

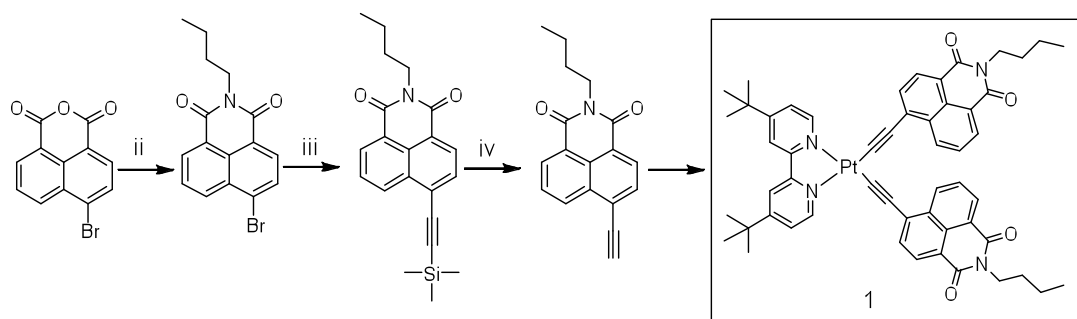
Supporting Information for:

Naphthalimide Phosphorescence Finally Exposed in a Platinum(II) Diimine Complex

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Synthesis of *N*-butyl-4-ethynynaphthalimide (NI-C≡C-H). 4-Bromonaphthalene anhydride (4.00 g, 14 mmol) and *N*-butylamine (1.28 g, 1.2 equiv.) was heated in ethanol (300 mL) at 60 °C. Then solution was cooled to room temperature. The light yellow precipitate was collected and washed with water. The product (*N*-butyl-4-bromonaphthalimide) was obtained. ¹H NMR (400 MHz, CDCl₃) 8.66 (d, 1H, *J* = 4.0 Hz), 8.56 (d, 1H, *J* = 8.4 Hz), 8.41 (d, 1H, *J* = 6.4 Hz), 8.04 (d, 1H, *J* = 8.4 Hz), 7.86 (t, 2H,

$J = 8.4$ Hz), 4.17 (t, 2H, $J = 8.4$ Hz), 1.75–1.68 (m, 2H), 1.50–1.40 (m, 2H), 0.98 (t, 3H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ : 163.57, 163.54, 133.14, 131.99, 131.17, 131.10, 130.52, 130.18, 128.89, 128.10, 123.12, 122.26, 40.48, 30.26, 20.50, 13.98. TOF-MS: $\text{C}_{16}\text{H}_{14}\text{BrNO}_2$, Calculated, $m/z = 331.0208$, found $m/z = 331.0211$.

Under an Ar atmosphere, *N*-butyl-4-bromonaphthalimide (1.00 g, 3.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (42.0 mg, 0.06 mmol), PPh_3 (32.0 mg, 0.12 mmol) and CuI (23.0 mg, 0.12 mmol) were mixed in THF (10 mL) and triethylamine (10 mL). Then trimethylsilylacetylene (414 mg, 4.2 mmol) was added. The mixture was heated for 6 h under an Ar atmosphere. The reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and then was purified with the column chromatography (silica gel, DCM: ethyl acetate = 10:1, V/V). The third fraction was collected. Then the silyl group was removed by treatment with anhydrous potassium carbonate in methanol at room temperature. The residue was taken up with dichloromethane, washed with water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified with column chromatography (silica gel, DCM : ethyl acetate = 10:1, V/V), yellow powder was obtained, 600.0 mg, 56.0 %. ^1H NMR (400 MHz, CDCl_3): δ 8.59 (m, 2H), 8.48 (d, $J = 7.6$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.78 (t, $J = 8.2$ Hz, 1H), 4.15(t, $J = 7.6$ Hz, 2H), 3.74 (s, 1H), 1.50 (m, 2H), 1.46 (m, 2H), 0.97 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): 164.09, 163.82, 132.32, 132.10, 131.82, 130.29, 128.05, 127.85, 126.31, 123.16, 123.00, 86.64, 80.49, 40.53, 30.36, 20.56, 14.04. TOF-MS: $\text{C}_{18}\text{H}_{15}\text{NO}_2$, Calculated, $m/z = 277.1111$, found, $m/z = 277.1103$.

Synthesis of Title Complex 1. Pt(dbbpy)Cl₂ (50 mg, 0.09 mmol), CuI (5 mg, 0.09 mmol) and diisopropylamine (1.0 mL) were dissolved in CH₂Cl₂ (5 mL), the mixture was stirred for 10 min. The mixture was purged with Ar, then NI-C≡C-H (100 mg, 0.36 mmol) was added and the mixture was stirred at room temperature for 24 h. The mixture was evaporated to dryness, the residue was purified by column chromatography (silica gel, CH₂Cl₂: CH₃OH = 150:1, v/v). The product was collected as the third fraction. 82.0 mg of yellow powder was obtained, yield: 86.0 %. ¹H NMR (400 MHz, CDCl₃): δ 9.68 (d, *J* = 6.0 Hz, 2H), 9.14 (d, *J* = 8.0 Hz, 2H), 8.51 (t, *J* = 7.6 Hz, 4H), 8.05 (s, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 5.2 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 4.16 (t, *J* = 7.6 Hz, 4H), 1.71 (m, 4H), 1.48 (m, 24H), 0.96 (t, *J* = 7.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 164.63, 164.43, 156.40, 151.45, 134.26, 33.26, 133.15, 131.24, 130.99, 130.10, 128.52, 126.64, 125.19, 122.90, 119.60, 119.26, 101.55, 100.12, 40.34, 36.16, 30.44, 20.61, 14.03. HR-MALDI-MS: C₅₄H₅₆NaN₄Pt, Calculated *m/z* = 1038.3534, found, *m/z* = 1038.3608.

Photophysical Measurements. Static UV-Vis absorption spectra were measured with a Varian 50 Bio spectrophotometer or a Hewlett-Packard 8453 diode array spectrophotometer. Uncorrected steady-state luminescence spectra were obtained by a PTI Instruments spectrofluorimeter equipped with an R-928 PMT using single photon counting detection. This fluorimeter operates under the control of Felix32 software from PTI. All photophysical measurements were conducted at ambient temperature, 22 ± 2 °C with the exception of low temperature glasses maintained at 77 K in a

liquid N₂ bath inside a quartz-tipped finger dewar. All luminescence samples were prepared with spectroscopic grade MTHF in 1 cm² anaerobic quartz cells (Starna Cells), degassed by solvent-saturated high purity argon for at least 35 minutes prior to the measurements and maintained under argon atmosphere throughout the experiments. Transient absorption spectra were collected on a Proteus Nanosecond Transient Absorption spectrometer (Ultrafast Systems) equipped with a 150 W Xe-arc lamp (Newport), a Bruker Optics monochromator and photodiode detectors (DET 10A and DET 10C, Thorlabs). Excitation at 420 nm (2 mJ/pulse) from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an optical absorbance of 0.4 at the excitation wavelength. The data consisting of a 128-shot average were analyzed by Origin 8.0 software.