Supporting Information for:

Towards Globular Macromolecules with Functionalized Interiors: Design and Synthesis of Dendrimers with an Interesting Twist

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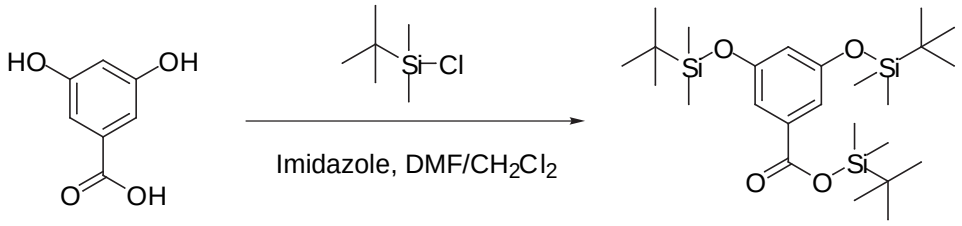
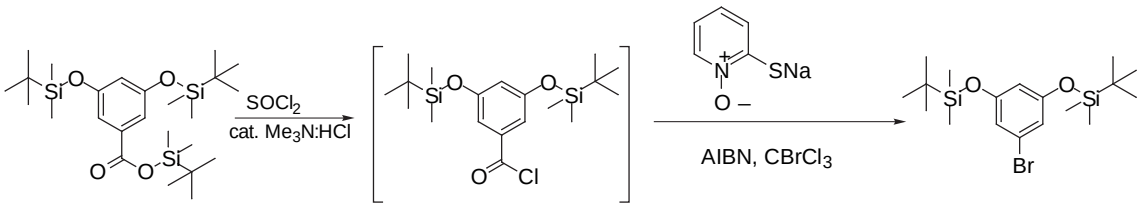
Experimental Details

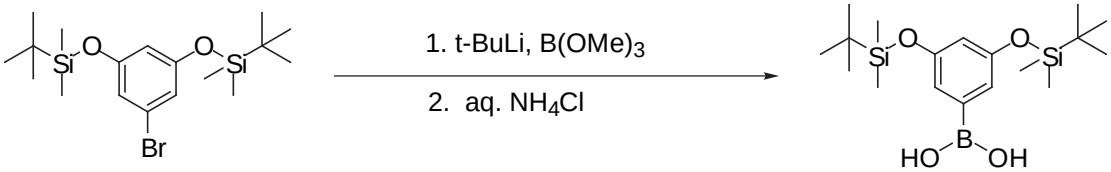
^{1}H-NMR spectra were recorded on a 400 MHz or a 500 MHz FT NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; d of d, doublet of a doublet; m, multiplet; b, broad. ^{13}C-NMR spectra were proton decoupled and recorded on a 400 MHz or a 500 MHz FT NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. MALDI ToF mass spectra was obtained at the Coordinated Instrumentation Facility of Tulane University or at the mass spectrometric facility at the University of Notre Dame. Flash chromatography was performed with EM science 37-75 μm silica gel. Analytical thin layer chromatography was performed on EM Science silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using the molybdic acid stain mixture. THF was distilled over Na / Ph_2CO ketyl. All other chemicals obtained from commercial sources were used without further purification, unless otherwise mentioned.



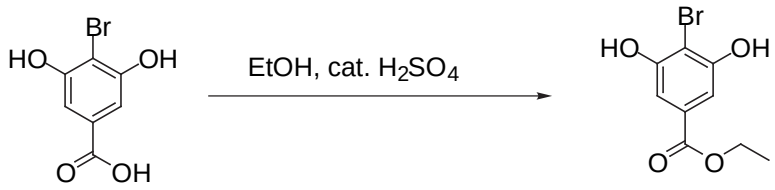
Silylation of 3,5-dihydroxybenzoic acid: In DMF(15 mL)/CH_2Cl_2(15 mL) 3,5-dihydroxybenzoic acid (1.00 g, 6.49 mmol) was dissolved and *tert*-butyl dimethylsilyl chloride (3.42 g, 22.70 mmol), and imidazole (1.55 g, 22.70 mmol) were added to this. Th reaction mixture was stirred at ambient temperature under nitrogen for 16 h. Water was added to this and organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic part was dried over anhydrous $MgSO_4$ and solvent was removed in vacuo. The crude product was column purified using silica gel and ethylacetate/hexane (20:80) mixture as eluent to afford 2.61 g (81%) of the ester as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J*=2.0 Hz, 2H), 6.36 (t, *J*=2.0 Hz, 1H), 0.77 (s, 27H), 0.00 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 157.0, 131.2, 118.2, 115.4, 25.9, 18.5, -4.1. GC/MS m/z (r. i.): 496 (3, M^+), 481 (3), 442 (5), 441 (20), 440 (42), 439 (100), 397 (7), 323 (4), 147 (6), 133 (6), 73 (54), 57 (11).



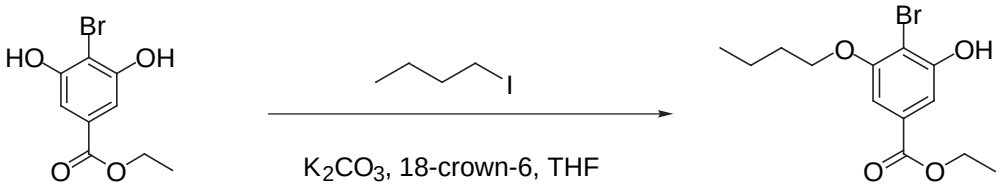
Synthesis of bis-(*O*-t-butyldimethylsilyl)-5-bromoresorcinol: To a flask containing the silyl ester (2.10 g, 4.23 mmol) and trimethylamine hydrochloride (0.01 g, 0.08 mmol) was added distilled dichloromethane (15 mL). To this solution was added distilled thionyl chloride (0.38 mL, 5.08 mmol) dropwise under nitrogen. After the addition, the mixture was heated at reflux for 3 h. Solvent was removed in vacuo and the residue was vacuum dried (190 ^{o}C/6mm Hg). The crude acid chloride thus obtained was taken in bromotrichloromethane (15 mL) along with 2,2'-azobisisobutyronitrile (0.10 g, 0.63 mmol). This homogeneous solution was added dropwise to a refluxing solution of 2-mercaptopyridine *N*-oxide sodium salt hydrate (0.76 g, 5.08 mmol) in bromotrichloromethane (10 mL). After heating at reflux for 2 hours, solvent was removed in vacuo. The mixture was purified by silica gel chromatography using hexane as eluent to afford 1.10 g (62%) of the bis-(*O*-t-butyldimethylsilyl)-5-bromoresorcinol as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 2H), 6.10 (s, 1H), 0.81 (s, 18H), 0.03 (s, 12H). ^{13}C NMR (100 MHz $CDCl_3$) δ 161.5, 126.7, 121.4, 115.6, 30.1, 22.6, 0.0. GC/MS m/z (r. i.): 418 (16, M^{+}), 416 (14), 361 (55), 359 (51), 319 (66), 317 (61) 280 (23), 265 (56), 223 (13), 137 (16), 73 (100), 41 (14).



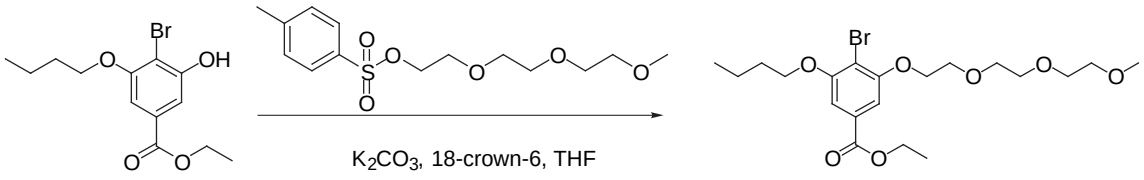
Preparation of boronic acid from the bis(*O*-t-butyldimethylsilyl)-5-bromo-resorcinol: To a solution of bis(*O-t*-butyldimethylsilyl)-5-bromo-resorcinol (31.77 mmol, g) was added *t*-BuLi (111.12 mmol, 65.4 mL of 1.7 M pentane solution) at -78 ^{o}C and stirred for 15 min. The $B(OMe)_3$ (62 mmol, 6.9 mL) was added and stirred at -78 to 20 ^{o}C for 8h. The reaction was quenched with a satd. NH_4Cl solution and extracted with ethylacetate. The solvent was removed in vacuo and the crude boronic acid was taken to the next step without further purification or characterization.



Synthesis of ethyl- 4-bromo-3,5-dihydroxybenzoate: To a solution of 4-bromo-3,5-dihydroxybenzoic acid (6.83 g, 0.03 mol) in ethyl alcohol (80 mL) was added 8~10 drops of fuming sulfuric acid. The mixture was refluxed overnight. Then the reaction mixture was concentrated in vacuo. The crude mixture was separated between ether and aqueous sodium bicarbonate aqueous solution. The organic layer was dried over sodium sulfate and concentrated to afford 7.28 g (95%) of the ester as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.07 (s, 2H); 7.16 (s, 2H); 4.28 (q, *J*=7.2 Hz, 2H); 1.32 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 165.5, 155.5, 130.8,108.0, 103.7, 61.0, 13.9. GC/MS m/z (r. i.): 262 (47), 260 (46, M^+), 234 (30), 232 (30), 217 (100), 215 (97), 190 (27), 189 (28), 188 (29), 187 (26), 108 (19), 107 (12), 79 (22), 51 (25)

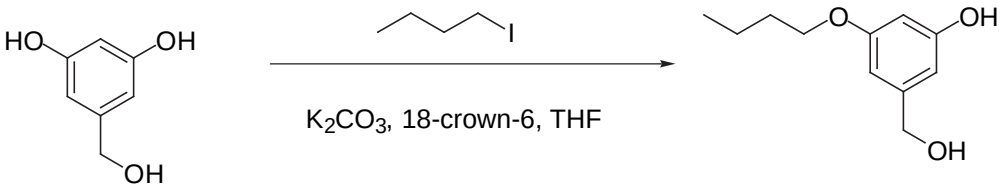


Synthesis of ethyl-4-bromo-3-hydroxy-5-butyloxy-benzoate: Ethyl-4-bromo-3,5-dihydroxybenzoate (7.05 g, 0.03 mol), potassium carbonate (3.73 g, 0.03 mol), 18-crown-6 (0.36 g, 1.35 mmol), and 1-iodobutane (2.46 mL, 0.02 mol) were all dissolved in 100 mL acetone. The mixture was refluxed under nitrogen for 12 hours. The reaction mixture was concentrated in vacuo and residue was purified by silica gel chromatography using ethylacetate/CH_2Cl_2 (5:95) to afford 2.92 g (46%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H); 7.11 (s, 1H); 5.85 (s, 1H); 4.35 (q, *J*=7.2 Hz, 2H); 4.07 (t, *J*=6.4 Hz, 2H); 1.81 (m, 2H); 1.53 (m, 2H); 1.37 (t, *J*=7.2 Hz, 3H); 0.98 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 156.2, 153.5, 131.2, 109.6, 105.8, 105.4, 69.4, 61.6, 31.2, 19.4, 14.4, 14.0. GC/MS m/z (r. i.): 318 (36), 316 (35, M^+), 262 (99), 260 (100), 234 (75), 232 (77), 218 (47), 217 (81), 216 (54), 215 (83), 190 (37), 188 (42).

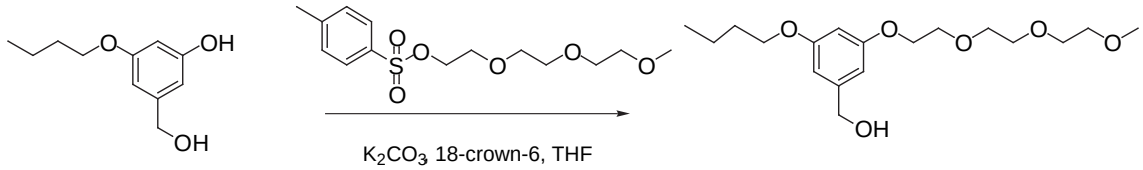


Synthesis of 3: Ethyl-4-bromo-3-hydroxy-5-butyloxy-benzate (14.04 g, 0.04 mol), potassium carbonate (9.18 g, 0.07 mol), 18-crown-6 (0.59 g, 2.20 mmol), and tosylate of

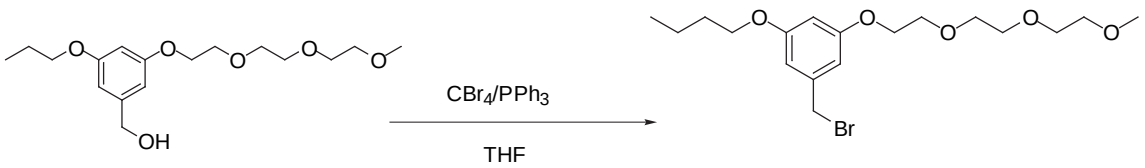
triethyleneglycolmonomethyl ether (14.11 g, 0.04 mol) were dissolved in 150 mL acetone. The solution was refluxed under nitrogen for 12 hours. The reaction mixture was concentrated in vacuo and residue was purified by silica gel chromatography using ethylacetate/CH_2Cl_2 (20:80) to afford 18.86 (92%) of compound **3** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H); 4.34 (q, *J*=7.2 Hz, 2H); 4.21 (t, *J*=5.2 Hz, 2H); 4.05 (t, *J*=6.4 Hz, 2H); 3.90 (t, *J*=4.8 Hz, 2H); 3.77 (m, 2H); 3.61~3.66 (m, 4H); 3.51 (m, 2H); 3.34 (s, 3H); 1.78 (m, 2H); 1.50 (m, 2H); 1.36 (t, *J*=6.8 Hz, 3H); 0.95 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 156.5, 156.2, 130.2,107.6, 106.6, 106.4, 71.8, 71.0, 70.6, 70.4, 69.3, 69.2, 69.1, 61.3, 58.9, 31.0, 19.1, 14.3, 13.7. GC/MS m/z (r. i.): 464 (0.3), 462 (0.3, M^+), 360 (1), 351 (3), 318 (19), 316 (19), 263 (17), 262 (25), 260 (24), 234 (11), 232 (11), 136 (12), 59 (100), 45 (19), 41 (14).



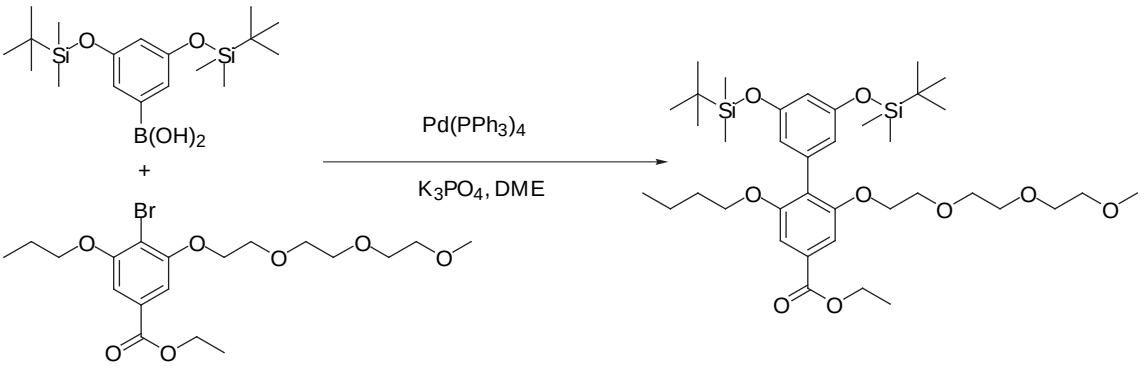
Synthesis of 3-hydroxy-5-butyloxy-benzyl alcohol: Procedure similar to the synthesis of ethyl-4-bromo-3-hydroxy-5-butyloxy-benzoate was adapted using 3,5-dihydroxybenzyl alcohol (20.00 g, 0.14 mol) as the substrate to afford 12.20 g (54%) of 3-hydroxy-5-butoxy-benzyl alcohol as a yellow liquid using ethylacetate/CH_2Cl_2 (25:75). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H); 6.40 (s, 1H); 6.34 (s, 1H); 4.51 (s, 2H); 3.86 (t, *J*=6.4 Hz, 2H); 1.72 (m, 2H); 1.46 (m, 2H); 0.99 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.4, 143.0, 106.6, 105.7, 101.5, 68.0, 65.1, 31.4, 19.4, 14.1. GC/MS m/z (r. i.): 196 (57, M^+), 140 (100), 122 (38), 111 (77), 94 (22), 65 (15), 41 (21).



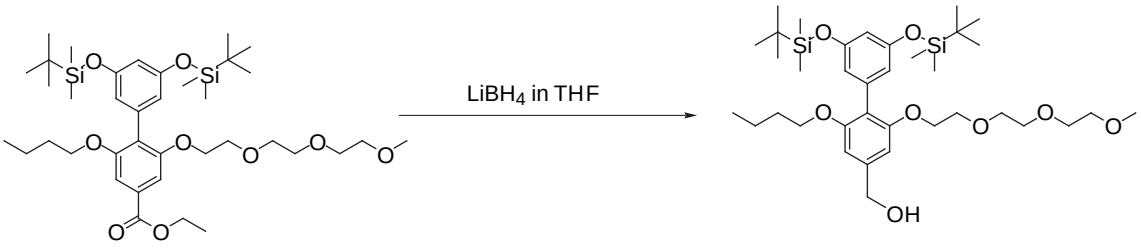
Synthesis of 3-butyloxy-5-triethyleneglycoxy-benzyl alcohol: Procedure similar to the synthesis of compound **3** was adapted using 3-hydroxy-5-butyloxy-benzyl alcohol (12.20 g, 62.18 mmol) as the substrate to afford 14.69 (69%) of the product as a colorless liquid using ethylacetate/CH_2Cl_2 (35:75) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (t, *J*=2.4 Hz, 2H); 6.33 (t, *J*=2.4 Hz, 1H); 4.54 (d, *J*=4.8 Hz, 2H); 4.05 (t, *J*=5.2 Hz, 2H); 3.87 (t, *J*=6.4 Hz, 2H); 3.77 (t, *J*=4.8 Hz, 2H); 3.67 (m, 2H); 3.57~3.62 (m, 4H); 3.48 (m, 2H); 3.31 (s, 3H); 1.69 (m, 2H); 1.41 (m, 2H); 0.90 (t, *J*=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.3, 143.5, 105.6, 105.2, 100.9, 72.1, 71.0, 70.9, 70.8, 69.9, 68.0, 67.7, 65.5, 59.3, 31.5, 19.5, 14.1. GC/MS m/z (r. i.): 342 (22, M^+), 310 (3), 266 (5), 240 (5), 220 (7), 196 (47), 165 (38), 141 (59), 140 (43), 123 (24), 111 (27), 59 (100), 45 (25), 41 (20).



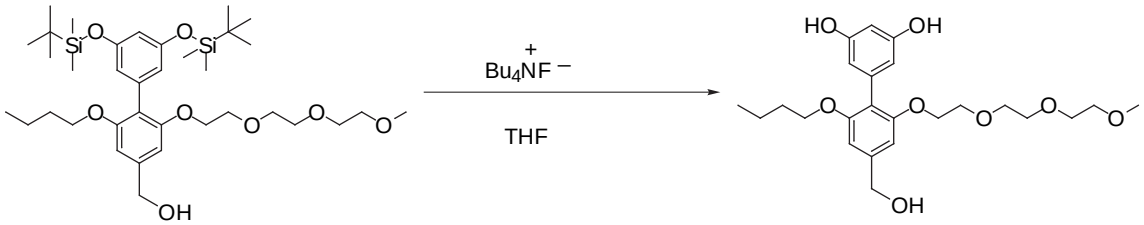
Synthesis of 3-butyloxy-5-triethyleneglycoxy-benzylbromide: To a stirred solution of 3-butyloxy-5-triethyleneglycoxy-benzyl alcohol (14.60 g, 42.64 mmol) and carbon tetrabromide (22.63 g, 68.22 mmol) in minimal THF was added a solution of triphenyl phosphine in THF at 0°C. The mixture was allowed to reach room temperature and stirred for 2 hours. Then, more PPh_3 (2.24 g, 8.54 mmol) and CBr_4 (2.83 g, 8.54 mmol) were added to force the reaction to completion. The mixture was stirred for another hour and separated between dichloromethane and water. The organic layer was concentrated and the residue was purified by silica gel chromatography to afford 14.06 g (82%) of compound as an oil using ethylacetate/CH_2Cl_2 (20:80) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J*=1.6 Hz, 2H); 6.45 (t, *J*=2.4 Hz, 1H); 4.44 (s, 2H); 4.15 (t, *J*=4.8 Hz, 2H); 3.98 (t, *J*=6.4 Hz, 2H); 3.89 (t, *J*=4.8 Hz, 2H); 3.77 (m, 2H); 3.69~3.74 (m, 4H); 3.60 (m, 2H); 3.43 (s, 3H); 1.79 (m, 2H); 1.53 (m, 2H); 1.02 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 160.2, 139.8,108.0, 107.6, 101.8, 72.1, 71.0, 70.9, 70.8, 69.9, 68.0, 67.7, 59.3, 33.9, 31.5, 19.4, 14.1. GC/MS m/z (r. i.): 406 (2), 404 (2, M^+), 348 (1), 346 (1), 293 (9), 261 (10), 260 (10), 259 (9), 258 (9), 205 (65), 179 (71), 151 (36), 149 (39), 123 (26), 77 (15), 59 (100), 45 (33).



Procedure for the Suzuki coupling: To a solution of the crude boronic acid (31.77 mmol), bromoester (24.8 mmol, 11.5 g) and K_3PO_4 (95.31 mmol, 20.23 g) in DME was added $Pd(PPh_3)_4$ (3.17 mmol, 3.66 g) and the mixture was refluxed for 30 h. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography to afford 7.55 g(42%) of the biphenyl product using ethylacetate/hexane (20:80) as eleunt. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 6.40(d, J=1.76 Hz, 2H), 6.29 (t, J=1.72 Hz, 1H), 4.39 (q, *J*=7.12 Hz, 2H), 4.08 (t, *J*=5.1 Hz, 2H), 3.93 (t, *J*=6.40 Hz, 2H), 3.68 (t, *J*=5.07 Hz, 2H), 3.60-3.50 (m, 8H), 3.36 (s, 3H), 1.59 (m, 2H), 1.41 (t, *J*=6.62 Hz, 3H), 1.29 (m, 2H), 0.98 (s, 18H), 0.85 (t, *J*=7.37 Hz, 3H), 0.18 (s, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 156.9, 156.5, 155.4, 135.1, 130.3, 125.0, 115.7, 110.7, 106.7, 71.7, 69.1, 68.8, 68.3, 60.9, 58.8, 30.9, 25.5, 18.9, 18.0, 14.2, 13.5, -4.5.



Reduction of ester to alcohol: A solution of $LiBH_4$ in THF (150 mL) was refluxed for 1h, then cooled to room temperature and a solution of ester (10 mmol, 7.21 g) in THF (20 mL) was added dropwise. After addition the mixture was refluxed for 12 h. The reaction was quenched with ethylacetate. Solvent was removed in vacuo, the residue was treated with a satd. NH_4Cl solution and the resulting mixture was extracted with ethylacetate (3 x 100 mL). The combined organic extracts was dried over anhydrous $MgSO_4$ and the filtered organic layer was evaporated to dryness. The crude product was purified by silicagel column chromatography to afford 5.97 g (88%) of the alcohol. ^{1}H-NMR (100 MHz, $CDCl_3$) δ 6.49 (s, 1H), 6.46 (s, 1H), 6.23 (d, *J*=1.74 Hz, 2H), 6.09 (t, *J*=1.73 Hz, 1H), 4.51 (s, 2H), 3.92 (t, *J*=5.1 Hz, 2H), 3.85 (t, *J*=6.4 Hz, 2H), 3.50-3.30 (m, 8H), 3.21 (s, 3H), 1.41(m, *J*=1.94, 2H), 1.05 (m, *J*=7.41 Hz, 2H), 0.8 (s, 18H), 0.65 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.5, 157.2, 155.6, 142.1, 136.1, 120.0, 116.5, 110.7, 104.7, 104.5, 72.0, 71.0, 70.8, 70.5, 69.6, 69.1, 68.6, 65.4, 60.6, 59.1, 31.4, 25.9, 19.3, 13.9, 18.0. EI-MS (m/z) 679 (M^+), 622.

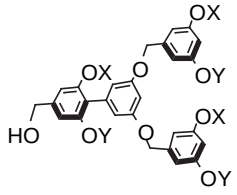


Desilylation procedure for the synthesis of 1: To the solution of alcohol (7 mmol, 4.75 g) in THF (125 mL) was added TBAF (60 mmol, 60 mL of 1.0 M THF solution) and stirred at room temperature under nitrogen for 20 h. The solvent was removed with rotavapor. The residue was treated with a 10% HCl (50 mL) and the organic compound was extracted with ethylacetate. The crude was column chromatographed and the compound **1** was isolated using hexane/ethylacetate (20:80) mixture as eluent (Yield 2.87g, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.4 (broad singlet, 2H), 6.21-6.53 9 (m, 5H), 4.5 (s, 2H), 4.02 (t, *J*=5.1Hz, 2H), 3.81(t, *J*=6.4 Hz, 2H), 3.71 (t, *J*=5.06 Hz, 2H), 3.60-3.40 (m, 8H), 3.21 (s, 3H), 1.51 (m, 2H), 1.24 (m, 2H), 0.7 (t, *J*=7.33 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.2, 157.0, 156.7, 141.8, 136.0, 119.5, 110.6, 104.1, 101.6, 71.8, 71.0, 70.7, 70.3, 69.6, 68.9, 65.1, 60.7, 58.9, 31.3, 19.2, 13.9. EI-MS (m/z) 450 (M^+).

General procedure for the Synthesis of Dendritic hydroxymethyl compounds 5-8: A mixture of the appropriate, bromomethyl compound (1 eq.) the compound **1** (0.5 eq), potassium carbonate (10-15 eq.) and 18-crown-6 (10-15 mol %) in THF was heated at

reflux and stirred vigorously under nitrogen for 36 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was treated with water and organic compounds were extracted with ethylacetate. The aqueous layer was extracted with ethylacetate and combined extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silicagel column chromatography.

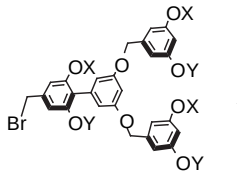
General procedure for the Synthesis of Dendritic bromomethyl compounds: To a solution of the appropriate dendritic benzyl alcohol in the minimum amount of dry THF was added PPh_3 and CBr_4. The reaction mixture was stirred at room temperature under nitrogen and was monitored by TLC. The reaction mixture was treated with water and extracted with ethylacetate. The combined extracts were dried over $MgSO_4$ and the solvent was rotavaped. The crude product was purified by silicagel column chromatography.



X=Bu; Y=TEG

3-mer-OH

Synthesis of 3-mer-OH, 5: This reaction was carried out in 6.99 mmol scale of **1** and the yield of the reaction was 72% using ethylacetate/1,4-dioxane (90:10) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.60-6.37 (m, 11H), 4.88 (s, 4H), 4.59 (s, 2H), 4.07 (t, *J*=5.13 Hz, 6H), 3.99 (t, *J*=6.41 Hz, 6H), 3.89-3.77 (m, 14H), 3.67-3.57 (m, 8H), 3.49-3.39 (m, 8H), 3.32 (s, 3H), 3.30(s, 3H), 3.24 (s, 3H), 1.72-1.69 (m,4H), 1.57-1.53 (m, 4H), 1.33-1.27 (m, 4H). 0.91 (t, 6H, *J*=7.42 Hz), 0.81 (t, 3H, *J*=7.32 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.6, 160.2, 159.2, 157.4, 157.1, 142.4, 139.2, 119.4, 110.5, 106.3, 105.8, 104.4, 101.0, 72.1, 72.0, 70.9, 70.9, 70.8, 70.7, 70.5, 70.1, 69.8, 69.7, 69.0, 68.5, 67.9, 67.6, 59.2, 59.1, 31.4, 31.3, 19.4, 19.4, 14.0, 13.9.

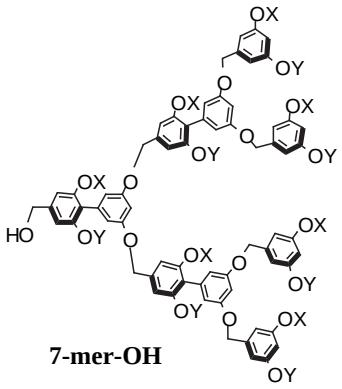


X=Bu; Y=TEG

3-mer-Br

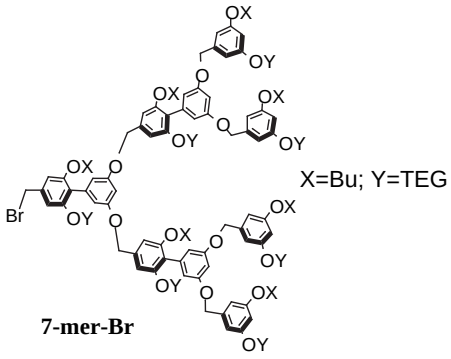
Synthesis of 3-mer-Br: This reaction was carried out in 14.3 mmol scale and the yield of the reaction was 69% using ethylacetate/1,4-dioxane (80:20) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.63-6.39 (m, 11H), 4.90 (s, 4H), 4.46 (s, 2H), 4.09 (t, J=4.09 Hz, 6H), 4.02 (t, J=4.29 Hz, 6H), 3.91-3.61 (m, 14H), 3.53-3.44 (m, 8H), 3.38 (s, 3H), 3.33 (s, 3H), 3.28 (s, 3H), 1.75-1.69 (m, 4H), 1.60-1.55 (m 4H), 1.36-1.29 (m 4H), 0.94 (t, J=7.41 Hz, 6H), 0.83 (t, J=7.21 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.6, 160.2, 159.2, 157.4, 157.1, 139.5, 138.4, 135.7, 120.5, 110.3, 106.7, 106.3, 105.8, 101.1, 100.9,

72.1, 72.0, 70.9, 70.8, 70.7, 70.5, 70.1, 69.8, 69.6, 69.0, 68.6, 67.9, 67.9, 67.6, 67.2, 59.2, 59.1, 34.2, 31.4, 31.2, 19.4, 19.3, 14.0, 13.9.



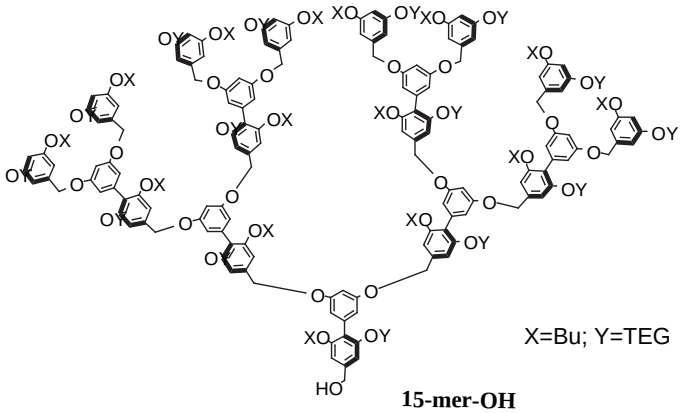
7-mer-OH

Synthesis of 7-mer-OH, 6: This reaction was carried out in 1.4 mmol (of **1**) scale and the yield of the reaction was 88%. The compound was isolated using ethylacetate/1,4-dioxane (80:20) as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.61-6.38 (m, 27H), 4.98 (s, 4H), 4.90 (s, 8H), 4.67 (s, 2H), 4.06 (t, *J*=5.3 Hz, 14H), 3.98 (t, *J*=6.1 Hz, 14H), 3.90-3.79(m, 14H), 3.69-3.67 (m, 32H), 3.64-3.59 (m, 16H), 3.50-3.41 (m, 8H), 3.32 (s, 18H), 3.29 (s, 3H), 1.70 (m, 8H), 1.54 (m, 6H), 1.44 (m, 8H), 1.30 (m,6H), 0.92 (t, *J*=7.11 Hz, 18H), 0.82 (t, *J*=7.22 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.3, 159.9, 159.0, 158.9, 157.1, 156.9, 156.8, 142.5, 139.3, 137.8, 136.1, 135.8, 119.6, 117.4, 115.5, 110.1, 106.1, 105.6, 105.0, 104.9, 104.6, 104.3, 100.7, 71.8, 71.9, 71.7, 70.7, 70.5, 70.4, 70.3, 70.2, 69.8, 69.6, 69.3, 68.7, 68.3, 67.6, 67.3, 65.3, 60.3, 58.9, 58.8, 31.1, 31.0, 30.8, 19.1, 14.1, 13.7, 13.7. MALDI-TOF 2635.18 (Calcd. for $C_{144}H_{210}O_{42}$ ($M+Na^+$)= 2635.82).



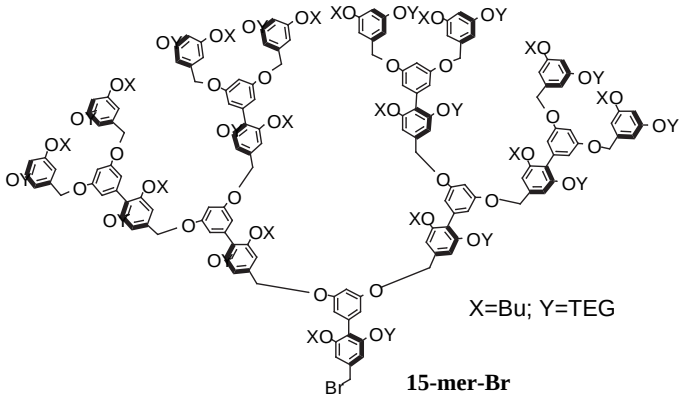
7-mer-Br

Synthesis of 7-mer-Br: This reaction was carried out in 0.531 mmol (of **1**) scale and the yield of the reaction was 42%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.61-6.38 (m, 27H), 4.99 (s, 4H), 4.92 (s, 8H), 4.01 (t, *J*=5.11 Hz, 8H), 3.94 (t, *J*=6.6 Hz, 8H), 3.90- 3.79(m, 14H), 3.69-3.67 (m, 14H), 3.64-3.59 (m, 24H), 3.50-3.41 (m, 32H), 3.32 (s, 18H), 3.29 (s, 3H), 1.70 (m, 8H), 1.54 (m, 6H), 1.44 (m, 8H), 1.30 (m,6H), 0.92 (t, *J*=7.43 Hz, 18H), 0.82 (t, *J*=7.11 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_{13}$) δ 160.2, 159.8, 158.9, 158.8, 157.1, 156.8, 139.2, 137.9, 137.7, 135.7, 135.6, 120.1, 119.6, 110.1, 110.0, 106.1, 106.0, 105.5, 105.0, 104.8, 100.8, 100.6, 71.7, 71.6, 70.6, 70.4, 70.3, 70.2, 70.1, 69.7, 69.5, 69.3, 69.2, 68.7, 68.2, 67.5, 67.2, 58.8, 58.7, 46.4, 31.1, 30.9, 19.0, 13.7, 13.6 MALDI-TOF: 2698.65 (Calcd: for $C_{144}H_{209}Br0_{41}$ ($M+Na^+$=2698.08).



15-mer-OH

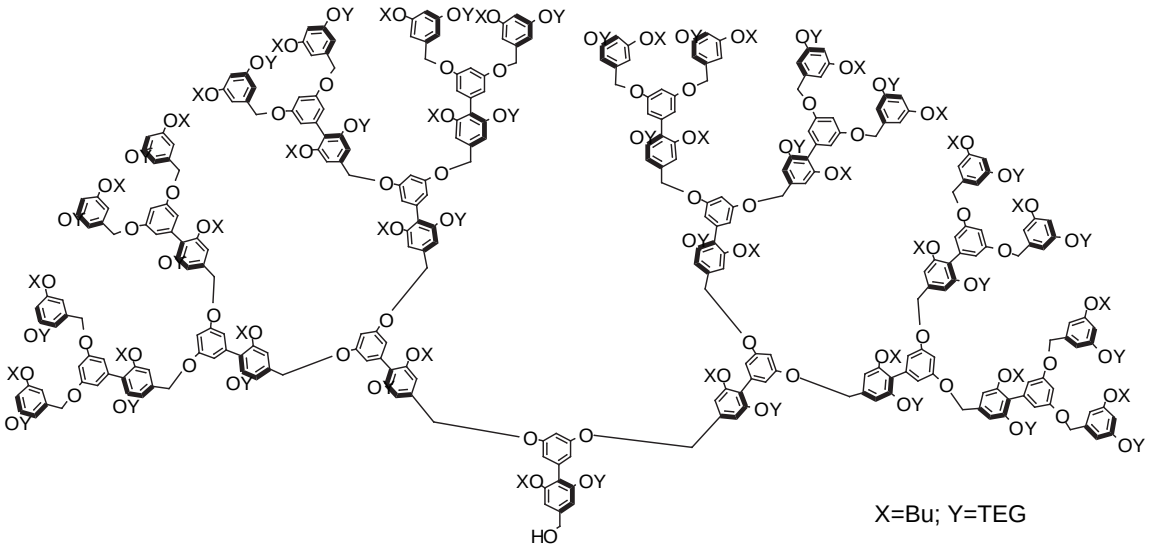
Synthesis of 15-mer-OH, 7: This reaction was carried out in 0.106 mmol (of **1**) scale and the yield of the reaction was 50%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.69-6.37 (m, 59H), 4.97(s, 12H), 4.89 (s, 16H), 4.64 (s, 2H), 4.06 (t, *J*=5.11 Hz, 30H), 3.98 (t, *J*=6.34 Hz, 30H), 3.90- 3.79(m, 30H), 3.69-3.67 (m, 96H), 3.64-3.59 (m, 16H), 3.50-3.41 (m, 8H), 3.32 (s, 42H), 3.29 (s, 3H), 1.70 (m, 30H), 1.54 (m, 16H), 1.44 (m, 8H), 1.30 (m,6H), 0.92 (t, *J*=7.11 Hz, 36H), 0.82 (t, *J*=7.22 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.1, 159.6, 159.1, 158.9, 157.2, 156.9, 139.3, 137.7, 136.0, 135.8, 119.7, 110.1, 106.1, 105.6, 105.2, 105.0, 100.7, 71.8, 71.7, 70.7, 70.6, 70.5, 70.3, 70.2, 69.8, 69.6, 69.4, 69.3, 68.8, 68.3, 67.6, 67.3, 58.9, 58.8, 31.2, 31.1, 31.0, 19.2, 19.1, 13.7, 13.6. MALDI-TOF: 5662.38 (Calcd: for $C_{312}H_{450}0_{90}$ ($M+Na^{+}$) 5662.86).



15-mer-Br

Synthesis of 15-mer-Br: This reaction was carried out in 0.049 mmol scale and the yield of the reaction was 76%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.69-6.37 (m, 59H), 4.95(s, 12H), 4.87 (s, 16H), 4.41 (s, 2H), 4.06 (t, *J*=5.11 Hz, 30H), 3.98 (t, *J*=6.34 Hz, 30H), 3.91- 3.80(m, 30H), 3.68-3.65 (m, 96H), 3.63-3.59 (m, 16H), 3.51-3.40 (m, 8H), 3.33 (s, 42H), 3.28 (s, 3H), 1.71 (m, 30H), 1.54 (m, 16H),

1.44 (m, 8H), 1.30 (m,6H), 0.92 (t, *J*=7.11 Hz, 36H), 0.82 (t, *J*=7.22 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_{13}$) δ 160.3, 159.7, 158.8, 158.8, 157.1, 156.8, 139.2, 137.9, 137.7, 135.7, 135.6, 120.1, 119.6, 110.1, 110.0, 106.1, 106.0, 105.5, 105.0, 104.8, 100.8, 100.6, 71.7, 71.6, 70.6, 70.4, 70.3, 70.2, 70.1, 69.7, 69.5, 69.3, 69.2, 68.7, 68.2, 67.5, 67.2, 58.7, 58.6, 46.5, 31.1, 30.8, 19.0, 13.6, 13.5.



31-mer-OH

Synthesis of 31-mer-OH, 8: This reaction was carried out in 0.0105 mmol (of **1**) scale and the yield of the reaction was 51%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.69-6.37 (m, 123H), 4.97(s, 28H), 4.89 (s, 32H), 4.60 (s, 2H), 4.04 (t, *J*=5.33 Hz, 62H), 3.98 (t, *J*=6.13 Hz, 62H), 3.90- 3.79(m, 62H), 3.69-3.67 (m, 56H), 3.64-3.59 (m, 194H), 3.50-3.41 (m, 34H), 3.32 (s, 18H), 3.29 (s, 86H), 1.70 (m, 16H), 1.54 (m, 24H), 1.44 (m, 32H), 1.30 (m,24H), 0.92 (t, *J*=7.11 Hz, 72H), 0.82 (t, *J*=7.22 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.3, 159.9, 159.0, 158.9, 157.2, 156.9, 139.3, 137.7, 136.0, 135.8, 119.7, 110.1, 106.1, 105.6, 105.2, 105.0, 100.7, 71.8, 71.7, 70.7, 70.6, 70.5, 70.3, 70.2, 69.8, 69.6, 69.4, 69.3, 68.8, 68.3, 67.6, 67.3, 58.9, 58.8, 31.2, 31.1, 31.0, 19.2, 19.1, 13.8, 13.7. MALDI-TOF: 11695.0, (Calcd: for $C_{648}H_{930}0_{186}$ 11696.2).