Supporting Information for:

Fluorophore-cored dendrimers for patterns in metalloprotein sensing

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Experimental Section:

General Methods:

All dendrimers were synthesized according to the procedures previously reported.[1] Other chemicals and solvents used in these studies were obtained from commercial sources and used as received unless otherwise mentioned.

^{1}H-NMR spectra were recorded on a 300 or 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; quin; quintet; d of d, doublet of doublet; m, multiplet; br, broad. ^{13}C-NMR spectra were proton decoupled and recorded on a 75 or 100 MHz spectrometer using the carbon signal of the deuterated solvents as the internal standard. MALDI-ToF, EI, and FAB mass spectra were obtained at the Molecular Weight Characterization Facility at the University of Massachusetts. Flash chromatography was performed with 40-60 μm silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using an iodine chamber. THF was distilled over Na/Ph_2CO ketyl. All other chemicals were obtained from commercial sources and used as received.

Spectroscopic Measurements:

The UV-visible absorption spectra were recorded on a Varian (model EL 01125047) spectrophotometer using quartz cells. Fluorescence spectra were recorded on a Jasco (FP-6500) fluorimeter. The spectra were recorded using a 100 μL quartz cuvette. Excitation and emission bandwidth was kept at 3 nm. For Stern-Volmer quenching studies, optical value at peak wavelength was set between 0.1- 0.3 to avoid self-absorption effects.

Dendritic Stock Solution Preparation:

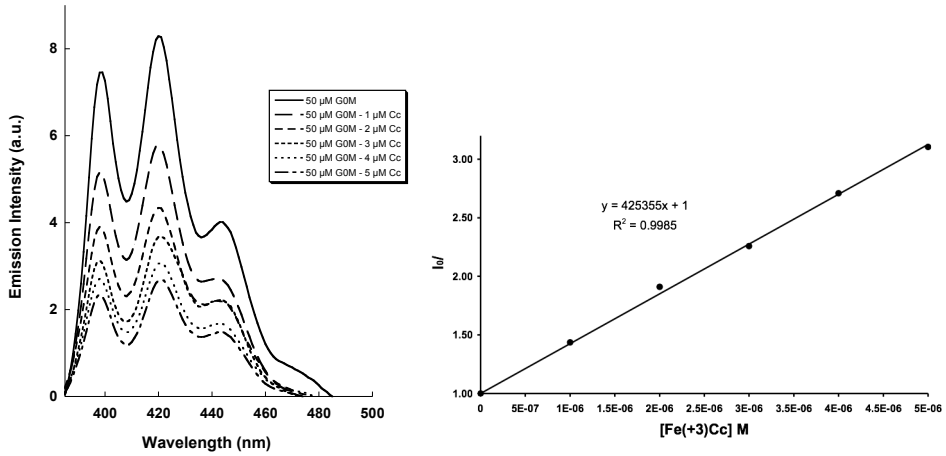
To the dendritic compound was added KOH (1 equivalent per carboxylic acid functionality) in 1 mL MilliQ water. The solution mixture was sonicated at 60 °C for 15 minutes and then 9 mL of sodium phosphate buffer (pH 7.4) was added to adjust volume to 10 mL. The final concentration of the dendrimer stock solution was 50 μM.

Stern-Volmer Quenching Studies:

For fluorescence studies, 50 μM of dendritic stock solution was incubated with different concentration of analytes (10-50 μM protein) in 5 mM sodium phosphate buffer pH 7.4 and measurements were taken after 30 minutes.

The fluorescence data were fitted either using linear ($I_0/I = 1 + K_{SV}[Q]$) or exponential fit ($I_0/I = e^{Ksv[Q]}$). At low concentration of protein, we got a linear fit whereas increasing the concentration of quencher (protein) leads to superlinear behavior which is consistent with the previous reports.[2-4] The K_{SV} value is similar[3,4] (within 5% experimental error) which is also closely matches with previous reported.[3,4] The superlinear behavior at higher concentration of quencher is attributed to the presence of quencher molecule within the sphere of action which is about 40 nm.[3, 4]

G0M-cytochrome c



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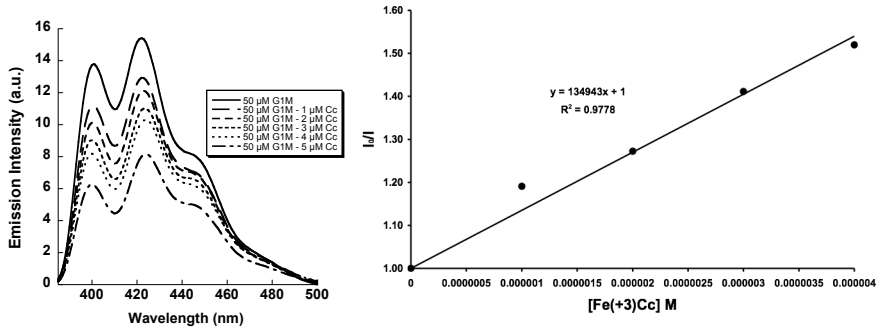

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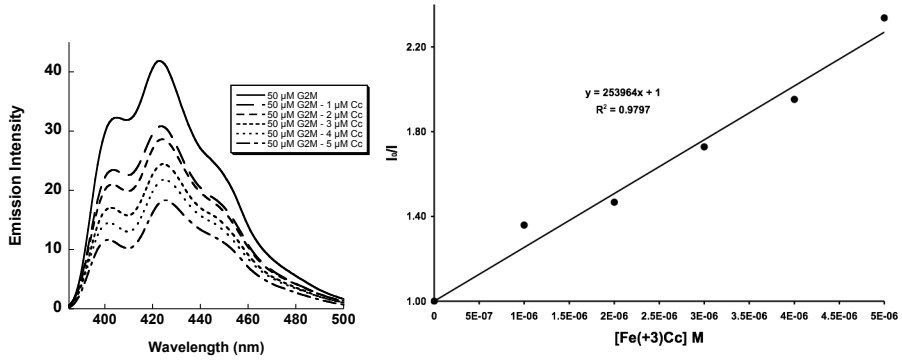

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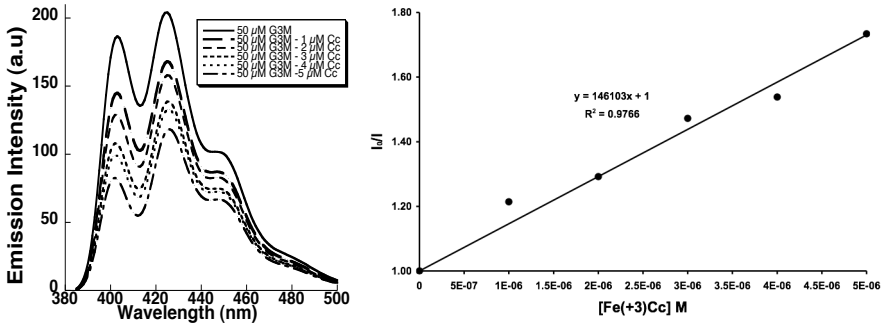

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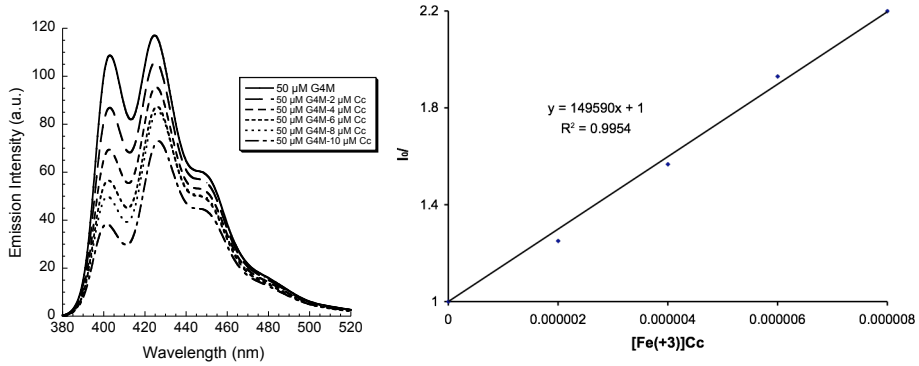

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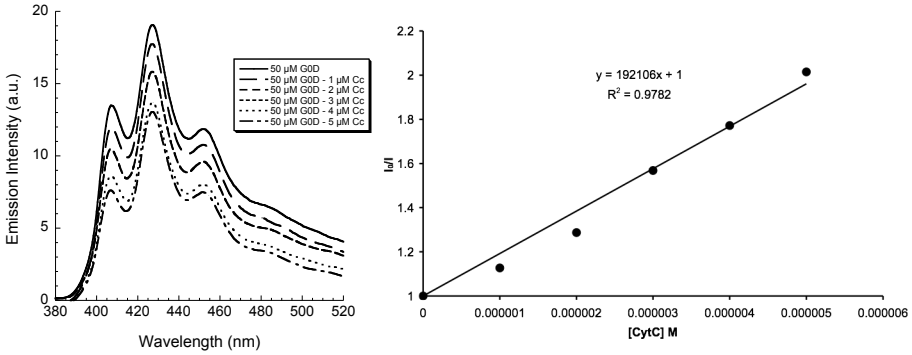

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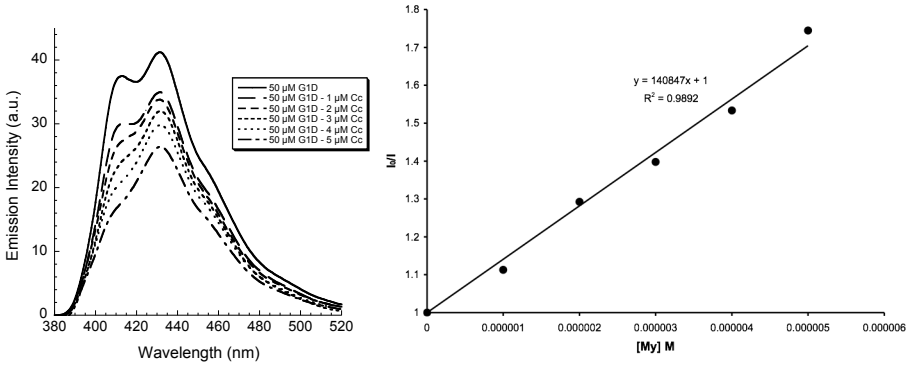

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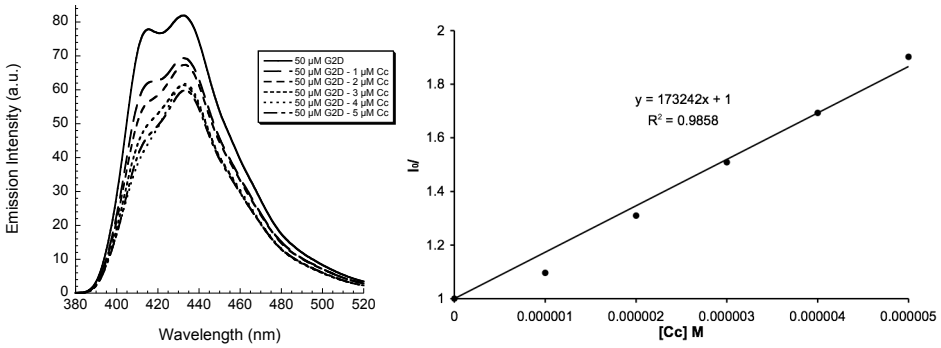

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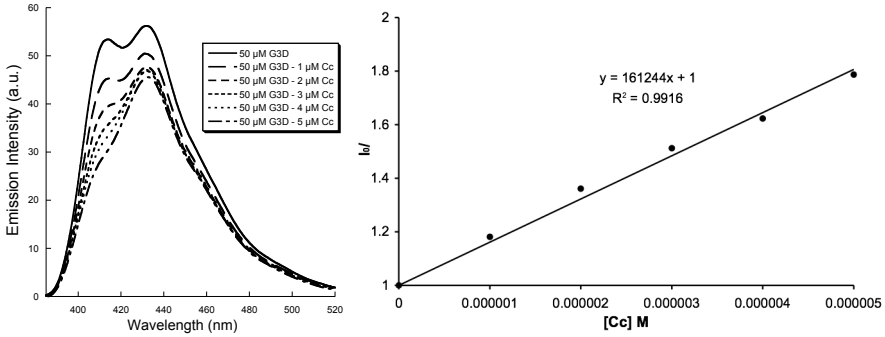

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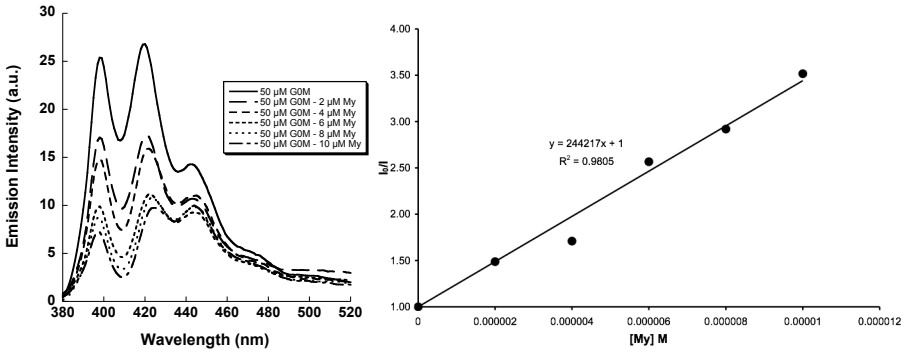

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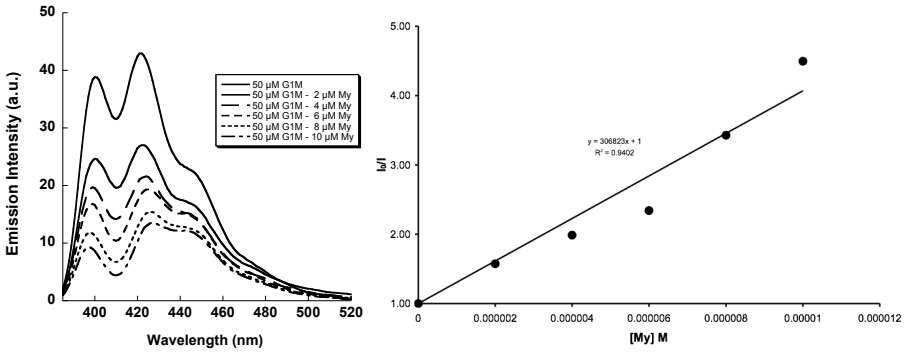

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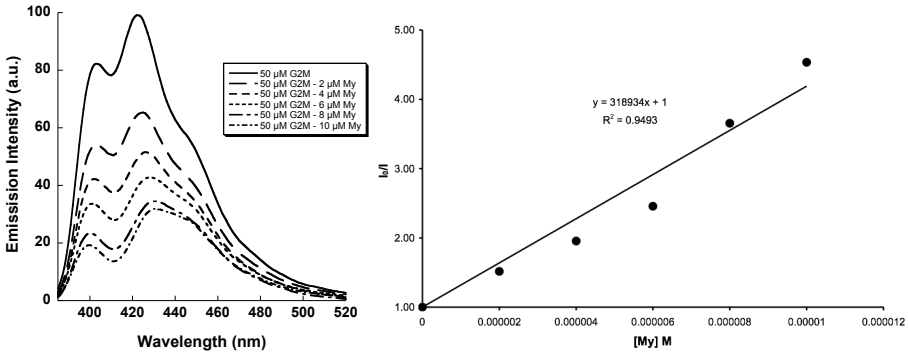

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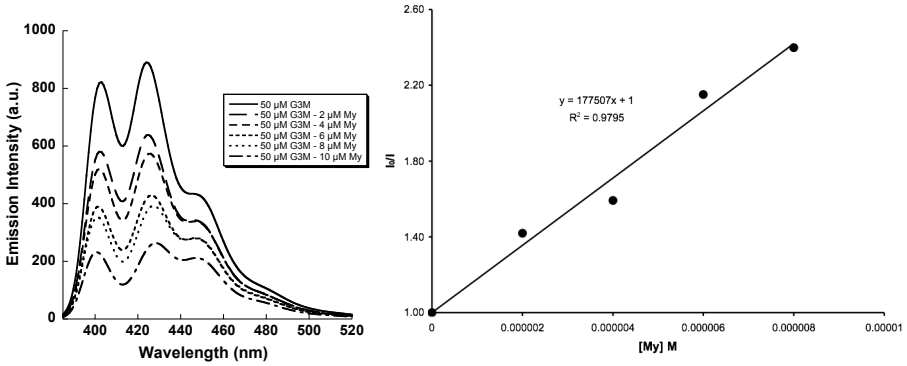

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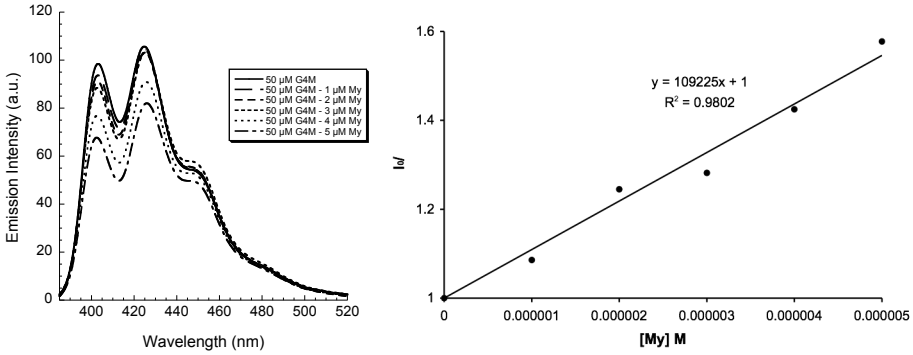

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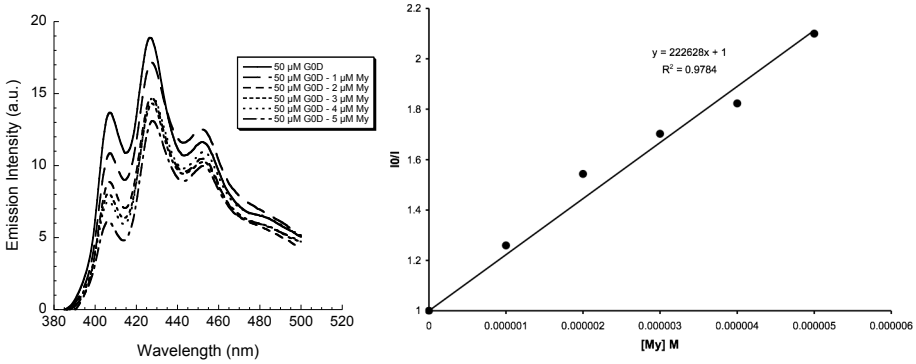

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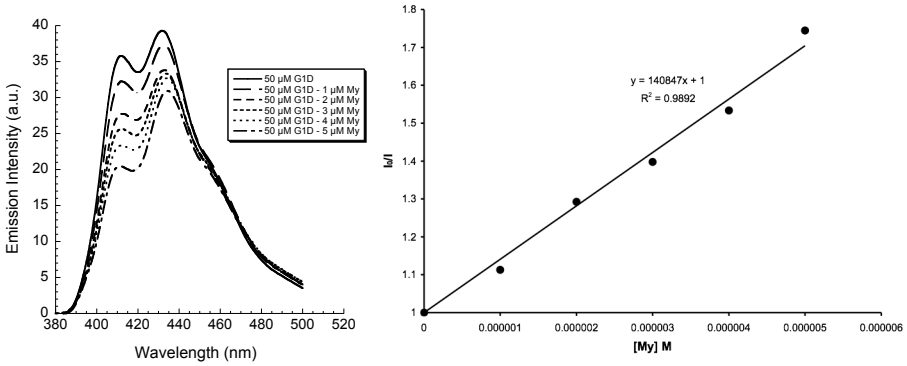

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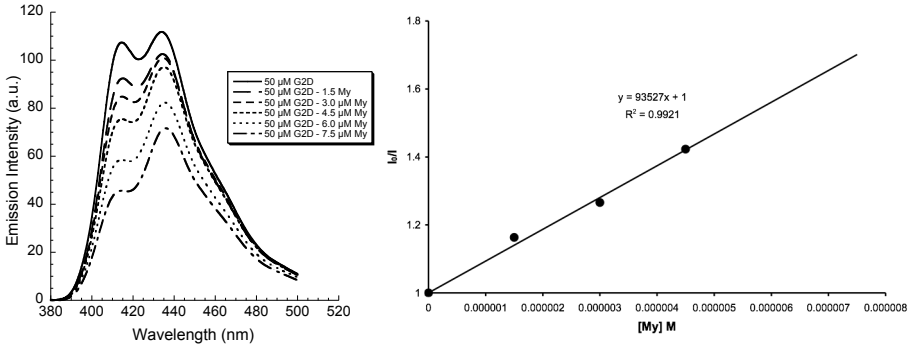

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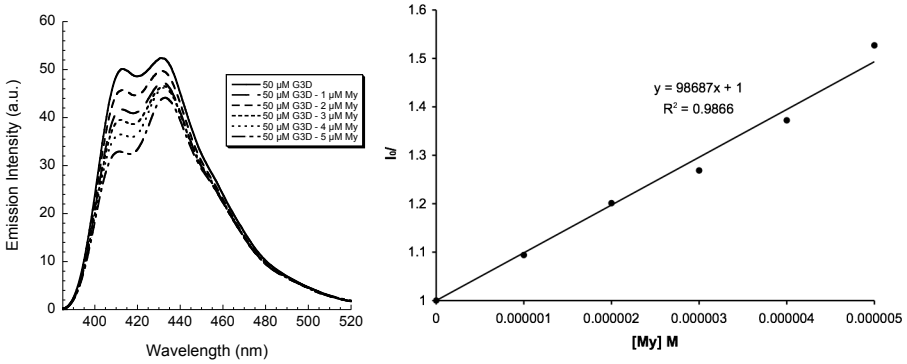

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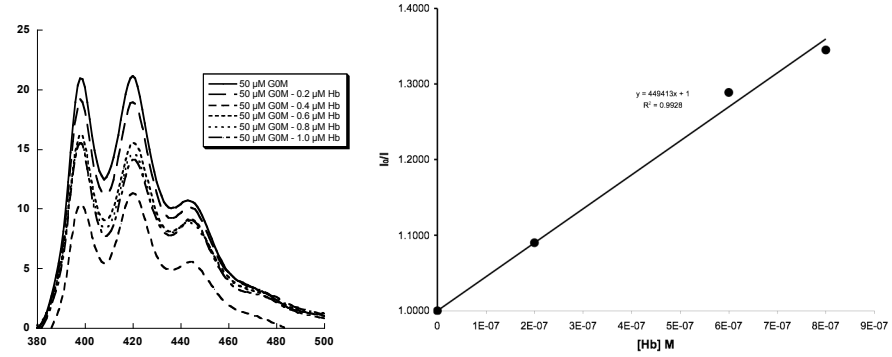

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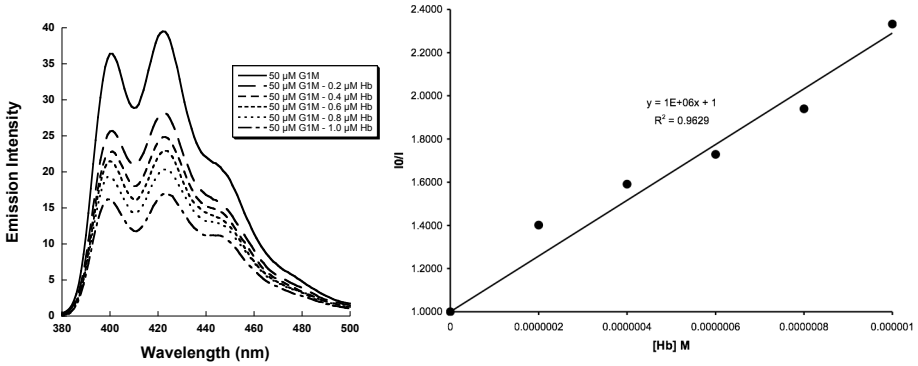

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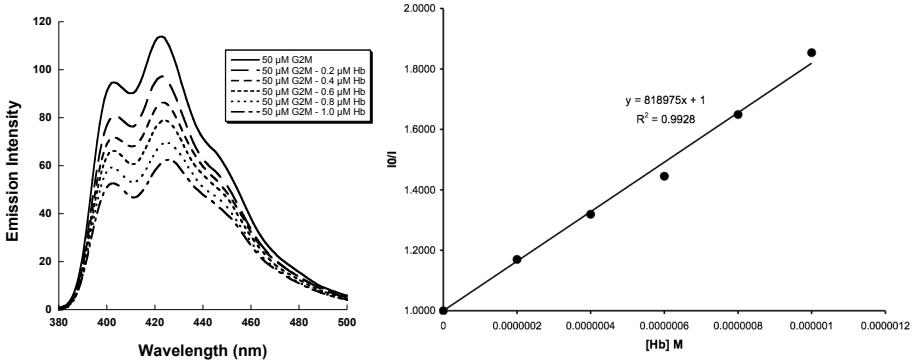

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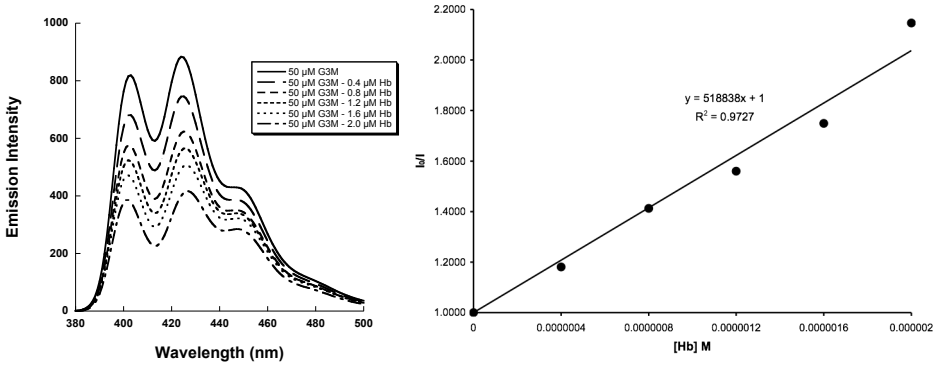

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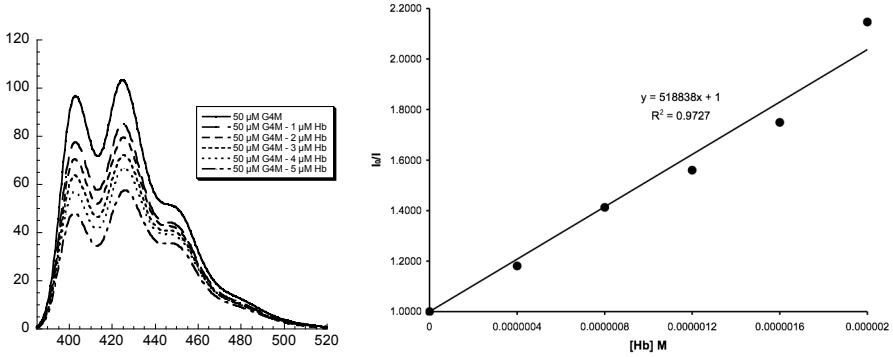

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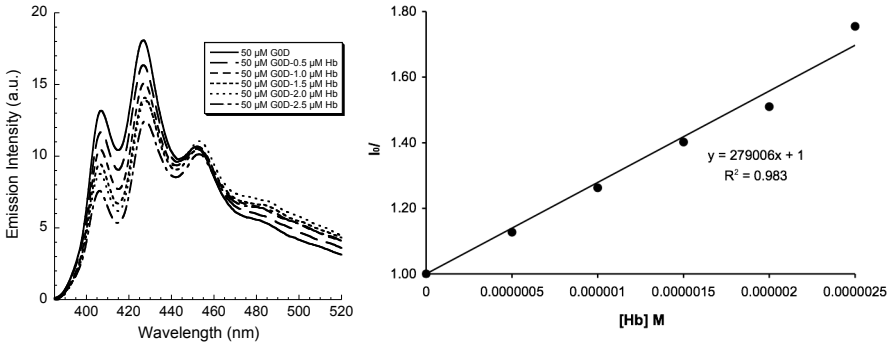

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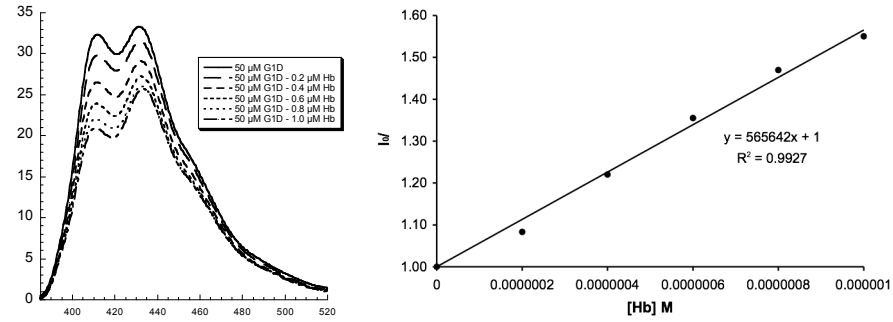

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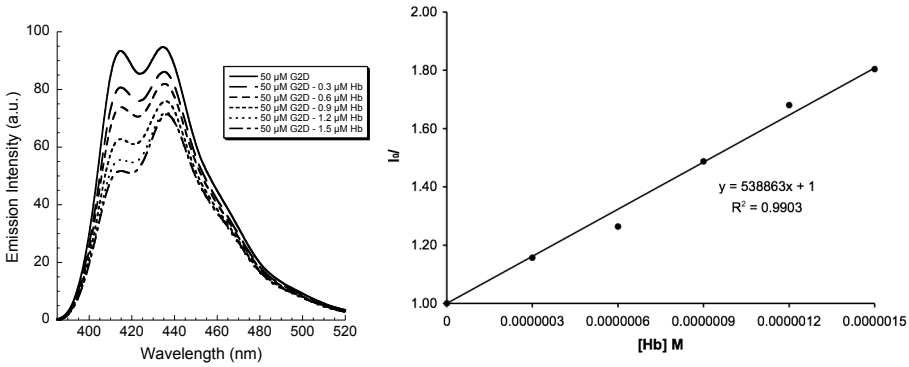

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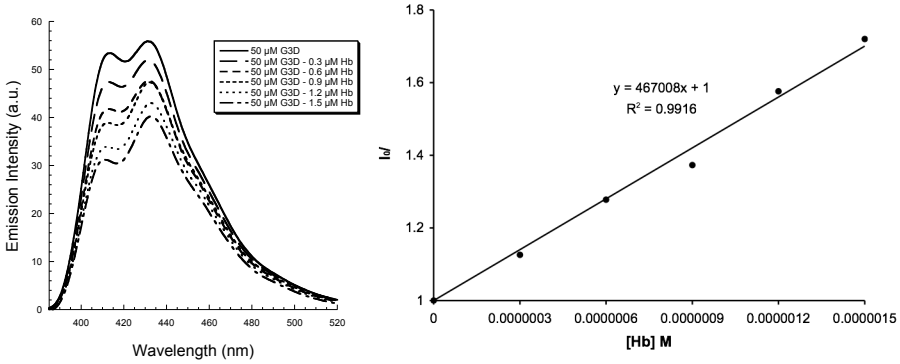

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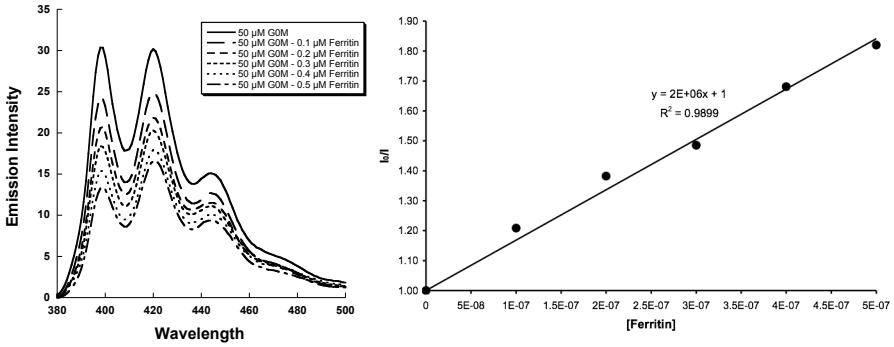

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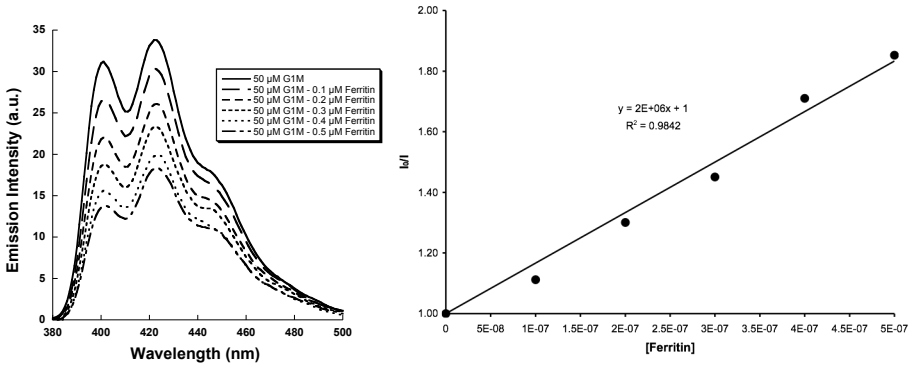

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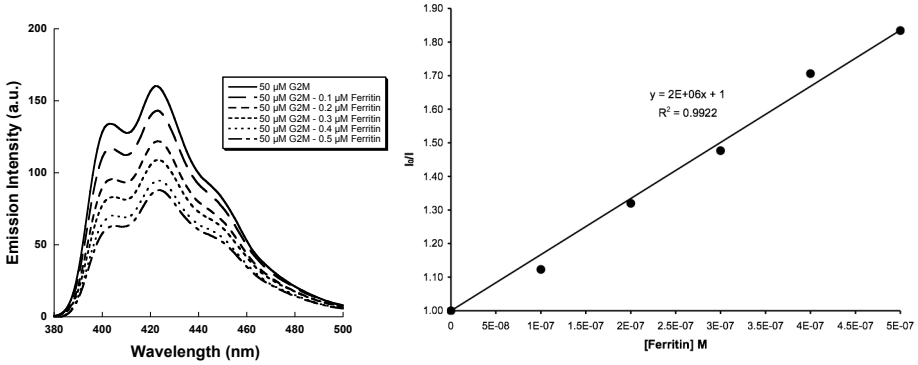

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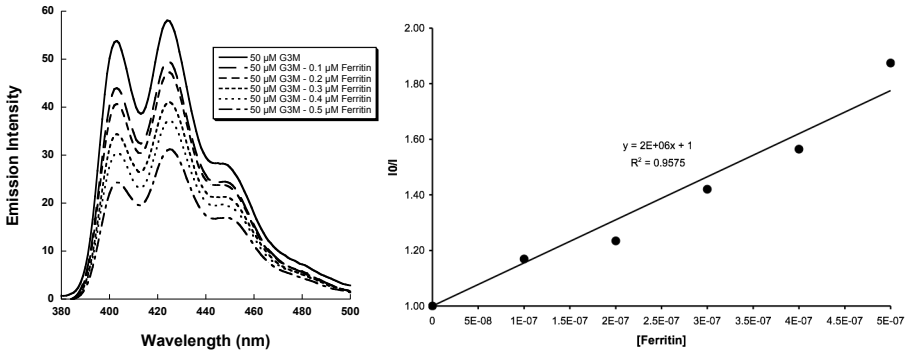

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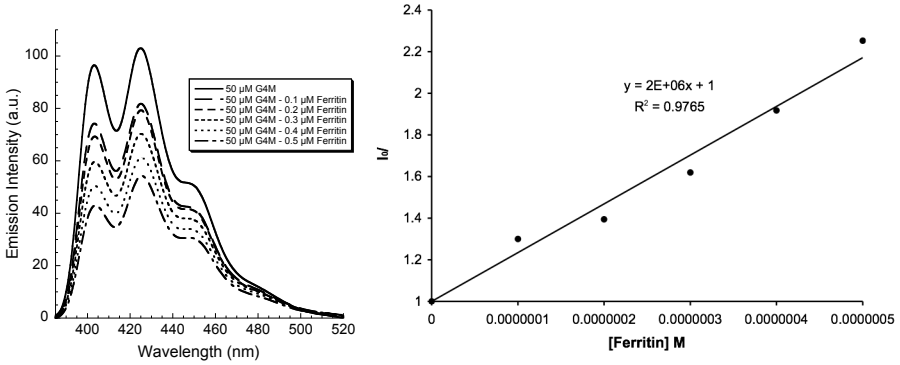

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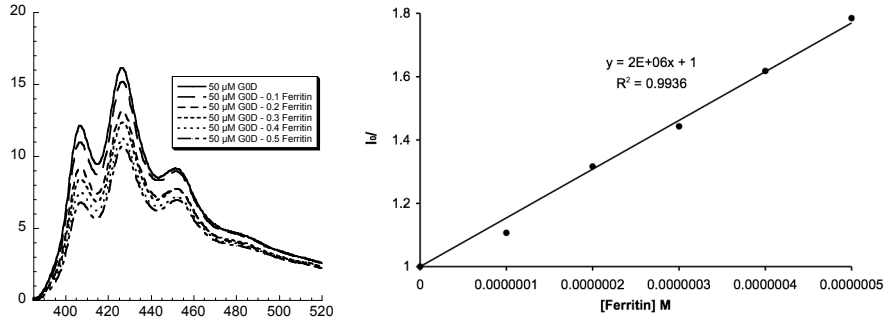

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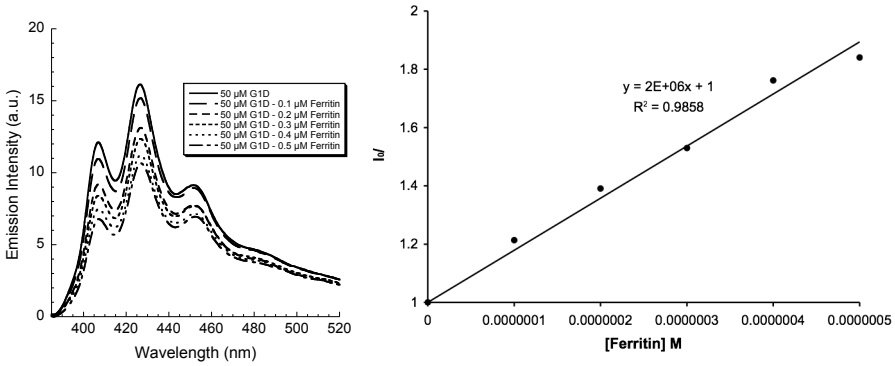

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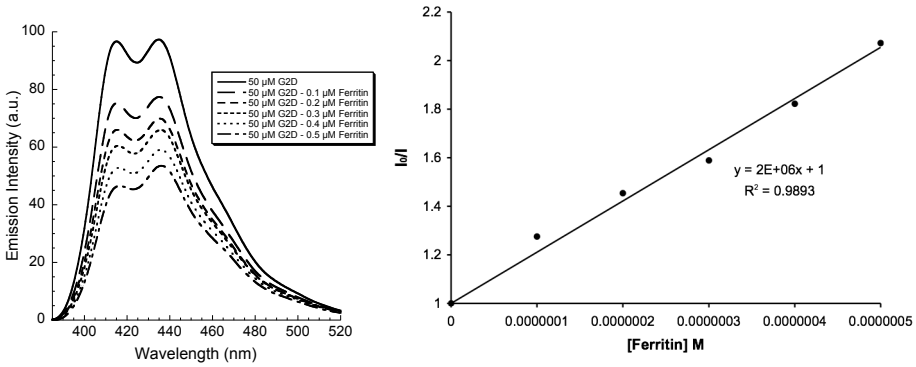

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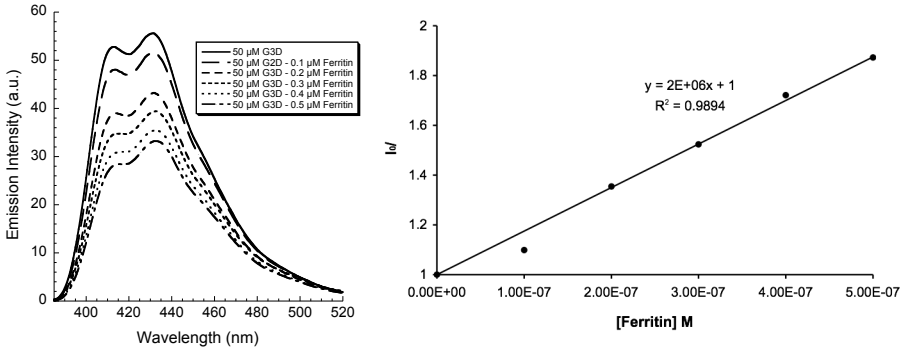
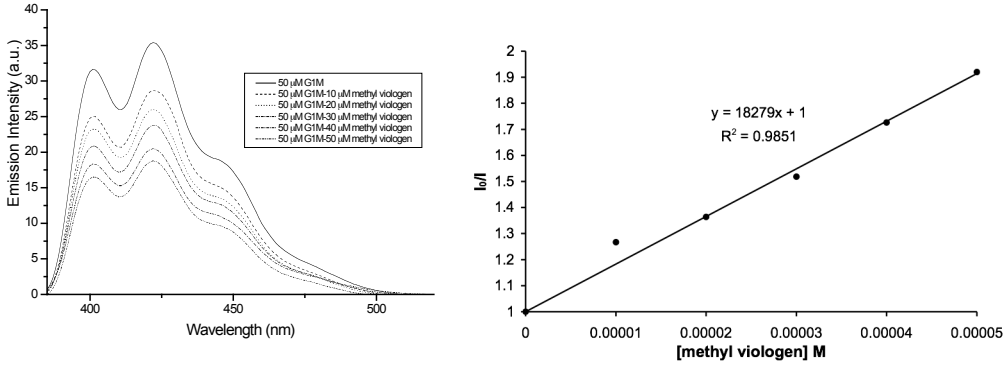


G1M - Methyl viologen



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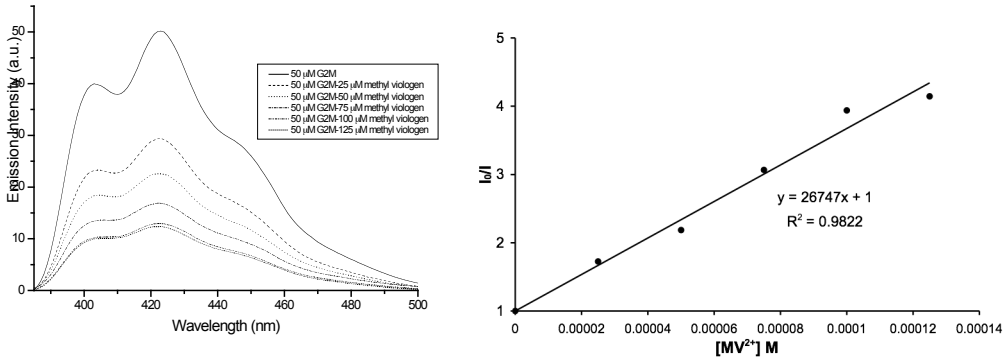

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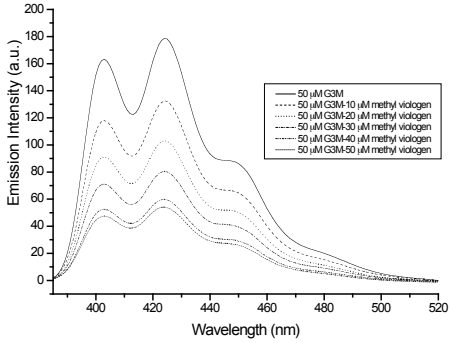

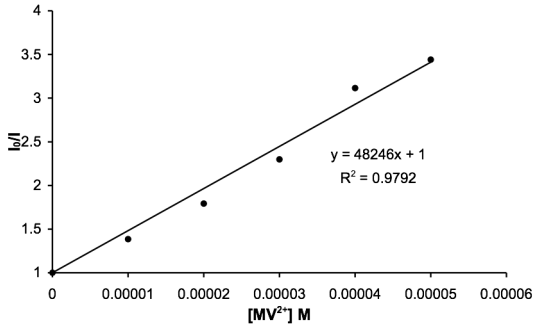

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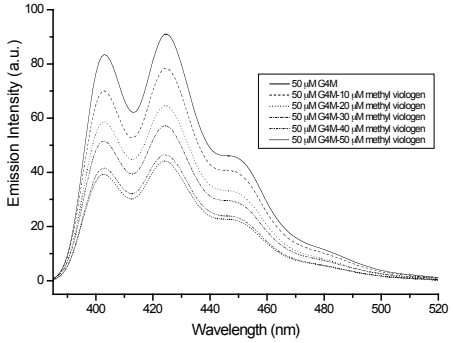
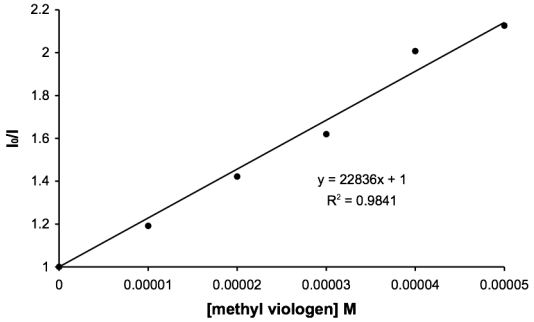
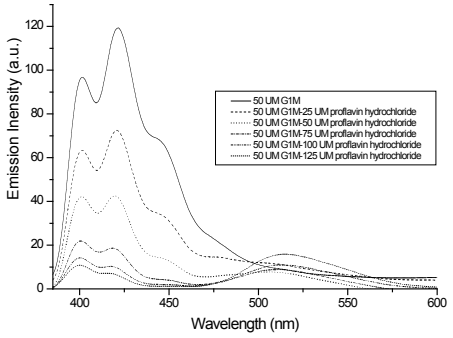
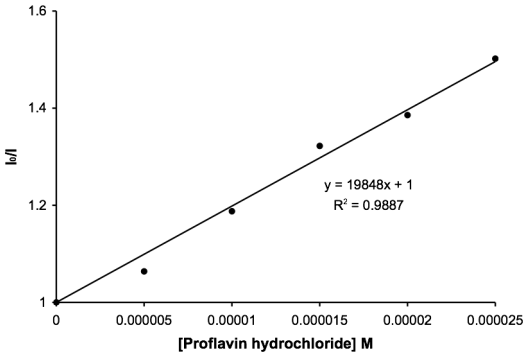




G1M - Proflavin





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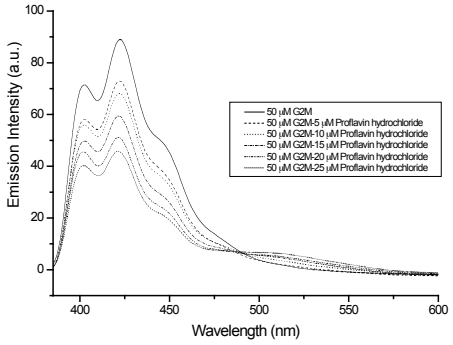

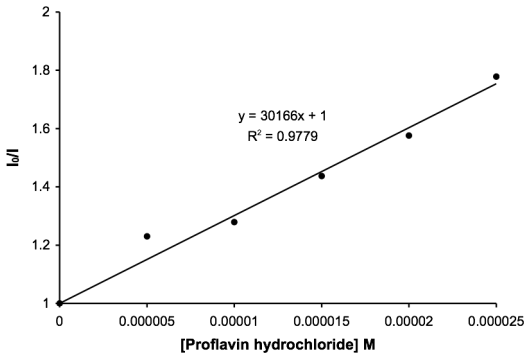

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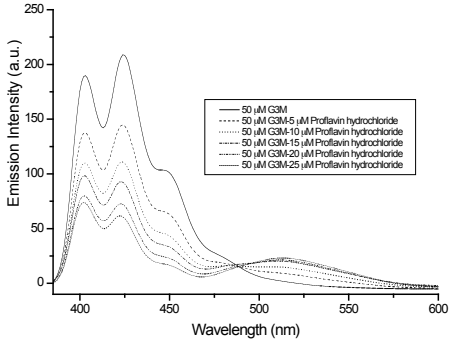

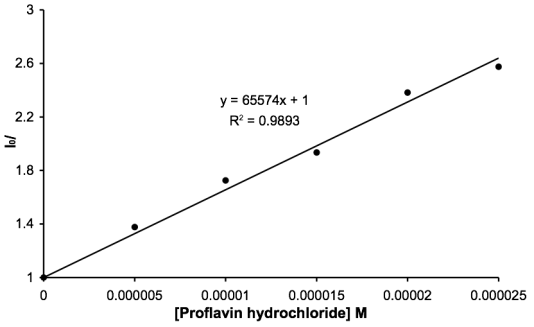

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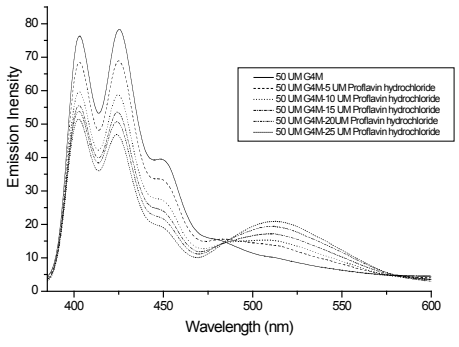
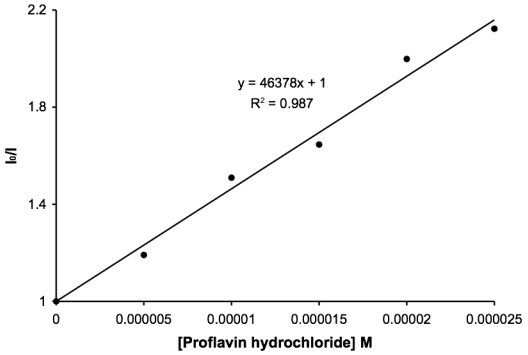
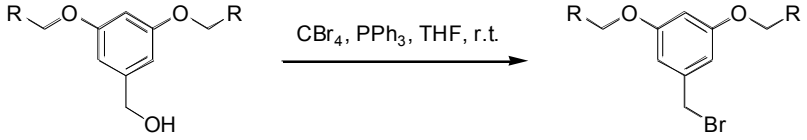




Dendritic Scaffold Syntheses:

Synthesis of dendron G1 to G4-OH was achieved from 3, 5-dihydroxybenzyl alcohol. We have followed the experimental procedure which has been reported by Fréchet *et al.*[1]

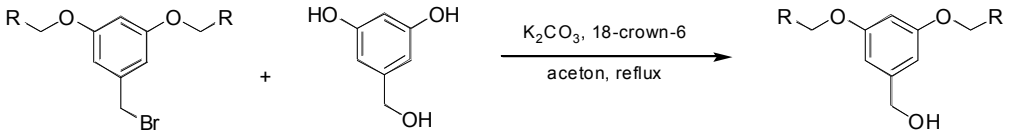
General Procedure I



Gn-OH **Gn-Br**

To a stirring solution of appropriate benzyl alcohol (1 equiv), CBr_4 (1.2 equiv), and PPh_3 (1.2 equiv) was added portion wise under argon. The reaction was monitored until completion by TLC. If the reaction was not complete after 20 min, an additional 0.3 equiv of PPh_3 and CBr_4 were added. Upon completion of the reaction, water was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was then purified by column chromatography (SiO_2, hexanes/ethyl acetate).

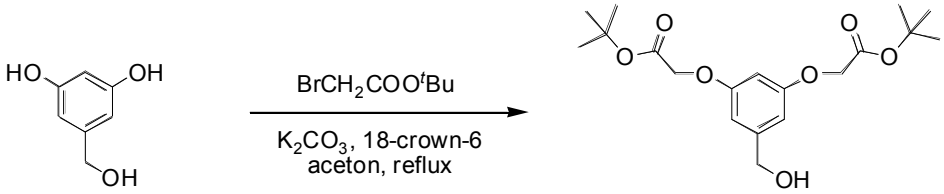
General Procedure II



Gn-OH

The bromobenzyl compound (2 equiv) and the appropriate phenolic compound (1 equiv) were taken along with K_2CO_3 (6-9 equiv), 18-crown-6 (catalytic amount) in THF and the resultant solution was refluxed under argon for 24-48 hours. Water was added to the reaction mixture. The aqueous layer was extracted wit ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The crude product was purified by column chromatography (SiO_2, hexanes/ethyl acetate).

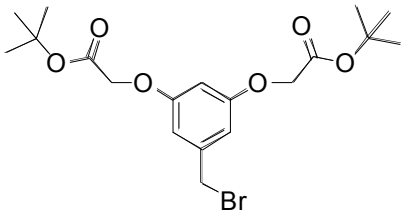
Synthesis of G0-OH



G0-OH

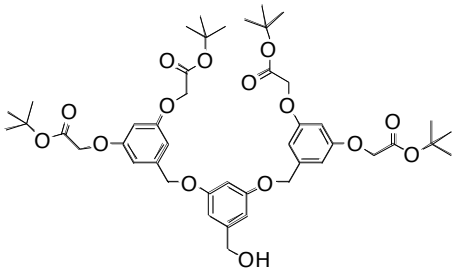
The reaction of 3, 5-dihydroxybenzyl alcohol with 2 equiv. of tert-butyl bromoacetate under alkylation condition afforded **G0-OH.** This compound was synthesized using general procedure II. Yield (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (d, J = 2.3 Hz, 2H), 6.39 (t, J = 2.3 Hz, 1H), 4.60 (s, 2H), 4.47 (s, 4H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 159.5, 143.9, 106.2, 101.4, 82.8, 66.0, 65.4, 28.4. EI/MS m/z (r.i.): 368.2 (M+, 68), 312.1 (24), 256.0 (61), 212.0 (41), 101.0 (42), 57.0 (100).

Synthesis of G0-Br



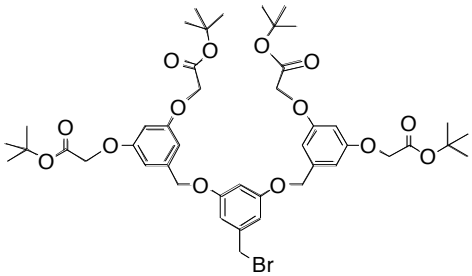
This compound was synthesized by using general procedure I, Yield (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (d, J = 2.3 Hz, 2H), 6.41 (t, J = 2.3 Hz, 1H), 4.48 (s, 4H), 4.37 (s, 2H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 159.5, 140.2, 108.7, 102.4, 82.9, 66.1, 33.5, 28.4. EI/MS m/z (r.i.): 432.1, (M+1, 30), 430.1 (M+, 30), 239.0 (39), 69.1 (56), 57.0 (100).

Synthesis of G1-OH



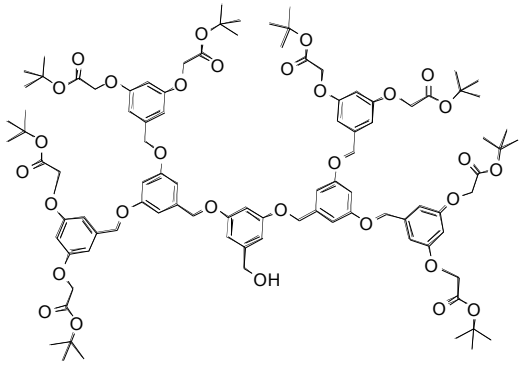
This compound was synthesized by using general procedure II, Yield (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57-6.55 (m, 6H), 6.44 (t, J = 2.3 Hz, 1H), 6.40 (t, J = 2.3 Hz, 2H), 4.92 (s, 4H), 4.59 (s, 2H), 4.46 (s, 8H), 1.46 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.3, 159.5, 143.9, 139.8, 106.8, 106.2, 143.9, 82.8, 70.1, 66.1, 65.6, 28.4. FAB/MS m/z (r.i.): 836.9 (16), 598.9 (18), 476.9 (9), 358.9 (5), 238.9 (100), 181.2 (15), 124.0 (10).

Synthesis of G1-Br



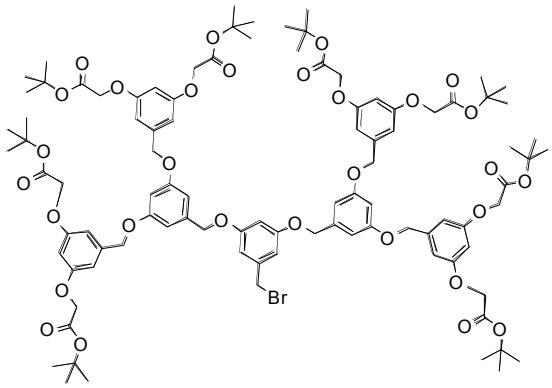
This compound was synthesized by using general procedure I, Yield (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60-6.54 (m, 6H), 6.47 (t, J = 2.3 Hz, 1H), 6.44 (t, J = 2.0 Hz, 2H), 4.90 (s, 4H), 4.49 (s, 8H), 4.40 (s, 2H), 1.48 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.2, 159.6, 140.1, 139.5, 108.5, 106.8, 102.4, 101.8, 82.8, 70.1, 66.0, 33.1, 28.4. FAB/MS m/z (r.i.): 904.3 (M+,100), 903.3 (45.5), 902.3 (M+, 88.5), 836.8, 598.9, 530.9, 476.8, 474.8, 360.9, 238.9, 181.2, 124.0.

Synthesis of G2-OH



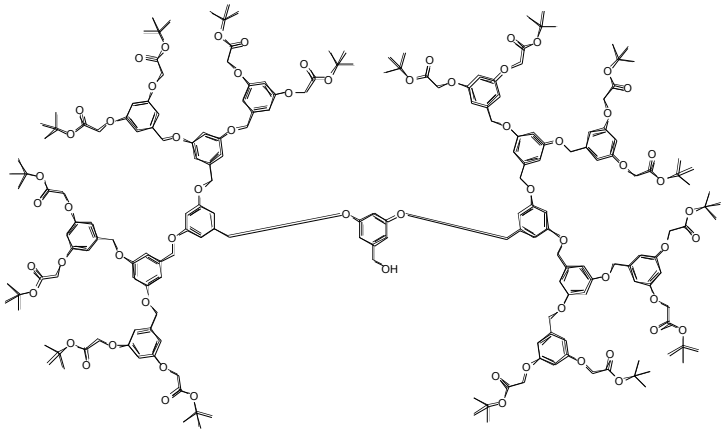
This compound was synthesized by using general procedure II, Yield (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, J = 2.3 Hz, 4H), 6.58 (d, J =2.5 Hz, 10H), 6.51 (t, J = 2.3 Hz, 1H), 6.49 (t, J = 2.3 Hz, 2H), 6.42 (t, J = 2.3 Hz, 4H), 4.94 (s, 12H), 4.46 (s, 2H), 4.48 (s, 16), 1.47 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.3, 160.2, 159.5, 139.7, 139.6, 106.7, 106.6, 105.9, 101.8, 101.7, 101.4, 82.7, 70.1, 70.0, 66.0, 28.3. MALDI-ToF m/z calcd. for $C_{97}H_{124}O_{31}$+Na^{+}:1809.0; found: 1809.1.

Synthesis of G2-Br



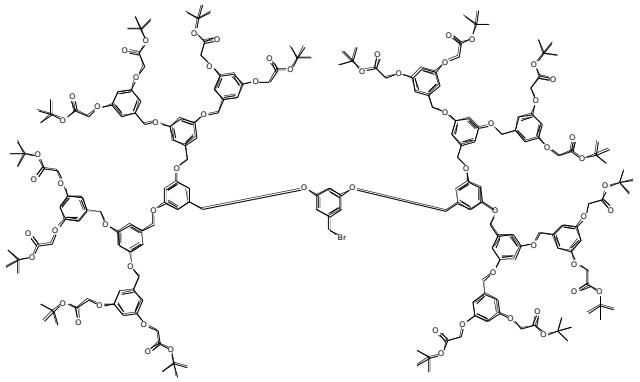
This compound was synthesized by using general procedure I, Yield (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (br, 6H), 6.59 (d, J = 2.3 Hz, 8H), 6.53 (s, 1H), 6.51 (t, J = 2.3 Hz, 2H), 6.43 (t, J = 2.3 Hz, 4H), 4.95 (s, 12H), 4.49 (s, 16H), 4.42 (s, 2H), 1.48 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.6, 140.1, 139.7, 139.4, 108.5, 106.8, 102.4, 101.9, 101.8, 82.8, 70.4, 70.2, 66.1, 33.9, 28.4.

Synthesis of G3-OH



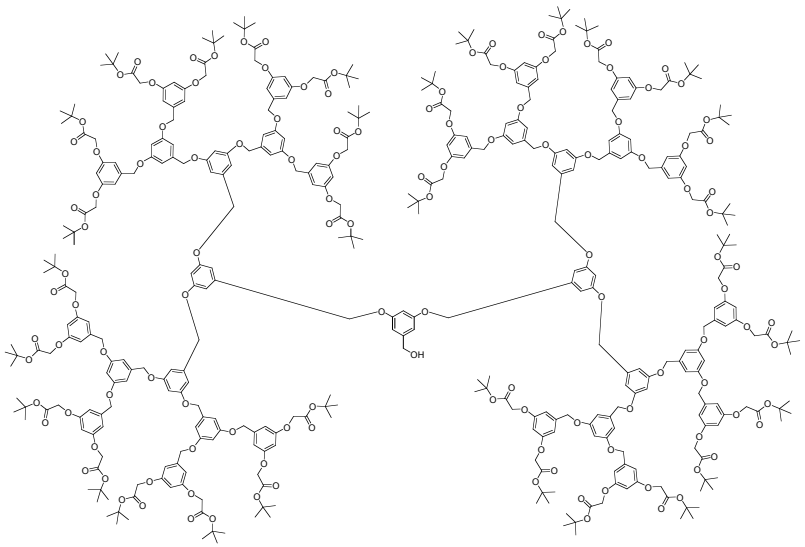
This compound was synthesized by using general procedure II, Yield (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, J = 2.3 Hz, 14H), 6.58 (d, J = 2.2 Hz, 16H), 6.48 (t, J = 2.0 Hz, 7H), 6.41 (t, J = 2.2 Hz, 8H), 4.95 (s, 28H), 4.61 (s, 2H), 4.47 (s, 32H), 1.48 (s, 144H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.4, 160.3, 159.6, 139.7, 139.6, 106.8, 101.7, 100.3, 82.7, 70.3, 70.1, 70.0, 66.1, 28.4. MALDI-ToF m/z calcd. for $C_{201}H_{252}O_{63}$+Na^{+}: 3699.1; found: 3696.4.

Synthesis of G3-Br



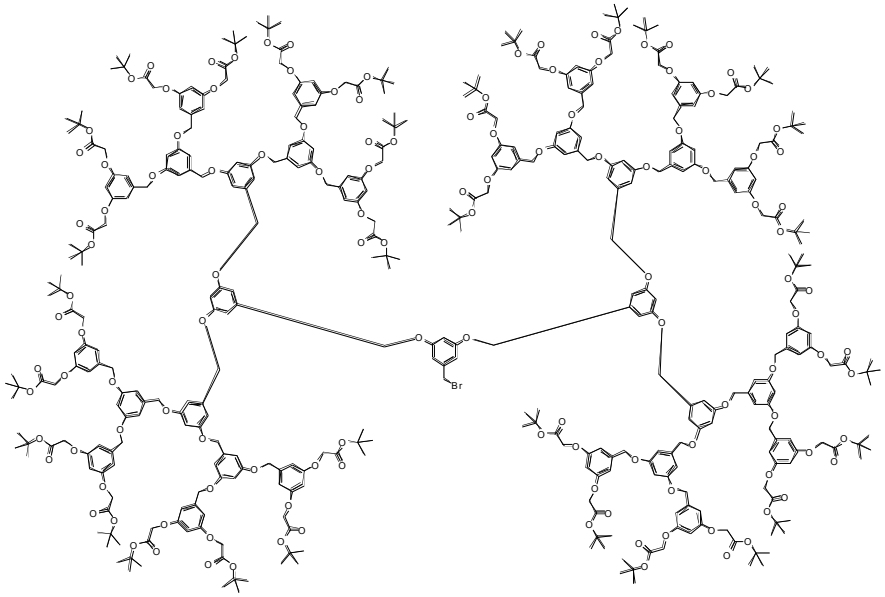
This compound was synthesized by using general procedure I, Yield (76%). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (d, J=2.3 Hz, 4H), 6.65 (d, J=2.0 Hz, 8H), 6.58 (d, J=2.3 Hz, 19H), 6.49 (d, J=2.0 Hz, 6H), 6.42 (t, J=2.3 Hz, 8H), 4.93 (s, 28H), 4.61 (s, 2H), 4.47 (s, 32H), 1.46 (s, 144H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.5, 160.3, 159.6, 139.7, 139.5, 106.8, 101.8, 101.7, 100.3, 82.7, 70.3, 70.1, 66.1, 33.9, 28.4.

Synthesis of G4-OH



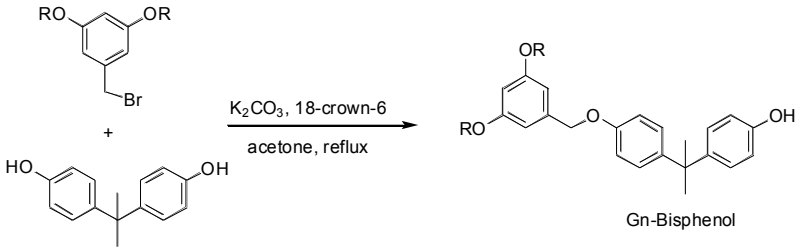
This compound was synthesized by using general procedure II, Yield (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (br, 12H), 6.65 (br, 18H), 6.59-6.57 (m, 33H), 6.53-6.51 (br, 6H), 6.48 (m, 8H), 6.41 (t, J=2.3 Hz, 16H), 4.92 (s, 60H), 4.58 (s, 2H), 4.45 (s, 64H), 1.45 (s, 288H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.4, 160.3, 159.5, 139.6, 139.5, 106.8, 101.7, 101.6, 100.2, 82.7, 70.3, 70.2, 70.0, 66.0, 28.4. MALDI-ToF m/z calcd. for $C_{408}H_{508}O_{127}$+Na^+: 7479.3; found 7486.5.

Synthesis of G4-Br



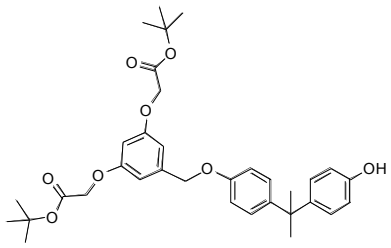
This compound was synthesized by using general procedure II, Yield (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73-6.68 (br, 12H), 6.67-6.63 (br, 18H), 6.60-6.56 (br, 39H), 6.49-6.46 (br, 8), 6.43-6.37 (br, 16H), 4.91 (s, 60H), 4.61 (s, 2H), 4.45 (s, 64H), 1.46 (s, 288H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 160.3, 160.2, 159.4, 159.4, 139.6, 139.4, 139.3, 106.7, 101.7, 101.6, 82.5, 70.3, 70.2, 69.9, 65.9, 33.8, 28.2.

General Procedure III



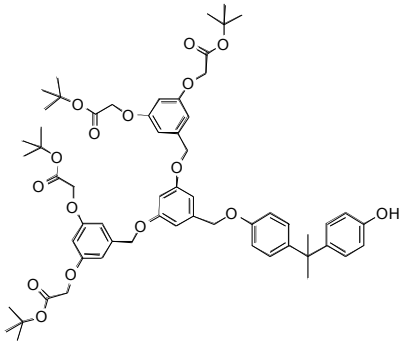
Appropriate bromomethyl compound (1 equiv), bisphenol-A (2 equiv), K_2CO_3 (6-9 equiv), 18-crown-6 (catalytic amount), and THF were refluxed under argon for 24-48 hours. Water was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate, dried over Na_2SO_4 anhydrous, and concentrated by rotary evaporator. Crude product was purified by column chromatography (SiO_2, hexanes/ethyl acetate).

Synthesis of G0-Bisphenol



This compound was synthesized by using general procedure III, Yield (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (dd, *J*= 8.8, 12.1 Hz, 4H), 6.82 (d, *J*= 8.8 Hz, 2H), 6.73 (d, *J*= 8.8 Hz, 2H), 6.59 (d, *J*= 2.3 Hz, 2H), 6.43 (t, *J*= 2.3 Hz, 1H), 5.61 (s, 1H), 4.93 (s, 2H), 4.48 (s, 4H), 1.62 (s, 6H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.4, 156.7, 153.9, 143.9, 143.1, 140.2, 128.1, 128.0, 115.0, 114.4, 106.7, 101.6, 82.9, 70.0, 66.0, 41.9, 31.4, 28.3. FAB/MS (r.i.) m/z 578.0 (19), 466.0 (40), 373.0 (20), 295.0 (15), 238.9 (100), 181.0 (38), 135.0 (100), 57.4 (100).

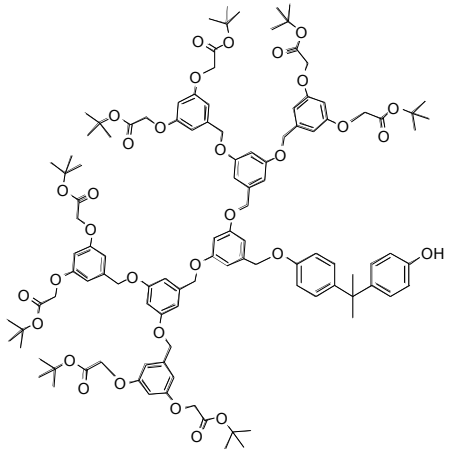
Synthesis of G1-Bisphenol



This compound was synthesized by using general procedure III, Yield (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J*= 8.8 Hz, 2H), 7.05 (d, *J*= 8.8 Hz, 2H), 6.83 (d, *J*= 8.8 Hz, 2H), 6.72 (d, *J*= 8.8 Hz, 2H), 6.62 (d, *J*= 2.0 Hz, 2H), 6.58 (d, *J*= 2.3 Hz, 4H), 6.49 (t, *J*= 2.3 Hz, 1H), 6.42 (t, *J*= 2.3 Hz, 2H), 4.97 (s, 2H), 4.92 (s, 4H), 4.48 (s, 8H), 1.62 (s, 6H),

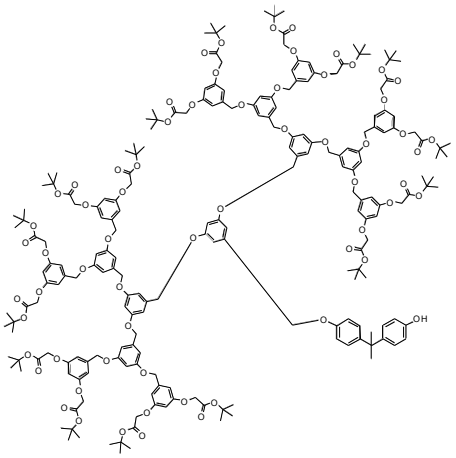
1.48 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 160.2, 159.5, 156.7, 153.9, 143.8, 143.5, 140.1, 139.7, 128.2, 128.0, 115.0, 114.6, 106.9, 106.5, 101.7, 82.9, 70.1, 70.0, 66.1, 42.0, 31.3, 28.4. MALDI-ToF m/z calcd. for $C_{60}H_{74}O_{16}$+Na^+: 1074.2; found: 1073.3.

Synthesis of G2-Bisphenol



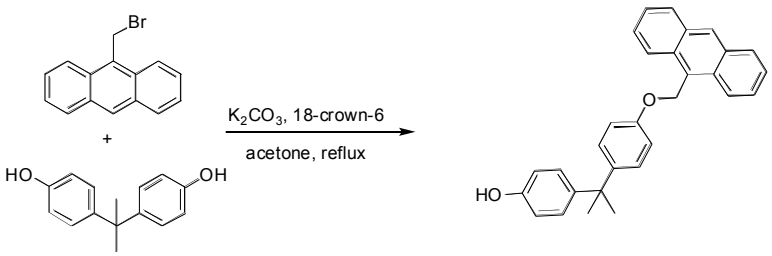
This compound was synthesized by using general procedure III, Yield (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (m, J= 8.8 Hz, 4H), 6.81 (d, J= 8.8 Hz, 2H), 6.70 (d, J= 8.8 Hz, 2H), 6.64 (br, 6H), 6.59 (d, J= 2.3 Hz, 8H), 6.56 (br, 1H), 6.50 (br, 2H), 6.43 (t, J= 2.3 Hz , 4H), 4.95 (s, 12H), 4.50 (s, 2H), 4.48 (s, 16H), 1.67 (s, 6H), 1.47 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 156.8, 154.0, 143.8, 143.1, 140.2, 139.7, 139.6, 128.1, 115.0, 114.6, 106.8, 106.6, 101.8, 101.7, 82.8, 70.3, 70.2, 70.1, 66.1, 41.9, 31.3, 28.4. MALDI-ToF m/z calcd. for $C_{112}H_{138}O_{32}$+Na^+: 2019.3; found: 2019.0.

Synthesis of G3-Bisphenol



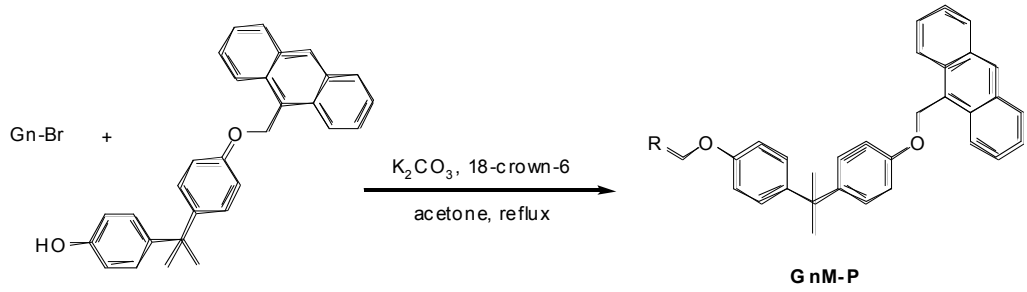
This compound was synthesized by using general procedure III, Yield (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (m, J = 8.8 Hz, 4H), 6.87 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.6 Hz, 6H), 6.65, (s, 8H), 6.59 (s, 17H), 6.49 (s, 6H), 6.42 (s, 8H), 4.93 (s, 28H), 4.60 (s, 2H), 4.48 (s, 32H), 1.62 (s, 6H), 1.47 (s, 144H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 156.8, 154.3, 143.9, 142.7, 140.1, 139.7, 139.5, 128.0, 127.9, 115.0, 114.4, 106.8, 106.7, 101.8, 101.7, 82.7, 70.3, 70.2, 70.1, 66.0, 41.9, 31.3, 28.3. MALDI-ToF m/z calcd. for $C_{216}H_{266}O_{64}$+Na^+: 3909.4; found 3908.1.

Synthesis of Mono-Anthracene-Bisphenol



Bromomethyl antrancene (1 equiv), bisphenol-A (1.5 equiv), K_2CO_3 (6-9 equiv), 18-crown-6 (catalytic amount), and THF were refluxed under argon for 24-48 hours. Water was added to the reaction mixture. The aqueous layer was extracted wit ethyl acetate, dried over Na_2SO_4 anhydrous, and concentrated by rotary evaporator. Crude product was purified by column chromatography (SiO_2, Hexane/Ethyl acetate), Yield (44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.29 (d, J = 8.8 Hz, 2H), 8.04 (d, J= 8.8 Hz, 2H), 7.51 (m, 4H), 7.23 (2, J = 8.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 5.94 (s, 2H), 4.61 (s, 1H), 1.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 153.3, 143.7, 143.3, 131.5, 131.1, 129.1, 129.0, 128.0, 127.9, 127.0, 126.5, 125.1, 124.1, 114.8, 114.2, 62.6, 41.8, 31.1. FAB/MS m/z (r.i.): 418.1 (M+. 11), 391.1 (12), 307.0 (55), 289.0 (30), 239.0 (23), 191.0 (100), 153.9 (100), 137.0 (100), 106.9 (65), 57.4 (65).

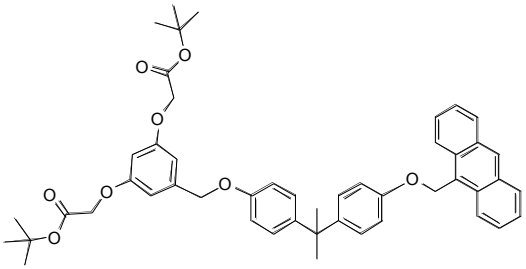
Synthesis of monodendron with anthracene core:



General procedure IV

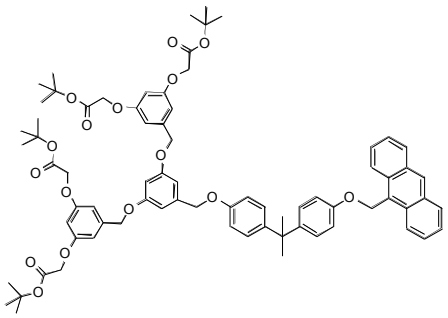
Appropriate bromomethyl dendron (1 equiv), monoanthracene bisphenol (1 equiv), K_2CO_3 (6-9 equiv), 18-crown-6 (catalytic amount), and THF were refluxed under argon for 24-48 hours. Water was added to the reaction mixture. The aqueous layer was extracted wit ethyl acetate, dried over Na_2SO_4 anhydrous, and concentrated by rotary evaporator. Crude product was purified by column chromatography (SiO_2, hexanes/thy acetate).

Synthesis of G0M-P



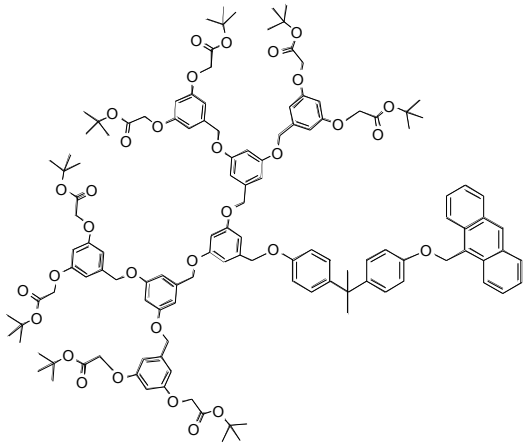
This compound was synthesized by using general procedure IV, Yield (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.28 (d, J = 8.6 Hz, 2H), 8.03 (d, J = 7.3 Hz, 2H), 7.50 (m, J = 8.6 Hz, 4H), 7.25 (dd, J = 7.3, 8.6 Hz, 4H), 7.07 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 2.0 Hz, 2H), 6.49 (t, J = 2.0 Hz, 1H), 5.88 (s, 2H), 4.99 (s, 2H), 4.53 (s, 4H), 1.73 (s, 6H), 1.53 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 159.4, 156.8, 153.9, 143.8, 143.7, 140.2, 131.7, 131.2, 139.3, 139.1, 128.1, 128.0, 127.2, 126.7, 125.2, 124.3, 114.5, 114.4, 106.6, 101.5, 82.6, 69.9, 66.0, 62.7, 42.0, 31.3, 28.3. FAB/MS (r.i.) m/z 767.1 (M+, 12), 655.0 (8), 476.9 (11), 429.0 (12), 373.0 (15), 251.9 (15), 238.9 (100), 192.1 (100), 135.9 (70).

Synthesis of G1M-P



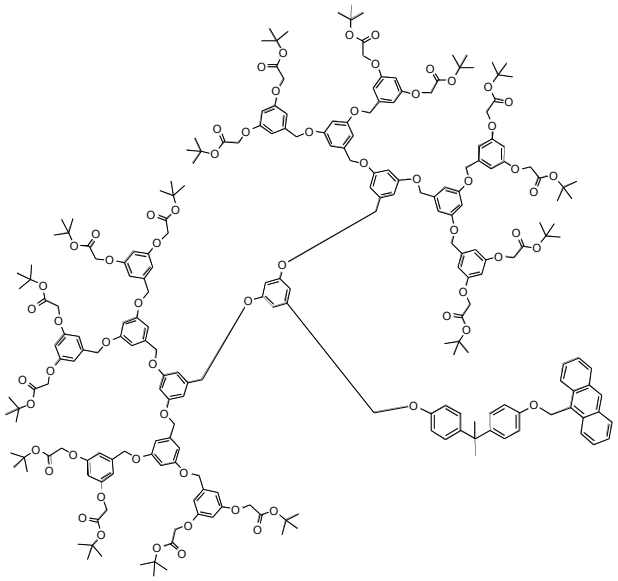
This compound was synthesized by using general procedure IV, Yield (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.29 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 9.3 Hz, 2H), 7.51 (m, J = 8.3 Hz, 4H), 7.21 (m, J = 8.3 Hz, 4H), 7.07 (m, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 2.3 Hz, 2H), 6.60 (d, J = 2.0 Hz, 4H), 6.50 (m, 1H), 6.47 (t, J = 2.0 Hz, 2H), 5.94 (s, 2H), 4.97 (s, 2H), 4.95 (s, 4H), 4.48 (s, 8H), 1.55 (s, 6H), 1.47 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.3, 159.5, 157.3, 156.9, 143.9, 143.7, 140.0, 139.7, 131.7, 131.3, 129.3, 129.2, 128.1, 128.0, 127.3, 126.7, 125.3, 124.3, 114.5, 114.4, 106.7, 106.6, 101.7, 82.7, 70.1, 70.0, 66.0, 62.6, 42.0, 31.2, 28.3. MALDI-ToF m/z calcd. for $C_{60}H_{74}O_{16}$+Na^{+}: 1264.5; found: 1263.5.

Synthesis of G2M-P



This compound was synthesized by using general procedure IV, Yield (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.28 (d, J = 8.3 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.48 (m, 4H), 7.22 (m, 4H), 7.06 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.72 (s, 2H), 6.67 (d, J = 2.0 Hz, 4H), 6.60 (d, J = 2.0 Hz, 9H), 6.51 (s, 2H), 6.44 (s, 4H), 5.92 (s, 2H), 4.95 (s, 14H), 4.49 (s, 16H), 1.70 (s, 6H), 1.48 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 157.4, 156.9, 143.9, 143.7, 140.0, 139.7, 139.5, 131.8, 131.3, 129.4, 129.2, 128.1, 128.0, 127.3, 126.8, 125.3, 124.4, 114.5, 114.4, 106.8, 106.7, 101.8, 101.7, 82.7, 70.3, 70.2, 70.1, 66.0, 62.9, 42.1, 31.4, 28.3. MALDI-ToF m/z calcd. for $C_{127}H_{148}O_{32}$+Na^{+}: 2209.5; found: 2206.7.

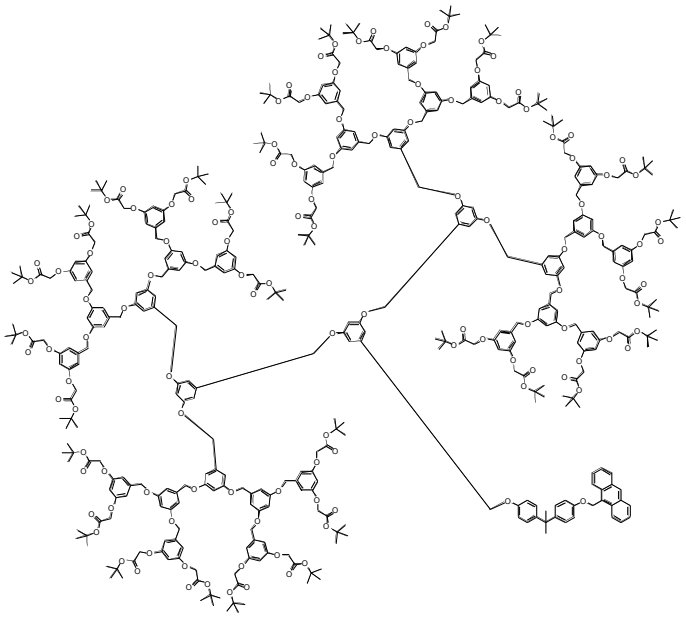
Synthesis of G3M-P



This compound was synthesized by using general procedure IV, Yield (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.28 (d, J= 8.3 Hz, 2H), 8.03 (d, J= 8.8 Hz, 2H), 7.50 (m, J= 8.6 Hz, 4H), 7.22 (m, J= 8.8 Hz, 4H), 7.05 (d, J= 8.6 Hz, 2H), 6.90 (d, J= 8.6 Hz, 2H), 6.67 (br, 6H), 6.64 (d, J= 2.0 Hz, 8H), 6.57 (d, J=2.0 Hz, 19H), 6.48 (t, J= 2.0 Hz, 4H), 6.40 (t, J= 2.0 Hz, 8H), 5.92 (s, 2H), 4.94 (s, 30H), 4.48 (s, 32H), 1.68 (s, 6H), 1.46 (s, 144H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 157.0, 156.9, 143.9, 143.2,

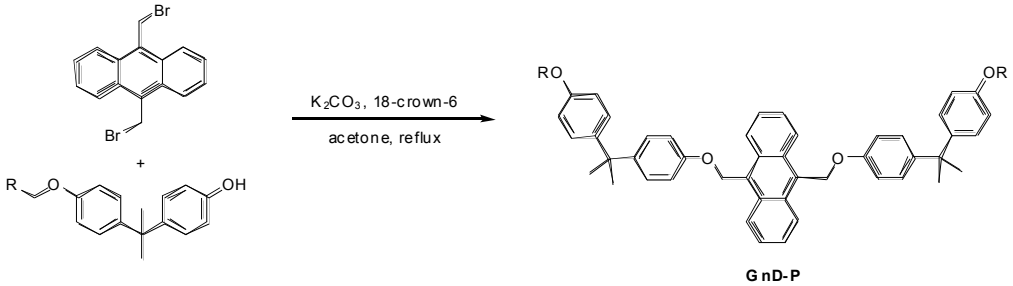
139.7, 139.4, 138.7, 131.8, 131.3, 128.3, 128.2, 128.1, 127.4, 126.8, 125.4, 124.4, 114.6, 114.4, 106.8, 101.8, 101.7, 82.7, 70.3, 70.2, 70.1, 66.1, 62.9, 42.1, 31.4, 28.4. MALDI-ToF m/z calcd. for $C_{231}H_{276}O_{64}$-anthracene+Na^+: 3922.4; found: 3921.0.

G4M-P



This compound was synthesized by using general procedure IV, Yield (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.27 (d, J = 8.6 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.47 (m, J = 8.0 Hz, 4H), 7.20 (m, 4H), 7.04 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.71 (br, 14H), 6.65 (br, 16H), 6.58 (br, 39H), 6.50 (t, J = 2.0 Hz, 8H), 6.42 (t, J = 2.0 Hz, 16H), 5.90 (s, 2H), 4.93 (s, 62H), 4.47 (s, 64H), 1.67 (s, 6H), 1.46 (s, 288H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 157.4, 156.9, 143.9, 143.6, 139.7, 139.4, 138.7, 131.8, 131.3, 129.4, 129.3, 128.2, 128.1, 127.4, 126.8, 125.4, 124.4, 114.6, 114.5, 106.8, 101.8, 101.7, 82.7, 70.3, 70.1, 66.0, 62.9, 42.1, 31.9, 28.4.

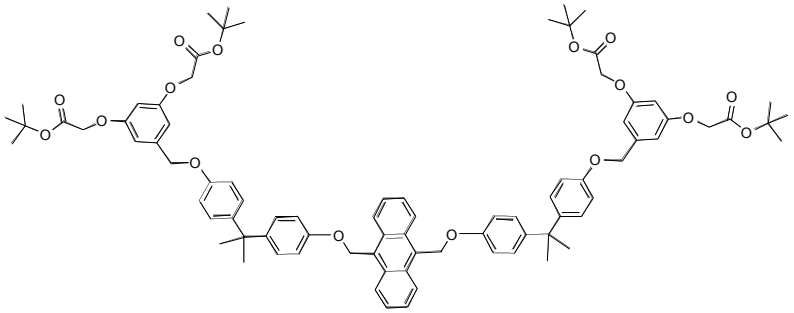
Synthesis of monodendron with anthracene core



General procedure V

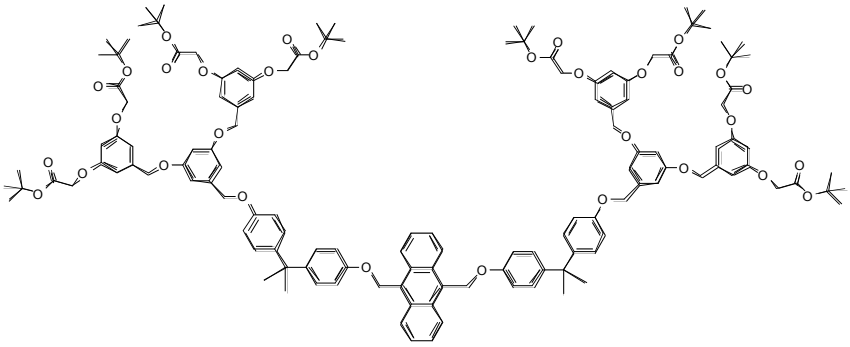
Appropriate Gn-Bisphenol compound (2 equiv), 9,10-bromomethyl anthracene, K_2CO_3 (6-9 equiv), 18-crown-6 (catalytic amount), and THF were refluxed under argon for 24-48 hours. Water was added to the reaction mixture. The aqueous layer was extracted wit ethyl acetate, dried over Na_2SO_4 anhydrous, and concentrated by rotary evaporator. Crude product was purified by column chromatography (SiO_2, hexanes/ethyl acetate).

Synthesis of G0D-P



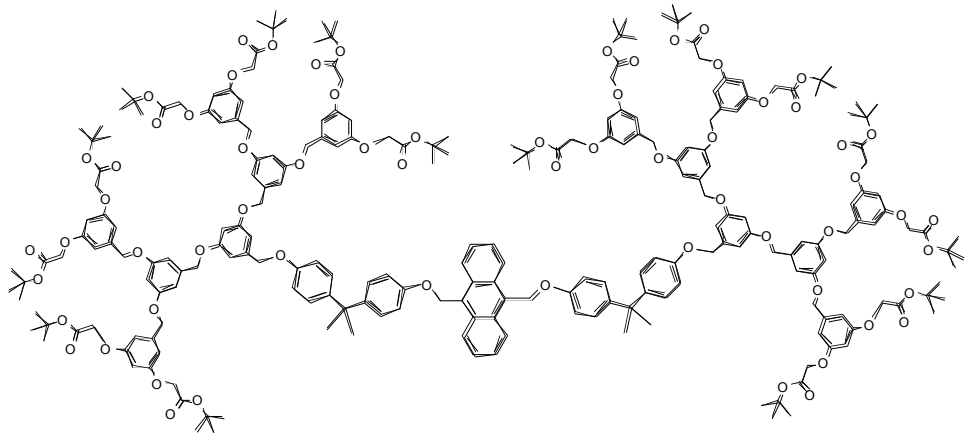
This compound was synthesized by using general procedure IV, Yield (39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (m, J = 3.2 Hz 4H), 7.53 (m, J = 3.0 Hz, 4H), 7.20 (d, J = 8.8 Hz, 8H), 7.08 (d, J = 8.8 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 6.60 (d, J = 2.7 Hz, 4H), 6.43 (t, J = 2.27 Hz, 2H), 5.97 (s, 4H), 4.97 (s, 4H), 4.49 (s, 8H), 1.68 (s, 12H), 1.48 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 159.5, 157.3, 156.8, 144.0, 143.8, 140.2, 131.2, 129.5, 128.1, 128.0, 126.5, 125.1, 115.0, 114.5, 106.7, 101.6, 82.8, 70.0, 66.0, 42.1, 31.4, 28.4. MALDI-ToF m/z calcd. for $C_{84}H_{94}O_{16}$+Na^+: 1382.6; found: 1381.9.

Synthesis of G1D-P



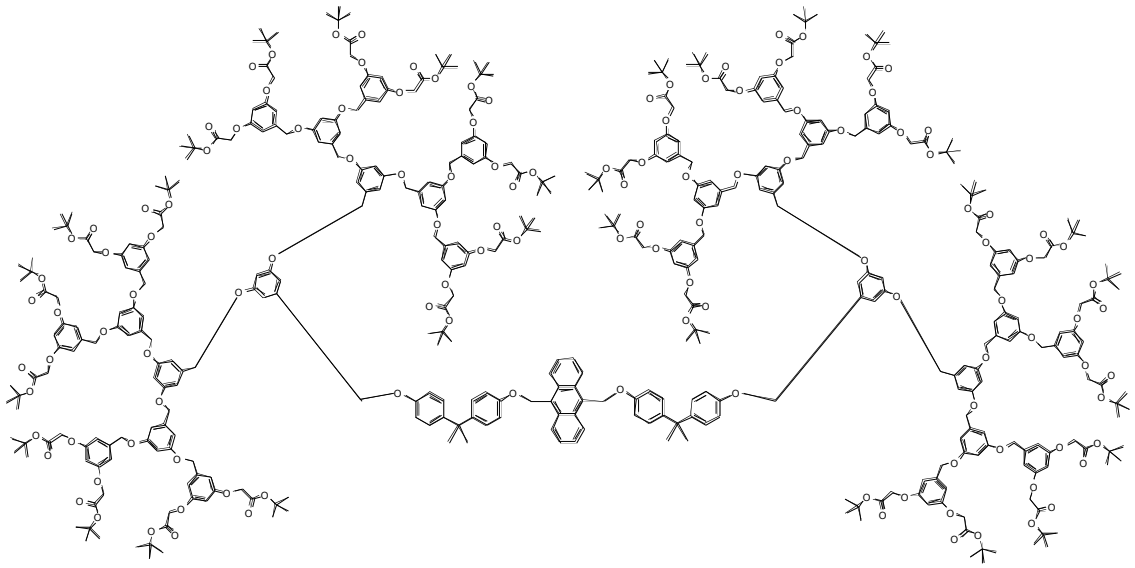
This compound was synthesized by using general procedure IV, Yield (29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (m, 4H), 7.53 (m, 4H), 7.23 (m, 8H), 7.06 (d, J = 8.8 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.62 (s, 4H), 6.60 (s, 8H), 6.51 (s, 2H), 6.43 (s, 4H), 5.96 (s, 4H), 4.97 (s, 12H), 4.49 (s, 16H), 1.69 (s, 12H), 1.48 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 160.2, 159.5, 157.3, 156.7, 154.2, 143.9, 143.7, 142.9, 139.7, 131.6, 129.5, 128.1, 128.0, 126.4, 125.0, 115.0, 114.4, 106.7, 106.5, 101.7, 82.7, 70.1, 70.0, 66.0, 62.9, 41.8, 31.3, 28.3. MALDI-ToF m/z calcd. for $C_{136}H_{158}O_{32}$+Na^+: 2327.7; found: 2328.2.

Synthesis of G2D-P



This compound was synthesized by using general procedure IV, Yield (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (m, 4H), 7.52 (m, 4H), 7.21 (m, 8H), 7.05 (d, J = 8.8 Hz, 4H), 6.90 (d, J = 8.8 Hz, 4H), 6.70 (s, 4H), 6.66 (s, 8H), 6.59 (s, 18H), 6.50 (s, 4H), 6.43 (s, 8H), 5.94 (s, 4H), 4.94 (s, 28H), 4.48 (s, 32H), 1.68 (s, 12H), 1.48 (s, 144H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 157.0, 143.7, 143.1, 139.9, 139.7, 139.5, 131.1, 129.5, 128.2, 128.1, 126.4,125.2, 114.5, 114.4, 106.8, 101.8, 101.7, 82.7, 70.3, 70.2, 70.1, 66.1, 42.1, 31.5, 28.4. MALDI-ToF m/z calcd. for $C_{240}H_{286}O_{64}^{+}$: 4194.8; found: 4196.8.

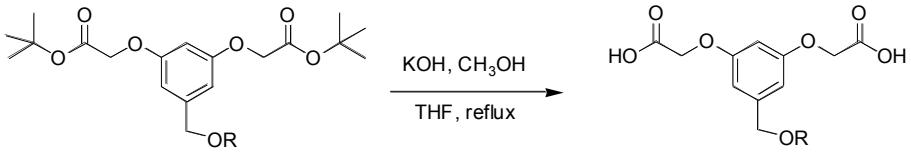
Synthesis of G3D-P



This compound was synthesized by using general procedure IV, Yield (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (m, 4H), 7.51 (m, 4H), 7.21 (m, 8H), 7.05 (br, 4H), 6.88 (br, 4H), 6.71 (m, 12H), 6.65 (s, 16H), 6.58 (d, J = 2.0 Hz, 34H), 6.54 (br, 4H), 6.50 (br, 8H), 6.42 (t, J = 2.3 Hz, 16H), 5.91 (s, 4H), 4.93 (s, 60H), 4.47 (s, 64H), 1.68 (s, 12H), 1.46 (s, 288H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 160.4, 160.3, 159.5, 156.9, 153.4, 144.5, 142.3,

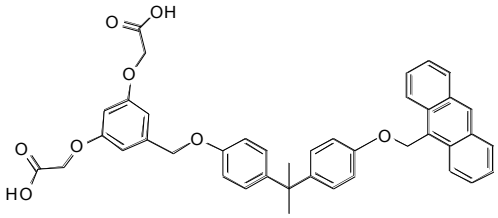
139.7, 139.5, 134.4, 129.3, 128.3, 128.1, 128.0, 127.5, 115.0, 114.4, 106.8, 106.8, 101.8, 101.7, 82.7, 70.3, 70.1, 68.3, 66.0, 53.6, 31.2, 28.4.

General Procedure VI



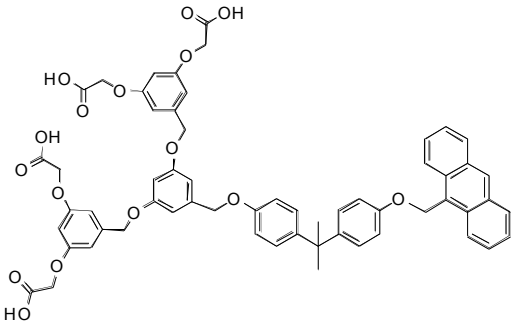
To solution of dendrimers in 10 ml THF/ 5 ml methanol was added KOH solution. After refluxing for overnight, solvent was removed followed by the addition of water then reaction the mixture was refluxed for overnight. The mixture was cooled to ambient temperature then HCl solution (20%) was added drop-wise to get white precipitate. Solid compound was dried under vacuum.

Synthesis of G0M



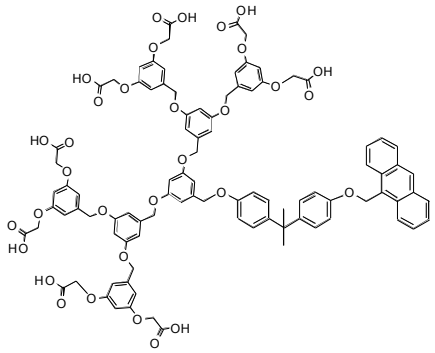
This compound was synthesized by using general procedure VI, Yield (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.22 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 7.8 Hz, 2H), 7.43 (m, 4H), 7.14 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 2.3 Hz, 2H), 6.41 (t, J = 2.3 Hz, 1H), 5.87 (s, 2H), 4.91 (s, 2H), 4.51 (s, 4H), 1.62 (s, 6H). The ^{1}H NMR was compared with the unhydrolyzed version **G0M-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{41}H_{36}O_8^+$: 656.7; found: 656.3.

Synthesis of G1M



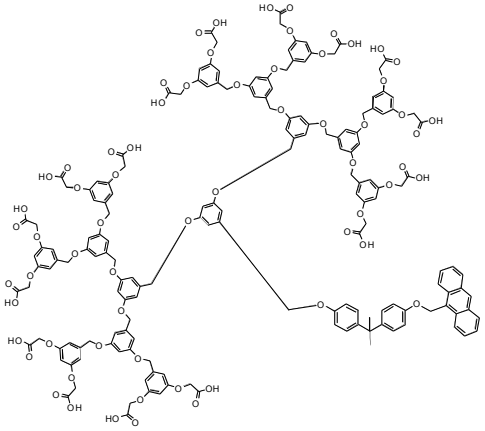
This compound was synthesized by using general procedure VI, Yield (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.38 (d, J = 8.3 Hz, 2H), 8.20 (d, J = 7.8 Hz, 2H), 7.61 (m, J = 8.3 Hz, 4H), 7.20 (t, J = 9.6 Hz, 4H), 7.11 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 2.0 Hz, 2H), 6.65 (d, J = 2.0 Hz, 5H), 6.46 (t, J = 2.0 Hz, 2H), 6.03 (s, 2H), 5.04 (s, 6H), 4.69 (s, 8H), 1.66 (s, 6H). The ^{1}H NMR was compared with the unhydrolyzed version **G1M-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{59}H_{52}O_{160}^+$: 1017.0; found: 1017.3.

Synthesis of G2M



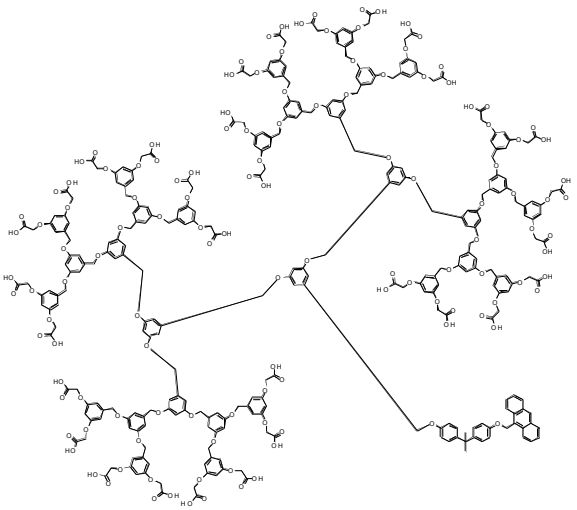
This compound was synthesized by using general procedure VI, Yield (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.40 (d, J = 9.8 Hz, 2H), 8.18 (d, J = 7.8 Hz, 2H), 7.58 (m, 4H), 7.21 (t, 4H), 7.12 (d, 2H), 6.95 (d, 2H), 6.74 (br, 5H), 6.65 (br, 8H), 6.47 (s, 4H), 6.03 (s, 2H), 5.04 (s, 14H), 4.69 (s, 16H), 1.66 (s, 6H). The ^{1}H NMR was compared with the unhydrolyzed version **G2M-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{95}H_{84}O_{32}$+Na^+: 1760.7; found: 1757.9.

Synthesis of G3M



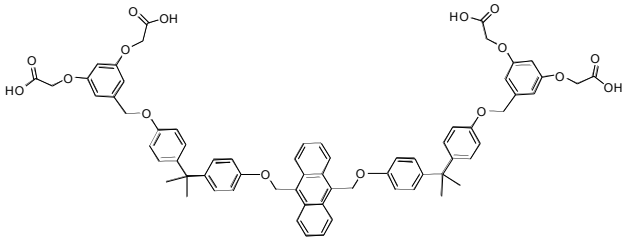
This compound was synthesized by using general procedure VI, Yield (40%). ^{1}H NMR (400 MHz, CD_3CO): δ 8.67 (s, 1H), 8.38 (d, J = 9.0 Hz, 2H), 8.15 (m, J = 6.0 Hz, 2H), 7.56 (m, J = 8.3 Hz, 4H), 7.23 (m, 4H), 7.08 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 9.6 Hz, 2H), 6.76 (br, 15H), 6.72 (br, 20H), 6.52 (s, 8H), 6.02 (s, 2H), 5.05 (s, 30H), 4.73 (s, 32H), 1.67 (s, 6H). The ^{1}H NMR was compared with the unhydrolyzed version **G3M-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{59}H_{52}O_{160}$+Na^+: 3201.9; found: 3202.7.

Synthesis of G4M



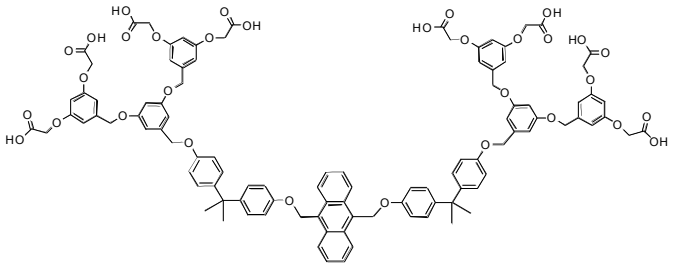
This compound was synthesized by using general procedure VI, Yield (95%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.75 (s, 1H), 8.38 (d, 2H), 8.19 (d, 2H), 7.60 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 7.01 (d, 2H), 6.76 (br, 30H), 6.65 (br, 47H), 6.46 (br, 16H), 6.03 (s, 2H), 5.04 (s, 62H), 4.69 (s, 64H), 1.66 (s, 6H). The ^{1}H NMR was compared with the unhydrolyzed version **G4M-P** to make sure that tert-butyl ester was hydrolyzed.

Synthesis of G0D



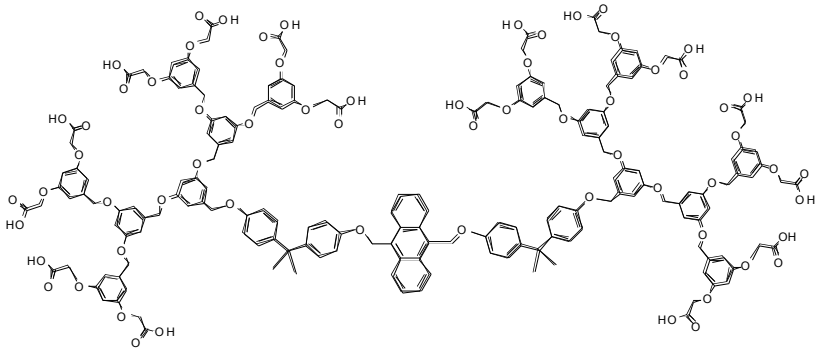
This compound was synthesized by using general procedure VI, Yield (87%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.45 (m, J = 3.0 Hz, 4H), 7.65 (m, J = 3.0 Hz, 4H), 7.21 (t, J = 9.3 Hz, 8H), 7.13 (d, J = 8.6 Hz, 4H), 6.95 (d, J = 8.8 Hz, 4H), 6.65 (d, J = 2.0 Hz, 4H), 6.46 (t, J = 2.0 Hz, 2H), 6.07 (s, 4H), 5.03 (s, 4H), 4.70 (s, 8H), 1.66 (s, 12H). The ^{1}H NMR was compared with the unhydrolyzed version **G0D-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{68}H_{62}O_{16}$+Na^+: 1135.2; found: 1134.7.

Synthesis of G1D



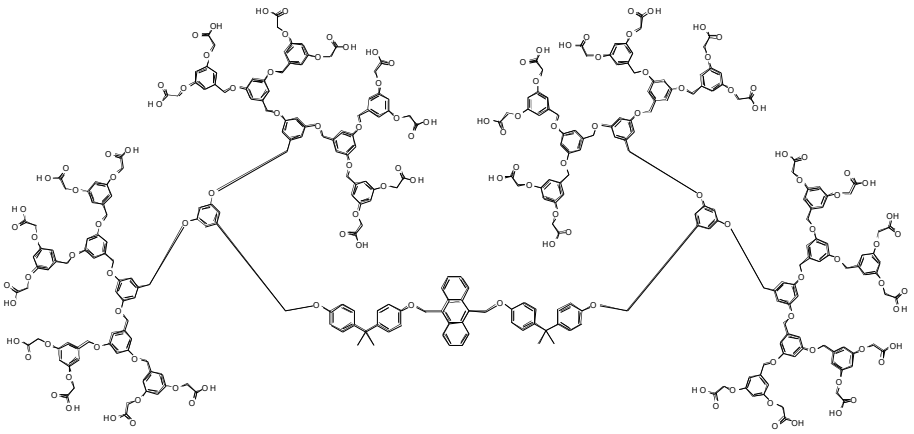
This compound was synthesized by using general procedure VI, Yield (93%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.45 (m, *J*= 3.0 Hz, 4H), 7.65 (m, *J*= 3.0 Hz, 4H), 7.21 (t, *J* = 9.3 Hz, 8H), 7.12 (d, *J* = 8.6 Hz, 4H), 7.02 (d, *J* = 8.6 Hz, 4H), 6.73 (m, 4H), 6.65 (br, 10H), 6.46 (t, 4H), 6.07 (s, 4H), 5.04 (s, 12H), 4.68 (s, 16H), 1.66 (s, 12H). The ^{1}H NMR was compared with the unhydrolyzed version **G1D-P** to make sure that tert-butyl ester was hydrolyzed. MALDI-ToF m/z calcd. for $C_{104}H_{94}O_{32}$+Na^+: 1878.8; found: 1878.1.

Synthesis of G2D



This compound was synthesized by using general procedure VI, Yield (11%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.27 (m, *J* = 2.5 Hz, 4H), 7.98 (m, *J* = 2.5 Hz, 4H), 7.12 (d, 8H), 7.02 (d, *J* = 8.6 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.75 (br, 12H), 6.66 (br, 22H), 6.46 (s, 8H), 6.30 (s, 4H), 5.08 (s, 28H), 4.69 (s, 32H), 1.57 (s, 12H). The ^{1}H NMR was compared with the unhydrolyzed version **G2D-P** to make sure that tert-butyl ester was hydrolyzed.

Synthesis of G3D



This compound was synthesized by using general procedure VI, Yield (53%). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.28 (m, 4H), 8.00 (m, 4H), 7.10 (m, 8H), 7.02 (br, 4H), 6.88 (br, 4H), 6.76 (br, 28H), 6.65 (br, 46H), 6.46 (s, 16H), 6.30 (s, 4H), 5.04 (s, 60H), 4.68 (s, 64H), 1.57 (s, 12H). The ^{1}H NMR was compared with the unhydrolyzed version **G3D-P** to make sure that tert-butyl ester was hydrolyzed.

References:

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