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Supporting Information

Dendrimers with 9-Phenylcarbazole Dendrons and Tetraphenylsilane Core: Synthesis, Photophysics, and Electrochemical Behavior

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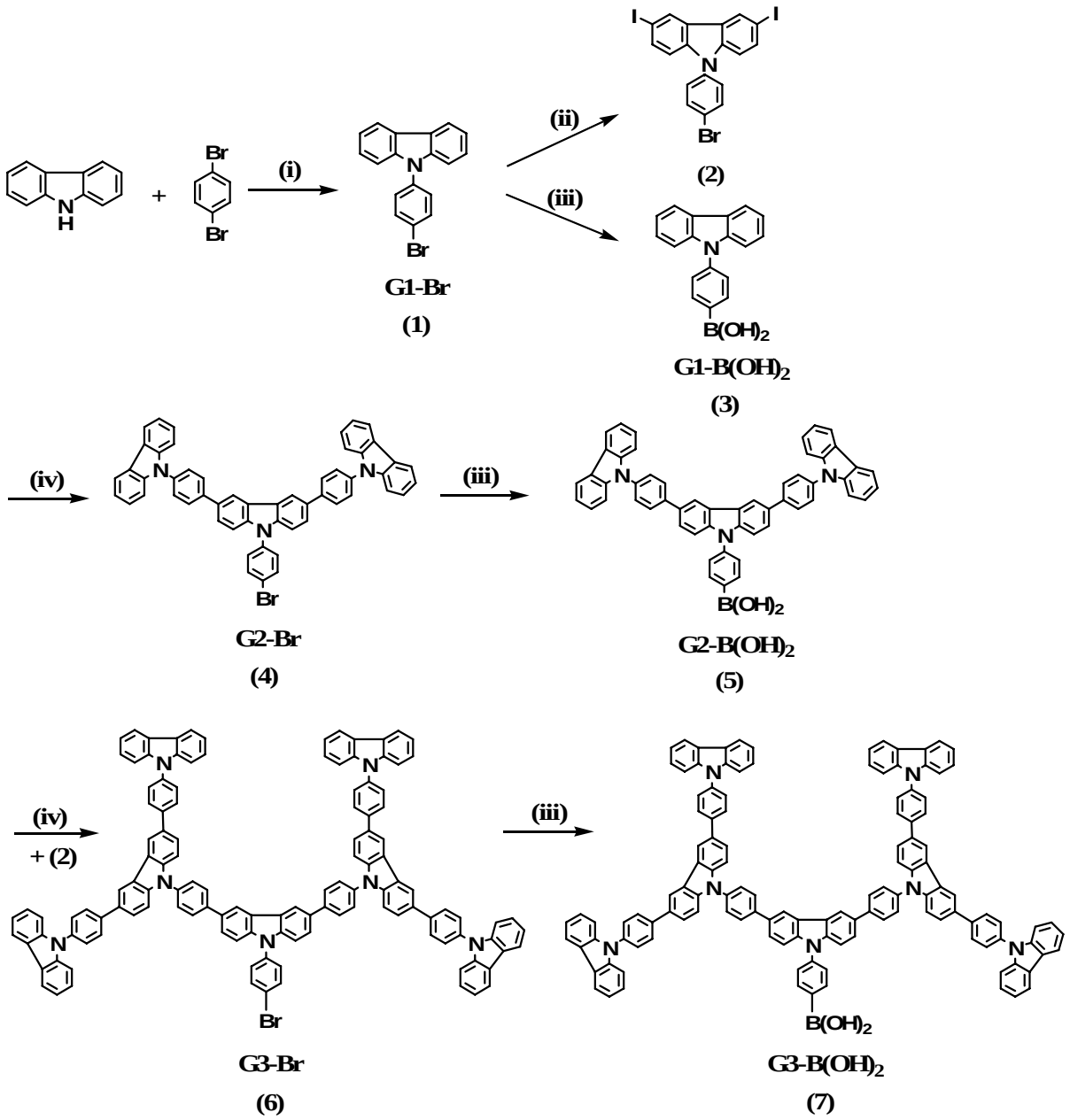

Scheme 1. Synthesis of 9-phenylcarbazole based dendrons and endrimers[a]

[a] Reagents and conditions: (i) CuI, K_2CO_3, 18-Crown-6, DMPU, 170 °C, 11h; (ii) KI, KIO_3, acetic acid, 80 °C, 4h; (iii) (a) n-BuLi, THF, -78 °C, 1h, (b) $(i\text{-PrO})_3B$, -78 °C, 1h; (iv) $Pd(PPh_3)_4$, K_2CO_3, Toluene, 50 °C, overnight.

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Synthesis procedures for G1-G3 dendrons:

Synthesis of 9-(4-bromophenyl)-9H-carbazole G1-Br (1). 9-(4-Bromophenyl)-9H-carbazole was prepared to a method with some modification.[1] A mixture of CuI (1.14 g, 6 mmol), 18-Crown-6 (0.53 g, 2 mmol), K_2CO_3 (16.6 g, 120 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (2 mL), dibromobenzene (14.2 g, 60 mmol) and carbazole (10 g, 60 mmol) was heated at 170 °C for 11 h under nitrogen. The cooled mixture was quenched with 1 N HCl, the precipitate was filtered and washed with NH_3H_2O and water. The residual solid was purified with column chromatography using hexane as eluant to afford the desired product as a white solid (11.7 g, 71% yield) ^{1}HNMR (400 MHz, CDCl3): δ (ppm) = 8.13 (d, 2 H, J = 7.6 Hz)， 7.72 (d, 2 H, J = 8.8 Hz), 7.45 (d, 2 H, J = 8.8 Hz), 7.41–7.37 (dt, 4H, J_1 = 6.8 Hz, J_2 = 6.8 Hz), 7.30 (t, 2H, J = 6.6 Hz). Elemental analysis: calculated for $C_{18}H_{12}BrN$, C 67.10%, H 3.75%, N 4.35%; found, C 67.21%, H 3.70%, N 4.29%.

Synthesis of 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole (2). 9-(4-Bromophenyl)-3,6-diiodo-9H-carbazole was prepared in a modified method given in the literature.[2] 4-Carbazolyl-1-bromobenzene (0.65 g, 2 mmol) was dissolved in boiling glacial acetic acid (40 mL) and potassium iodide (0.66 g, 3.96 mmol) and potassium iodate (0.96 g, 4.5 mmol) were added. The solution was refluxed at 80 °C for 4 h. Then the mixture was poured into water, the precipitate was filtered and washed with water. A purified product was obtained as a white solid by recrystallization from chloroform/ethanol. (3.64 g, 85% yield). ^{1}HNMR (400 MHz, CDCl3): δ (ppm) =8.38 (s, 2H), 7.74(d, 2H, J = 8.8 Hz), 7.67(d, 2H, J = 8.8 Hz), 7.37(d, 2H, J = 8.2 Hz), 7.11(d, 2H, J = 8.8 Hz). Elemental analysis: calculated for $C_{18}H_{10}BrI_2N$, C 37.66%, H 1.76%, N 2.44%; found, C 37.56%, H 1.80%, N 2.40%.

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Synthesis of 4-carbazolyl-1-bromophenylboronic acid G1-B(OH)$_2$ (3). 4-Carbazolyl-1-bromophenylboronic Acid was carried out in reference to the procedure described previously.[3] Using a syringe, 7.2 mL of 2.5 M *n*-BuLi (18 mmol) in hexane was added dropwise to a solution of 9-(4-bromophenyl)-9H-carbazole (4.3 g, 15 mmol) in THF (40 mL) at -78 °C with stirring. After stirring for 1h, and triisopropyl borate (32 mL, 18 mmol) was added using a syringe. The reaction mixture was stirred at -78 °C for additional 1 h and then was gradually warmed to room temperature and stirred overnight. The clear solution was diluted with ether (100 mL) and washed with water. The organic layer was dried over $MgSO_4$, and the solvents were concentrated below 40 °C using a rotary evaporator. Flash column chromatography of the residue over silica gel with a mixture of hexane and ethyl acetate mixture as a gradient eluent to afford a white solid with an isolated yield of 87% (3.3 g). ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.56 (d, 2H, *J* = 8.0 Hz), 8.18 (d, 2H, *J* = 7.6 Hz), 7.80 (d, 2H, *J* = 8.0 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 7.46 (t, 2H, *J* = 7.2 Hz), 7.33 (t, 2H, *J* = 7.6 Hz). Elemental analysis: calculated for $C_{18}H_{14}BNO_2$, C 75.30%, H 4.91%, N 4.88%; found, C 75.36%, H 4.82%, N 4.81%.

9,9'-((9-(4-bromophenyl)-9H-carbazole-3,6-diyl)bis(4,1-phenylene))bis(9H-carbazole), G2-Br (4). 9,9'-((9-(4-Bromophenyl)-9H-carbazole-3,6-diyl)bis(4,1-phenylene))bis(9H-carbazole) was carried out in a method briefly given in the literature.[3] To a mixture of G1-B(OH)$_2$ (495 mg, 1.72 mmol), 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole (449 mg, 0.78 mmol), and tetrakis(triphenylphosphine)-palladium(0)(18 mg) in a 100 mL-round-bottom flask equipped with a magnetic stirrer, a N_2 purge, and a reflux condenser was added toluene (30 mL) and 2 M K_2CO_3 (4 mL). The solution mixture was heated to 50 °C for overnight. The reaction mixture was poured

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into water and then extracted with chloroform. The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether/$CHCl_2$ as eluent affording 571 mg (91%) of an orange solid. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.55 (s, 2H), 8.17 (d, 4H, J = 8.0 Hz), 7.97 (d, 4H, J = 8.0 Hz), 7.82 (m, 4H), 7.70 (d, 4H, J = 8.4 Hz), 7.57 (m, 4H), 7.52 (d, 4H, J = 8.8 Hz), 7.44 (t, 4H, J = 7.2 Hz), 7.30 (t, 4H, J = 7.2 Hz). Elemental analysis: calculated for $C_{54}H_{34}BrN_3$, C 80.59%, H 4.26%, N 5.22%; found, C 80.51%, H 4.33%, N 5.14%.

Synthesis of 4-[3',6'-di(4'-carbazolylbenzene-1'-yl)carbazolyl] phenylboronic acid, G2-B(OH)$_2$ (5). This compound was prepared according to the procedure for the synthesis of G1-B(OH)$_2$, using G2-Br, in 54% yield. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.99 (s, 2H), 8.17 (m, 6H), 8.20 (m, 6H), 7.82 (d, 2H, *J* = 7.6 Hz), 7.83 (d, 4H, *J* = 8.8 Hz), 7.78 (d, 2H, *J* = 8.0 Hz), 7.66 (d, 2H, *J* = 7.6 Hz), 7.56-7.50 (m, 8H), 7.37 (t, 4H, *J* = 6.4 Hz). Elemental analysis: calculated for $C_{54}H_{36}BN_3O_2$, C 84.26%, H 4.71%, N 5.46%; found, C 84.20%, H 4.77%, N 5.53%.

Synthesis of 9,9',9'',9'''-((9,9'-((9-(4-bromophenyl)-9H-carbazole-3,6-diyl)bis(4,1-phenylene))bis(9H-carbazole-9,6,3-triyl))tetrakis(benzene-4,1-diyl))tetrakis(9H-carbazole), G3-Br (6). This compound was prepared according to the procedure for the synthesis of G2-Br in 69% yield from the intermediate G2-B(OH)$_2$ and 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.62 (s, 2H), 8.59 (s, 4H), 8.17 (d, 8H, *J* = 8.0 Hz), 8.06 (d, 4H, *J* = 8.4 Hz) , 7.99 (d, 8H, *J* = 8.0 Hz), 7.88-7.81 (m, 12H), 7.71-7.68 (m, 12H), 7.59 (d, 4H, *J* = 8.8Hz), 7.52 (d, 8H, *J* = 8.0 Hz), 7.45 (t, 8H, *J* = 7.6 Hz), 7.32 (t, 8H, *J* = 7.2 Hz). Elemental analysis: calculated for $C_{126}H_{78}BrN_7$, C 85.50%, H 4.44%, N 5.54%; found, C 85.45%, H 4.41%, N 5.58%.

Synthesis of

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4-(3,6-bis(4-(3,6-bis(4-(9H-carbazol-9-yl)phenyl)-9H-carbazol-9-yl)phenyl)-9H-carbazol-9-yl) phenylboronic acid, G3-B(OH)$_2$ (7). This compound was prepared according to the procedure for the synthesis of G1-B(OH)$_2$, using G2-Br, in 50% yield. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.62 (s, 2H), 8.59 (s, 4H), 8.17 (d, 8H, *J* = 8.0 Hz), 8.07 (d, 4H, *J* = 8.4 Hz) , 7.99 (d, 8H, *J* = 8.0 Hz), 7.87-7.76 (m, 12H), 7.71-7.63 (m, 16H), 7.52 (d, 8H, *J* = 8.4Hz), 7.45 (t, 8H, *J* = 7.6 Hz), 7.31 (t, 8H, *J* = 7.6 Hz). Elemental analysis: calculated for $C_{126}H_{80}BN_7O_2$, C 87.23%, H 4.65%, N 5.65%; found, C 87.19%, H 4.68%, N 5.61%.

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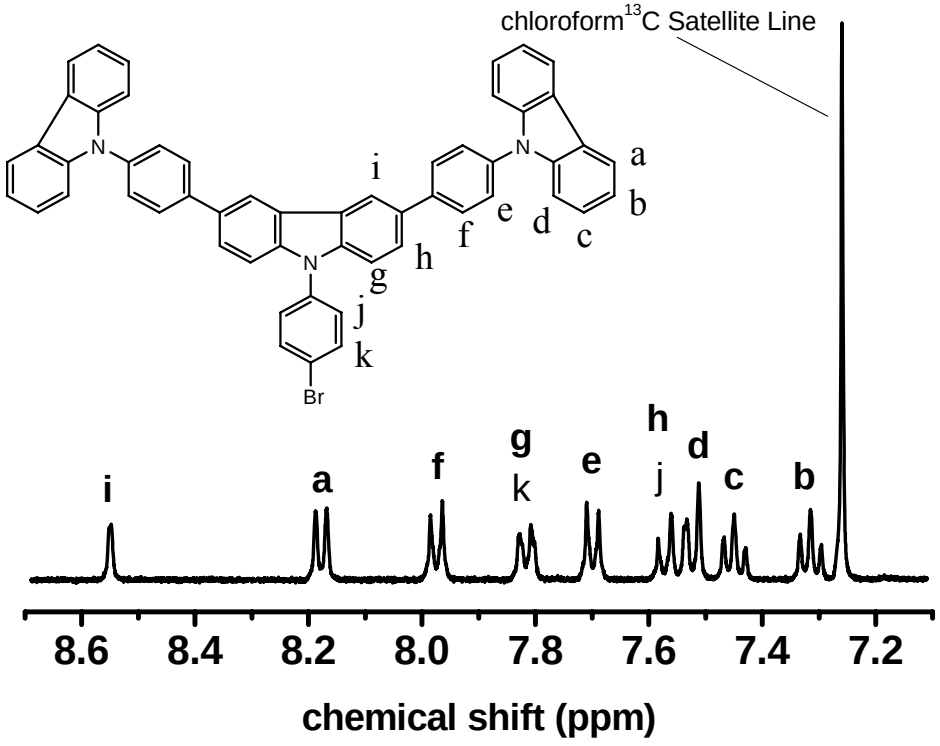

Figure 1S. ^{1}H NMR spectrum of G2-Br in chloroform-d.

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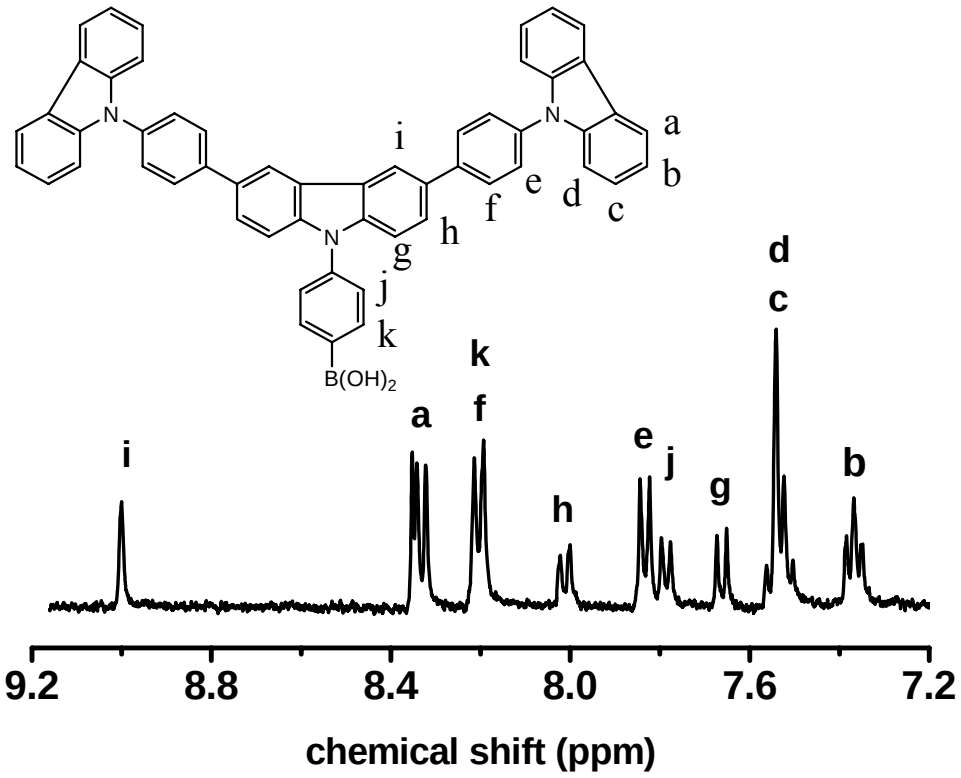

Figure 2S. ^{1}H NMR spectrum of G2-B(OH)$_2$ in chloroform-d.

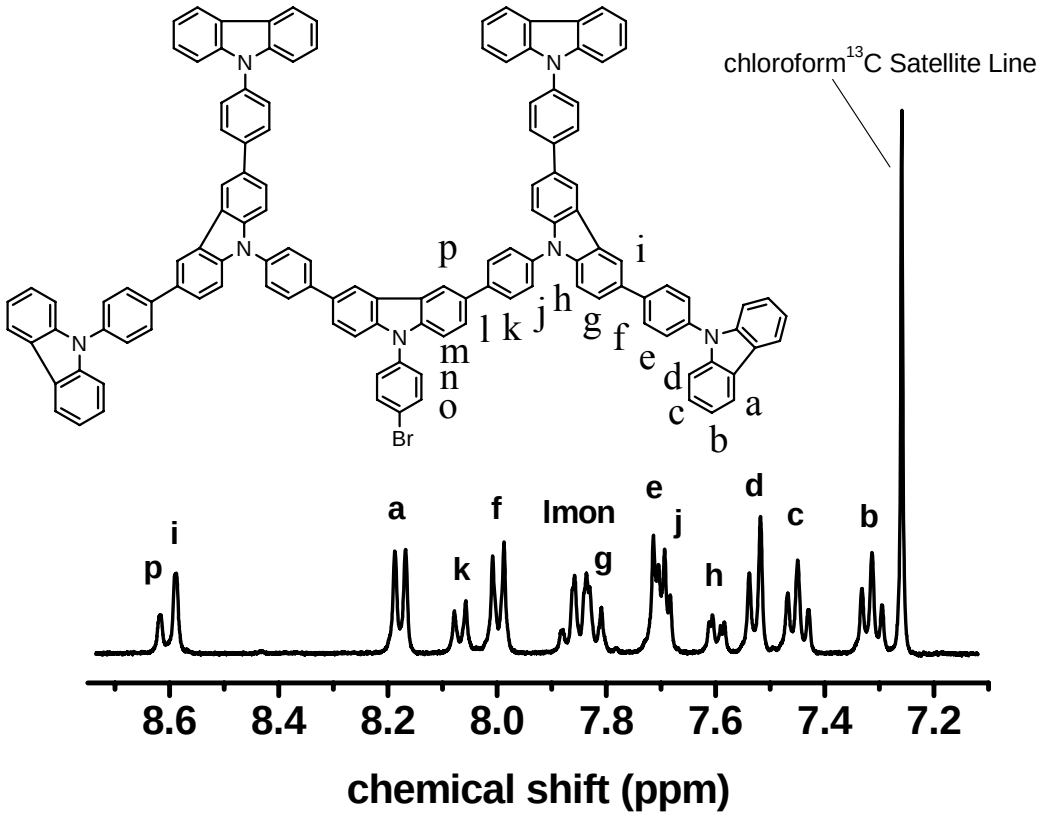

Figure 3S. ^{1}H NMR spectrum of G3-Br in chloroform-d.

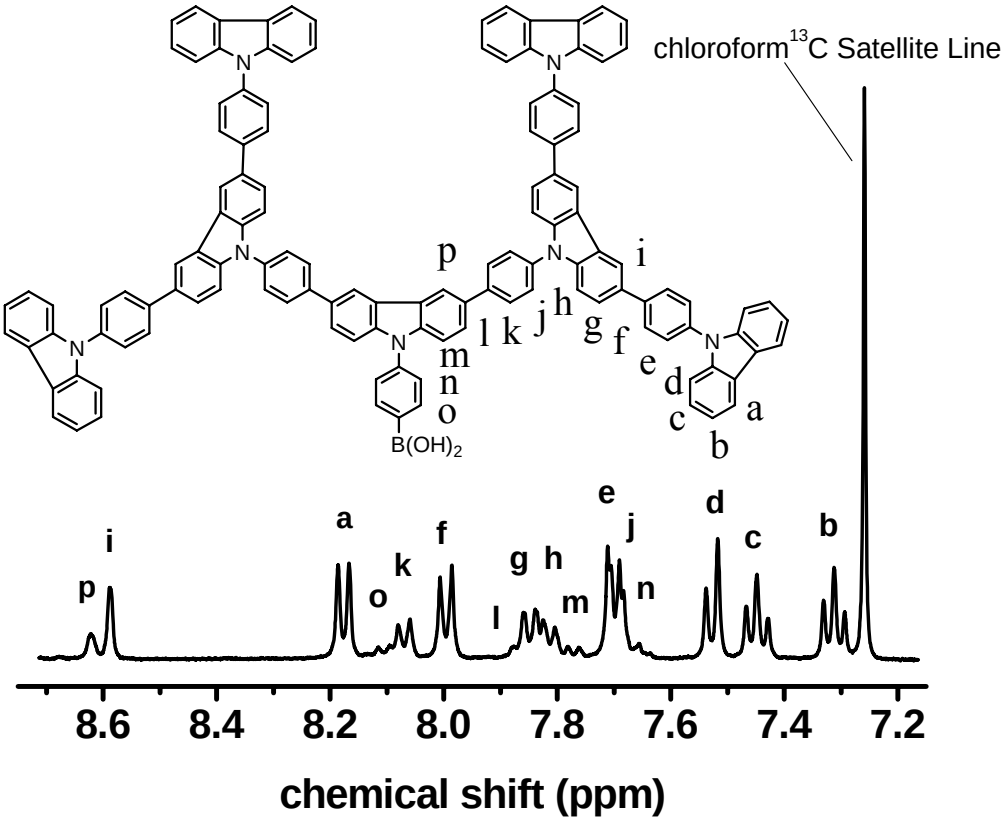

Figure 4S. ^{1}H NMR spectrum of G3-B(OH)$_2$ in chloroform-d.

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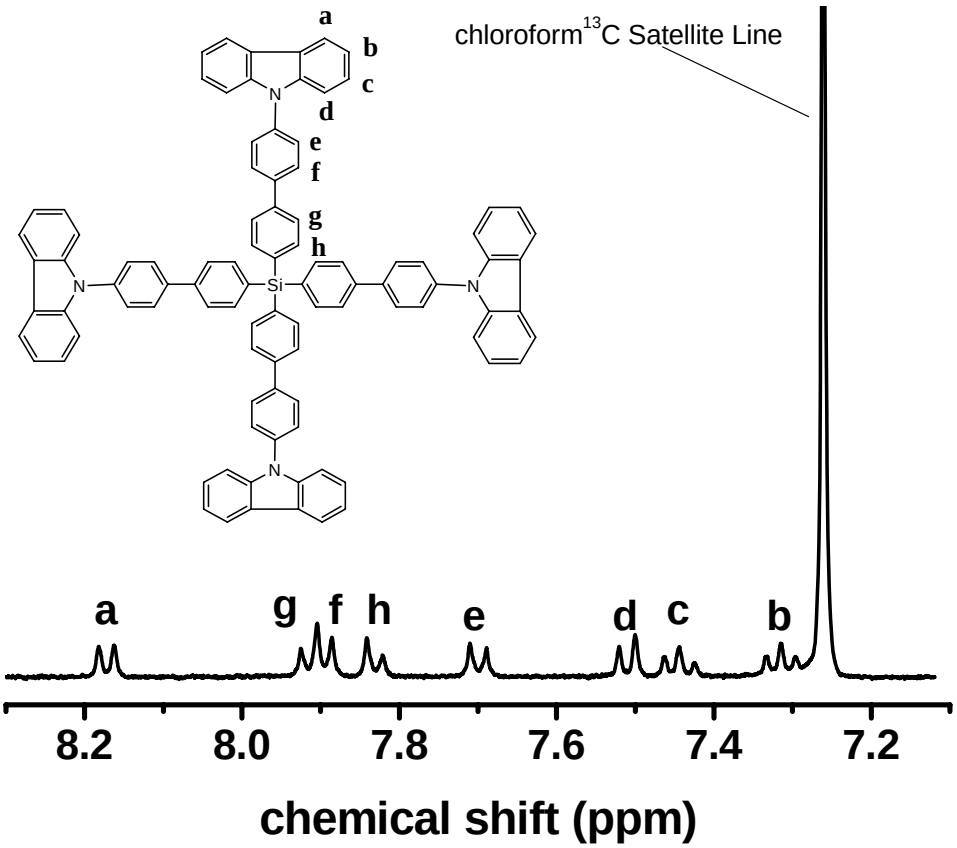

Figure 5S. ^{1}H NMR spectrum of **G1** in chloroform-d.

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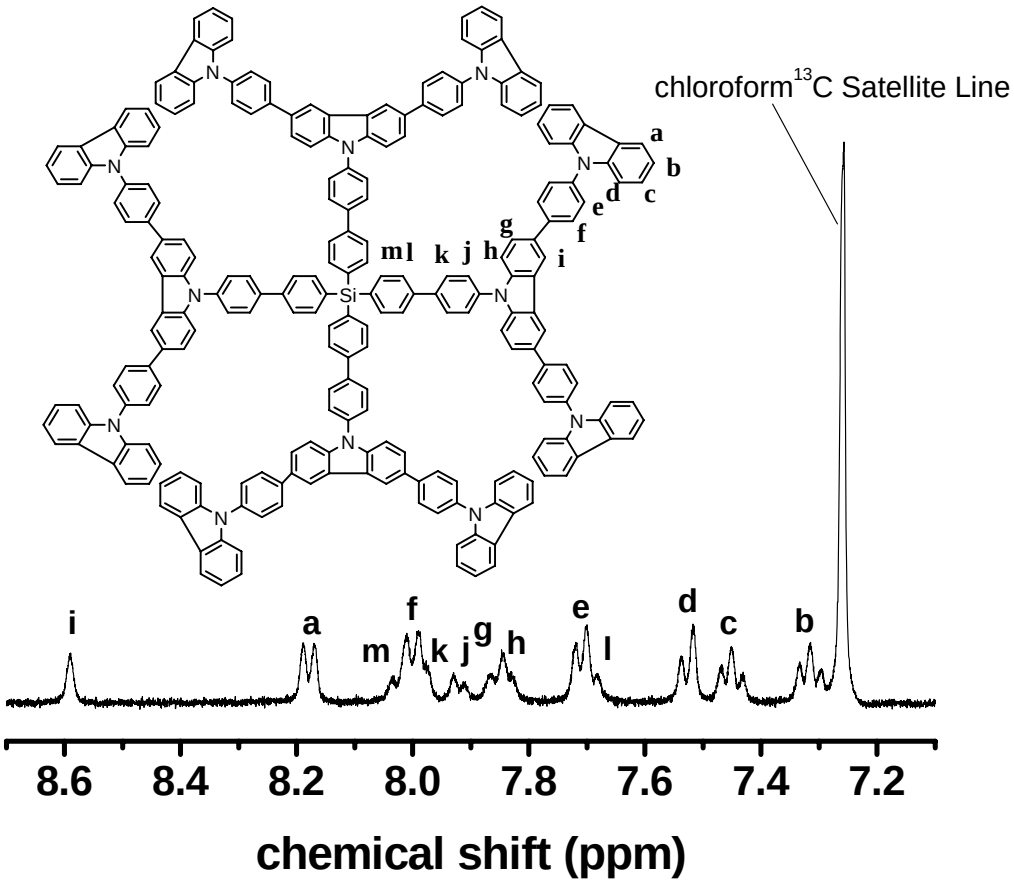

Figure 6S. ^{1}H NMR spectrum of **G2** in chloroform-d.

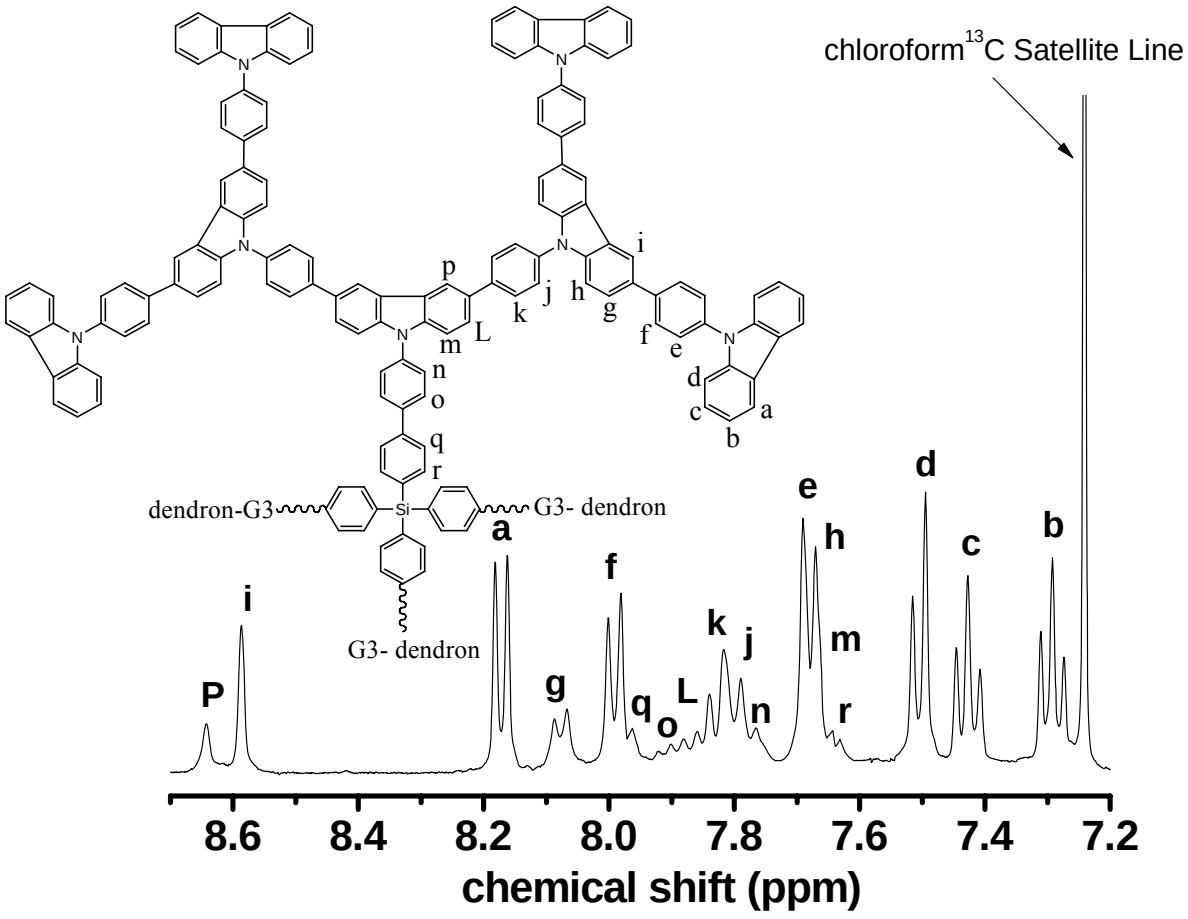

Figure 7S. ^{1}H NMR spectrum of **G3** in chloroform-d.