Supporting Information for

Directed Assembly of Chiral Organometallic Squares that Exhibit Dual Luminescence

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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 the reactions were dried by standard procedures. UV-Visible spectra were obtained using a Shimadzu UV-2401PC spectrophotometer. Circular dichroism (CD) spectra were recorded on a Jasco J-720 spectropolarimeter. The IR spectra were recorded from KBr pellets on a Nicolet Magna-560 FT-IR spectrometer. NMR spectra were recorded on a Bruker NMR 400 DRX spectrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform (δ 7.26). $^{13}C\{^{1}H\}$ 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 chloroform-d_1 (δ 77.0). Mass spectra were recorded on an Agilent 1100 series LC/MSD, MALDI-TOF from UIUC mass spectrometry laboratory, and FAB from UIUC mass spectrometry laboratory and MSU mass spectrometry facility.

6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthalene was synthesized by bromination of 1,1'-bi-2-naphthol in 99.9% yield according to the literature procedures,[1] while 6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene was obtained from 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene in quantitative yield according to the literature procedures.[2] 4,4'-dibromo-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthalene, 4,4'-dibromo-6,6'-dichloro-2,2'-dimethoxy-1,1'-binaphthalene, 6,6'-dichloro-2,2'-dibenyloxy-4,4'-dibromo-1,1'-binaphthalene, 6,6'-dichloro-2,2'-dimethoxy-4,4'-bis(ethynyl)-1,1'-binaphthalene (**L_{1a}**), and 6,6'-dichloro-2,2'-diethoxy-4,4'-bis(ethynyl)-1,1'-binaphthalene (**L_{2a}**) were prepared according to the procedures published by us previously.[3] *cis*-$Pt(PEt_3)_2Cl_2$ was prepared by following modified literature procedures.[4]

6,6'-dichloro-2,2'-dibenzyloxy-4,4'-bis(ethynyl)-1,1'-binaphthalene (L_{3a}). A mixture of 4,4'-dibromo-6,6'-dichloro-2,2'-dibenzyloxy-1,1'-binaphthalene (900 mg, 1.3 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol), CuI (20 mg, 1 mmol), and trimethylsilylacetylene (1.3 g, 13 mmol) in 6.5 mL of toluene and 6.5 mL of triethylamine was refluxed under N_2 atmosphere for 48 h. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to

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[1]. Dotsevi Yao Sogah, G.; Cram, D.J. *J. Am. Chem. Soc.* **1979**, *101*, 3035-3042.

[2]. Duessen, H.J.; Hendrickx, E.; Boulton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjornholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841.

[3]. (a) Lee, S.J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554. (b) Lee, S.J.; Hu, A-G.; Lin, W. *J. Am. Chem. Soc.*, **2002**, *124*, 12948.

[4]. Parshall, G.W. *Inorg. Synth.* **1970**, *12*, 26-33.

afford yellow powdery product which was purified by silica-gel column chromatography (hexane/ethyl acetate: 10:0.25 (v/v)) to afford pure 6,6'-dichloro-2,2'-dibenzyloxy-4,4'-bis(trimethylsilylethynyl)-1,1'-binaphthalene intermediate.

6,6'-Dichloro-2,2'-dibenzyloxy-4,4'-bis(trimethylsilylethynyl)-1,1'-binaphthalene obtained from the above reaction was treated with K_2CO_3 (525 mg, 3.8 mmol) in a mixture of THF (18 mL) and MeOH (18 mL) for 2 h. After workup, pale yellow powdery crude product was purified by silica-gel column chromatography (ethyl acetate/hexane: 1:9 (v/v)) to afford 312 mg of pure 6,6'-dichloro-2,2'-dibenzyloxy-4,4'-bis(ethynyl)-1,1'-binaphthalene (41% overall yield). ^{1}H NMR ($CDCl_3$): δ 8.36 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 7.67 (s, 2H), 7.20 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 7.14 (m, 6H), 7.04 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 6.93 (d, $J_{H\text{-}H}$ = 7.64 Hz, 4H), 5.03 (s, 4H), 3.57 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.44, 136.56, 132.07, 131.14, 130.34, 128.32, 128.09, 127.67, 127.22, 126.64, 125.11, 121.65, 121.09, 120.67, 83.07, 81.04, 71.21. IR (cm^{-1}): 3288.2(m), 3061.7(w), 3030.4(w), 2935.9(w), 1734.4(m), 1700.9(w), 1576.7(s), 1559.5(m), 1487.8(m), 1453.2(m), 1372.5(s), 1345.4(s), 1319.8(s), 1267.7(w), 1222.9(s), 1145.6(w), 1122.0(m), 1090.3(s), 1027.0(m), 815.9(m), 734.6(m), 695.5(m), 611.2(m). MS (LCMS) *m/z* 583 (Calcd *m/z* 583.5 for M$^+$).

6,6'-dichloro-2,2'-dimethoxy-4- trimethylsilylethynyl -4'-ethynyl-1,1'-binaphthalene (L_1). A solution of **L_{1a}** (500 mg, 1.16 mmol) in THF (10 mL) was allowed to cool down to -78°C and n-BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol) was added slowly. After the addition was completed, the reaction mixture was allowed to warm to room temperature. After the reaction mixture was again cooled down to -78°C, trimethylbromosilane (0.19 mL, 1.4 mmol) was added dropwise. The reaction mixture was then allowed to stir for 6 h at RT. The volatiles were removed under reduced pressure and the residue was extracted with EtOAc. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to afford yellow oily product which was purified by silica-gel column chromatography (ethyl acetate/hexane: 1:9 (v/v)) to afford pure 6,6'-dichloro-2,2'-dimethoxy-4- trimethylsilylethynyl -4'-bis(ethynyl)-1,1'-binaphthalene (315.4 mg, 54% yield). ^{1}H NMR ($CDCl_3$): δ 8.35 (d, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 8.31 (d, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 7.67 (s, 1H), 7.64 (s, 1H), 7.19 (dd, $^3J_{H\text{-}H}$ = 9.2, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 7.18 (dd, $^3J_{H\text{-}H}$ = 9.2, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H), 6.99 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 1H), 6.98 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.58 (s, 1H), 0.39 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.21, 154.19, 131.92, 131.88, 130.86, 130.67, 130.10, 130.00, 128.06, 127.99, 126.95, 126.87, 125.31, 125.09, 121.71, 120.64, 120.60, 120.03, 119.33, 118.76, 102.22, 100.90, 82.98, 81.10, 56.68, 56.65, 0.03. IR (cm^{-1}): 3296.9(m), 2957.1(m), 2937.4(m), 2841.1(m), 2152.34(m), 1576.8(s), 1559.6(m), 1488.5(m), 1458.1(m), 1334.3(s), 1320.7(s), 1263.2(m), 1231.6(m), 1230.6(m), 1203.3(m), 1145.1(m), 1125.9(s), 1092.5(s), 1068.2(m), 1046.2(m), 948.4(w), 900.5(w), 881.15(m), 857.6(s), 844.5(s), 814.9(m), 760.3(m), 711.4(m). MS (LCMS) *m/z* 501 (Calcd *m/z* 502.1 for M$^+$).

6,6'-dichloro-2,2'-diethoxy-4- trimethylsilylethynyl -4'-bis(ethynyl)-1,1'-binaphthalene (L_2). A solution of $\mathbf{L_{2a}}$ (456 mg, 1 mmol) in THF (15 mL) was allowed to cool down to -78°C and n-BuLi (1.6 M in hexane, 1 mmol, 0.625 mL) was added slowly. After the addition was completed, the reaction mixture was allowed to warm to room temperature. After the reaction mixture was again cooled down to -78°C, trimethylbromosilane (1.2 mmol, 0.158 mL) was added dropwise. The reaction mixture was allowed to stir for 6 h at RT. The volatiles were removed under reduced pressure and the residue was extracted with EtOAc. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to afford yellow oily product which was purified by silica-gel column chromatography (ethyl acetate/hexane: 0.5:9.5 (v/v)) to afford pure 6,6'-dichloro-2,2'-diethoxy-4- trimethylsilylethynyl -4'-ethynyl-1,1'-binaphthalene (276 mg, 52% yield). ^1H NMR ($CDCl_3$): δ 8.34 (d, $^4J_{H-H}$ = 2.0 Hz, 1H), 8.30 (d, $^4J_{H-H}$ = 2.0 Hz, 1H), 7.64 (s, 1H), 7.61 (s, 1H), 7.19 (dd, $^3J_{H-H}$ = 9.2, $^4J_{H-H}$ = 2.0 Hz, 2H), 7.00 (d, $^3J_{H-H}$ = 9.2 Hz, 1H), 6.99 (d, $^3J_{H-H}$ = 9.2 Hz, 1H), 4.02 (m, 4H), 3.57 (s, 2H), 1.06 (m, 6 H), 0.38 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.65, 132.09, 132.05, 130.82, 130.65, 130.14, 130.05, 127.82, 127.75, 127.18, 127.10, 125.26, 125.03, 121.64, 121.44, 120.89, 120.37, 120.32, 102.37, 100.70, 82.79, 82.77, 81.21, 65.21, 65.15, 14.82, 0.03. IR (cm^{-1}): 3291.6(br), 2976.7(m), 2930.5(m), 2896.9(w), 2363.3(w), 2151.4(m), 1653.1(w), 1576.5(s), 1558.9(s), 1539.9(w), 1489.6(m), 1372.6(m), 1332.7(s), 1320.0(s), 1262.4(w), 1249.8(m), 1225.9(m), 1199.4(w), 1145.7(m), 1124.2(s), 1091.8(s), 1047.9(m), 879.6(w), 856.4(s), 843.6(s), 815.7(m), 759.4(m), 668.3(m). MS (LCMS) *m/z* 532 (Calcd *m/z* 531.5 for M^+).

6,6'-dichloro-2,2'-dibenzyloxy-4- trimethylsilylethynyl -4'-bis(ethynyl)-1,1'-binaphthalene (L_3). A solution of $\mathbf{L_{3a}}$ (1.2 g, 2 mmol) in THF (18 mL) was allowed to cool down to -78°C and n-BuLi (1.6 M in hexane, 1.25 mL, 2 mmol) was added slowly. After the addition was completed, the reaction mixture was allowed to warm to room temperature. After the reaction mixture was again cooled down to -78°C, trimethylbromosilane (0.33 mL, 2.4 mmol) was added dropwise. The reaction mixture was allowed to stir for 6 h at RT. The volatiles were removed under reduced pressure and the residue was extracted with EtOAc. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to afford yellow oily product which was purified by silica-gel column chromatography (ethyl acetate/hexane: 0.5:9.5 (v/v)) to afford pure 6,6'-dichloro-2,2'-dibenzyloxy-4- trimethylsilylethynyl -4'-bis(ethynyl)-1,1'-binaphthalene (590 mg, 45% yield). ^{1}H NMR ($CDCl_3$): δ 8.35 (d, $^4J_{H\text{-}H}$ = 2.1 Hz, 1H), 8.32 (d, $^4J_{H\text{-}H}$ = 2.1 Hz, 1H), 7.67 (s, 1H), 7.66 (s, 1H), 7.19 (m, 2H), 7.15 (m, 6H), 7.04 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 1H), 7.02 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 1H), 6.93 (m, 4H), 5.04 (s, 2H), 5.02(s, 2H), 3.57 (s, 1H), 0.39 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.54, 153.45, 136.65, 136.57, 132.13, 132.06, 131.12, 130.98, 130.34, 130.30, 128.32, 128.27, 128.05, 127.99, 127.65, 127.61, 127.22, 127.19, 126.68, 126.62, 125.34, 125.08, 121.79, 121.74, 121.33, 121.10, 120.60, 120.57, 102.23, 101.04, 83.02, 81.08, 71.23, 71.21, 0.03. IR (cm^{-1}): 3291.3(br), 3062.6(w), 3034.1(w), 2958.1(m), 2148.8(m), 2112.6(sh), 1701.1(w), 1576.7(s), 1488.1(m), 1453.4(m), 1333.9(s), 1319.8(s), 1262.2(m), 1249.5(s), 1223.6(s), 1193.0(w), 1146.1(m), 1123.2(m), 1092.0(s), 1053.1(m), 1027.4(s), 961.6(w), 880.57(w), 843.6(s), 815.7(m), 759.3(m), 733.5(m), 694.5(s), 657.5(m), 618.9(w). MS (LCMS) *m/z* 654 (Calcd *m/z* 654.2 for M$^+$).

***cis*-Pt(PEt_3)$_2$(L_1)$_2$ (Pt-2L_1).** To a 200 mL two-necked round bottom flask containing *cis*-Pt(PEt_3)$_2$$Cl_2$ (116 mg, 0.23 mmol), **L_1** (260 mg, 0.52 mmol) and CuCl (6 mg, 0.06 mmol) was added diethylamine (70 mL) and the reaction mixture was allowed to stir at room temperature for 12 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford yellow powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 3:1 v/v) to give *cis*-Pt(PEt$_3$)$_2$(L$_1$)$_2$ (244 mg, 74 %). ^{1}H NMR (CDCl$_3$), 8.69 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 8.27 (d, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 7.62 (s, 2H), 7.61(s, 2H), 7.15 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 7.06 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 2.3 Hz, 2H), 7.04 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 6.87 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 3.73 (s, 6H), 3.63(s, 6H), 2.23 (m, 12H), 1.30 (m, 18H), 0.37(s, 18H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.67, 153.49, 132.36, 131.91, 130.74, 130.58, 130.14, 129.35, 127.69, 127.49, 127.09, 126.75, 126.38, 125.12, 121.74, 121.11, 119.32, 117.60, 116.33, 110.72 (dd, $^2J_{\text{trans P-C}}$ = 142.3, $^2J_{\text{cis P-C}}$ = 22.1), 104.93 (t, $^3J_{\text{P-C}}$ = 16.8), 102.59, 100.39, 56.86, 56.57, 17.46 (t, $J_{\text{P-C}}$ = 17.7), 8.59, 0.05. ^{31}P{^{1}H} NMR (CDCl$_3$): 3.56 (s, $J_{\text{Pt-P}}$ = 2266.7). IR (cm^{-1}): 2962.1(m), 2932.9(m), 2841.2(w), 2150.3(m), 2105.7(m), 1574.2(s), 1486.7(s), 1457.9(m), 1332.9(s), 1317.5(s), 1249.7(s), 1227.3(s), 1201.2(m), 1125.5(s), 1143.5(m), 1092.6(s), 1069.1(w), 1039.7(s), 952.7(w), 845.8(s), 815.7(m), 761.0(m), 724.7(w). MS (FAB): m/z 1434.4 (calculated *m/z* 1436.4 for [M]$^+$).

***cis*-Pt(PEt$_3$)$_2$(L$_2$)$_2$ (Pt-2L$_2$).** To a two-necked round bottom flask containing *cis*-Pt(PEt$_3$)$_2$Cl$_2$ (83 mg, 0.16 mmol), **L$_2$** (200 mg, 0.38 mmol) and CuCl (3 mg, 0.03 mmol) was added diethylamine (75 mL) and the reaction mixture was allowed to stir at room temperature for 12 h under N$_2$ atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$. The extract was washed with water, dried over anhydrous MgSO$_4$ and evaporated to afford yellow powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 1:1 (v/v)) to give *cis*-Pt(PEt$_3$)$_2$(L$_2$)$_2$ (212 mg, 89 %). ^{1}H NMR (CDCl$_3$), 8.68 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 8.27 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 7.58 (s, 4H), 7.14 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 2.1 Hz, 2H), 7.08 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 7.04 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ =

2.1 Hz, 2H), 6.91 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 2H), 3.99 (m, 4H), 3.90 (m, 4H), 2.23 (m, 12H), 1.30 (m, 18H), 1.02 (t, $^3J_{H\text{-}H}$ = 6.9, 6H), 0.93 (t, $^3J_{H\text{-}H}$ = 6.9, 6H), 0.37 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.02, 153.84, 132.44, 131.99, 131.02, 130.45, 130.11, 129.23, 127.69, 127.37, 127.09, 126.79, 126.65, 126.53, 125.00, 122.77, 120.92, 120.72, 119.02, 117.24, 111.66 (dd, $^2J_{\text{trans P-C}}$ = 145.0, $^2J_{\text{cis P-C}}$ = 22.4), 104.72 (t, $^3J_{\text{P-C}}$ = 17.4), 102.63, 100.15, 65.31, 64.81, 17.43 (t, $J_{\text{P-C}}$ = 17.4), 14.86, 8.56, 0.033. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 3.59 (s, $J_{\text{Pt-P}}$ = 2267.1). IR (cm^{-1}): 2966.7(m), 2933.6(m), 2148.3(m), 2106.2(m), 1573.8(s), 1486.2(m), 1453.2(w), 1450.0(w), 1370.8(s), 1330.4(s), 1318.9(s), 1249.8(m), 1222.0(m), 1196.3(w), 1166.7(m), 1143.9(m), 1123.6(s), 1091.9(s), 1040.2(s), 843.4(s), 815.2(m), 760.8(s), 723.3(m), 698.7(m), 642.8(m), 623.7(m). MS (FAB): m/z 1493.4 (calculated *m/z* 1492.5 for $[M]^+$).

***cis*-Pt(PEt$_3$)$_2$(L$_3$)$_2$ (Pt-2L$_3$).** To a 250 mL two-necked round bottom flask containing *cis*-$Pt(PEt_3)_2Cl_2$ (161 mg, 0.32 mmol), **L$_3$** (511.4 mg, 0.78 mmol) and CuCl (6 mg, 0.06 mmol) was added diethylamine (120 mL) and the reaction mixture was allowed to stir at room temperature for 12 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford yellow powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 1:1 (v/v)) to give *cis*-$Pt(PEt_3)_2(L_3)_2$ (420 mg, 74 %). ^1H NMR ($CDCl_3$), δ 8.74 (d, $^4J_{H\text{-}H}$ = 1.9 Hz, 2H), 8.28 (d, $^4J_{H\text{-}H}$ = 1.9 Hz, 2H), 7.62 (s, 2H), 7.61(s, 2H), 7.12 (m), 7.06 (m), 6.98 (m), 6.90 (m), 6.82 (d), 4.97 (s, 4H), 4.91 (s, 4H), 2.21 (m, 12H), 1.29 (m, 18H), 0.37(s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.89, 153.72, 137.21, 136.90, 132.49, 132.07, 131.00, 130.79, 130.37, 129.61, 128.20, 128.05, 127.75, 127.68, 127.40, 127.27, 127.21, 127.14, 126.77, 126.69, 126.68, 126.04, 125.09, 122.92, 121.08, 121.04, 119.13, 117.40, 111.09 (dd, $^2J_{\text{trans P-C}}$ = 135.9, $^2J_{\text{cis P-C}}$ = 19.0), 104.55 (t, $^3J_{\text{P-C}}$ = 16.0), 102.55, 100.46, 71.36, 70.95, 17.47 (t, $J_{\text{P-C}}$ = 18.1), 8.59, 0.05. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 3.56 (s, $J_{\text{Pt-P}}$ = 2264.8). IR (cm^{-1}): 3062.5(w), 2961.3(m), 2874.3(m), 2146.4(m), 2106.6(s), 1572.5(s), 1486.6(m), 1453.4(m), 1411.5(w), 1375.6(m), 1331.7(s), 1318.6(s), 1249.4(s), 1219.6(m), 1187.9(w), 1144.5(m), 1122.6(m), 1092.2(s), 1038.8(s), 1027.5(s), 880.7(w), 844.5(s), 814.8(m), 760.6(m), 733.4(m), 694.8(m). MS (FAB): m/z 1739.8 (calculated *m/z* 1740.7 for $[M]^+$).

***cis*-Pt(PEt$_3$)$_2$(L$_{1a}$)$_2$ (Pt-2L$_{1a}$).** To a 25 mL two-necked round bottom flask containing **Pt-2L$_1$** (230 mg, 0.16 mmol), and K_2CO_3 (140 mg, 1 mmol) was added a mixture of THF (4 mL) and MeOH (4 mL), and the reaction mixture was allowed to stir at room temperature for 2 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 5:1 (v/v)) to give **Pt-2L$_{1a}$** (167 mg, 81 %). ^1H NMR ($CDCl_3$), δ 8.70 (d, $^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 8.12 (d, $^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 7.65 (s, 2H), 7.62 (s, 2H), 7.18 (dd, $^3J_{\text{H-H}}$ = 9.0, $^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 7.067 (dd, $^3J_{\text{H-H}}$ = 9.0, $^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 7.065 (d, $^3J_{\text{H-H}}$ = 9.0 Hz, 2H), 6.89 (d, $^3J_{\text{H-H}}$ = 9.0 Hz, 2H), 3.72 (s, 6H), 3.65 (s, 6H), 3.55 (s, 2H), 2.23 (m, 12H), 1.31 (m, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.67, 154.46, 132.37, 131.89, 130.79, 130.75, 130.24, 129.38, 127.79, 127.55, 127.46, 127.14, 126.78, 126.36, 124.92, 122.11, 120.13, 119.86, 117.52, 116.16, 112.52 (dd, $^2J_{\text{trans P-C}}$ = 132.6, $^2J_{\text{cis P-C}}$ = 24.6), 104.67 (t, $^3J_{\text{P-C}}$ = 21.9), 82.57, 81.36, 56.89, 56.56, 17.46 (t, $J_{\text{P-C}}$ = 16.8), 8.60 (t, ${}^2J_{\text{P-C}}$ = 11.2). ^{31}P{^{1}H} NMR (CDCl$_3$): 3.49 (s, $J_{\text{Pt-P}}$ = 2265.1). IR (cm^{-1}): 3292.1(br), 3061.6(m), 2962.2(m), 2934.3(m), 2839.8(w), 2106.8(m), 1575.4(s), 1486.7(s), 1458.1(s), 1331.2(s), 1317.8(s), 1261.1(w), 1227.8(s), 1200.37(w), 1124.1(s), 1143.4(m), 1090.2(s), 10067.8(m), 1039.6(s), 897.7(m), 814.2(m), 767.6(s), 724.1(m). MS (FAB): m/z 1291.3 (calculated *m/z* 1292.0 for [M]$^+$).

***cis*-Pt(PEt$_3$)$_2$(L$_{2a}$)$_2$ (Pt-2L$_{2a}$).** To a 50 mL two-necked round bottom flask containing *cis*- **Pt-2L$_2$** (540 mg, 0.36 mmol), and K$_2$CO$_3$(193 mg, 1.4 mmol) was added a mixture of THF (20ml) and MeOH (20ml), and the reaction mixture was allowed to stir at room temperature for 2 h under N$_2$ atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH$_2$Cl$_2$. The extract was washed with water, dried over anhydrous MgSO$_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 3:1 (v/v)) to give *cis*- **Pt-2L$_{2a}$** (393 mg, 81 %). ^{1}H NMR (CDCl$_3$), δ 8.69 (d, ${}^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 8.30 (d, ${}^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 7.62 (s, 2H), 7.59 (s, 2H), 7.16 (dd, ${}^3J_{\text{H-H}}$ = 9.1, ${}^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 7.10 (d, ${}^3J_{\text{H-H}}$ = 9.1 Hz, 2H), 7.05 (dd, ${}^3J_{\text{H-H}}$ = 9.1, ${}^4J_{\text{H-H}}$ = 2.1 Hz, 2H), 6.91 (d, ${}^3J_{\text{H-H}}$ = 9.1 Hz, 2H), 3.98 (m, 4H), 3.92 (m, 4H), 3.54 (s, 2H), 2.24 (m, 12H), 1.30 (m, 18H), 1.03 (t, ${}^3J_{\text{H-H}}$ = 7.0, 6H), 0.95 (t, ${}^3J_{\text{H-H}}$ = 7.0, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.02, 153.83, 132.49, 132.01, 130.79, 130.68, 130. 23, 129.29, 127.77, 127.51, 127.17, 126.87, 126.69, 126.55, 124.83, 123.12, 121.46, 119.77, 118.99, 117.14, 112.46 (dd, ${}^2J_{\text{trans P-C}}$ = 142.5, ${}^2J_{\text{cis P-C}}$ = 23.1), 105.08 (t, ${}^3J_{\text{P-C}}$ = 17.1), 82.40, 81.43, 65.39, 64.82, 17.49 (t, $J_{\text{P-C}}$ = 17.4), 14.87, 8.59 (t, ${}^2J_{\text{P-C}}$ = 10.5). ^{31}P{^{1}H} NMR (CDCl$_3$): 3.49 (s, $J_{\text{Pt-P}}$ = 2267.9). IR (cm^{-1}): 3288.2(m), 3060.7(w), 2966.4(m), 2931.2(m), 2873.1(m), 2101.9(m), 1670.7(s), 1576.2(s), 1555.3(s), 1487.1(m), 1369.0(s), 1350.1(s), 1320.3(s), 1316.8(s), 1260.5(w), 1221.6(m), 1196.6(w), 1143.3(m), 1120.7(m), 1089.3(s), 1039.2(s), 1003.8(sh), 875.5(m), 769.2(m),720.9(m). MS (FAB): m/z 1349.4 (calculated *m/z* 1348.1 for $[M]^+$).

***cis*-Pt(PEt$_3$)$_2$(L$_{3a}$)$_2$ (Pt-2L$_{3a}$).** To a 50 mL two-necked round bottom flask containing *cis*- **Pt-2L$_3$** (370 mg, 0.21 mmol), and K_2CO_3 (175 mg, 1.26 mmol) was added a mixture of THF (10ml) and MeOH (10ml), and the reaction mixture was allowed to stir at room temperature for 2 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/hexane: 3:2 (v/v)) to give **Pt-2L$_{3a}$** (293 mg, 87 %). ^{1}H NMR (CDCl$_3$), δ 8.75 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H), 8.32 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H), 7.631 (s, 2H), 7.629 (s, 2H), 7.13 (m), 7.06 (m), 7.00 (m), 6.94 (m), 6.82 (d), 4.98 (s, 6H), 4.94 (s, 6H), 2.21 (m, 12H), 1.29 (m, 18H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.89, 153.64, 137.21, 136.83, 132.52, 132.03, 131.02, 130.97, 130.42, 129.65, 128.25, 128.05, 127.78, 127.46, 127.35, 127.24, 127.18, 126.81, 126.71, 126.66, 12.87, 123.24, 121.62, 119.98, 119.13, 117.29, 110.41 (dd, $^2J_{\text{trans P-C}}$ = 139.8, $^2J_{\text{cis P-C}}$ = 21.2), 105.04 (t, $^3J_{\text{P-C}}$ = 17.2), 82.60, 81.31, 71.36, 70.97, 17.47 (t, $J_{\text{P-C}}$ = 16.9), 8.60. ^{31}P{^{1}H} NMR (CDCl$_3$): 3.50 (s, $J_{\text{Pt-P}}$ = 2264.7). IR (cm^{-1}): 3288.2(m), 3060.9(w), 3028.9(w), 2964.3(m), 2930.2(m), 2873.0(m), 2102.2(s), 1572.6(s), 1486.5(s), 1452.9(s), 1375.4(m), 1329.8(s), 1316.9(s), 1261.5(w), 1219.4(m), 1188.4(m), 1144.2(m), 1120.8(m), 1090.8(s), 1027.2(s), 917.2(w), 898.9(m), 880.6(w), 835.5(s), 814.5(m), 767.8(m), 733.4(s), 695.3(s), 668.4(m). MS (FAB): m/z 1596.5 (calculated *m/z* 1596.4 for $[M]^+$).

[*cis*-Pt$(PEt_3)_2(L_{1a})]_4$ (1). To a 25 mL two-necked round bottom flask containing **Pt-2L_{1a}** (34.9 mg, 0.027 mmol), *cis*-Pt$(PEt_3)_2Cl_2$ (13.6 mg, 0.027 mmol) and CuCl (0.8 mg, 0.008 mmol) were added CH_2Cl_2 (13.5 ml) and diethylamine (0.6 ml) at -5 ^{o}C, and the reaction mixture was allowed to stir at 0^{o}C for 12 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/ethyl acetate/hexane: 2:2:3 (v/v)) to give [*cis*-Pt$(PEt_3)_2(L_{1a})]_4$ (19 mg, 41 %). ^{1}H NMR ($CDCl_3$), δ 8.66 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 8H), 7.60 (s, 8H), 7.03 (dd, $^3J_{H\text{-}H}$ = 9.1, $^4J_{H\text{-}H}$ = 2.2 Hz, 8H), 6.94 (d, $^3J_{H\text{-}H}$ = 9.1 Hz, 8H), 3.64 (s, 24H), 2.22 (m, 48H), 1.28 (m, 72H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.87, 132.28, 130.86, 129.20, 126.92, 126.82, 126.77, 126.55, 118.11, 117.76, 111.65 (dd, $^2J_{\text{trans P-C}}$ = 147.0, $^2J_{\text{cis P-C}}$ = 22.3), 104.83 (t, $^3J_{\text{P-C}}$ = 16.4), 56.85, 17.47 (t, $J_{\text{P-C}}$ = 17.7), 8.59. ^{31}P{^{1}H} NMR ($CDCl_3$): 3.54 (s, $J_{\text{Pt-P}}$ = 2263.2). IR (cm^{-1}): 3446.8(br), 3061.9(w), 2962.9(m), 2932.4(m), 2872.8(m), 2839.5(w), 2105.6(s), 1653.2(m), 1570.8(s), 1559.1(s), 1539.1(w), 1485.6(m), 1457.1(m), 1436.8(w), 1419.2(w), 1352.5(s), 1328.3(m), 1314.8(m), 1225.4(m), 1198.5(w), 1123.5(m), 1142.0(w), 1090.5(s), 1067.1(w), 1037.9(s), 948.9(w), 898.2(m), 856.4(w), 767.7(s), 724.7(m), 668.3(w), 636.4(w). MS (FAB): m/z 3442.4 (calculated *m/z* 3442.7 for $[M]^+$). Anal. Calcd for $C_{152}H_{176}Cl_8O_8P_8Pt_4 \cdot 2CHCl_3$: C, 50.24; H, 4.87. Found: C, 49.64; H, 4.70.

[*cis*-Pt$(PEt_3)_2(L_{2a})]_4$ (2). To a 25 mL two-necked round bottom flask containing **Pt-2L_{2a}** (24 mg, 0.018 mmol), *cis*-Pt$(PEt_3)_2Cl_2$ (9 mg, 0.018 mmol) and CuCl (0.8 mg, 0.004 mmol) were added CH_2Cl_2 (9 mL) and diethylamine (0.4 mL) at -20^{o}C, and the reaction mixture was allowed to stir at -20°C for 12 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/ethyl acetate/hexane: 2:2:5 v/v) to give [*cis*-Pt(PEt_3)$_2$(L_{2a})]$_4$ (15 mg, 46 %). ^{1}H NMR ($CDCl_3$), δ 8.65 (d, $^4J_{H\text{-}H}$ = 2.0 Hz, 8H), 7.57 (s, 8H), 7.03 (dd, $^3J_{H\text{-}H}$ = 8.9, $^4J_{H\text{-}H}$ = 2.0 Hz, 8H), 6.99 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 8H), 3.88 (m, 16H), 2.23 (m, 48H), 1.28 (m, 72H), 0.91 (t, $^3J_{H\text{-}H}$ = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.23, 132.38, 130.92, 130.88, 129.09, 127.16, 126.50, 126.42, 119.85, 118.82, 111.45 (dd, $^2J_{\text{trans P-C}}$ = 137.1, $^2J_{\text{cis P-C}}$ = 20.8), 104.65 (t, $^3J_{\text{P-C}}$ = 16.8), 65.11, 17.66 (t, $J_{\text{P-C}}$ = 17.4), 14.91, 8.58. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 3.68 (s, $J_{\text{Pt-P}}$ = 2262.8). IR (cm^{-1}): 3466.7(br), 2967.1(m), 2930.6(m), 2870.8(w), 2104.9(m), 1570.1(m), 1559.4(m), 1540.0(m), 1505.1(m), 1486.6(m), 1457.4(m), 1350.2(s), 1314.3(m), 1253.5(w), 1220.0(w), 1192.7(w), 1142.0(m), 1121.1(m), 1121.1(m), 1089.3(m), 1039.2(m), 914.2(w), 877.1(w), 860.8(w), 765.7(m), 722.6(w). MS (MALDI-TOF): m/z 3554.6 (calculated *m/z* 3555.0 for $[M]^+$). Anal. Calcd for $C_{160}H_{192}Cl_8O_8P_8Pt_4{\cdot}CHCl_3$: C, 52.63; H, 5.29. Found: C, 52.61; H, 4.72.

[*cis*-Pt(PEt_3)$_2$(L_{3a})]$_4$ (3). To a 25 mL two-necked round bottom flask containing **Pt-2L_{3a}** (28.7 mg, 0.018 mmol), *cis*-Pt(PEt_3)$_2$$Cl_2$ (9.1 mg, 0.018 mmol) and CuCl(0.8mg, 0.008 mmol) were added CH_2Cl_2 (9 ml) and diethylamine (0.4 ml) at -10°C, and the reaction mixture was allowed to stir at -10°C for 12 h under N_2 atmosphere with exclusion of light. The volatiles were removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous

$MgSO_4$ and evaporated to afford white powdery product which was further purified by silica-gel column chromatography (dichloromethane/ethyl acetate/hexane: 2:2:3 (v/v)) to give [*cis*-$Pt(PEt_3)_2(L_{3a})]_4$ (12 mg, 34 %). ^1H NMR ($CDCl_3$), δ 8.70 (d, $^4J_{H\text{-}H}$ = 2.0, 2H), 7.60 (s, 2H), 7.03 (d, $^3J_{H\text{-}H}$ = 9.0, 2H), 7.00 (dd, $^3J_{H\text{-}H}$ = 9.0, $^4J_{H\text{-}H}$ = 2.0 Hz, 2H), 6.89 (m, 3H), 6.79 (m, 2H), 4.89 (s, 4H), 2.19 (m, 12H), 1.27 (m, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.02, 137.36, 132.40, 131.07, 129.46, 127.97, 127.15, 127.01, 126.88, 126.66, 126.61, 126.55, 118.84, 111.52 (dd, $^2J_{\text{trans P-C}}$ = 143.2, $^2J_{\text{cis P-C}}$ = 23.2), 104.58 (t, $^3J_{\text{P-C}}$ = 17.42), 71.19, 17.43 (t, $J_{\text{P-C}}$ = 17.2), 8.57. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 3.60 (s, $J_{\text{Pt-P}}$ = 2261.3). IR (cm^{-1}): 3447.3(br), 3057.1(w), 2965.1(m), 2932.9(m), 2873.2(m), 2362.8(m), 2343.1(m), 2107.3(m), 1570.1(s), 1559.1(s), 1486.4(m), 1453.2(m), 1436.9(w), 1374.2(m), 1350.5(s), 1313.9(s), 1217.0(m), 1120.5(m), 1090.7(s), 1038.6(s), 905.2(w), 857.2(w), 815.5(w), 767.8(m), 732.8(m), 695.7(m), 668.5(w), 635.0(w). MS (FAB): m/z 4052.4 (calculated *m/z* 4051.5 for $[M]^+$). Anal. Calcd for $C_{200}H_{208}Cl_8O_8P_8Pt_4\cdot 4CHCl_3$: C, 54.10; H, 4.72. Found: C, 53.98; H, 4.11.

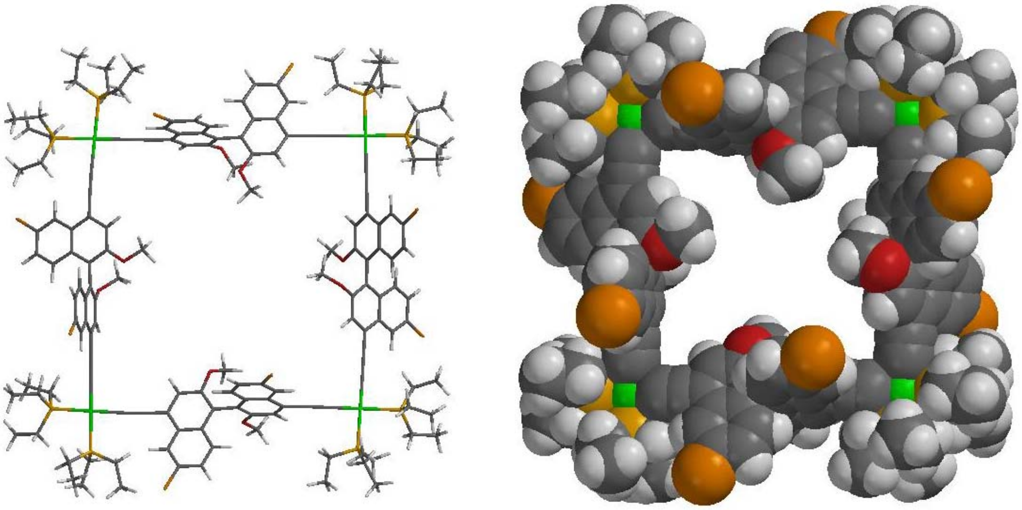

Figure S1. Energy-minimized structures of **1.**

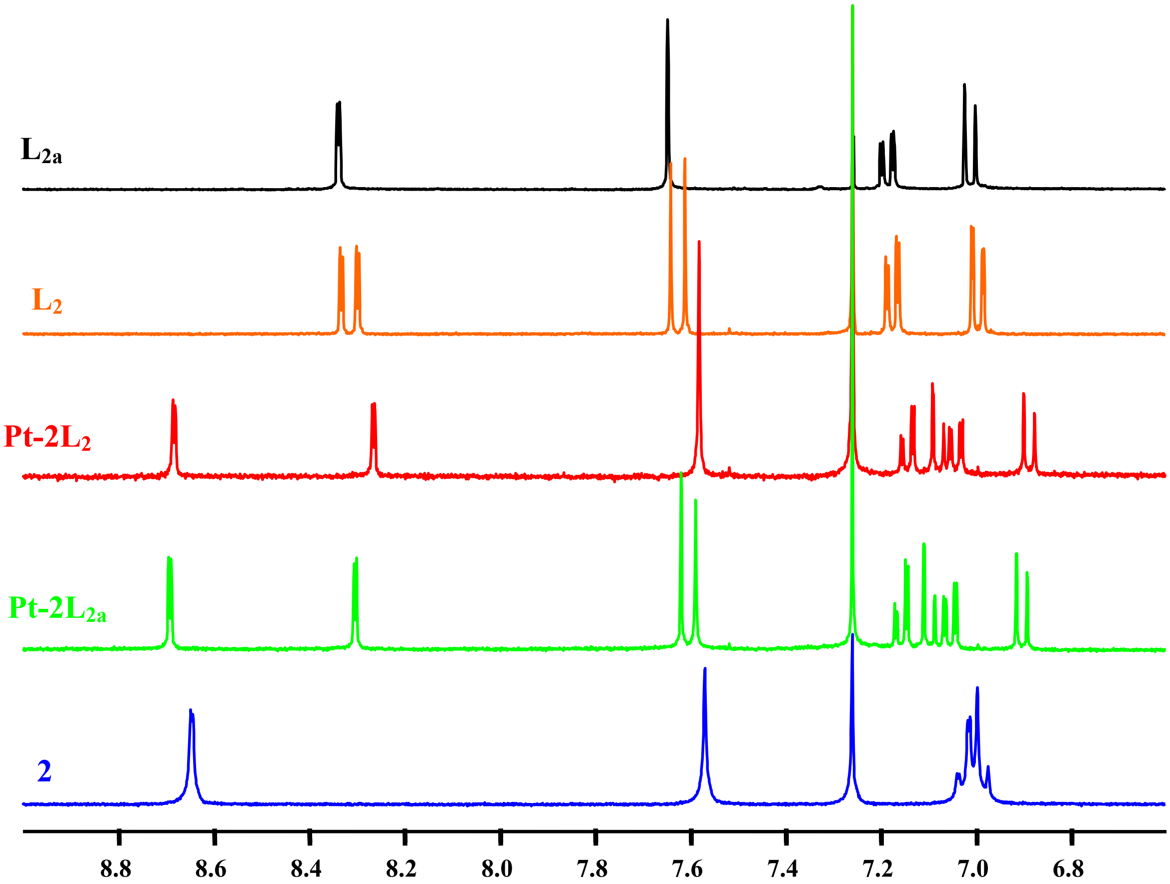

Figure S2. ^{1}H NMR spectra of $\mathbf{L_{2a}}$, $\mathbf{L_2}$, **Pt-2**$\mathbf{L_2}$, **Pt-2**$\mathbf{L_{2a}}$, and **2**.

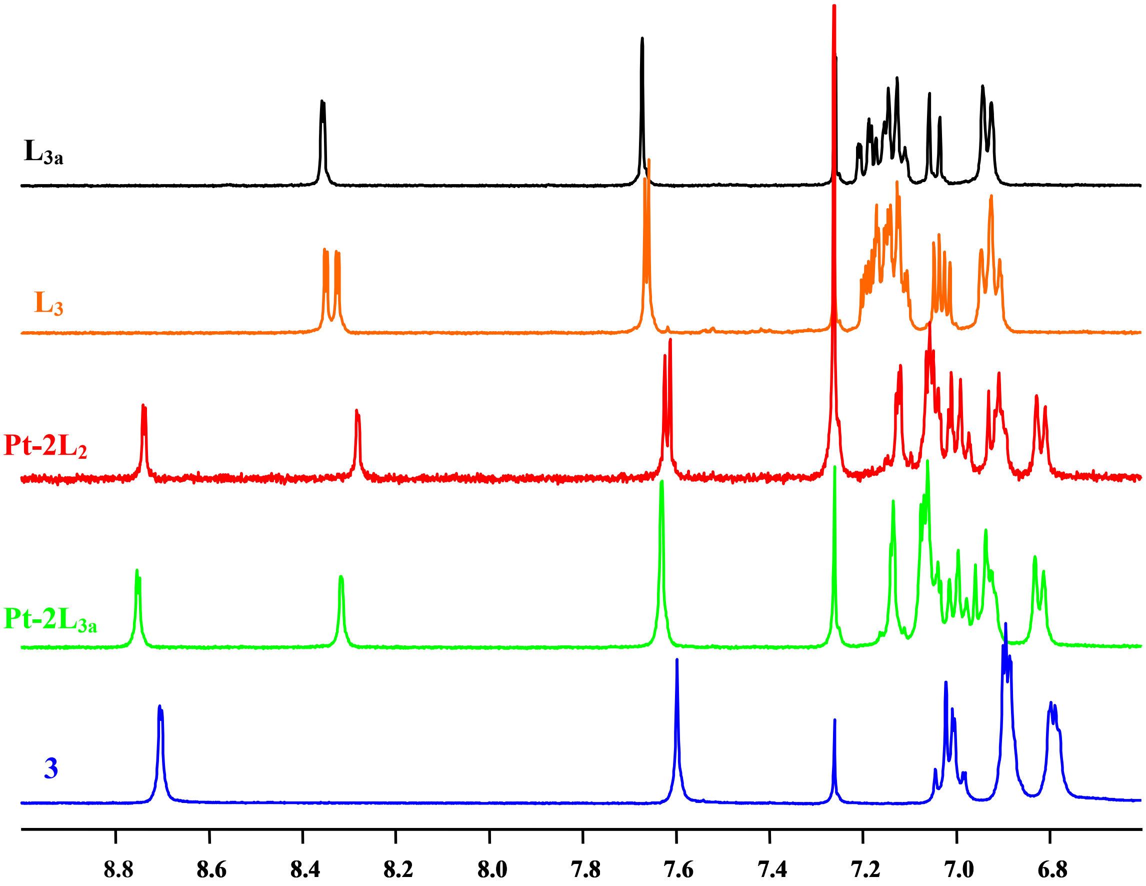

Figure S3. ^{1}H NMR spectra of **L_{3a}**, **L_3**, **Pt-2L_3**, **Pt-2L_{3a}**, and **3**.

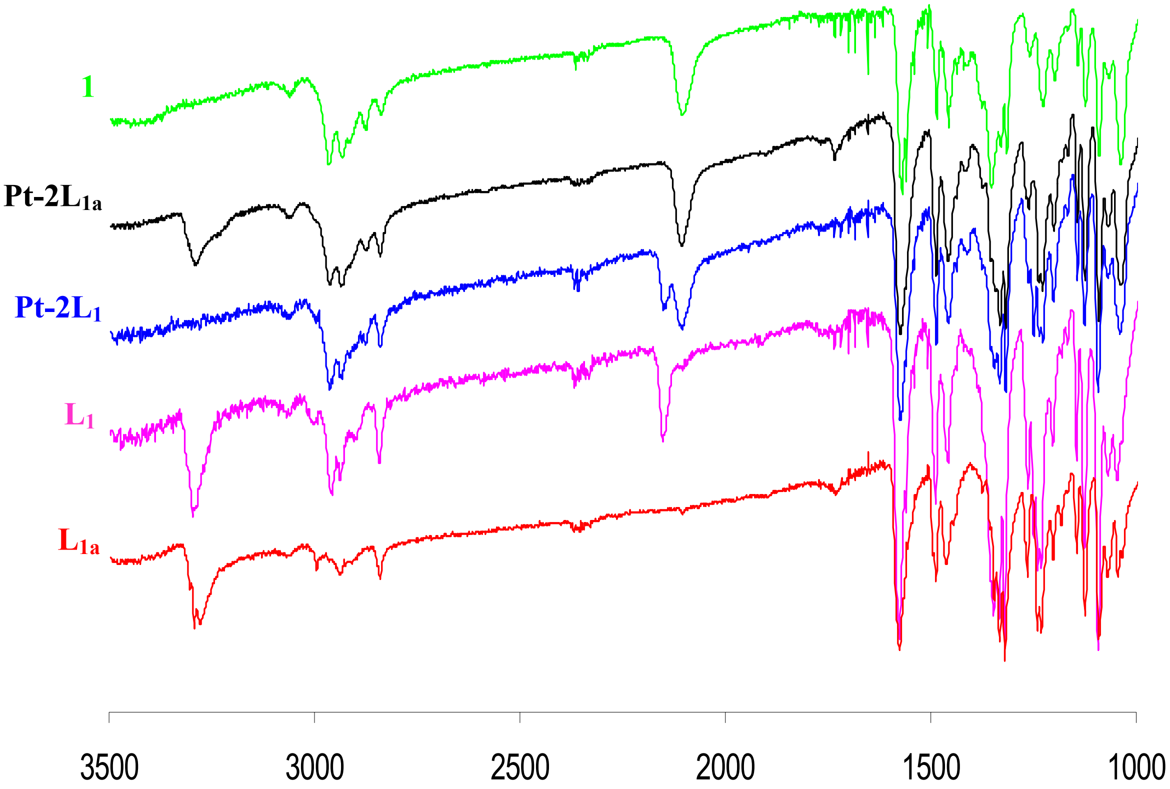

Figure S4. IR spectra of $\mathbf{L_{1a}}$, $\mathbf{L_1}$, **Pt-2**$\mathbf{L_1}$, **Pt-2**$\mathbf{L_{1a}}$, and **1**.

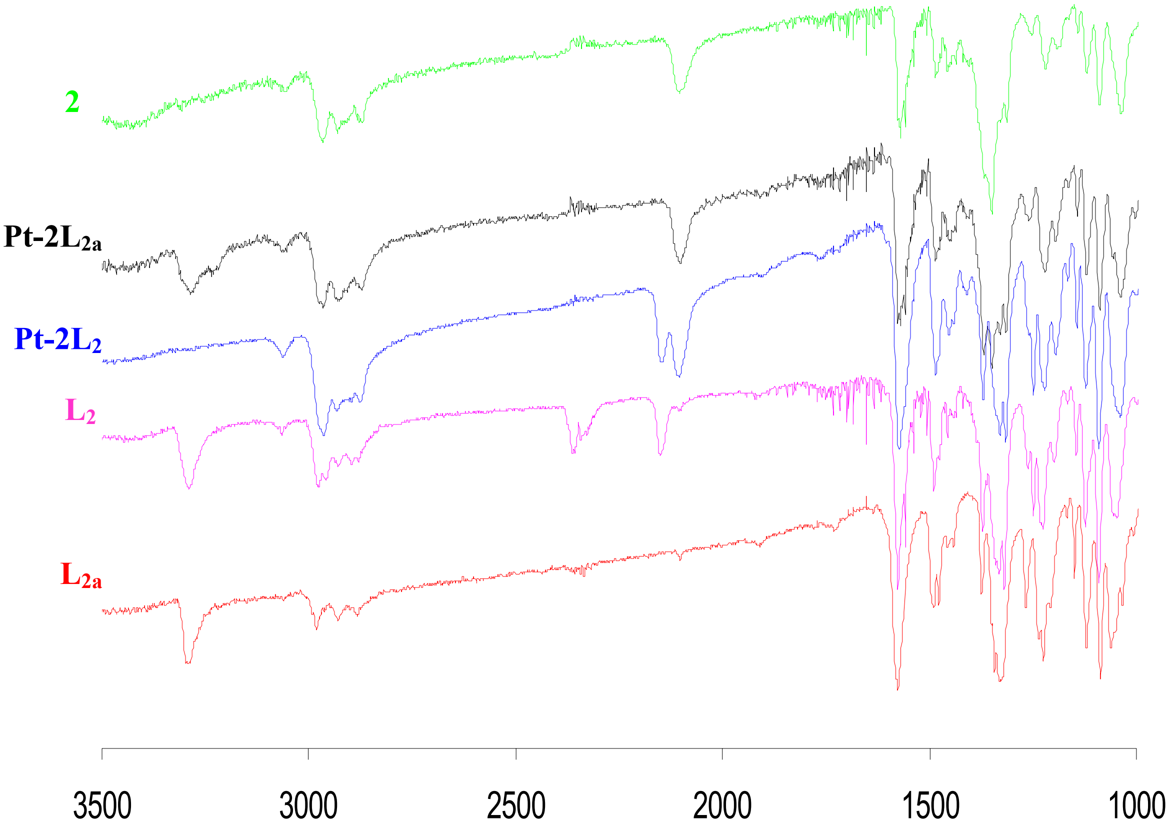

Figure S5. IR spectra of $\mathbf{L_{2a}}$, $\mathbf{L_2}$, **Pt-2**$\mathbf{L_2}$, **Pt-2**$\mathbf{L_{2a}}$, and **2**.

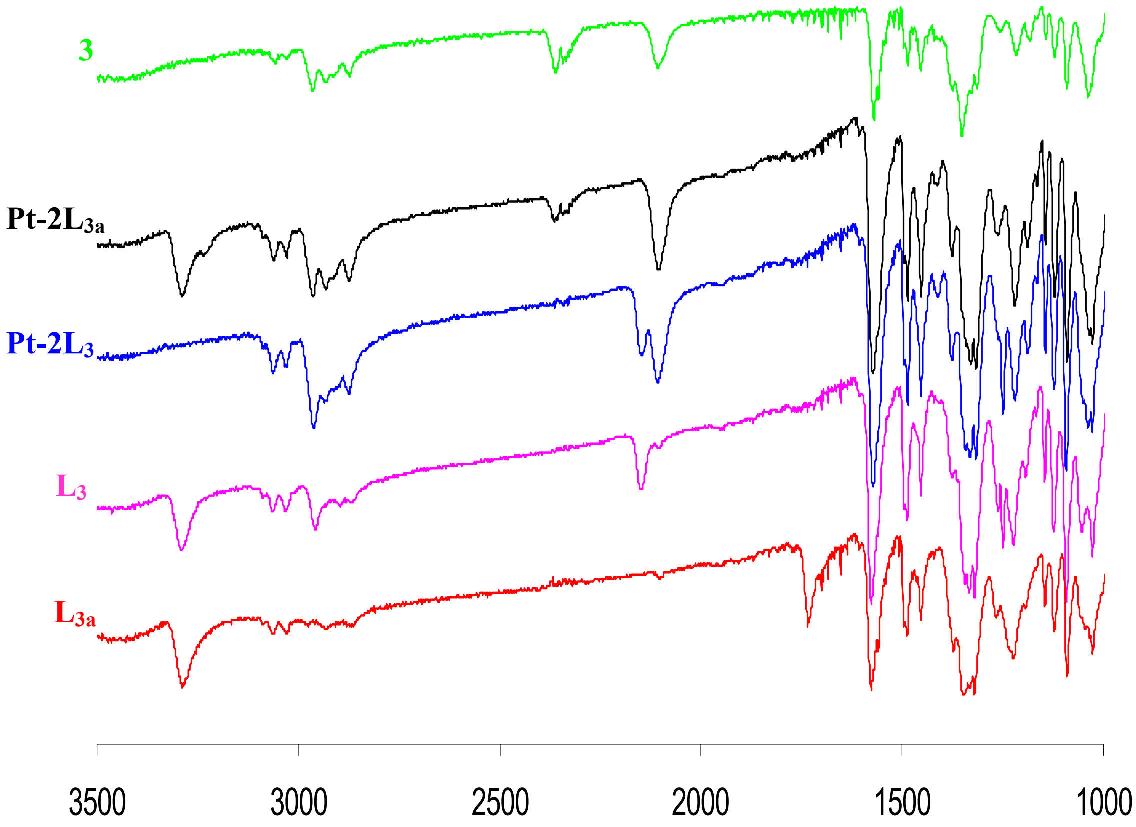

Figure S6. IR spectra of **L_{3a}**, **L_3**, **$Pt\text{-}2L_3$**, **$Pt\text{-}2L_{3a}$**, and **3**.

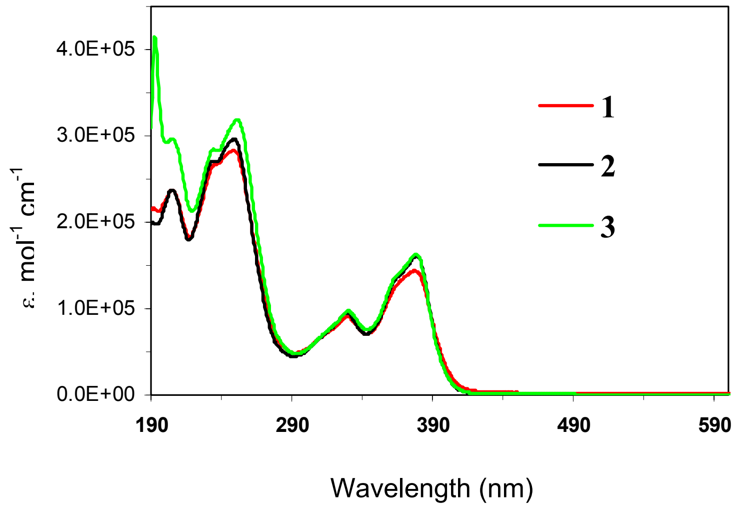

Figure S7. UV-Vis spectra of **1**-**3**.

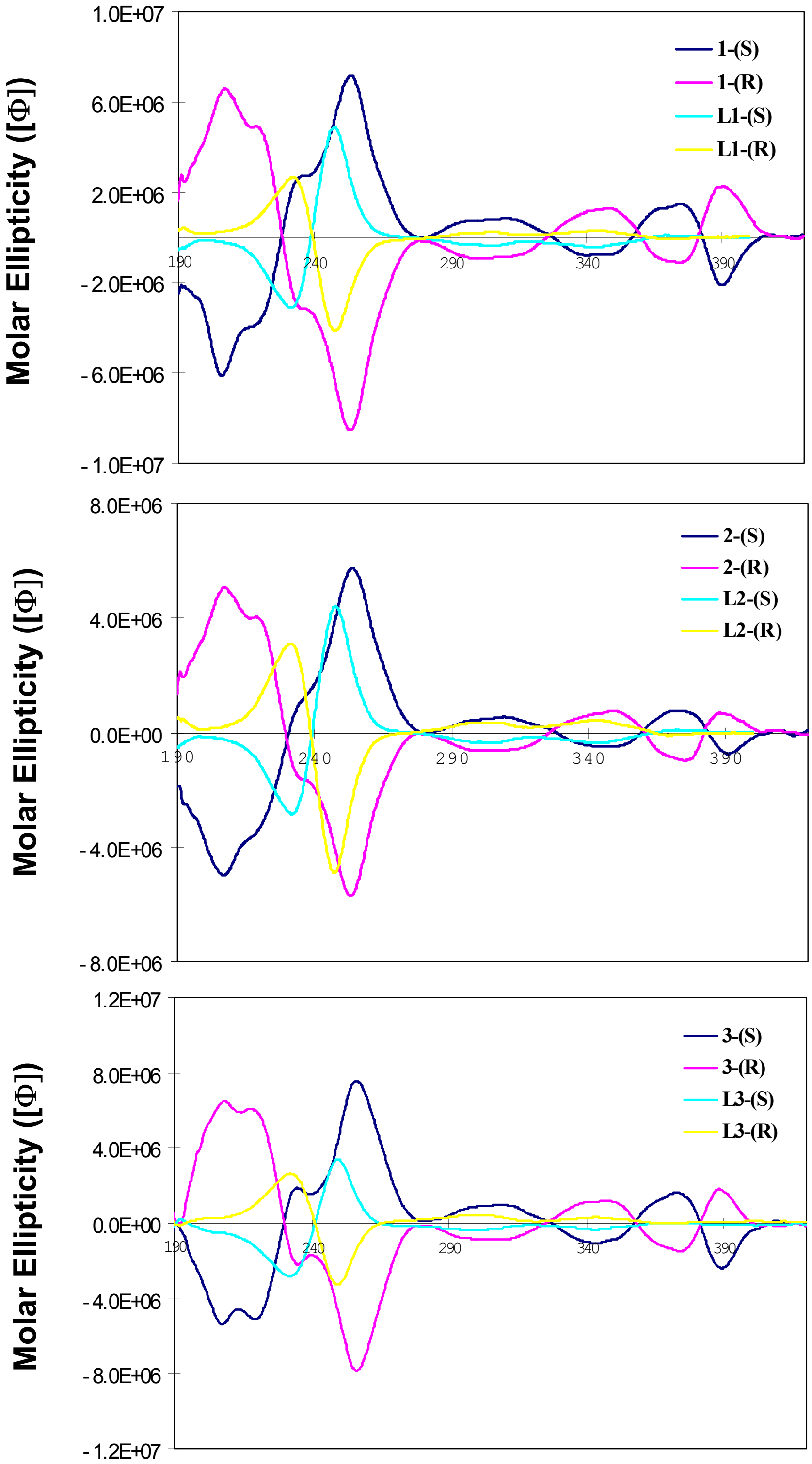

Figure S8. CD spectra of $\mathbf{L_{1a\text{-}3a}}$ and **1-3**.

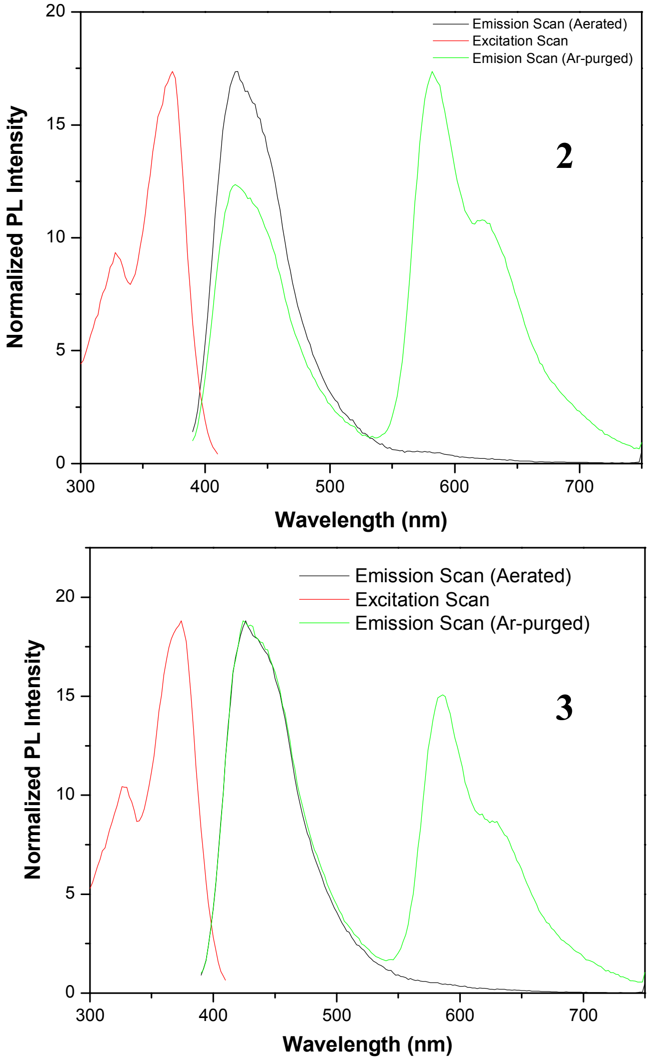

Figure S9. Excitation and emission spectra of **2** and **3** in CH_2Cl_2.