Synthesis of Unsymmetrical Branched Polyether Dendrons from 3,4-Methylene-dioxybenzaldehyde

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Unsymmetrical dendrons 1, 2 and 3 were easily prepared according to a novel convergent strategy from 3, 4-methylene-dioxybenzaldehyde as starting material.

Keywords dendrimer, convergent synthesis, piperonal

Introduction

Dendrimers, well defined macromolecules with highly branched structures, since their discovery about 20 years ago,[1] have stimulated an almost explosive research effort and many synthetic, analytical and application-related issues have been addressed.[2] Even industrially applicable synthesis was developed.[3] Now, chiral dendrimers[4] are of particular interest because these materials have the potential for enantioselective clathration, leading to applications in separation, catalysis and sensor technology. Recent studies showed that dendrimers constructed with Fréchet-type polyether dendritic wedges which were pioneered by Fréchet through convergent approach[5] are comformationally quite flexible,[6] moreover, several theoretical[7] and experimental[8] studies demonstrated that significant inward folding of the chain termini occurs in these systems, resulting in a density maximum near the core rather than at the periphery. Meijer[9] observed that an enantiomerically pure dendrimer, which was constructed using three constitutionally different Fréchet-type dendritic wedges attached to a central carbon atom, exhibited no optical activity. Later, Parquette[10] modified the symmetrical 3,5-disubstitution pattern of a Fréchet-type wedge to an unsymmetrical 2,3-branched pattern to restrict flexibility in the branch segments and synthesized unsymmetrically branched dendrimeric wedges up to the fourth generation based on 2,3-dihydroxybenzyl alcohol.

We recently reported a novel" convergent-growth "approach to dendritic macromolecules,[11] using gallic acid and α-resorcylic acid (3,5-dihydroxybenzyl acid) as starting materials to synthesize the second and the fourth generation dendrimers respectively. By using Wittig reaction to prolong branch unit, higher generation dendrimers could be synthesized with less steric hindrance and more spacious cavities to trap larger molecules, thus these new dendrimers may have more potential for medicine manufacture. Benzyl ethers were selected as protecting groups since it can afford a dendrimer with phenolic chain ends by catalytic hydrogenolysis that does not affect the aliphatic ether linkages within the dendrimers, and further modification of the chain end will be readily accomplished. Later, the symmetrical 3,5-disubstitution pattern of this type of wedges was modified to an unsymmetrical 3,4-branched pattern. In this paper, the synthesis of unsymmetrical branched dendrons **1**, **2** and **3** from 3,4-methylene-dioxybenzaldehyde (piperonal), which is commercially available, is reported (Fig. 1).

Results and discussion

The synthesis progressed by the new convergent growth approach was shown in Scheme 1. Accordingly, 3,4-methylenedioxybenzaldehyde (**4**) reacted with ylide reagent followed by catalytic hydrogenation with Pd/C to afford ester **5** in 85% yield. The methylene moiety of **5** was removed using a standard procedure[12] to produce ester **6**. This ester was protected as their bisbenzyl ethers, and subsequent reduction of the ester functionality by treatment with $LiAlH_4$ gave alcohol **7**. The deprotection of the alcohol **7** by catalytic hydrogenolysis with Pd/C afforded the desired monomer **8**. On the other hand, activation of the hydroxyl group of **7** by reaction with CBr_4/PPh_3 in dry THF at r.t. generated bromide **9** in 94% yield. The bromide **9** (2.1 equiv.) was allowed to react with the diphenolic monomer unit **8** to afford the first-generation alcohol **10** (**[G-1]**-OH). The first-generation alcohol **10** was converted to the first-generation bromide **11** (**[G-1]**-Br) in 94% yield with CBr_4/PPh_3. Reaction of **11** (2.1 equiv.) with monomer **8** as above, gave the second-generation alcohol **1** (**[G-2a]**-OH) in 82% yield, which was

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Received May 6, 2003; revised July 28, 2003; accepted August 25, 2003.

Project supported by the National Natural Science Foundation of China (QT program No. 20021001) and the Natural Science Foundation of Gansu Province (QT program No. ZS011-A25-003-Z).

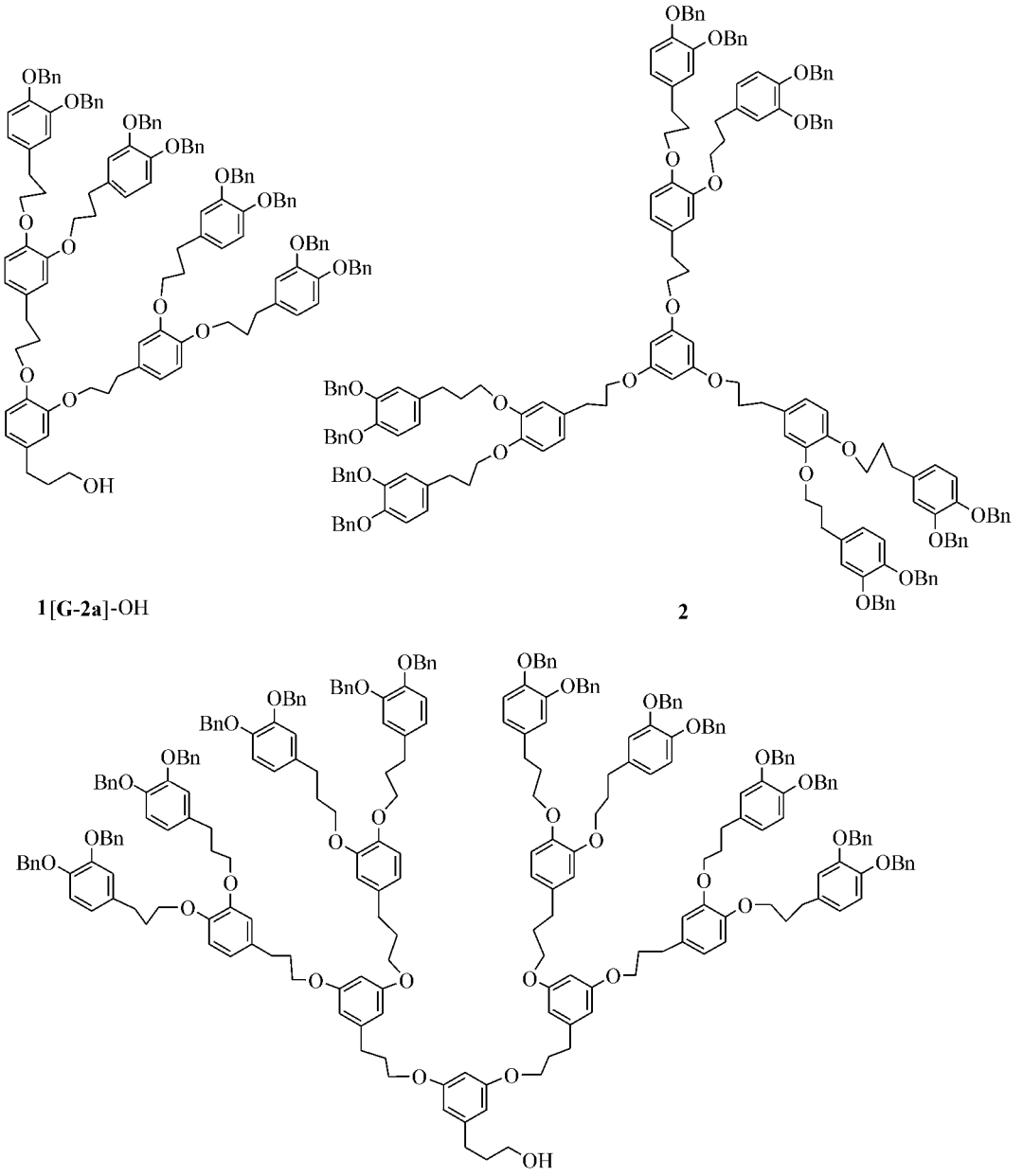


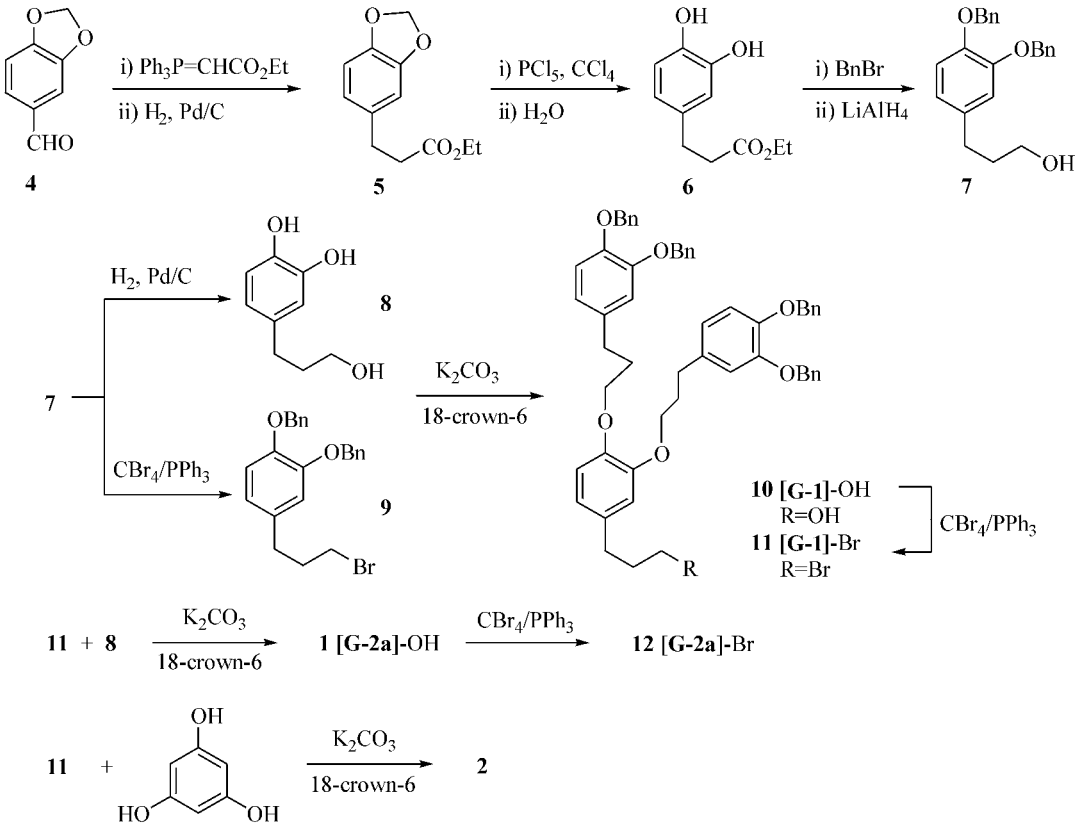
Fig. 1 Structure of dendrons **1**, **2** and **3**.

brominated with CBr_4/PPh_3 to give **12** (**[G-2a]**-Br) in 93% yield. Probably due to its great steric inhibition occurring at the focal functional group with increasing dendron size which inhibits its anchoring to the monomer, the second-generation bromide **12** did not react with monomer **8**. When bromide **11** (**[G-1]**-Br) reacted with phloroglucinol (1,3,5-trihydroxybenzene), a novel spherical dendron **2** was generated in 79% yield under similar conditions for coupling reaction described above.

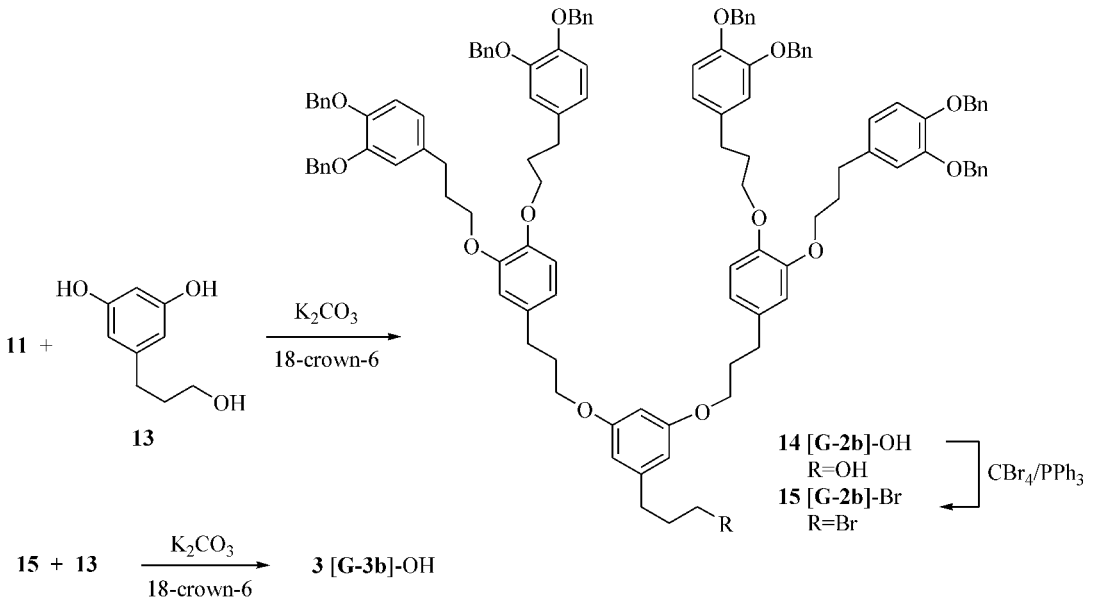
Then, we chose another difunctional monomer 3-(3,5-dihydroxyphenyl)-1-propanol (**13**) which had less steric hindrance to synthesize higher generation dendrimers. The preparation of **13** was described in detail in previous paper from our laboratory.[11] Reaction of the first-generation bromide **11** (**[G-1]**-Br) with monomer **13** (K_2CO_3, 18-crown-6, acetone, reflux for 3 d) gave the second-generation alcohol **14** (**[G-2b]**-OH) in 78% yield. Alcohol **14** was brominated with CBr_4/PPh_3 to produce the corresponding bromide **15** (**[G-2b]**-Br) in 90% yield. After coupling reaction of **15** with monomer **13** and purification by flash chromatography, the third-generation alcohol **3** (**[G-3b]**-OH) was isolated in 75% yield (Scheme 2).

All of these dendrons were extremely soluble in a vast range of organic solvents such as dichloromethane, chloroform, ethyl acetate and acetone. As with our previous studies, ^1H and ^{13}C NMR data, high resolution mass spectra data are very useful for the structure identification and determination of the purity of dendrons **1**, **2** and **3** as well

Scheme 1 Synthesis of dendrons **1** and **2**



Scheme 2 Synthesis of dendron **3**



as the intermediates. As can be seen in Fig. 2, in the ^1H NMR spectrum of the second-generation alcohol **1** ([**G-2a**]-OH), which has eight terminal phenyl rings, there is a set of multiplet peaks at δ 7.26—7.39 for the phenyl ring while the resonance for the aromatic protons of the internal dioxyphenyl groups is observed at δ 6.66—6.94. Resonance at δ 5.00—5.06 can be attributed to the protons of benzylmethylene group and other signals result from the alkyl branched moieties at six separate regions (δ_H 1.76—1.84, 1.96—2.10, 2.53—2.61, 2.68—2.78, 3.58—3.64, 3.83—3.96). Since the focal point/other moiety ratio decreases with the increase of generation, the

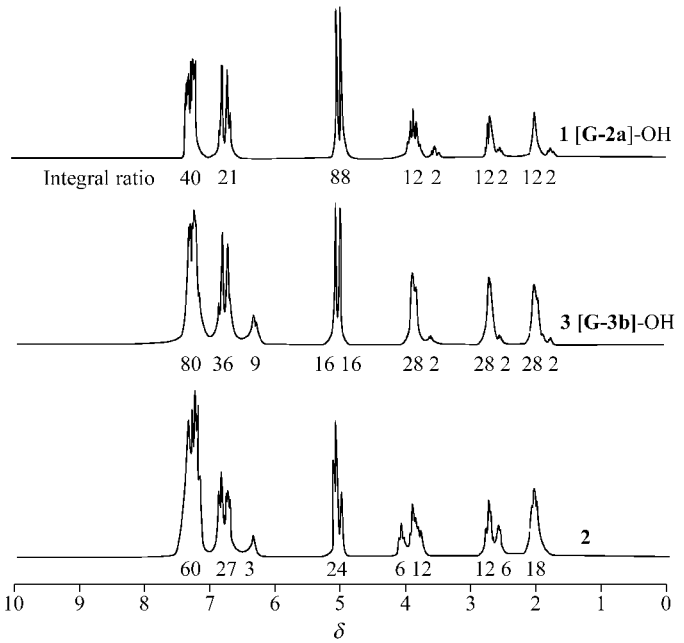


Fig. 2 ^{1}H NMR spectra of **1**, **2** and **3**.

higher the generation, the smaller the relative integral intensities of the hydroxymethylene group moiety proton signals (δ 3.58—3.64) at the focal point to those of the signals resulting from the benzylic and alkyl branching moieties. This can be observed distinctly in comparison with the ^{1}H NMR spectrum of the third-generation alcohol **3** ([**G-3b**]-OH). The ^{1}H NMR spectrum of **3** also reveals the different types of internal moieties and additional resonance for 3,5-dioxyphenyl protons occurring at δ 6.35—6.50. So, integral intensities of these respective moieties and their comparison with each other confirm not only the generation number but also the structure. In the ^{1}H NMR spectrum of dendrimer **2**, the multiplet at δ 6.40—6.46 is due to the core protons, and additional complexity is also observed in the benzylic methylene protons at δ 5.01—5.10. Although ^{13}C NMR spectra of the various dendrons are overlaped seriously, the greater differences can be found between the resonances for the CH_2OH and CH_2Br functional groups, the former occurring at δ 62.15—66.88 and the latter at δ 31.59—34.18.

Conclusion

We described a convenient synthesis of unsymmetrical branched dendritic wedges with benzyl ether periphery for application to dendrimer synthesis and each generational growth step proceeded with high efficiency at least up to the third generation. This kind of dendrons with good solubility in organic solvents could be easily isolated by flash chromatography and they can be further modified easily. Moreover, dendrimers with optical activity arising entirely from unsymmetrical branch segments are a relatively new development and represent an exciting area for future study, and at the moment the synthesis of these compounds is an important goal in our further research.

Experimental

General methods and materials

IR spectra were record on a Nicolet 170 SX FT-IR spectrophotometer with KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Avance DRX-200 or Bruker 80 spectrometer. Mass spectra (MS) data were obtained on a V.G. ZAB-HS and high resolution mass spectra data were obtained on a Bruker Daltonics APEXII mass spectrometer. All materials were used directly as obtained commercially.

Ethyl 3-(3, 4-*methylene-dioxyphenyl*)-*propanoate* (**5**) A mixture of piperonal (10.0 g, 0.07 mol) and $Ph_3P=CHCO_2Et$ (27.8 g, 0.08 mol) in benzene was stirred at r.t. for 4 h, the resulting ester (13.3 g, 0.06 mol) was allowed to the hydrogen atmosphere (10% Pd/C catalyst, 0.1 equiv.) to give the ester **5** (12.6 g) in 85% yield. ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 1.18 (t, J = 7.0 Hz, 3H, CH_3), 2.38—2.59 (m, 2H, CH_2), 2.72—2.93 (m, 2H, CH_2), 4.07 (q, J = 7.0 Hz, 2H, CH_2), 5.83 (s, 2H, OCH_2O), 6.52—6.73 (m, 3H, 3 × ArH). MS (EI) m/z (%): 222 (M^+, 81), 151 (75), 135 (100), 119 (38), 91 (60), 77 (65).

Ethyl 3-(3,4-*dihydroxyphenyl*)-*propanoate* (**6**) It was prepared from ester **5** in 79% yield by the same method given in the literature.[12] ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 1.20 (t, J = 7.0 Hz, 3H, CH_3), 2.51—2.80 (m, 4H, 2 × CH_2), 4.12 (q, J = 7.0 Hz, 2H, CH_2), 6.51—6.85 (m, 3H, 3 × ArH), 7.01 (br, 2H, 2 × OH); MS (EI) m/z (%): 210 (M^+, 77), 136 (95), 123 (100), 91 (26), 77 (30).

3-(3,4-*Dibenzyloxyphenyl*)-*propanol* (**7**) It was prepared from **6** in 79% yield by the method given in the

literature.[11] ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.75—1.86 (m, 2H, CH_2), 2.61 (t, J = 7.0 Hz, 2H, CH_2), 3.60 (t, J = 7.0 Hz, 2H, C**H**$_2$OH), 5.09—5.16 (m, 4H, 2 × $PhCH_2O$), 6.69—6.90 (m, 3H, 3 × ArH), 7.31—7.48 (m, 10H, 10 × ArH); HRMS calcd for $C_{23}H_{25}O_3$ [M + H$^+$] 349.1798; found 349.1793.

3-(3,4-*Dihydroxyphenyl*)-*propanol* (**8**) It was prepared from **7** in 87% yield by the same method given in the literature.[11] ^{1}H NMR (CD_3COCD_3, 200 MHz) δ: 1.69—1.83 (m, 2H, CH_2), 2.49 (t, J = 7.0 Hz, 2H, CH_2), 3.57 (t, J = 7.0 Hz, 2H, C**H**$_2$OH), 6.45—6.70 (m, 3H, 3 × ArH), 7.56 (br, 2H, 2 × OH); MS (FAB) m/z (%): 168 (M$^+$, 16).

3-(3,4-*Dibenzyloxyphenyl*)-1-*bromopropane* (**9**) A mixture of the alcohol **7** (1.0 mol equiv.), carbon tetrabromide (1.2 mol equiv.) and triphenylphosphine (1.2 mol equiv.) was stirred in dry THF at r.t. for 9 h. The reaction was monitored by thin layer chromartography until all materials disappeared. The reaction mixture was filtered and filter cake was washed with dry ether. The combined filtrate was evaporated *in vacuo* to leave a residue, which was then purified by silica gel column chromatography (EtOAc/hexane = 1/10 graded to 1/5) to give the bromide **9** in 94% yield. ^{1}H NMR ($CDCl_3$, 80 MHz,) δ: 2.03—2.09 (m, 2H, CH_2), 2.63—2.81 (m, 2H, CH_2), 3.37 (t, J = 7.1 Hz, 2H, CH_2Br), 5.18 and 5.20 (double s, 4H, 2 × $PhCH_2O$), 6.99—6.70 (m, 3H, 3 × ArH), 7.33—7.53 (m, 10H, 10 × PhH); IR (KBr) ν: 3379, 2923, 1595, 1370, 1155, 879 cm^{-1}; HRMS calcd for $C_{23}H_{23}BrO_2Na$ [M + Na$^+$] 433.0774; found 433.0773.

General procedure for the synthesis of dendritic bromides **[G-*n*]**-Br (***n*** = **1, 2**) **11, 12, 15** followed that for the preparation of compound **9**

[G-1]-Br (**11**) This compound was prepared as an oil from **10** (**[G-1]**-OH) in 94% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.00—2.07 (m, 6H, 3 × CH_2), 2.58—2.74 (m, 6H, 3 × CH_2), 3.30 (t, J = 7.1 Hz, 2H, CH_2), 3.86—3.94 (m, 4H, 2 × CH_2), 4.96—5.03 (m, 8H, 4 × $PhCH_2O$), 6.64—6.81 (m, 9H, 9 × ArH), 7.24—7.35 (m, 20H, 20 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 30.94, 31.04, 31.51, 33.10, 33.67, 34.15, 67.91, 68.02, 71.16, 71.64, 114.21, 114.54, 115.40, 115.68, 120.79, 121.24, 127.24, 127.30, 127.83, 128.31, 133.41, 135.06, 137.47, 147.17, 147.40, 148.97; IR (KBr) ν: 3399, 2925, 1595, 1450, 1378, 1155, 696 cm^{-1}; HRMS calcd for $C_{55}H_{55}BrO_6Na$ [M + Na$^+$] 913.3074; found 913.3057.

[G-2a]-Br (**12**) This compound was prepared as an oil from **1** (**[G-2a]**-OH) in 93% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.05 (br, 14H, 7 × CH_2), 2.74 (br, 14H, 7 × CH_2), 3.38 (t, J = 7.1 Hz, 2H, CH_2Br), 3.92—3.95 (m, 12H, 6 × CH_2), 5.01—5.07 (m, 16H, 8 × $PhCH_2O$), 6.67—6.84 (m, 21H, 21 × ArH), 7.26—7.40 (m, 40H, 40 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 30.50, 32.37, 33.13, 33.87, 34.18, 66.70, 68.35, 69.91, 70.01, 98.97, 99.09, 99.59, 105.81, 106.37, 107.12, 107.67, 127.49, 127.68, 128.49, 136.69, 136.75, 142.76, 143.87, 159.72, 159.92, 160.02, 160.21; IR (KBr) ν: 3429, 2925, 1595, 1448, 1155, 1065, 736 cm^{-1}; HRMS calcd for $C_{119}H_{120}BrO_{14}$ [M + H$^+$] 1851.7856; found 1851.7886.

[G-2b]-Br (**15**) This compound was prepared as an oil from **14** (**[G-2b]**-OH) in 90% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.05—2.17 (m, 14H, 7 × CH_2), 2.70—2.77 (m, 14H, 7 × CH_2), 3.39 (t, J = 7.2 Hz, 2H, CH_2Br), 3.90—3.95 (m, 12H, 6 × CH_2), 5.04—5.10 (m, 16H, 8 × $PhCH_2O$), 6.35—6.46 (m, 3H, 3 × ArH), 6.71—6.88 (m, 18H, 18 × ArH), 7.26—7.42 (m, 40H, 40 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 31.03, 31.59, 66.86, 67.94, 68.12, 71.20, 71.51, 107.12, 114.23, 114.57, 115.43, 115.69, 120.74, 121.27, 127.28, 127.34, 127.65, 128.35, 134.48, 134.63, 135.10, 137.35, 137.52, 142.78, 147.21, 148.93, 160.28; IR (KBr) ν: 3387, 2923, 1735, 1511, 806, 736, 696 cm^{-1}; HRMS calcd for $C_{119}H_{120}BrO_{14}$ [M + H$^+$] 1851.7856; found 1851.7886.

General procedure for the synthesis of dendritic alcohols **[G-*n*a]**-OH or **[G-*n*b]**-OH (***n*** = **1—3**) **10, 1, 14, 3**

A mixture of the dendritic bromide **[G-(*n* – 1)]**-Br (2.1 mol equiv.), 3-(3,4-dihydroxyphenyl)-propanol (**8**) or 3-(3,5-dihydroxyphenyl)-propanol (**13**) (1.0 mol equiv.), potassium carbonate (6.0 mol equiv.) and 18-crown-6 (0.1 mol equiv.) was refluxed in acetone. The reaction time required was 2, 3, and 4 d for n = **1** to **3** respectively. The reaction mixture was filtered through a pad of silica gel to remove the inorganic materials. After concentration of the filtrate *in vacuo*, the crude product was purified by silica gel column chromatography (EtOAc/hexane = 1/4).

[G-1]-OH (**10**) This compound was prepared as an oil from **9** and monomer **8** in 85% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.74—1.88 (m, 2H, CH_2), 2.03—2.09 (m, 4H, 2 × CH_2), 2.59 (t, 2H, CH_2), 2.71—2.78 (m, 4H, 2 × CH_2), 3.62 (t, J = 7.0 Hz, 2H, CH_2OH), 3.90—4.02 (m, 4H, 2 × CH_2), 5.00—5.11 (m, 8H, 4 × $PhCH_2O$), 6.69—6.85 (m, 9H, 9 × ArH), 7.28—7.40 (m, 20H, 20 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 31.01, 31.58, 34.29, 62.23, 67.94, 68.15, 71.25, 71.56, 114.30, 114.53, 115.49, 115.78, 120.66, 121.33, 127.30, 127.36, 127.67, 128.37, 134.86, 135.12, 137.36, 137.53, 147.24, 148.95; IR (KBr) ν: 3403, 2924, 1595, 1453, 1155, 697 cm^{-1}; HRMS calcd for $C_{55}H_{56}O_7Na$ [M + Na$^+$] 851.3918; found 851.3935.

[G-2a]-OH (**1**) This compound was prepared as an oil from **11** (**[G-1]**-Br) and monomer **8** in 82% yield. ^{1}H NMR ($CDCl_3$, 200 MHz,) δ: 1.76—1.84 (m, 2H,

CH_2), 1.96—2.10 (m, 12H, 6 × CH_2), 2.53—2.61 (m, 2H, CH_2), 2.68—2.78 (m, 12H, 6 × CH_2), 3.61 (t, J = 7.1 Hz, 2H, CH_2OH), 3.83—3.96 (m, 12H, 6 × CH_2), 5.00 (s, 8H, 4 × $PhCH_2O$), 5.06 (s, 8H, 4 × $PhCH_2O$), 6.66—6.94 (m, 21H, 21 × ArH), 7.26—7.39 (m, 40H, 40 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 29.81, 30.49, 30.98, 32.14, 32.36, 63.30, 66.74, 69.99, 99.10, 99.60, 99.69, 107.20, 107.37, 107.79, 127.11, 127.51, 127.91, 128.12, 128.51, 136.91, 143.75, 143.91, 156.75, 159.95, 160.19, 160.33, 171.21; IR (KBr) ν: 3437, 2932, 1595, 1452, 1156 cm^{-1}; HRMS calcd for $C_{119}H_{120}O_{15}Na$ [M + Na^+] 1811.8519; found 1811.8554.

[G-2b]-OH **(14)** This compound was prepared as an oil from **11** (**[G-1]**-Br) and monomer **13** in 78% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.88 (t, J = 7.1 Hz, 2H, CH_2), 2.06—2.09 (m, 12H, 6 × CH_2), 2.60—2.78 (m, 14H, 7 × CH_2), 3.66 (t, J = 7.1 Hz, 2H, CH_2OH), 3.94—3.97 (m, 12H, 6 × CH_2), 5.05—5.11 (m, 16H, 8 × $PhCH_2O$), 6.36—6.40 (m, 3H, 3 × ArH), 6.73—6.89 (m, 18H, 18 × ArH), 7.33—7.44 (m, 40H, 40 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 30.99, 31.55, 33.92, 62.15, 66.76, 67.90, 68.09, 71.17, 71.47, 106.96, 114.20, 114.55, 115.39, 115.65, 120.72, 121.24, 127.25, 127.32, 127.63, 128.33, 134.59, 135.07, 137.31, 137.48, 144.15, 147.18, 148.89, 160.17; IR (KBr) ν: 3457, 2928, 1735, 1594, 1158, 737, 697 cm^{-1}; HRMS calcd for $C_{119}H_{120}O_{15}Na$ [M + Na^+] 1811.8519; found 1811.8554.

[G-3b]-OH **(3)** This compound was prepared as an oil from **15** (**[G-2b]**-Br) and monomer **13** in 75% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.75—1.85 (m, 2H, CH_2), 1.98—2.07 (m, 28H, 14 × CH_2), 2.52—2.62 (m, 2H, CH_2), 2.68—2.78 (m, 28H, 14 × CH_2), 3.62 (t, J = 7.2 Hz, 2H, C**H**$_2$OH), 3.84—3.95 (m, 28H, 14 × CH_2), 5.00 (s, 16H, 8 × $PhCH_2O$), 5.06 (s, 16H, 8 × $PhCH_2O$), 6.35—6.50 (m, 9H, 9 × ArH), 6.60—7.00 (m, 36H, 36 × ArH), 7.23—7.42 (m, 80H, 80 × PhH); ^{13}C NMR ($CDCl_3$, 50 MHz,) δ: 31.04, 31.60, 32.49, 66.88, 67.96, 68.13, 71.19, 71.50, 98.95, 107.08, 114.21, 114.55, 115.67, 120.73, 121.27, 127.28, 127.35, 127.65, 128.36, 134.53, 135.10, 137.34, 137.51, 147.20, 148.92, 160.23; IR (KBr) ν: 3497, 2933, 1591, 1161, 1022, 912, 808, 697 cm^{-1}; HRMS calcd for $C_{247}H_{248}O_{31}Na$ [M + Na^+] 3732.7722; found 3732.7686.

Spherical dendron **2** This compound was prepared as an oil from **11** (**[G-1]**-Br) and phloroglucinol in 79% yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.00—2.08 (b, 18H, 9 × CH_2), 2.55—2.59 (m, 6H, 3 × CH_2), 2.70—2.74 (m, 12H, 6 × CH_2), 3.86—3.93 (m, 12H, 6 × CH_2), 4.06—4.12 (m, 6H, 3 × CH_2), 5.01—5.10 (m, 24H, 12 × $PhCH_2O$), 6.40—6.46 (m, 3H, 3 × ArH), 6.71—6.88 (m, 27H, 27 × ArH), 7.26—7.40 (m, 60H, 60 × ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 31.60, 71.35, 71.55, 115.49, 115.71, 121.30, 127.31, 127.38, 127.68, 128.40, 135.17, 137.37, 137.54, 147.23, 148.96; IR (KBr) ν: 2927, 1586, 1134, 1023, 735, 696 cm^{-1}; HRMS calcd for $C_{171}H_{169}O_{21}$ [M + H^+] 2558.2151; found 2558.2170.

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(E0305065 PAN, B. F.; LU, Z. S.)