Supporting Information for:

Design and Synthesis of Non-Conjugated Monodendrons with Triarylamine Repeating Units

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Experimental Details

^{1}H-NMR spectra were recorded on a 400 MHz 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 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. Smaller molecules were also analyzed using an EI mass spectrometer integrated with a HP gas chromatograph. 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. Toluene was distilled over calcium hydride. All other chemicals obtained from commercial sources were used without further purification, unless otherwise mentioned.

Synthesis of 3,5-Dimethoxy-4'-methyl-3''-bromotriphenylamine (6): To a flame dried three neck round bottom flask were added $Pd_2(dba)_3$ (0.44 g, 0.48 mmol) and DPPF (0.39 g, 0.72

mmol) under N_2. Dry toluene (150 ml) was added followed by p-bromotoluene to the stirring reaction mixture. Then NaO^tBu (3.99 g, 40.0 mmol) and 3,5-dimethoxyaniline (5.00 g, 32.8 mmol) were added to the reaction mixture. The system was then purged with N_2 for 10 min. The mixture was heated at 90 °C for 5 h, at which time the reaction was complete as assessed by TLC. To the reaction mixture was added NaO^tBu (3.99 g, 40.0 mmol) and1,3-dibromobenzene (6.77 g, 40.0 mmol); and the mixture as stirred at 90 °C for 48 h. The mixture was then cooled and water was added. The aqueous layer was extracted with toluene and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 10% ethyl acetate in hexanes) to afford 4.96 g (38% yield) of product **6**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.18-7.14 (m, 3 H), 7.10-7.07 (m, 2 H), 7.02-6.99 (m, 2 H), 6.96-6.94 (m, 1 H), 6.24-6.23 (t, J = 2.2, 1 H), 6.18 (d, J = 2.2 Hz, 2 H), 3.68 (s, 6 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 161.7, 149.6, 148.9, 144.3, 134.0, 130.7, 130.2, 125.8, 124.8, 124.4, 122.2, 121.1, 102.7, 95.3, 54.7, 20.0. MS (*m/z*, r.i.)399 (M+, 99), 397 (100).

Synthesis of 3,5-Dihydroxy-4'-methyl-3''-bromotriphenyamine from 6: To a flame dried round bottom flask, **6** (5.00 g, 12.6 mmol) was added and dissolved in dry CH_2Cl_2 (80 ml). The reaction mixture was cooled to –78 °C. To the stirring solution, BBr_3 (4.0 ml, 43.8 mmol) was added under N_2. The solution was allowed to warm-up to room temperature and continued to stir for 65 h. Then, saturated sodium bicarbonate was slowly added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 6% acetone in CH_2Cl_2) to afford 4.20 g (91% yield) of 3,5-dihydroxy-4'-methyl-3''-bromotriphenyamine. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.20 (s, 2 H), 7.14-6.93 (bm, 8 H),

6.09 (b, 1 H), 6.01 (b, 2 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 159.2, 149.7, 149.0, 144.4, 133.9, 130.5, 130.1, 125.8, 124.8, 124.1, 122.1, 121.1, 102.8, 98.3, 20.0. MS (*m/z*, r.i.) 272 (34), 257 (40), 231 (65), 229 (100) 132 (86).

Synthesis of 3,5-Di(^{t}butyldimethylsilyl)-4'-methyl-3''-bromotriphenylamine (7): In a round bottom flask, 3,5-dihydroxy-4'-methyl-3''-bromotriphenylamine (4.13g, 11.2 mmol) was dissolved in a 1:1 mixture of CH_2Cl_2 and DMF (80 ml). To the reaction mixture, imidazole (4.24 g, 67.2 mmol) and TBS-Cl (10.13g, 67.2 mmol) were added. The reaction mixture was stirred under N_2 for 17 h. Water was added to the reaction mixture at the end of the 17 h period. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 5% CH_2Cl_2 in hexanes) to afford 5.99 g (90% yield) of product **7**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.07-7.03 (m, 3 H), 6.99-6.96 (m, 2 H), 6.89-6.87 (m, 2 H), 6.83-6.81 (m, 1 H), 6.02 (d, *J* = 2.1 Hz, 2 H), 5.95 (t, *J* = 2.1 Hz, 1 H), 2.17 (s, 3 H), 0.79 (s, 18 H), 0.01 (s, 12 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 201.6, 163.0, 154.0, 149.2, 138.1, 135.9, 135.3, 134.0, 130.6, 130.1, 128.6, 126.5, 118.9, 114.3, 112.9, 30.3, 25.2, 23.1. MS (*m/z*) 599.2 (M^+ calcd. for $C_{31}H_{44}BrNO_2Si_2$: 597.2).

Synthesis of 3,5-Di(^{t}butyldimethylsilyl)-4'-methyltriphenylamine-3''-carboxaldehyde (8): To a flame dried round bottom flask, **7** (6.00g, 10.1 mmol) was added. The solid was dissolved in dry THF (200 ml) under N_2. Once completely dissolved, the reaction mixture was cooled to –78 °C. To the stirring reaction mixture, 1.7 M solution of ^{t}BuLi (17.8 ml, 30.2 mmol) was added and allowed to stir for 15 min. This was followed by the addition of dry DMF (2.57 ml, 35.2 mmol) and allowed to stir for 30 min. The reaction mixture was then removed from the bath and allowed to stir at room temperature for 21 h. Then, water was used to quench any

unreacted ^{t}BuLi. The aqueous layer was extracted with ether and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 30 % CH_2Cl_2 in hexanes) to afford 4.94 g (90% yield) of product **8**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.81 (s, 1 H), 7.41-7.33 (m, 3 H), 7.19-7.17 (m, 1 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.04 (d, *J* = 2.1 Hz, 2 H), 5.96 (t, *J* = 2.1 Hz, 1 H), 2.19 (s, 3 H), 0.79 (s, 18 H), 0.00 (s, 12 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.6, 197.0, 162.4, 154.2, 154.0, 135.4, 135.2, 133.8, 130.8, 128.6, 127.7, 114.1, 112.4, 30.3, 25.2, 23.4, 0.0. MS (*m/z*) 548.3 (M^+ calcd. for $C_{32}H_{45}NO_3Si_2$: 547.3).

Synthesis of 3,5-Di(^{t}butyldimethylsilyl)-4'-methyl-3''-hydroxymethyltriphenylamine from 8: In a round bottom flask, **8** (4.89g, 8.98 mmol) was dissolved in ethanol (150 ml). To this solution, $NaBH_4$ (0.41 g, 10.8 mmol) was added and allowed to stir under N_2. After 2 h, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 70% CH_2Cl_2 in hexanes) to afford 3.61 g (74% yield) of 3,5-di(^{t}butyldimethylsilyl)-4'-methyl-3''-hydroxymethyltriphenylamine. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.12-7.08 (m, 1 H), 7.00-6.97 (m, 3 H), 6.90 (d, *J* = 7.4 Hz, 1 H), 6.86-6.84 (m, 2 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 5.99-5.98 (t, *J* = 2.0, 1 H), 5.89-5.88 (m, 2 H), 4.43 (d, *J* = 5.9 Hz, 1 H), 4.09-4.05 (m, 2 H), 2.16 (s, 3 H), 0.79 (s, 18 H), 0.00 (s, 12 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 162.1, 154.8, 152.7, 150.1, 148.9, 138.1, 135.0, 134.0, 130.3, 127.8, 127.4, 126.2, 113.1, 111.1, 68.6, 30.3, 25.1, 23.0, 0.0. MS (*m/z*) 550.2 (M^+ calcd. for $C_{32}H_{47}NO_3Si_2$: 549.3).

Synthesis of 3,5-Dihydroxy-4'-methyl-3''-hydroxymethyltriphenylamine (1): In a round bottom flask, 3,5-di(^{t}butyldimethylsilyl)-4'-methyl-3''-hydroxymethyltriphenylamine (2.43g,

4.45 mmol) was dissolved in 30 ml tetrabutylammonium fluoride (1.0 M solution in THF). The reaction mixture was allowed to stir for 20 h, followed by the addition of water. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 40% acetone in hexanes) to afford 1.40 g (97% yield) of product **1**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.10 (s, 2 H), 7.22 (t, *J* = 7.8 Hz, 1 H), 7.12-7.10 (m, 3 H), 7.0-6.90 (m, 4 H), 6.03 (t, *J* = 2.1 Hz, 1 H), 5.98 (d, *J* = 2.1, 2 H), 4.55 (s, 2 H), 4.30 (s, 1 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 159.2, 150.2, 148.2, 145.6, 143.8, 132.9, 130.0, 129.1, 125.4, 123.0, 122.6, 121.1, 102.0, 97.3, 63.8, 20.2. MS (*m/z*) 322.2 (M^+ calcd. for $C_{20}H_{14}NO_3$: 321.1).

Synthesis of 3,5-Dimethoxy-4'-methyltriphenylamine-3''-carboxaldehyde from 6: To a flame dried round bottom flask, **6** (2.0 g, 5.0 mmol) was added and dissolved in dry THF (50 ml). Once completely dissolved, the reaction mixture was cooled to –78 °C under N_2. To the reaction mixture, 1.7 M solution of ^{t}BuLi (8.9 ml, 15 mmol) was added and allowed to stir for 15 min. This was followed by the addition of dry DMF (1.3 ml, 18.0 mmol) and allowed to stir for 30 min. The reaction mixture was then removed from the bath and allowed to stir at room temperature for 20 h. Then, water was added to quench any unreacted ^{t}BuLi. The aqueous layer was extracted with ether and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 20 % ethyl acetate in hexanes) to afford 1.42 g (81% yield) of 3,5-dimethoxy-4'-methyltriphenylamine-3''-carboxaldehyde. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.92 (s, 1 H), 7.51-7.43 (m, 3 H), 7.30-7.27 (m, 1 H), 7.17-7.14 (m, 2 H), 7.03-7.01 (m, 2 H), 6.24-6.23 (t, *J* = 2.2 Hz, 1 H), 6.18 (d, *J* = 2.2 Hz, 2 H), 3.67 (s, 6 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 191.9, 161.7,

149.1, 148.8, 144.4, 137.9, 133.9, 130.2, 129.8, 128.1, 125.6, 123.2, 122.2, 102.5, 95.2, 54.7, 20.0. MS (*m/z*, r.i.) 347 (M, 100), 330 (24), 318 (30), 288 (23).

Synthesis of 3,5-Dimethoxy-4'-methyl-3''-hydroxymethyltriphenylamine (2): In a round bottom flask, 3,5-dimethoxy-4'-methyltriphenylamine-3''-carboxaldehyde (1.41 g, 4.1 mmol) was dissolved in ethanol (50 ml). To this solution, $NaBH_4$ (0.18 g, 4.9 mmol) was added and allowed to stir under N_2 for 8 h. Then, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 2% ethyl acetate in CH_2Cl_2) to afford 1.35 g (95% yield) of product **2**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.22 (t, *J* = 7.8 Hz, 1 H), 7.13 (bd, 3 H), 7.11-6.97 (m, 3 H), 6.92-6.90 (bm, 1 H), 6.15 (t, *J* = 2.1 Hz, 1 H), 6.12 (d, *J* = 2.3, 2 H), 4.55 (d, *J* = 5.9 Hz, 2 H), 4.22 (t, *J* = 5.8 Hz, 1 H), 3.66 (s, 6 H), 2.26 (s, 3 H). ^{13}C NMR (100 MHz, CD3COCD3): δ 161.7, 150.1, 148.0, 146.0, 144.1, 133.2, 130.1, 129.1, 125.4, 122.9, 122.5, 121.2, 101.6, 94.1, 63.8, 54.6, 20.2. MS (*m/z*, r.i.) 349 (M, 100), 318 (30), 288 (25).

Synthesis of 3,5-Dimethoxy-4'-methyl-3''-bromomethyltriphenylamine (9): In a round bottom flask, **2** (0.75 g, 2.2 mmol) was dissolved in dry THF (12 ml). To the stirring reaction mixture, CBr_4 (1.03 g, 3.1 mmol) and Ph_3P (0.82 g, 3.1 mmol) were added under N_2. The reaction was monitored until completion by TLC. If the reaction was not complete, additional 0.2 equivalents of CBr_4 and Ph_3P were added. Once the reaction was complete, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 10% ethyl acetate in hexanes) to afford 0.63 g, (69% yield) of product **9**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.26-7.21 (m, 1 H), 7.16-7.13 (m, 3 H), 7.09-

7.06 (m, 1 H), 7.01-6.98 (m, 2 H), 6.95-6.92 (m, 1 H), 4.56 (s, 2 H), 3.65 (s, 6 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 162.3, 149.6, 148.7, 145.8, 139.6, 133.7, 130.3, 129.7, 129.6, 125.7, 124.1, 123.5, 123.3, 54.9, 33.7, 33.6, 20.3. MS (*m/z*, r.i.) 333 (M-Br, 100), 334 (27), 332 (18).

Synthesis of 3-Mer-OH, 10: In a round bottom flask, **1** (200 mg, 0.62 mmol) and **9** (513 mg, 1.25 mmol) were dissolved in dry THF (15 ml). To the reaction mixture, 18-crown-6 (99 mg, 0.37 mmol) and K_2CO_3 (258 mg, 1.87 mmol) were added. The solution was refluxed for 20 h under N_2. After the 20 h period, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 30% ethyl acetate in hexanes) to afford 385 mg (63% yield) of product **10**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.26-7.18 (m, 3 H), 7.11-7.08 (m, 9 H), 7.02-6.89 (m, 12 H), 6.23 (t, *J* = 2.1 Hz, 3 H), 6.16-6.11 (m, 6 H), 4.89 (s, 4 H), 4.54 (d, *J* = 5.7 Hz, 2 H), 4.18 (t, *J* = 5.8 Hz, 1 H), 3.63 (s, 12 H), 2.27 (s, 9 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 161.7, 160.6, 150.1, 149.9, 148.2, 148.0, 147.8, 145.9, 145.1, 144.5, 144.1, 142.0, 138.7, 133.4, 130.2, 129.9, 129.5, 129.2, 125.5, 125.4, 123.5, 123.2, 122.8, 122.5, 121.8, 121.4, 102.6, 101.9, 94.6, 69.6, 63.8, 54.8, 20.2. MS (*m/z*) 983.9 (M^+ calcd. for $C_{64}H_{61}N_3O_7$: 983.5).

Synthesis of 3-Mer-Br from 10: In a round bottom flask, **10** (337 mg, 0.342 mmol) was dissolved in dry THF (20 ml). To the stirring reaction mixture, CBr_4 (113 mg, 0.342 mmol) and Ph_3P (90 mg, 0.342 mmol) were added under N_2. The reaction was monitored until completion by TLC. If the reaction was not complete, additional 0.2 equivalents of CBr_4 and Ph_3P were added. Upon completion of the reaction, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure

to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 20% ethyl acetate in hexanes) to afford 296 mg (83% yield) of 3-mer-Br. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.23-6.90 (m, 24 H), 4.89 (s, 4 H), 4.53-4.52 (m, 2 H), 3.62 (s, 12 H), 2.30-2.13 (m, 9 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 161.4,_ 148.2, 145.1, 138.7, 133.4, 130.2, 125.5, 123.2, 69.6, 54.9, 33.7, 20.4. Overlap of some ^{13}C NMR peaks was assumed. MS (*m/z*) 1046.9 (M^+ calcd. for $C_{64}H_{60}BrN_3O_6$: 1045.4).

Synthesis of 7-Mer-OH, 11: In a round bottom flask, **1** (75 mg, 0.23 mmol) and 3-mer-Br (540 mg, 0.52 mmol) were dissolved in dry THF (40 ml). To the reaction mixture, 18-crown-6 (93 mg, 0.35 mmol) and K_2CO_3 (260 mg, 1.88 mmol) were added. The solution was refluxed for 24 h under N_2. Then, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 35% ethyl acetate in hexanes) to afford 370 mg (70% yield) of product **11**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.23-6.89 (m, 56 H), 6.20-6.10 (m, 21 H), 4.96-4.78 (m, 12 H), 4.56 (d, J = 5.9 Hz, 2 H), 3.58 (s, 24 H), 2.23 (2, 21 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 167.9, 161.7, 160.6, 149.8, 148.8, 148.1, 145.1, 145.0, 144.9, 138.7, 133.5, 133.3, 130.2, 130.0, 129.5, 125.5, 123.2, 123.1, 122.8, 121.8, 102.9, 101.9, 94.6, 69.6, 54.8, 20.3. Overlap of some ^{13}C NMR peaks was assumed. MS (*m/z*) 2257.2 (M^+ calcd. for $C_{148}H_{137}N_7O_{15}$: 2252.0).

Synthesis of 7-Mer-Br from 11: In a round bottom flask, **11** (270 mg, 0.120 mmol) was dissolved in dry THF (40 ml). To the stirring reaction mixture, CBr_4 (636 mg, 1.92 mmol) and Ph_3P (503 mg, 1.92 mmol) were added under N_2. The reaction was monitored until completion by TLC. If the reaction was not complete, additional 0.2 equivalents of CBr_4 and Ph_3P were added. Water was added to the reaction mixture upon completion. The aqueous layer was

extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 30% ethyl acetate in hexanes) to afford 130 mg (47% yield) of 7-mer-Br. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.08-6.73 (m, 56 H), 6.27-5.97 (m, 21 H), 4.78 (s, 2 H), 4.72-4.63 (m, 12 H), 3.46 (s, 24 H), 2.09 (s, 21 H). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 161.7, 160.8, 160.6, 149.8, 148.1, 145.1, 138.7, 133.3, 130.2, 129.9, 129.5, 125.5, 122.8, 102.9, 102.6, 101.9, 94.6, 69.6, 69.4, 69.3, 54.8, 20.3. Overlap of some ^{13}C NMR peaks was assumed. MS (*m/z*) 2311.9 (M^+ calcd. for $C_{148}H_{136}BrN_7O_{14}$: 2313.9).

Synthesis of 15-Mer-OH, 12: In a round bottom flask, **1** (7 mg, 0.023 mmol) and 7-mer-Br (110 mg, 0.047 mmol) were dissolved in dry THF (20 ml). To the stirring solution, 18-crown-6 (9 mg, 0.034 mmol) and K_2CO_3 (25 mg, 0,18 mmol) were added. The solution was refluxed for 24 h under N_2. After the 24 h period, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 40% ethyl acetate in hexanes) to afford 40 mg (37% yield) of product **12**. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.02-6.69 (m, 120 H), 6.03-5.97 (m, 45 H), 4.61-4.54 (m, 28 H), 4.35 (d, J = 5.7 Hz, 2 H), 3.43 (s, 48 H), 2.17-2.05 (m, 45 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3,160.5, 149.8, 148.0, 144.8, 137.9, 133.2, 130.1, 129.4, 125.5, 123.5, 123.1, 121.8, 102.9, 101.9, 96.1, 94.8, 70.0, 55.4, 21.0. Overlap of some ^{13}C NMR peaks was assumed. MS (*m/z*) 967.36 (M^+/5 calcd. for $C_{316}H_{289}N_{15}O_{31}$: 957.8).