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Supplemental Information For:

Towards Chemosensing Phosphorescent Conjugated Polymers: Cyclometalated Platinum(II) Poly(Phenylene)s

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4,4'-Dibromophenylpyridine: A mixture of 4.74 g (0.020 mol) of 2,5-dibromopyridine and 707 mg (0.612 mmol) tetrakis(triphenylphosphine)palladium (0) were stirred in 50 mL of 1,2-dimethoxyethane (DME) at room temperature while introducing Ar via a needle for 20 minutes. To this mixture was added 4.02 g (0.020 mol) of 4-bromophenylboronic acid in 50 mL absolute EtOH. This mixture was stirred was ambient temperature while introducing Ar via needle for an additional 20 minutes. To this mixture was added 30 mL of a 2.0 M aqueous solution of Na_2CO_3 and stirred for an additional 20 minutes with additional Ar bubbling. The argon needle was then removed, and the mixture heated to reflux under Ar for 20 hours. The flask was cooled to ambient temperature, and the solvent was removed *in vacuo* and to the residue was added 100 mL water and 75 mL CH_2Cl_2. The organic layer was separated and additional organics were extracted from the water layer with CH_2Cl_2 (2 x 75 mL). The organic layers were combined and washed with water (1 x 100 mL) and brine (1 x 100 mL), dried over $MgSO_4$, filtered, and dried *in vacuo*. The crude product was purified by column chromatography (SiO_2, 2:1 hexane:CH_2Cl_2) and recrystallized from hexanes to give 3.81 g (61% yield) of the pure desired product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (dd, 1H), 7.83 (m, 3H), 7.60 (m, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 119.9, 121.6, 124.1, 128.5, 132.2, 137.3, 139.6, 151.0, 154.9. MS calcd. for $C_{11}H_7NBr_2$ (M^+), 310.89; found, 310.90.

Dibromo Platinum (II) Complex 4: To a solution of K_2PtCl_4 (514 mg, 1.25 mmol) in 25 mL of water was added 783 mg (2.50 mmol) of 4,4'-dibromophenylpyridine and 75 mL of ethoxyethanol. The mixture was then heated to 90 ºC under Ar for 16 hours. Then mixture was then cooled to ambient temperature, and 100 mL of water were added. The solid was collected by filtration, redispersed in 300 mL water, stirred for 15 minutes, and again collected by filtration. The solid was then washed with EtOH in a similar fashion. The brown solid was extracted with CH_2Cl_2 for 16 hours in a Soxhlet apparatus for 18 hours. The remaining solid was then dispersed in 250 mL of CH_2Cl_2, sonicated for 15 minutes and filtered. This sonication/filtration procedure was repeated an additional two times. The filtrates were combined with the Soxhlet extract, and the solvent removed *in vacuo* to give 619 mg (91% yield) of the dichloride bridged dimer **3** as a yellow solid. This was used without further purification.

The dichloride bridged dimer (977 mg, 0.90 mmol) and 2.09 g (1.80 mmol) of **2** were then combined with 313 mg (1.35 mmol) of Ag_2O in 80 mL of ethoxyethanol and heated to 80 ºC under Ar overnight. After cooling to ambient temperature, the solvent was removed *in vacuo*. 200 mL of CH_2Cl_2 was added to the residue and this solution was washed with water (2 x 100 mL) and brine (1 x 200 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and dried *in vacuo*. The residue was purified by column chromatography (SiO_2, 1:2 hexanes:CH_2Cl_2) to yield 1.96 g (65% yield) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.16 (s, 1H), 7.88 (d, 1H), 7.78 (s, 1H), 7.38 (d, 1H), 7.2-7.3 (m, 5H), 6.63 (s, 1H), 4.2-4.0 (m, 12H), 1.9-1.7 (m, 12H), 1.6-1.2

(m), 0.88 (m, 18H). MS (MALDI-TOF) calcd. for $C_{86}H_{137}Br_2NO_8Pt$ $(M+H)^+$, 1665.8; found, 1666.0.

5-Dodec-1-ynyl-2-(4-dodec-1-ynyl-phenyl)-pyridine: A mixture of 4,4'-dibromophenylpyridine (939 mg, 3.00 mmol), 1-dodecyne (1.50 g, 9.02 mmol), dichlorobis(triphenylphosphine)palladium (II) (120 mg, 0.171 mmol) and CuI (29.0 mg, 0.152 mmol) were combined in 15 mL triethylamine and heated to reflux under Ar for 2 days. Upon cooling the flask to ambient temperature, the solvent was removed *in vacuo*. The residue was combined with 100 mL water, followed by extraction with CH_2Cl_2 (3 x 50 mL). The organic layers were combined, washed with water (2 x 100 mL) and brine (1 x 100 mL), dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2, 2:1 hexanes:CH_2Cl_2) to give 1.23 g (85% yield) of the desired product. ^1H NMR (300 MHz, $CDCl_3$): δ 8.67 (m, 1H), 7.91 (m, 2H), 7.71 (dd, 1H), 7.63 (dd, 1H), 7.48 (m, 2H), 2.43 (m, 4H), 1.61 (m, 4H), 1.46 (m, 4H), 1.28 (m, 28H), 0.88 (t, 6H). HRMS calcd. for $C_{35}H_{49}N$ $(M+H)^+$, 484.3938; found, 484.3938.

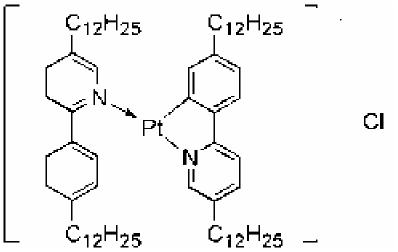
4,4'-didodecylphenylpyridine: A mixture of 5-dodec-1-ynyl-2-(4-dodec-1-ynyl-phenyl)-pyridine (1.23 g, 2.54 mmol) and 5% Pd on carbon (1.03 g) in 35 mL of ethyl acetate was reacted in a hydrogenator under 45 psi H_2 for 8 hours. The mixture was the filtered through Celite 545 and the solid was washed with 100 mL of CH_2Cl_2. The filtrate and wash were combined, and the solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2, 2:1 hexanes:CH_2Cl_2) to give 1.0 g of the desired product. ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, 1H), 7.88 (m, 2H), 7.61 (d, 1H), 7.51 (dd, 1H), 7.26 (d, 2H), 2.63 (q, 4H), 1.64 (m, 4H), 1.4-1.2 (m, 36H), 0.88 (t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.33, 22.90, 29.39, 29.52, 29.57, 29.66, 29.74, 29.79, 29.82, 29.86, 29.88, 31.39, 31.62, 32.14, 32.90, 120.00, 126.74, 128.98, 136.29, 136.72, 137.05, 143.76, 149.88, 155.26. HRMS calcd. for $C_{35}H_{57}N$ $(M+H)^+$, 492.4564; found, 492.4554.

Complex 5: To a mixture of complex **4** (94.0 mg, 0.056 mmol), 9,9-dioctylfluorene-2-boronic acid[1] and $Pd(PPh_3)_4$ (6.5 mg, 0.0056 mmol) in 1 mL toluene were added 1 mL of 2.0 M K_2CO_3 and Aliquat® 336 (3 drops), followed by introduction of nitrogen gas through a needle for 3 hours. Then, the mixture was vigorously stirred at 90 °C for 24 hours. Upon cooling, the aqueous phase was pipetted out and the organic was poured into CH_2Cl_2 (50 mL). This was washed with water (2 x 50 mL) and brine (1 x 50 mL). The organics were dried over $MgSO_4$, filtered, and solvent was removed *in vacuo*. The crude product was purified by column chromatography twice (SiO_2, 3:2 hexanes:CH_2Cl_2; followed by SiO_2, 8:1 hexanes:EtOAc) to give 48.0 mg (37% yield) of desired product. ^1H NMR (300 MHz, $CDCl_3$): δ 9.51 (d, 1H), 8.10 (m, 2H), 7.8-7.3 (m, 21H), 6.61 (s, 1H), 4.1-3.9 (m, 12H), 2.0 (m, 8H), 1.8-1.0 (m), 0.9-0.8 (m, 30H). MS (MALDI-TOF) calcd. for $C_{144}H_{219}NO_8Pt$ (M^+), 2285.64; found, 2285.59.

Complex 6: The dichloride bridged platinum dimer complex synthesized from phenylpyridine and K_2PtCl_4[2] (193 mg, 0.251 mmol) was reacted with β-ketonate ligand **2** (582 mg, 0.50 mmol) and Ag_2O (90 mg, 0.386 mmol) in 20 mL ethoxyethanol as described for the synthesis of complex **4**. The crude product was purified by column chromatography (SiO_2, 1:2 hexanes:CH_2Cl_2). The product was then further purified by precipitation into 20 mL MeOH and collection by centrifugation. It was precipitated a total of three times to give the 430 mg of the desired product (57% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 9.12 (m, 1H), 7.82 (m, 1H), 7.76 (dd, 1H), 7.67 (d, 1H), 7.50 (dd, 1H), 7.28 (s, 2H), 7.3-7.2 (m, 3H), 7.2-7.1 (m, 2H), 6.55 (s, 1H), 4.3-4.0 (m, 12H), 1.9-1.7 (m, 12H), 1.6-1.4 (m, 12H), 1.4-1.2 (m), 0.9-0.7 (m, 18H). MS (MALDI-TOF) calcd. for $C_{86}H_{129}NO_8Pt$ (M^+), 1509.0; found, 1509.0.

Complex 7:

To a solution of K_2PtCl_4 (623 mg, 1.50 mmol) in water (7.5 mL) were added 5-(1-dodecyl) -2-[(1-dodecyl)phenyl]pyridine (1.48 g, 3.01 mmol) and $EtOCH_2CH_2OH$ (30 mL). Then, the mixture was heated at 120 °C for 24 h under Ar. After cooling, the solvent was removed on a rotary evaporator, and the residue was subjected to water-CH_2Cl_2 extraction (150 mL/150 mL). The organic phase was washed with water (150 mL x 2) and sat. brine (150 mL), and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation, and the residue was purified by silica gel column chromatography (hexane/EtOAc, 8/1, v/v) to afford the intermediate complex pictured below (1.42 g, 1.17 mmol, 78%); ^1H NMR (300 MHz, $CDCl_3$) □ 0.85-0.90 (m, 12H), 1.25-1.30 (m, 72H), 1.42 (m, 2H), 1.50-1.72 (m, 6H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.49-2.68 (m, 6H), 5.92 (d, *J* = 1.4 Hz, 1H), 6.77 (dd, *J* = 1.7 and 8.0 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.71 (dd, *J* = 2.0 and 8.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 9.09 (d, *J* = 1.7 Hz, 1H), 9.41 (d, *J* = 1.7 Hz, 1H); MALDI-TOF Calcd for $C_{70}H_{113}N_2{}^{195}Pt$ ([M – Cl]): 1176.9. Found: 1176.0, 1177.0, 1178.0, 1179.0, 1180.0 (multiple); Anal. Calcd for $C_{70}H_{113}N_2{}^{195}PtCl$: C; 69.30, H; 9.39, N; 2.31. Found: C; 69.31, H; 9.20, N; 2.30.



This material was reacted with β-ketonate ligand **2** as described for complex **6**. The yield was 192 mg (35% yield) after purification by column chromatography (SiO_2, 1:1 hexanes:CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 8.92 (d, 1H), 7.65-7.25 (m, 8H), 6.93 (dd, 1H), 6.60 (s, 1H), 4.2-4.0 (m, 12H), 2.63 (t, 4H), 1.9-1.2 (m), 0.9 (m, 24H). MS (MALDI-TOF) calcd. for $C_{110}H_{187}NO_8Pt$ (M^+), 1845.39; found, 1845.50.

P1: To a mixture of monomer **4** (84.1 mg, 0.0504 mmol) and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (28.2 mg, 0.0505 mmol) and $Pd(PPh_3)_4$ (6.9 mg, 0.0050 mmol) in 1.25 mL toluene was added 1.25 mL of a 2.0 M aqueous solution of potassium carbonate and 3 drops of Aliquat® 336. This was subjected to Ar bubbling, and then heated at 80 ºC with vigorous stirring under Ar for 3 days. Upon cooling, the mixture was poured into 50 mL CH_2Cl_2 and washed with 50 mL water. The aqueous phase was thoroughly extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, washed with brine (3 x 100 mL), dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was dissolved in ca. 3 mL of THF and precipitated into a 2:1 (v/v) mixture of MeOH/acetone. The precipitate was collected by centrifugation. This precipitation was repeated again. 47 mg of polymer was isolated. GPC analysis: Mn = 12,000 g/mol; Mw = 31,000; PDI = 2.6.

P2: The corresponding dibromide Pt (II) monomer was synthesized by reaction of the bridged dichloride complex **3** and the chelating bis(*tert*-butyl) diketone ligand in the presence of Ag_2O as described for complex **6**. The yield of the dibromide monomer was 111 mg (32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (dd, 1H), 7.93 (dd, 1H), 7.75 (t, 1H), 7.45 (d, 1H), 7.26 (m, 2H), 5.84 (s, 1H), 1.29 (s, 9H), 1.28 (s, 9H). MS (MALDI-TOF) calcd for $C_{23}H_{25}Br_2O_2Pt$ $(M+H)^+$, 687.0; found, 687.1.

The polymer was synthesized as described for **P1**. In order to exclude low molecular weight oligomers were removed from the polymeric sample by preperative GPC to yield a sample with Mn = 11,000 g/mol, Mw = 13,000, PDI = 1.2. The optical properties of this sample are reported in the text.

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[1] J. Ding, M. Day, G. Robertson and J. Roovers, *Macromolecules*, 2002, **35**, 3474.

[2] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, **41**, 3055.