Supporting Information for

Chiral Hybrid Metal-Organic Dendrimers

Hua Jiang, Sukjoong Lee, and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599, wlin@unc.edu

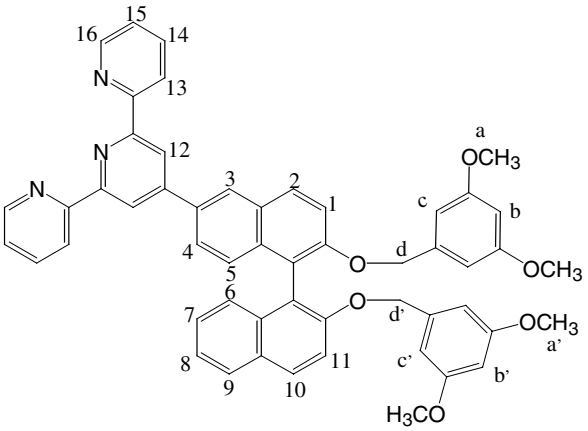
Experimental Section.

Materials and General Procedures. All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. UV-Visible spectra were obtained using a Hewlett Packard 8452A Diode array spectrophotometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. ^{1}H NMR spectra were recorded on Varian XL-400 spetrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26), or acetonitrile (δ 1.93). ^{13}C{^{1}H} NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of the methyl group of acetone-d_6 (δ 29.8), methylenechloride-d_2 (δ 53.8), or chloroform-d_1 (δ 77.0). Cyclic voltammetry (CV) experiments were carried out with a 0.5 mM solution of the desired compound under dried and deoxygenated methylenechloride on a BAS 100B

electrochemical analyzer, with a platinum disk (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a silver wire reference electrode. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the electrolyte.

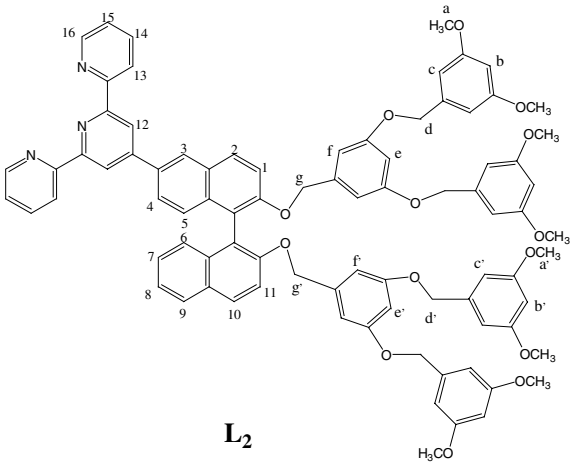
Synthesis.

1. 4'-[6-(2,2'-(dendritic benzoxyl)-1,1'-binaphthyl)]-2,2': 6'2''-terpyridine, (n=0), L_1. A mixture of 4'-[6-(2,2'-hydroxy-1,1'-binaphthyl)]-2,2':6'2''-terpyridine (250 mg, 0.483 mmol), dendritic benzyl bromide G_0Br (245 mg, 1.06 mmol), 18-crown -6 (30 mg, 0.114 mmol), and anhydrous potassium carbonate (333 mg, 2.41 mmol) in distilled acetone (10 mL) was refluxed for 3 days. After cooled to room temperature, the reaction mixture was added water and then CH_2Cl_2 was added to dissolve the product. The organic layer was dried over $MgSO_4$. After filtration and evaporation, the solid residue was chromatographied on silica gel with 1:1 ethyl acetate/hexane to give light yellow solid (348 mg, 88 %). ^{1}H NMR ($CDCl_3$): 8.80 (s, 2 H, H12), 8.70 (d, 4.3 Hz, 2 H, H16), 8.65 (d, 7.9 Hz, 2 H, H13), 8.42 (d, 1.8 Hz, 1 H, H3), 8.05 (d, 9.2 Hz, 1 H, H2), 7.94 (d, 9.2 Hz, 1 H, H10), 7.85 (d, 8.5 Hz, 1 H, H9), 7.84 (td, 7.9 Hz, 1.8 Hz, 2 H, H14), 7.76 (dd, 9.2 Hz, 1.8 Hz, 1 H, H4), 7.47 (t, 9.2 Hz, 2 H, H1 & H11), 7.353-7.254 (m, 5 H, H15 & H5 & H8), 7.274-7.229 (m, 2 H, H6 & H7), 6.21 (t, 1.8 Hz, 1 H, Hb or Hb'), 6.18 (t, 1.8 Hz, 1 H, Hb' or Hb), 6.12 (s, 4 H, Hc & Hc'), 5.01 & 5.00 (ss, 4 H, Hd & Hd'), 3.452 & 3.446 (ss, 12H, Ha & Ha'). $^{13}C\{^1H\}$ ($CDCl_3$): δ 160.6, 156.3, 155.9, 154.7, 154.0, 150.1, 149.1, 139.7, 136.8, 134.4, 134.1, 133.6, 130.0, 129.4, 128.5, 128.4, 127.9, 126.7, 126.5, 16.3, 125.4, 125.3, 123.8, 123.7, 121.3, 120.5, 120.2, 118.8, 116.1, 115.6, 104.0, 103.9, 99.9, 99.8, 71.0, 70.8, 55.04, 55.02.



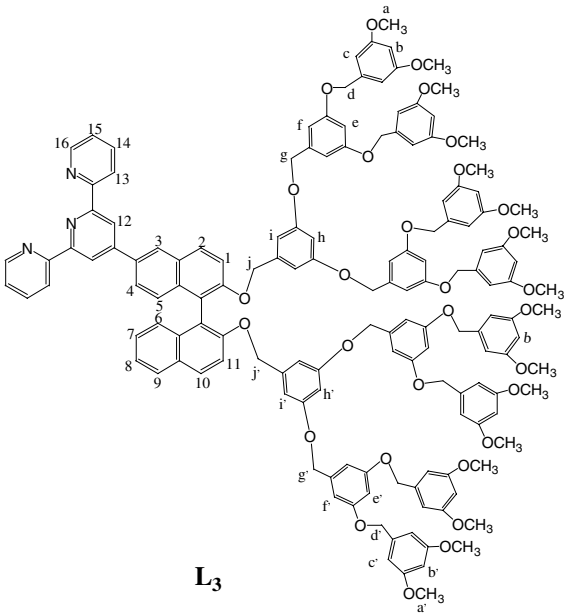
L_1

2. 4'-[6-(2,2'-(dendritic benzoxyl)-1,1'-binaphthyl)]-2,2': 6'2''-terpyridine, (n=1), L_2. By a procedure analogous to that described above, white solid was obtained (yield: 76 %). ^{1}H NMR ($CDCl_3$): 8.74 (s, 2 H, H12), 8.72 (d, 4.3 Hz, 2 H, H16), 8.67 (d, 7.3 Hz, 2 H, H13), 8.40 (s, 1 H, H3), 8.07 (d, 1 H, H2), 7.95 (d, 1 H, H10), 7.89 (td, 7.3 Hz, 1.2 Hz, 2 H, H14), 7.83 (d, 8.5 Hz, 1 H, H9), 7.80 (dd, 8.2 Hz, 1.8 Hz, 1 H, H4), 7.513 (t, 9.2 Hz, 2 H, H1 & H11), 7.381-7.287 (m, 5 H, H15 & H5 & H7 & H8), 7.27 (d, 4.9 Hz, 1 H, H6), 6.50 (d, 1.8 Hz, 4 H, Hc or Hc'), 6.41 (t, 1.8 Hz, 2 H, Hb or Hb'), 6.39 (d, 1.8 Hz, 4 H, Hc' or Hc), 6.35 (t, 2.4 Hz, 1 H, He or He'), 6.31 (t, 2.4 Hz, 1 H, He' or He), 6.26 (t, 1.8 Hz, , 2 H, Hb or Hb'), 6.22 (t, 2.7 Hz, 4 H, Hf & Hf'), 5.05 & 5.04 (ss, 4 H, Hg & Hg'), 4.56 & 4.50 (ss, 8 H, Hd & Hd'), 3.79 & 3.65 (ss, 24 H, Ha & Ha'). $^{13}C\{^1H\}$ ($CDCl_3$): δ 160.9, 160.7, 159.7, 159.6, 156.3, 155.7, 154.7, 154.0, 149.7, 149.0, 139.7, 139.0,136.7, 134.3, 134.1, 130.1, 129.5, 129.4, 128.0, 126.7, 126.6, 126.3, 125.3, 123.9, 123.7, 121.1, 120.5, 120.3, 118.5, 116.1, 115.6, 105.4, 105.3, 105.0, 104.9, 101.5, 99.8, 70.9, 70.7, 69.7, 55.3, 55.1.



L_2

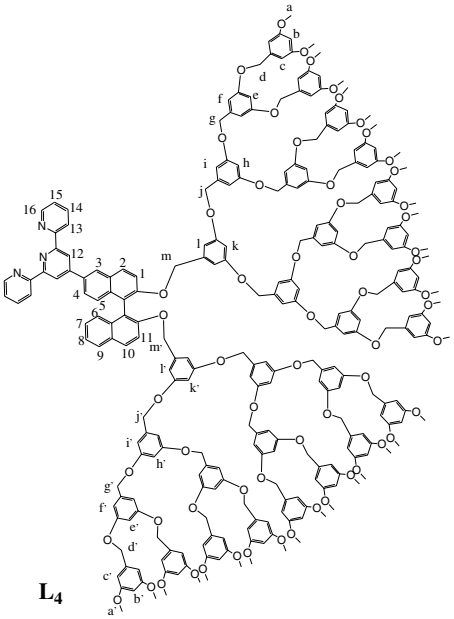
3. 4'-[6-(2,2'-(dendritic benzoxyl)-1,1'-binaphthyl)]-2,2': 6'2''-terpyridine, (n=2), L_3. A solution of 4'-[6-(2,2'-hydroxy-1,1'-binaphthyl)]-2,2':6'2''-terpyridine (105 mg, 0.203 mmol) in 1 mL of anhydrous DMF was added 60 % NaH which is dispersed in mineral oil (17 mg, 0.425 mmol). After stirred for 4 h at room temperature, the solution was added dendritic benzyl bromide L_2Br (470 mg, 0.448 mmol) in 1 mL of anhydrous DMF.



L_3

After stirred overnight at 60 ^{o}C, the reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$. After the solvent was evaporated, the solid was purified by silical gel column chromatography with ethyl acetate/hexane (1:1 v/v). The white solid was obtained. Yield: 470 mg (94 %). ^{1}H NMR ($CDCl_3$): 8.75 (s, 2 H, H12), 8.68 (d, 3.7 Hz, 2 H, H16), 8.61 (d, 7.9 Hz, 2 H, H13), 8.34 (s, 1 H, H3), 7.98 (d, 9.2 Hz, 1 H, H2), 7.87 (d, 9.2 Hz, 1 H, H10), 7.82 (td, 7.9 Hz, 1.8 Hz, 2 H, H14), 7.80 (dd, 7.3 Hz, 1.2 Hz, 1 H, H4), 7.75 (d, 8.5 Hz, 1 H, H9), 7.51 (d, 9.2 Hz, 1 H, H1), 7.48 (d, 9.2 Hz, 1 H, H11), 7.38 (d, 9.2 Hz, 1H, H5), 7.323-7.292 (m, 2 H, H15), 7.277-7.237 (m, 3 H, H6 & H7 & H8), 6.58 (d, 1.8 Hz, 4 H, Hf or Hf'), 6.57 (d, 1.8 Hz, 8 H, Hc or Hc'), 6.56 (t, 1.8 Hz, 2 H, He or He'), 6.50 (d, 2.4 Hz, 8 H, Hc' or Hc), 6.49 (d, 1.8 Hz, 4 H, Hf' or Hf), 6.43 (t, 1.8 Hz, 2 H, He' or He), 6.40 (t, 1.8 Hz, 4 H, Hb & Hb'), 6.37 (t, 1.8 Hz, 4 H, Hb' & Hb), 6.29 (t, 1.8 Hz, 1 H, Hh or Hh'), 6.25 (t, 1.8 Hz, 1 H, Hh' or Hh), 6.18 (d, 2.4 Hz, 2 H, Hi or Hi'), 6.17 (d, 2.4 Hz, 2 H, Hi' or Hi), 5.03 (s, 4 H, Hj & Hj'), 4.93 & 4.81 (ss, 16 H, Hd & Hd'), 6.49 & 6.45 (ss, 8 H, Hg & Hg'), 3.76 & 3.73 (ss, 48 H, Ha & Ha'). ^{13}C{^{1}H} ($CDCl_3$): δ 160.9, 160.8, 159.9, 159.8, 159.6, 156.2, 155.8, 154.6, 153.9, 149.8, 149.0, 139.7, 139.2, 139.0, 136.7, 134.3, 134.1, 133.5, 130.1, 129.5, 129.4, 128.0, 126.8, 126.6, 126.3, 125.4, 125.3, 123.9, 123.7, 121.3, 120.5, 120.2, 118.5, 116.0, 115.5, 106.6, 106.5, 105.2, 105.1, 104.9, 101.6, 101.3, 101.2, 99.9, 99.8, 70.8, 70.5, 69.9, 69.8, 69.6, 55.28, 55.25.

4. 4'-[6-(2,2'-(dendritic benzoxyl)-1,1'-binaphthyl)]-2,2': 6'2''-terpyridine, (n=3), L_4. By a procedure analogous to that described in experiment 1, white solid was obtained (yield: 53 %). ^{1}H NMR ($CDCl_3$): 8.74 (s, 2 H, H12), 8.66 (dz, 1 H, H2), 7.83 (d, 9.2 Hz, 1 H, H10), 7.82 (m, 3 H, H14 & H9), 7.72 (d, 7.3 Hz, 3.7 Hz, 2 H, H16), 8.59 (d, 7.9 Hz, 2 H, H13), 8.32 (s, 1 H, H3), 7.95 (d, 9.2 H, 1 H, H4), 7.45 (t, 9.2 Hz, 2 H, H1 & H11), 7.35 (d, 8.5 Hz, 1H, H6), 7.239 (broad, 5 H, H15 & H7 & H8), 6.64 (broad, 8 H, Hf or Hf'), 6.59 (broad, 8 H,

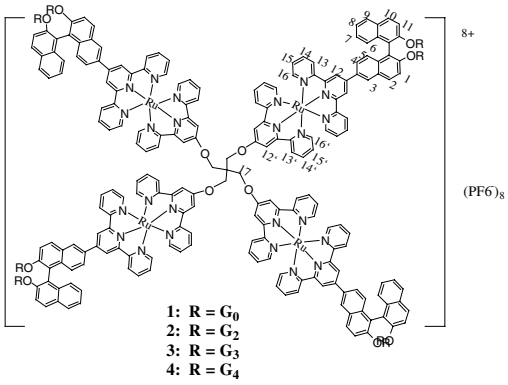


L_4

Hf' or Hf), 6.55 (broad, 4 H, He or He'), 6.52 (broad, 40 H, Hc & Hc' & Hi & Hi'), 6.47 (broad, 4 H, He' or He), 6.39 (broad, 4 H, Hh & Hh'), 6.36(), 6.26-6.22 (broad, 2 H, Hk & Hk'), 6.15 & 6.14 (broad, 4 H Hl & Hl'), 4.97 (broad, 4 H, Hm & Hm'), 4.88 & 4.87 (ss, broad, 40 H, Hd & Hd' & Hg), 4.76 (s, 8 H, Hg'), 4.43 & 4.39 (ss, 8 H, Hj & Hj'), 3.71 & 3.70 (ss, 96 H, Ha & Ha'). ^{13}C ($CDCl_3$): δ 160.9, 160.0, 159.95, 159.90, 159.8, 159.6, 155.6, 154.6, 153.8, 149.8, 148.9, 139.7, 139.3, 139.12, 139.10, 139.0, 136.9, 134.4, 134.0, 133.3, 130.2, 129.5, 129.3, 128.0, 126.8, 126.6, 126.3, 125.3, 123.9, 123.7, 123.2, 121.3, 120.4, 120.1, 118.6, 115.9, 115.4, 106.6, 106.5, 106.3, 106.2, 105.2, 105.0, 104.9, 101.6, 101.5, 101.4, 101.1, 99.9, 99.8, 70.6, 70.4, 69.95, 69.91, 69.90, 69.7, 55.2.

5. Ru (III) complexes. The above ligands were dissolved in a mixture of acetone and ethanol, and excess amount of $RuCl_3$ was added. The reaction mixture was refluxed overnight. After cooled down to room temperature, the solvents were evaporated and the residue was washed with ethanol. The solid was purified by preparative-scale thin layer chromatography with ethyl acetate. Dark brown solids were obtained. The yields for Ru(**L_{1-4}**)Cl_3 are 95 %, 76 %, 85 %, and 96 %, respectively.

6. **(Dendrimer-G_0)·(PF_6)$_8$, 1a.** To a solution of tetrakis(2,2': 6',2''-terpyridinyl-4'-oxymethyl)methane (10.5 mg, 0.00943 mmol) and 4-ethylmorpholine (0.1 mL) in ethane-1,2-diol (8 mL) was added Ru (**L_1**)Cl_3 (63 mg, 0.0401 mmol). The reaction mixture was stirred for 18 h at 120 °C. After cooled down to room temperature, saturated aqueous solution of KPF_6 was added to afford the red solid. After filtration, the red solid was recrystallized with CH_3CN/CH_3OH. The red solid was obtained (33 mg, 59 %). ^{1}H NMR (CD_3CN): 9.07 (s, 8 H, H12), 8.88 (s, 8 H, H12'), 8.82 (s, 4 H, H3), 8.72 (d, 8.5 Hz, 8 H, H13), 8.63 (d, 8.5 Hz, 8 Hz, H13'), 8.32 (d, 9.2 Hz, 4 H, H2), 8.12 (d, 9.2 Hz, 4 H, H10), 8.04 (d, 9.2 Hz, 4 H, H4), 7.99 (d, 7.9 Hz, 4 H, H9), 7.93-7.85 (m, 16 H, H14 & H14'), 7.77 (d, 9.2 Hz, 4 H, H1), 7.67 (d, 9.2 Hz, 4 H, H11), 7.52 (d, 6.5 Hz, 8 H, H16), 7.45-7.39 (m, 16 H, H16' & H5 & H8), 7.33 (t, 7.6 Hz,



4 H, H7), 7.21 (d, 8.5 Hz, 4 H, H6), 7.16-7.12 (m, 4 H, H15 & H15'), 6.26 (t, 1.8 Hz, 4 H, Hb or Hb'), 6.25 (t, 1.8 Hz, 4H, Hb' or Hb), 6.21 (s, 16H, Hc & Hc'), 6.56 (s, 8H, H17), 5.18-5.07 (m, 16H, Hd & Hd'), 3.533 & 3.526 (ss, 48H, Ha & Ha'). $^{13}C\ \{^{1}H\}$ (Acetone-d_6): δ 167.5, 161.7, 161.6, 159.4, 159.3, 157.0, 156.8, 15.4, 155.1, 153.4, 153.38, 153.30, 148.5, 140.8, 140.5, 138.8, 138.6, 135.5, 134.8, 132.5, 131.4, 130.6, 130.3, 129.0, 128.8, 128.6, 128.4, 127.3, 125.9, 125.6, 125.3, 124.5, 122.0, 121.2, 121.1, 121.0, 120.3, 117.1, 116.3, 112.9, 104.9, 104.8, 100.4, 100.3, 71.3, 71.0, 69.7, 55.4, 55.3.

7. **(Dendrimer-G_1)·$(PF_6)_8$, 1b.** By a procedure analogous to that described in experiment 6, red solid was obtained (yield: 57 %). ^{1}H NMR (CD_3CN): 8.91 (s, 8 H, H12), 8.75 (s, 4 H, H3), 8.73 (s, 8 H, H12'), 8.61 (d, 7.3 Hz, 8 H, H13), 8.48 (d, 7.9 Hz, 8 Hz, H13'), 8.28 (d, 9.8 Hz, 4 H, H2), 8.08 (d, 9.2 Hz, 4 H, H10), 8.01 (d, 9.2 Hz, 4 H, H4), 7.94 (d, 7.3 Hz, 4 H, H9), 7.89 (broad, 16 H, H14 & H14'), 7.74 (d, 9.2 Hz, 4 H, H1), 7.66 (d, 9.2 Hz, 4 H, H11), 7.51 (d, 4.9 Hz, 8 H, H16), 7.44 (d, 9.2 Hz, 4 H, H5), 7.39 (d, 4.9 Hz, 8 H, H16'), 7.36-7.29 (m, 8 H, H7 & H8), 7.20 (d, 7.9 Hz, 4 H, H6), 7.17-7.12 (broad, 16 H, H15 & H15'), 6.50 (d, 1.8 Hz, 16 H, Hc or Hc'), 6.46 (d, 1.8 Hz, 16 H, Hc' or Hc), 6.42 (t broad, 8 H, He & He'), 6.36 (t broad, 8 H, Hb or Hb'), 6.287 (broad, 16 H, (Hb' or Hb) & (Hf or Hf')), 6.26 (d broad, 8 H, Hf' or Hf), 5.52 (s broad, 8 H, H17), 5.11 (m, 16 H, Hg & Hg'), 4.67 & 4.60 (s s, 32 H, Hd & Hd'), 3.74 & 3.59 (s s, 96 H, Ha & Ha'). $^{13}C\ \{^{1}H\}$ (CD_2Cl_2): δ 167.2, 161.4, 160.2, 160.1, 159.0, 158.0, 156.3, 156.0, 155.8, 154.4, 153.3, 152.1, 148.1, 140.3, 140.0, 139.7, 139.6, 135.3, 134.4, 131.8, 131.1, 130.2, 129.9, 129.8, 128.6, 128.4, 127.6, 127.5, 127.1, 125.4, 125.2, 124.9, 124.4, 121.0, 120.8, 120.0, 116.9, 115.8, 112.4, 105.8, 105.6, 105.5, 101.8, 100.0, 99.8, 71.1, 71.0, 70.1, 70.0, 67.8, 55.7, 55.6, 30.1.

8. **(Dendrimer-G_2)·$(PF_6)_8$, 1c.** By a procedure analogous to that described in experiment 6, red solid was obtained (yield: 27 %). ^{1}H NMR (CD_3CN): 8.86 (s, 8 H, H12), 8.73 (s, 8 H, H12'), 8.66 (s, 4 H, H3), 8.59 (d, 7.3 Hz, 8 H, H13), 8.41 (d, 7.9 Hz, 8 Hz, H13'), 8.16 (d, 9.2 Hz, 4 H, H2), 7.99 (d, 8.5 Hz, 4 H, H10), 7.97 (d, 9.2 Hz, 4 H, H4), 7.87 (d, 7.3 Hz, 4 H, H9), 7.82-7.75 (m, 16 H, H14 & H14'), 7.67 (d, 9.8 Hz, 4 H,

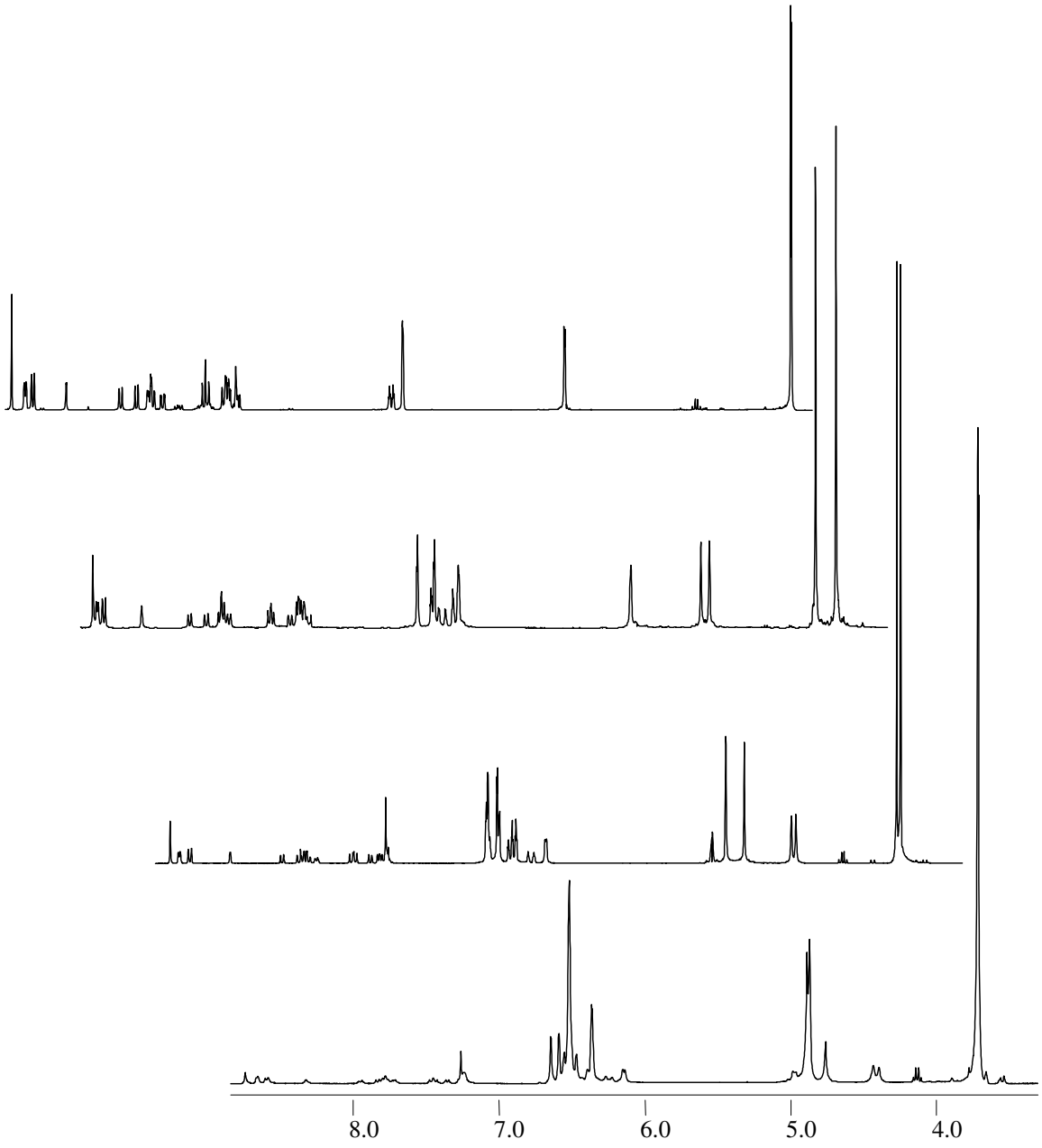
H1), 7.58 (d, 9.8 Hz, 4 H, H11), 7.48 (d, 4.3 Hz, 8 H, H16), 7.41 (d, 8.5 Hz, 4 H, H5), 7.35 (d, 4.3 Hz, 8 H, H16'), 7.31 (t, 7.3 Hz, 4 H, H8), 7.29 (t, 7.3 Hz, 4 H, H7), 7.17 (d, 7.3 Hz, 4 H, H6), 7.08 (t, 4.3 Hz, 8 H, H15), 7.03 (t, 4.3 Hz, 8 H, H15'), 6.52 (d, 1.8 Hz, 32 H, Hc), 6.51(broad, 32 H, Hf & He & He'), 6.39 (d, 1.8 Hz, 32 H, Hc'), 6.37 (broad, 32 H, Hf' & Hb), 6.29 (t, broad, 16 H, Hb'), 6.21 (broad, 16 H, Hi & Hh), 6.14 (broad, 4 H, Hh'), 6.10 (broad, 8 H, Hi'), 5.52 (s, broad, 8 H, H17), 5.00 (m, 16 H, Hj & Hj'), 4.87 & 4.76 (ss, 64 H, Hd & Hd'), 4.53 & 4.47 (ss, 32 H, Hg & Hg'), 4.67 & 4.60 (ss, 192 H, Ha & Ha'). $^{13}C\ \{^{1}H\}$ (CD_2Cl_2): δ 167.2, 161.4, 160.4, 160.2, 160.1, 159.0, 157.9, 156.3, 155.9, 155.7, 154.4, 153.3, 152, 148.2, 140.3, 139.9, 139.7, 139.5, 138.4, 138.0, 135.3, 134.3, 131.9, 131.1, 130.2, 129.9, 129.7, 128.6, 127.6, 127.1, 125.4, 125.2, 124.4, 124.2, 121.8, 121.7, 121.6, 121.0, 120.8, 120.0, 116.9, 115.8, 112.4, 106.9, 106.8, 105.7, 105.6, 101.8, 100.0, 99.9, 71.1, 70.8, 70.3, 70.0, 69.9, 66.0, 55.7, 55.6, 30.1.

9. **(Dendrimer-G_3)·$(PF_6)_8$, 1d.** By a procedure analogous to that described in experiment 6, red solid was obtained (yield: 20 %). ^{1}H NMR (CD_3CN): 8.79 (broad), 8.70 (broad), 8.51 (broad), 8.33 (broad), 7.92 (broad), 7.84 (broad), 7.65, (broad), 7.41(broad), 7.28 (broad), 7.14 (broad), 6.96 (broad), 6.91 (broad), 6.51 (broad), 6.40 (broad), 6.35 (broad), 6.28 (broad), 6.23 (broad), 6.13 (broad), 5.99 (broad), 5.87 (broad), 5.52 (8 H, H17), 4.72 (broad), 4.69 (broad), 4.57 (broad), 4.31 (broad), 4.25 (broad), 4.23 (broad), 3.56 (broad), 3.53 (broad). $^{13}C\ \{^{1}H\}$ (acetone-d_6): δ 161.85, 161.82, 160.9, 160.8, 160.7, 140.6, 140.5, 140.4, 140.3, 130.2, 107.2, 106.1, 102.0, 101.9, 100.2, 100.1, 70.3, 55.5.

Table S1. MS peaks and their assignments

Compd	Assignment	Observed M/Z	Expected M/Z
L_1	$(M + H)^+$	818.3232 (EI)	818.3230
L_2	$(M + H)^+$	1362.5322 (FAB)	1362.5327
L_3	$(M+H)^+$	2452.1 (FAB)	2451.7
L_4	M^+	4630.0 (MALDI-TOF)	4630.1
1a	$(M – 3PF_6)^{3+}$	1820.9 (ESI)	1820.7
	$(M – 4PF_6)^{4+}$	1329.6 (ESI)	1329.3
	$(M – 5PF_6)^{5+}$	1034.4 (ESI)	1034.4
	$(M – 6PF_6)^{6+}$	837.9 (ESI)	837.8
1b	$(M – PF_6 + Li)^+$	7935.7 (MALDI-TOF)	7935.8
1c	$(M – PF_6 + Li)^+$	12291.0 (MALDI-TOF)	12289.5
1d	$(M – 3PF_6 + 4Na + Li)^+$	20810.1 (MALDI-TOF)	20809.7

Figure S1. ^{1}H NMR spectra of L_1-L_4.



FigureS2. Fluorescence spectrum of 3,5-dimethoxybenzyl alcohol.

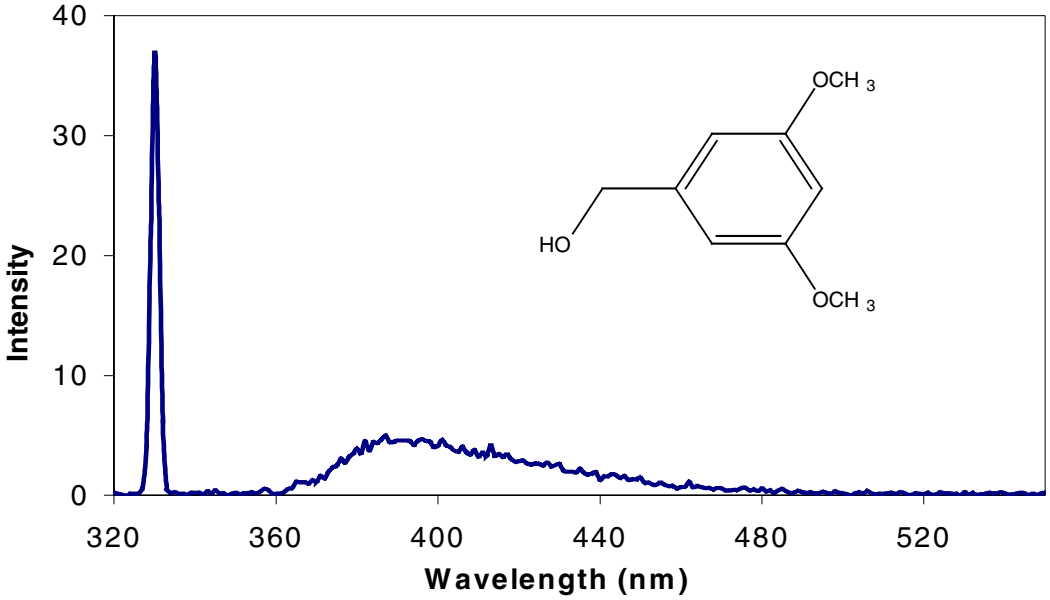


Fig S3. MALDI-TOF Spectrum of **1b**.

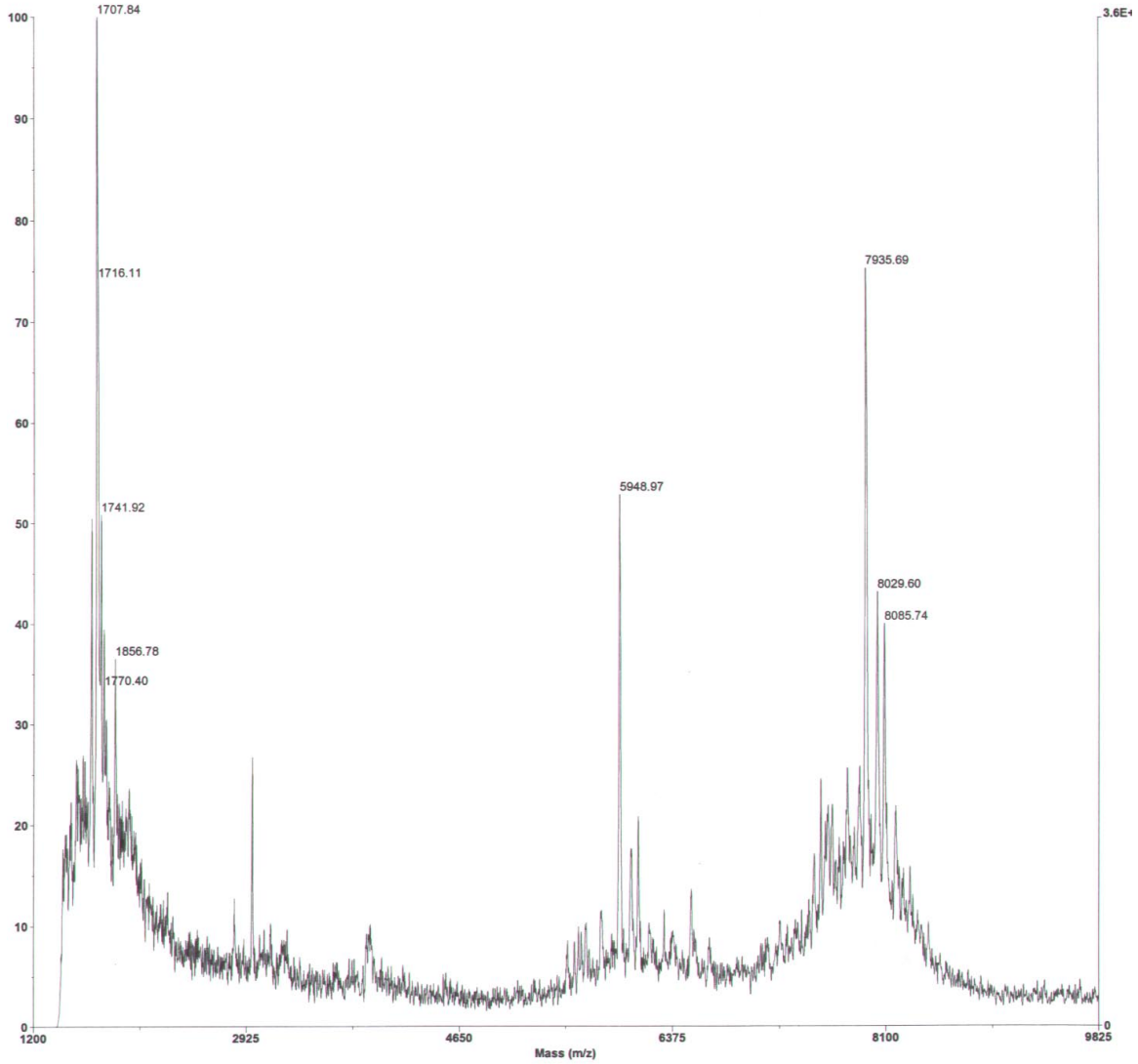


Fig S4. MALDI-TOF Spectrum of **1c**.

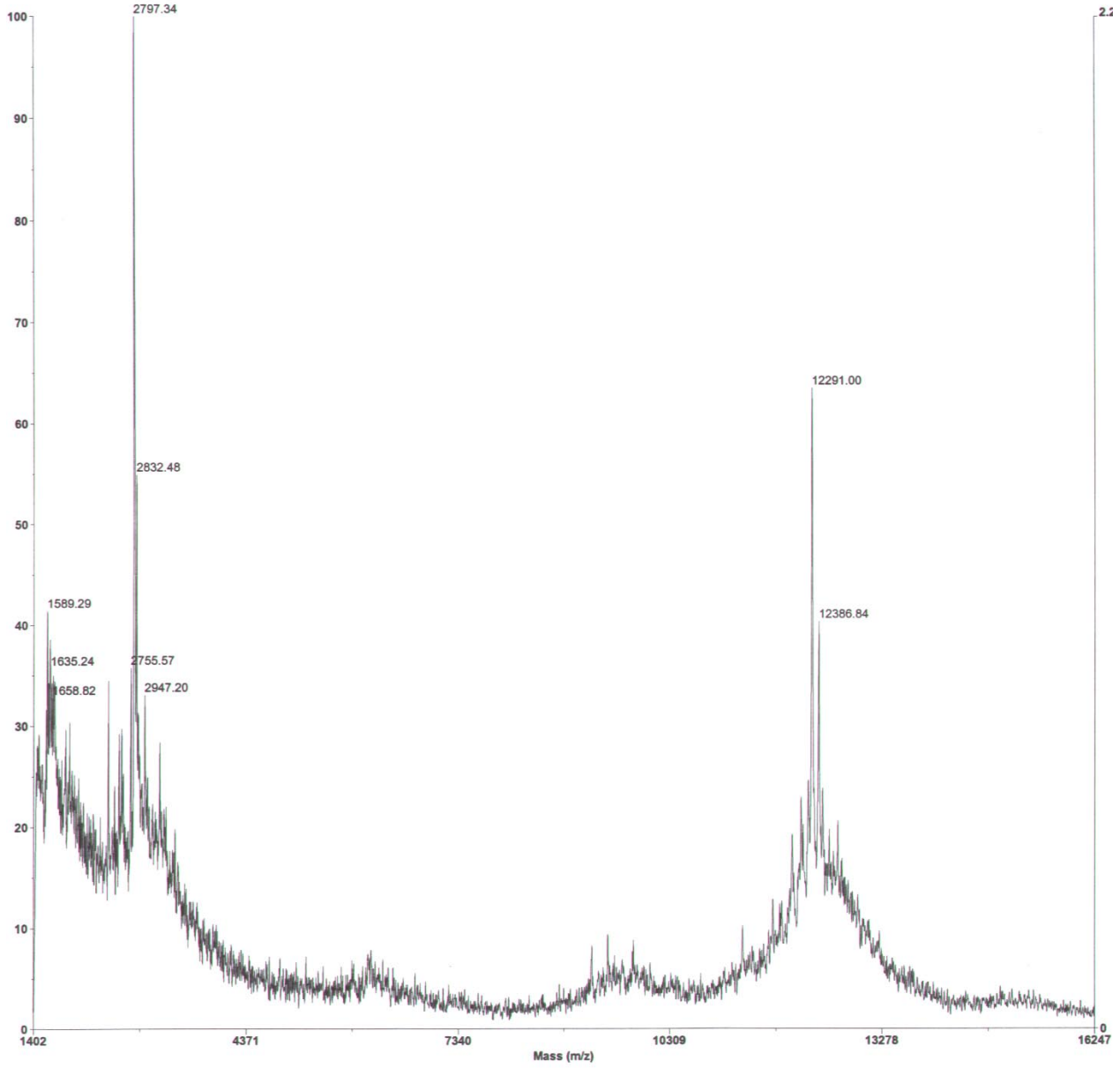
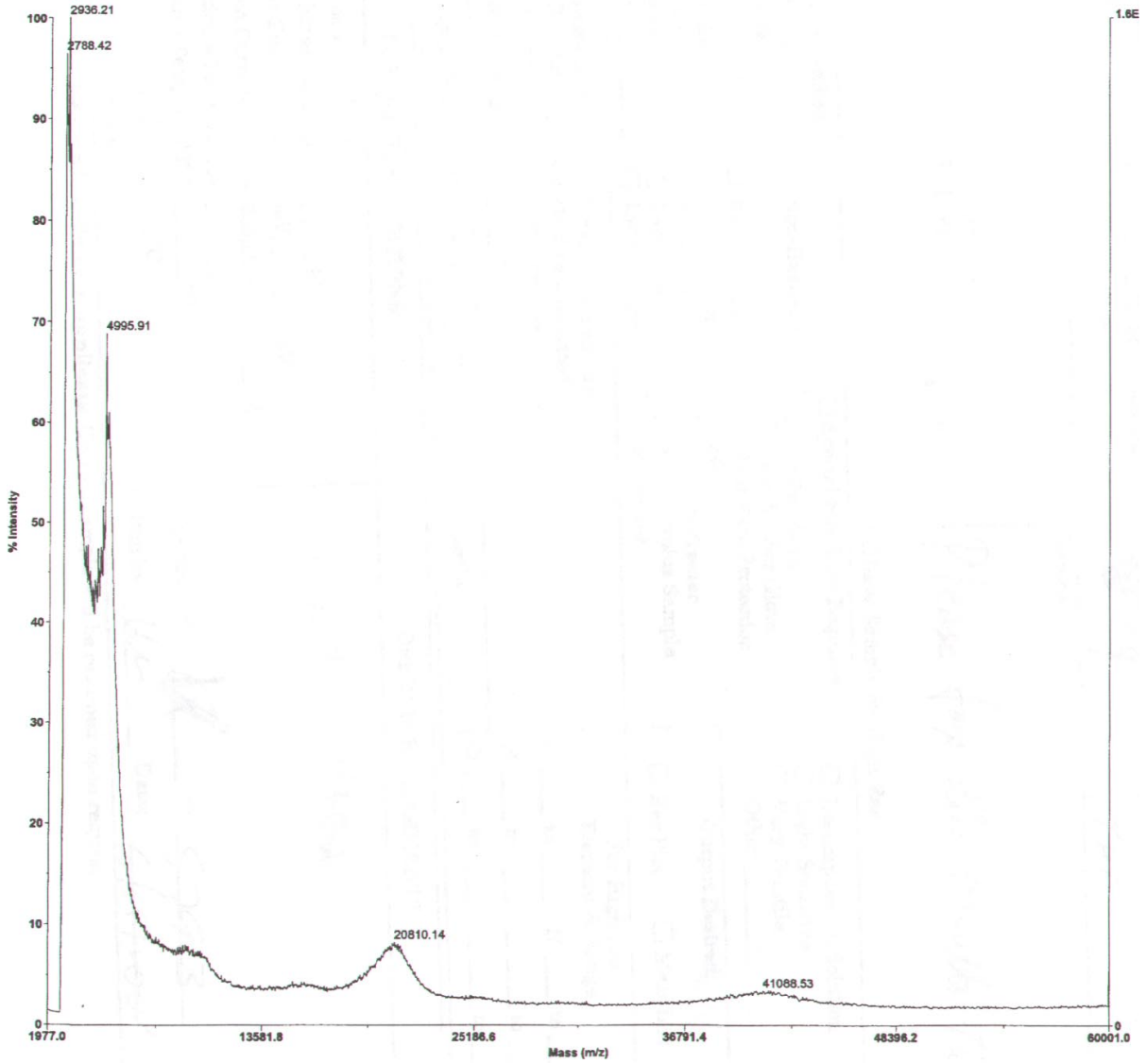



Fig S5. MALDI-TOF Spectrum of **1d**.