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Revised Supporting Information

3,4-Bis(hydroxymethyl)furan (2). To a cold (0 °C) suspension of $LiAlH_4$ (1.26 g, 33.2 mmol) in anhydrous ether (100 mL) was added with stirring dimethyl 3,4-furandicarboxylate (**1**) (2.70 g, 12.7 mmol). The reaction was warmed to rt while stirring (0.5 hr) and then quenched sequentially by slow addition of water (1.25 mL), 2N NaOH (1.25 mL), and water (3.75 mL). The reaction mixture was stirred for 45 min. and subsequently gravity filtered, dried ($MgSO_4$) and concentrated *in vacuo* yielding **2**[1] (1.33 g, 82%) as a colorless oil. ^{1}H NMR (400 MHz, acetone-d6) δ 7.42 (s, 2H), 4.51 (d, J = 5.6 Hz, 4H), 4.17 (t, J = 5.6 Hz, 2H).

3,4-Bis(benzyloxymethyl)furan (3a). A literature procedure was used with modifications as follows.[1] To a cold solution (0 °C) of 3,4-bis(hydroxymethyl)furan (**2**) (1.32 g, 10.3 mmol) in anhydrous DMF was added NaH (600 mg, 25.0 mmol) in three installments over 10 min. After 15 min., benzyl bromide (2.45 mL, 20.6 mmol) was added dropwise over 15 min. The reaction was warmed to rt, stirred under N_2, and monitored by TLC (SiO_2, 9:1 petroleum ether-ethyl acetate) until complete (15 hr). The reaction mixture was quenched with water (100 mL), and diluted with ethyl ether (100 mL). The organic layer was separated and the aqueous layer was extracted with ethyl ether (2 x 50 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated *in vacuo* to yield a crude yellow oil. Purification by flash chromatography (SiO_2, 9:1 petroleum ether-ethyl acetate) yielded **3a** (2.65 g, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.38-7.29 (m, 10 H), 4.53 (s, 4H), 4.48 (s, 4H).

[G-1]-DA dendron 5a. To a stirring solution of 3,4-bis(benzyloxymethyl)furan (**3a**) (1.13 g, 3.67 mmol) in 2:1 ethyl ether-ethyl acetate (15 mL) was added N-(4-hydroxyphenyl)maleimide (**4**) (694 mg, 3.67 mmol). The reaction stirred at rt until TLC (SiO_2, 3:2 petroleum ether-ethyl acetate) indicated consumption of starting materials (9 days). A white precipitate, which formed during the course of the reaction (2 days), was filtered and washed with copious amounts of ethyl ether. The precipitate was dried and the filtrate was concentrated *in vacuo* and purified by flash chromatography (SiO_2, 3:2 petroleum ether-ethyl acetate) yielding a 50/50 mixture of endo/exo isomers of [G-1]-DA dendron **5a** (941 mg) as a pale yellow glassy solid. The white precipitate isolated was determined to be pure exo isomer (432 mg) by ^{1}H NMR. The overall reaction produced a 66/33 percent mixture of exo/endo isomers of [G-1]-DA dendron **5a** (1.37 g, 75%). (exo isomer) mp 134-136 °C; ^{1}H NMR (exo isomer) (400 MHz, acetone-d6) δ 8.59 (s, 1H), 7.38-7.27 (m, 10H), 7.05 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.26 (s, 2H), 4.57 and 4.52 (AB pattern, J = 12 Hz, 4H), 4.36 and 4.32 (AB pattern, J = 12.8 Hz, 4H), 3.22 (s, 2H). ^{13}C NMR (exo isomer) (100 MHz, acetone-d6) δ 175.9, 156.0, 142.5, 137.4, 128.5, 128.0, 127.9, 127.7, 124.1, 116.1, 83.6, 72.8, 63.0, 48.2. Anal. Calcd for $C_{30}H_{27}NO_6$: C, 72.42; H, 5.47; N, 2.82. Found: C, 72.52; H, 5.42; N, 2.73.

[G-1]-DA Dendrimer 6a. A solution of exo [G-1]-DA dendron **5a** (202 mg, 0.406 mmol), THF (15 mL), and Et_3N (60 µL, 0.43 mmol) was stirred at rt for 10 min. 1,3,5-

Benzene tricarbonyltrichloride (36 mg, 0.14 mmol) was added to the stirring solution and a precipitate formed immediately. The reaction was stirred for 24 h after which time TLC (SiO_2, 3/2 ethyl acetate-petroleum ether) indicated consumption of starting materials. The crude reaction mixture was filtered and the resulting precipitate was washed with copious amounts of THF. The organic solvent was removed *in vacuo*, the solid residue was redissolved in methylene chloride (150 mL), washed with water (3 x 50 mL), dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by flash chromatography (SiO_2, 3/2 ethyl acetate-petroleum ether (250 mL), then acetone) and then precipitated from ethyl acetate-petroleum ether, yielding pure exo [G-1]-DA dendrimer **6a** (149 mg, 67%) as a colorless solid. mp 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 3H), 7.42-7.28 (s, 30H), 5.38 (s, 6H), 4.54 and 4.47 (AB pattern, *J* = 12 Hz, 12H), 4.19 (s, 12H), 3.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 162.8, 150.2, 142.5, 137.5, 136.2, 131.0, 129.7, 128.5, 127.9, 127.8, 127.7, 122.2, 83.8, 72.8, 63.0, 48.3. Anal. Calcd for $C_{99}H_{81}N_3O_{21}$: C, 72.12; H, 4.95; N, 2.55. Found: C, 71.92; H, 4.91; N, 2.53.

[G-2]-Furan dendron 3b. Following the procedure for **3a**, a solution of 3,4-bis(hydroxymethyl)furan (**2**) (246 mg, 1.92 mmol), [G-1]-Br (1.53 g, 3.83 mmol) anhydrous DMF (15 mL), and NaH (130 mg, 5.42 mmol) yielded [G-2]-furan **3b** (934 mg, 66%) as a colorless solid after purification by flash chromatography (SiO_2, 4:1 petroleum ether-ethyl acetate). mp 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 22H), 6.57 (d, *J* = 2.4 Hz, 4H), 6.52 (t, *J* = 2.4 Hz, 2H), 4.98 (s, 8H), 4.43 (s, 4H), 4.42 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 141.8, 140.6, 136.8, 128.5, 127.9, 127.5, 121.7, 106.6, 101.3, 71.7, 70.0, 62.4. Anal. Calcd for $C_{48}H_{44}O_7$: C, 78.67; H, 6.05. Found: C, 78.87; H, 6.21.

[G-2]-DA dendron 5b. A solution of [G-2]-furan dendron **3b** (884 mg, 1.20 mmol), ethyl acetate (20 mL), and N-(4-hydroxyphenyl)maleimide (**4**) (228 mg, 1.20 mmol) was stirred at rt until TLC (SiO_2, 7/3 petroleum ether-ethyl acetate) indicated consumption of starting materials (7 days). The crude reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2, 3/2 petroleum ether-ethyl acetate) to yield **5b** (832 mg, 77%) as a colorless solid. The ratio of exo/endo isomer was 66/33, respectively, as determined by ^{1}H NMR. Heating a sample neat for 48 hrs at 65 °C yielded pure exo isomer as determined by ^{1}H NMR. (exo isomer) mp 53-56 °C; ^{1}H NMR (exo isomer) (400 MHz, acetone-d6) δ 7.41 (m, 20 H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.58-6.53 (m, 6H), 6.02 (s (br), 1H), 5.36 (s, 2H), 5.01 (s, 8H), 4.46 and 4.41 (AB pattern, *J* = 12.0 Hz, 4H), 4.17 (s, 4H), 3.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 160.1, 156.2, 142.4, 139.9, 136.7, 128.5, 127.9 (two overlapping peaks), 127.5, 123.9, 116.1, 106.5, 101.5, 83.6, 72.6, 70.0, 63.0, 48.2. Anal. Calcd for $C_{58}H_{51}NO_{10}$: C, 75.56; H, 5.57; N, 1.52. Found: C, 75.28; H, 5.39; N, 1.47.

[G-2]-DA dendrimer 6b. Following the procedure for **6a**, a solution of [G-2]-DA dendron **5b** (570 mg, 0.618 mmol), Et_3N (90 µL, 0.65 mmol), 1,3,5-benzene tricarbonyltrichloride (56 mg, 0.21 mmol), and anhydrous THF (20 mL) yielded [G-2]

DA dendrimer **6b** (527 mg, 87%) as a colorless glass. Heating a sample neat for 48 hrs at 65 °C yielded pure exo isomer as determined by ^{1}H NMR. ^{1}H NMR (exo isomer) (400 MHz, $CDCl_3$) δ 9.24 (s, 3H), 7.44-7.28 (m, 72 H), 6.58-6.53 (m, 18H), 5.39 (s, 6H), 5.02 (s, 24 H), 4.47 and 4.42 (AB pattern, *J* = 12 Hz, 12H), 4.19 (s, 12H), 3.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 162.8, 160.1, 150.2, 142.4, 139.9, 136.8, 136.2, 131.1, 129.7, 128.5, 127.9, 127.8, 127.5, 122.2, 106.5, 101.5, 83.7, 72.7, 70.0, 63.0, 48.3. Anal. Calcd for $C_{183}H_{153}N_3O_{33}$: C, 75.22; H, 5.28; N, 1.44. Found: C, 74.86; H, 5.07; N, 1.36.

[G-3]-Furan dendron 3c. Following the procedure for **5a**, a solution of 3,4-bis-(hydroxymethyl)furan (**2**) (150 mg, 1.17 mmol), [G-2]-Br (1.87 g, 2.32 mmol), KH (122 mg, 3.05 mmol) and anhydrous THF (30 mL) yielded pure [G-3]-furan **5c** (1.36 g, 74%) as a colorless glass after purification by flash chromatography (SiO_2, 4:1 methylene chloride-petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 40 H), 6.63 (d, *J* = 2.4 Hz, 8H), 6.55 (d, *J* = 2.0 Hz, 4H), 6.53 (t, *J* = 2.4 Hz, 4H), 6.48 (t, *J* = 2.0 Hz, 2H), 4.96 (s, 16 H), 4.89 (s, 8H), 4.43 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.9, 141.9, 140.6, 139.3, 136.7, 128.5, 127.9, 127.5, 121.7, 106.5, 106.3, 101.5, 101.3, 71.8, 70.0, 69.8, 62.4. Anal. Calcd for $C_{104}H_{92}O_{15}$: C, 78.97; H, 5.86; Found: C, 79.37; H, 5.76.

[G-3]-DA dendron 5c. A solution of [G-3]-furan **5c** (1.28 g, 0.809 mmol), N-(4-hydroxyphenyl)maleimide (**4**) (154 mg, 0.814 mmol), and ethyl acetate (30 mL) were stirred and heated at 60 °C until TLC (SiO_2, 3:2 petroleum ether-ethyl acetate) indicated consumption of starting materials. Purification by flash chromatography (SiO_2, 3:2 petroleum ether-ethyl acetate) yielded **6c** (1.05 g, 73%) as a colorless glass. Heating a sample neat for 48 h at 65 °C yielded pure exo isomer as determined by ^{1}H NMR. ^{1}H NMR (exo isomer) (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 42H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 H, 2H), 6.67 (d, J = 2.4 Hz, 8H), 6.56 (d, *J* = 2.0 Hz, 4H), 6.54 (t, *J* = 2.2 Hz, 4H), 6.52 (t, *J* = 2.2 Hz, 2H), 5.36 (s, 2H), 5.28 (s (br), 1H), 4.97 (s, 16H) 4.94 (s, 8H), 4.46 and 4.40 (AB pattern, *J* = 12.4 Hz, 4H) 4.17 (s, 4H), 3.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 160.1, 160.0, 155.8, 142.4, 140.0, 139.2, 136.7, 128.5, 128.0, 127.9, 127.6, 124.2, 115.9, 106.3, 101.6, 101.5, 83.6, 72.6, 70.0, 69.9, 63.0, 48.3. Anal. Calcd for $C_{114}H_{99}NO_{18}$: C, 77.31; H, 5.63; N, 0.79; Found: C, 77.18; H, 5.64; N, 0.79.

[G-3]-DA dendrimer 6c. Following the procedure for **6a**, a solution of [G-3]-DA dendron (826 mg, 0.466 mmol), Et_3N (70 μL, 0.52 mmol), 1,3,5-benzene tricarbonyl-trichloride (42 mg, 0.16 mmol), and anhydrous THF (25 mL) yielded [G-3]- DA dendrimer **6c** (562 mg, 66%) as a colorless glass after purification by flash chromatography (SiO , 2:3 petroleum ether-ethyl acetate (400 mL), then ethyl acetate). Heating a sample neat for 24 h at 65 °C yielded pure exo isomer as determined by ^{1}H NMR. ^{1}H NMR (exo isomer) (400 MHz, $CDCl_3$) δ 9.18 (s, 3H), 7.37-7.25 (m, 132H), 6.64 (d, *J* = 2.4 Hz, 24H), 6.54 (d, *J* = 2.4 Hz, 12H), 6.52 (t, *J* = 2.2 Hz, 12H), 6.50 (t, J = 2.2 Hz, 6H), 5.37 (s, 6H), 4.96 (s, 48H), 4.92 (s, 24H), 4.46 and 4.40 (AB pattern, *J* = 12.4 Hz, 12H), 4.17 (s, 12H), 3.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 162.7, 160.0, 159.9, 150.0, 142.4, 139.9, 139.2, 136.7, 136.1, 130.9, 129.6, 128.5, 127.9, 127.7, 127.5, 122.1, 106.2, 101.5, 101.4, 83.7, 72.6, 70.0, 69.8, 63.0, 48.3. Anal. Calcd for $C_{351}H_{297}N_3O_{57}$: C, 77.08; H, 5.47; N, 0.79; Found: C, 76.68; H, 5.52; N, 0.87.

Molecular Weight Determination: Molecular weight data was obtained on a Polymer Labs GPC Model PL-GPC-210 with 2 columns (5 μM mixed-D, 200 - 400K MW) with a dual angle (15° and 90°) light scattering detector (Precision LSD PD-2040) in THF.

[G-1]-DA dendrimer 6a. MW = 1648.71 (calculated); Found: Mw = 1500, Mn = 1500, PD = 1.0.

[G-2]-DA dendrimer 6b. MW = 2922.17 (calculated); Found: Mw = 2600, Mn = 1800, PD = 1.4.

[G-3]-DA dendrimer 6c. MW = 5469.10 (calculated); Found: Mw = 6900, Mn = 6400, PD = 1.1.

References

(1) Meissner, R.; Garcias, X.; Mecozzi, S.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1997**, *119*, 77.