Supporting Information

Highly Efficient Orange Electrophosphorescence from a Trifunctional Organoboron-Pt(II) Complex

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S1. General Experimental Information

All reactions were carried out under a nitrogen atmosphere. Reagents were purchased from Aldrich chemical company and used without further purification. Thin-layer and flash chromatography were performed on silica gel. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400, 500 or 600 MHz spectrometers. Deuterated solvents were purchased from Cambridge Isotopes and used without further drying. Excitation and emission spectra were recorded using a Photon Technologies International QuantaMaster Model 2 spectrometer. UV/Visible spectra were recorded using an Ocean Optics CHEMUSB4 absorbance spectrophotometer. Cyclic voltammetry experiments were used to measure frontier orbital energy levels, and were performed using a BAS CV-50W analyzer with a scan rate of 0.2-1.0 V/sec using 1 mg sample in 0.5 mL dry DMF. The electrochemical cell was a standard three-compartment cell composed of a Pt working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode. CV measurements were carried out at room temperature with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte, with ferrocene/ferrocenium as internal standard ($E^{\circ} = 0.55$ V). Solution quantum yields were calculated using optically dilute solutions (A ≈ 0.1) relative to appropriate standards. The absolute solid-state quantum yield of Pt-BNPB was determined using an integration sphere. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia. Molecular orbital and molecular geometry calculations were performed using the Gaussian 03 program suite. Calculations were performed at the B3LYP level of theory using LANL2DZ as the basis set for Pt, and 6-31G* for all other atoms. The synthesis of 1a has been reported previously.^[1]

EL Device Fabrication: Devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool with a base pressure of $\sim 10^{-8}$ Torr without breaking vacuum. The ITO anode is commercially patterned and coated on glass substrates 50 x 50 mm² with a sheet resistance less than 15 Ω /square. Substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by UV ozone treatment for 15 min. The active area for all devices was 2 mm². The film thicknesses were monitored by a calibrated quartz crystal microbalance. I-V characteristics were measured using a HP4140B picoammeter in ambient air. Luminance measurements and EL spectra were taken using a Minolta LS-110 luminance meter and an Ocean Optics USB200 spectrometer with bare fiber, respectively. The external quantum efficiency of EL devices was calculated following the standard procedure.^[2] Additional details regarding device fabrication and characterization measurements have been described elsewhere.^[3]

S2. Synthetic Procedures



Synthesis of 1b: To a 250 mL Schlenk flask with stir bar and condenser was added **1a** (1.59 g, 3.8 mmol), 2,5-dibromopyridine (0.89 g, 3.8 mmol), Pd(PPh₃)₄ (0.13 g, 0.11 mmol), K₂CO₃ (1.56 g, 11.3 mmol), and 60 mL degassed THF:H₂O (1:1). The mixture was heated to 55°C under N₂ and allowed to stir overnight, after which the THF was evaporated *in vacuo* and the aqueous layer extracted with CH₂Cl₂. The combined organic layers were dried with MgSO₄, concentrated, and the residue purified by column chromatography on silica (4:3 hexanes:CH₂Cl₂ eluent) to 1.47 g **1b** (86%). ¹H NMR (400 MHz, CDCl₃) δ 8.76 (s, 1H), 8.05 (d, J = 8.4Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.92-7.85 (m, 3H), 7.84 (d, J = 8.5 Hz, 1H), 7.60-7.50 (m, 3H), 7.46 Hz (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 7.10 (t, J = 8.1 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 155.5, 150.4, 149.6, 147.7, 143.0, 139.0, 135.2, 131.1, 130.6, 129.2, 128.4, 127.5, 127.3, 126.8, 126.5, 126.3, 126.2, 124.1, 122.9, 122.7, 120.63, 120.59, 118.1 ppm; HRMS calc'd for C₂₇H₁₉BrN₂: 450.0732, found 450.0743.

Synthesis of BNPB2: To a 250 mL Schlenk flask with stir bar was added **1b** (1.29 g, 2.9 mmol) and 60 mL dry Et₂O. The mixture was cooled to -78° C under N₂ and allowed to stir for 30 min, at which point *n*-BuLi (2.3 mL, 3.4 mmol, 1.6 M in hexanes) was added dropwise. The mixture was stirred for 40 min, then FBMes₂ (1.02g, 90%, 3.4 mmol) in 20 mL Et₂O was added dropwise *via* cannula. The mixture was stirred 3h at -78° C, then 1 mL sat. aq. NH₄Cl was added. The mixture was warmed to room temperature and partitioned between Et₂O and water, and the aqueous layer was extracted further with Et₂O. The combined organic layers were then dried with MgSO₄, concentrated, and the residue purified by column

chromatography on silica (3:1 hexanes:CH₂Cl₂ eluent) to afford 1.42 g **BNPB2** as a yellow solid (80%). ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, J = 1.7 Hz, 1H), 8.01-7.96 (m, 3H), 7.93 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.81 dd, J = 8.1 Hz, J = 1.7 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 8.2 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.39 (t, J = 8.1 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.3 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), d, J = 8.9 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.88 (s, 4H), 2.36 (s, 6H), 2.10 (s, 12H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 157.3, 149.9, 147.7, 144.4, 143.0, 141.0, 140.7, 139.0, 137.2, 135.3, 131.1, 129.2, 128.4, 128.3, 128.1, 127.3, 126.9, 126.8, 126.5, 126.3, 126.2, 124.1, 123.1, 122.8, 120.5, 118.8, 23.5, 21.2 ppm; HRMS calc'd for C₄₅H₄₁BN₂: 620.3363, found 620.3381.

Synthesis of Pt-BNPB2: To a 100 mL Schlenk flask with stir bar and condenser was added **BNPB2** (200 mg, 0.32 mmol), PtCl(DMSO)(acac) (131 mg, 0.32 mmol) and NaOAc (0.32 mmol) in 30 mL degassed 1:1 THF:MeOH. The mixture was heated at reflux for two days, concentrated, then purified on silica (3:1 hexanes:CH₂Cl₂ eluent) to afford 69 mg **Pt-BNPB2** as an orange solid (23%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.89 (s, sat, J_{Pt-H} = 31.5 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.87 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.47-7.39 (m, 3H), 7.33-7.23 (m, 5H), 7.06 (t, J = 7.0 Hz, 1H), 6.91 (s, 4H), 6.61 (dd, J = 8.6 Hz, J = 2.4 Hz, 1H), 5.33 (s, 1H), 2.33 (s, 6H), 2.12 (s, 12H), 1.65 (s, 3H), 1.61 (s, 3H) ppm; ¹³C NMR (100 MHz, CD₂Cl₂) δ 186.3, 184.1, 170.2, 156.3, 150.1, 147.8, 146.3, 143.3, 143.1, 141.1, 140.8, 139.6, 136.9, 135.7, 135.2, 132.0, 129.4, 128.8, 128.5, 128.1, 127.3, 126.9, 126.7, 126.6, 125.6, 124.5, 124.2, 123.4, 120.6, 117.2, 115.4, 102.2, 27.7, 26.9, 23.8, 21.3 ppm; Anal. calc'd for C50H47BN2O2Pt: C 65.72, H 5.18, N 3.07, found C 65.74, H 5.41, N 3.02



S3. Solvent-Dependent Emission Spectra

Emission spectra for BNPB2 (top) and Pt-BNPB2 (bottom) at 10-5 M in various solvents. λ_{EX} = 365 nm for BNPB2 and 470 nm for Pt-BNPB2.



Luminescence of 10⁻⁵ M solutions of BNPB2 (top) and Pt-BNPB2 (bottom) in various solvents. From left to right: hexanes, toluene, Et₂O, CH₂Cl₂, acetone, methanol.

S4. Solid State Emission Spectra



Solid state emission spectra of BNPB2 and its Pt(II) complex.

S5. TD-DFT Calculations



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S6. Cyclic Voltammetry



Oxidation waves for BNPB2 and its Pt(II) complex measured in MeCN relative to $FeCp_2^{0/+}$.



Reduction waves for BNPB2 and its Pt(II) complex measured in DMF relative to $FeCp_2^{0/+}$.

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S7. Electroluminescence Data





Devices fabricated with a dedicated hole-blocking layer (HBL):

References:

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