

Supporting Information

Robust Phosphorescent Platinum(II) Complexes with Tetradentate O^NC^N Ligands. High Efficiency OLEDs with Excellent Efficiency Stability.

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(A) General Considerations

Grace Reveleris® iES Flash Chromatography System was employed to purify ligands **1–3** and Reveleris® Silica Flash Cartridge (Size 40 g, Davisil® silica) was used as stationary phase. The solvents used for synthesis were of analytical grade. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 500, 400 or DPX-300 FT-NMR spectrometer; the chemical shifts (in ppm) were reported relative to non-deuterated solvent residual or TMS (TMS = tetramethylsilane) as reference. Positive-ion-mode FAB mass spectra and EI mass spectra were recorded on a Finnigan MAT 95 mass spectrometer or Thermo Scientific DFS high resolution magnetic sector MS. Elemental analyses of the new complexes were performed at the Institute of Chemistry of the Chinese Academy of Sciences, Beijing. UV/Vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer or on a Perkin-Lambda 19 UV/Vis spectrophotometer. X-Ray diffraction data of single crystals were collected on a MAR PSD diffractometer with a 300 mm image plate detector or Bruker X8 Proteum diffractometer. The diffraction images were interpreted and diffraction intensities were integrated using program DENZO and the crystal structures were solved by direct methods employing SHELXS-97 program.

Emission and Lifetime Measurements

Steady-state excitation and emission spectra were obtained on a SPEX Fluorolog-3 spectrophotometer. All solutions for photophysical studies were degassed prior to the measurements. The solutions were in a two-compartment cell consisting of a 10 mL pyrex bulb and a 1 cm path-length quartz cuvette sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subjected to no less than three freeze-pump-thaw cycles. For measurement of emission spectrum at low-temperature (77 K), the solution or solid sample was loaded in a 5-mm-diameter quartz tube that was immersed in a liquid nitrogen Dewar flask equipped with quartz windows. The emission spectra were corrected for monochromator and photomultiplier efficiency and for Xenon-lamp stability. Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). Luminescence quantum yields were measured relative to that of a degassed benzene solution of 9,10-bis(phenylethynyl)anthracene (BPEA) as a standard reference ($\Phi_r = 0.85$). Errors for λ values (± 1 nm), τ (± 10 %), and Φ (± 10 %) are estimated.

OLED fabrication

TaPc, mCP, TmPyPB were purchased from from Luminescence Technology Corp. and used as received. Complexes **1** and **3** were synthesized by the authors and purified by gradient sublimation before use.

Glass slides with pre-patterned ITO electrodes used as substrates of OLEDs were cleaned in an ultrasonic bath of Decon 90 detergent and deionized water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of dionized water, acetone, and isopropanol, and subsequently dried in an oven for 1 h. OLEDs were fabricated in a Sunic multichamber high vacuum deposition system with a base pressure of 10^{-8} mBar. Substrates were treated by O₂ plasma in the Plasma Treating Chamber before transporting to the Organic Chamber, in which TaPc (70 nm), mCP: complex **1** or **3** (30 nm), TmPyPb (40 nm) were thermally deposited in sequence at a rate of 0.1 nm s⁻¹. The doping process in the emitting layer was realized by co-deposition of mCP and complex **1** or **3**. Afterwards, substrates with deposited organic layers were transferred to the Metal Chamber, in which LiF (0.5 nm) and Al (100 nm) were thermally deposited at rates of 0.03 and 0.2 nm s⁻¹, respectively. Film thicknesses were determined in-situ by calibrated oscillating quartz-crystal sensors. Finally, all fabricated devices were transferred to a N₂-filled glove box without exposure in air, inside which they were encapsulated together with an oxygen and moisture absorbing sheet with a glass lid and a UV curable epoxy resin.

The Commission Internationale de L'Eclairage (CIE) coordinates, luminance-current density-voltage characteristics (*L-J-V*), and electroluminescence (EL) spectra were measured simultaneously with a programmable Keithley model 2400 source-meter measurement unit and a Photoresearch PR-655 spectrascan spectroradiometer. All devices were characterized at room temperature after encapsulation. External quantum efficiency was calculated by assuming a Lambertian distribution.

(B) Synthetic Scheme for O[^]N[^]C[^]N Pt(II) Complexes:

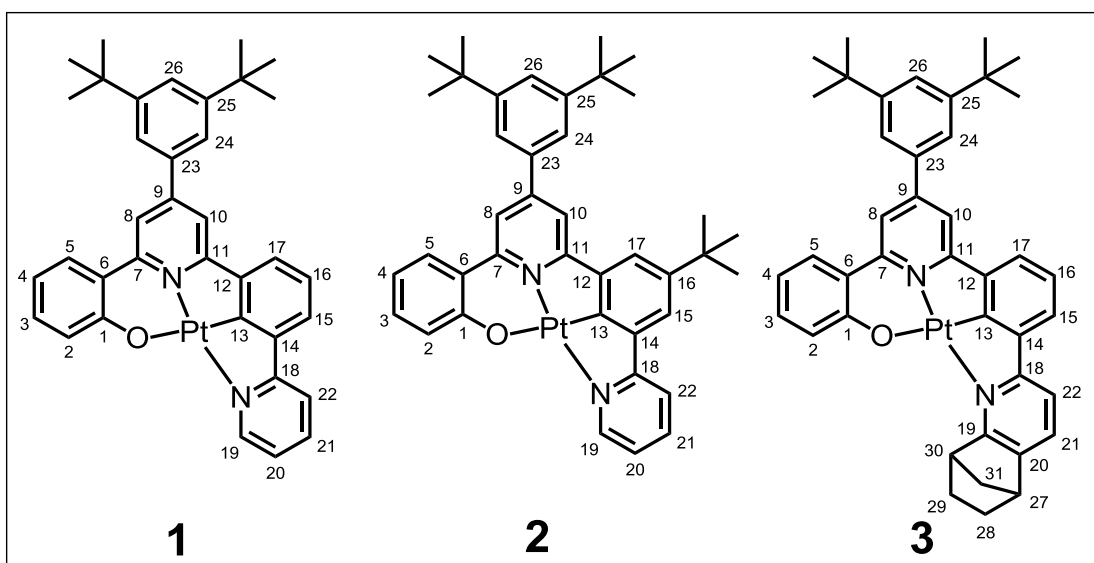
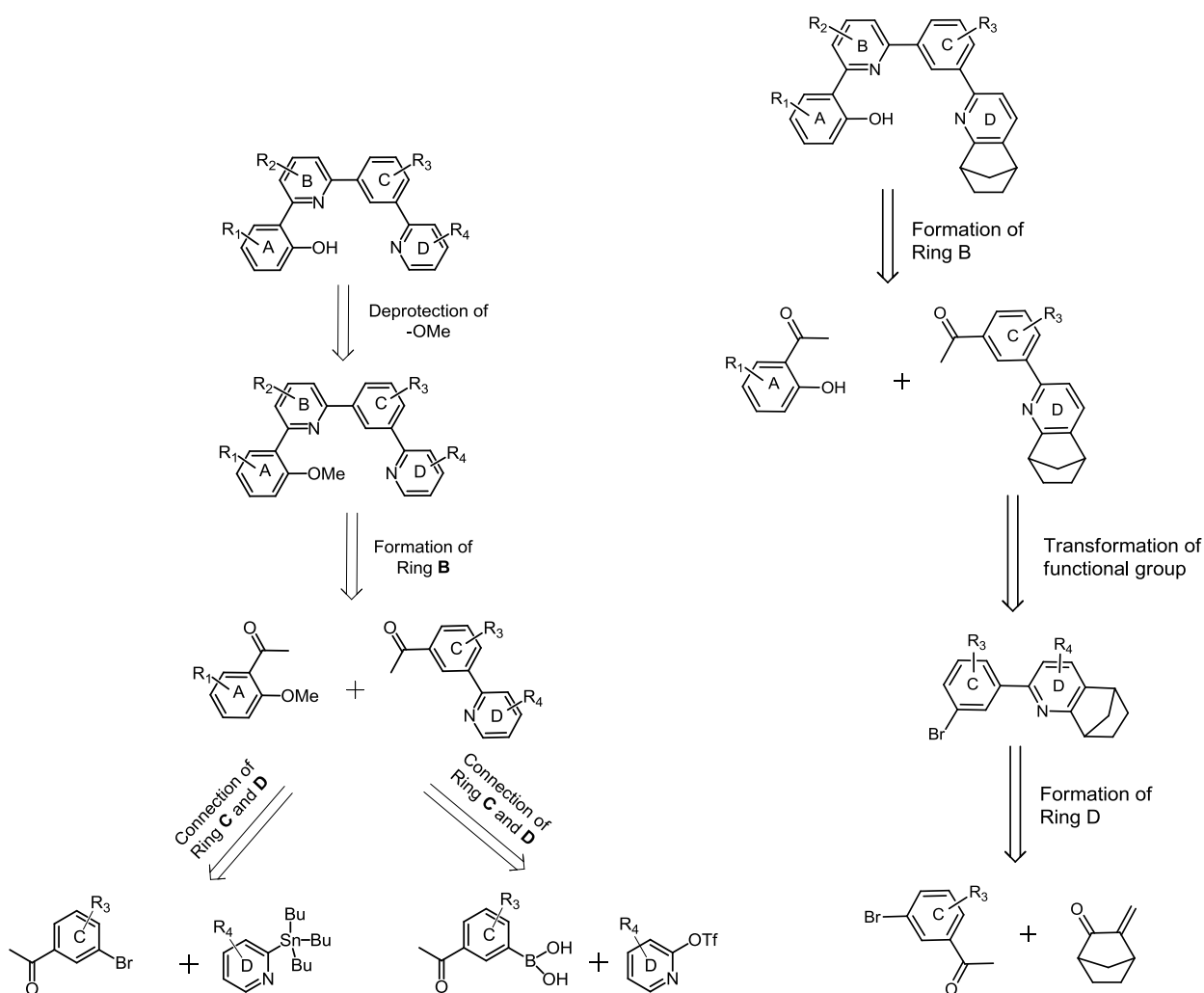
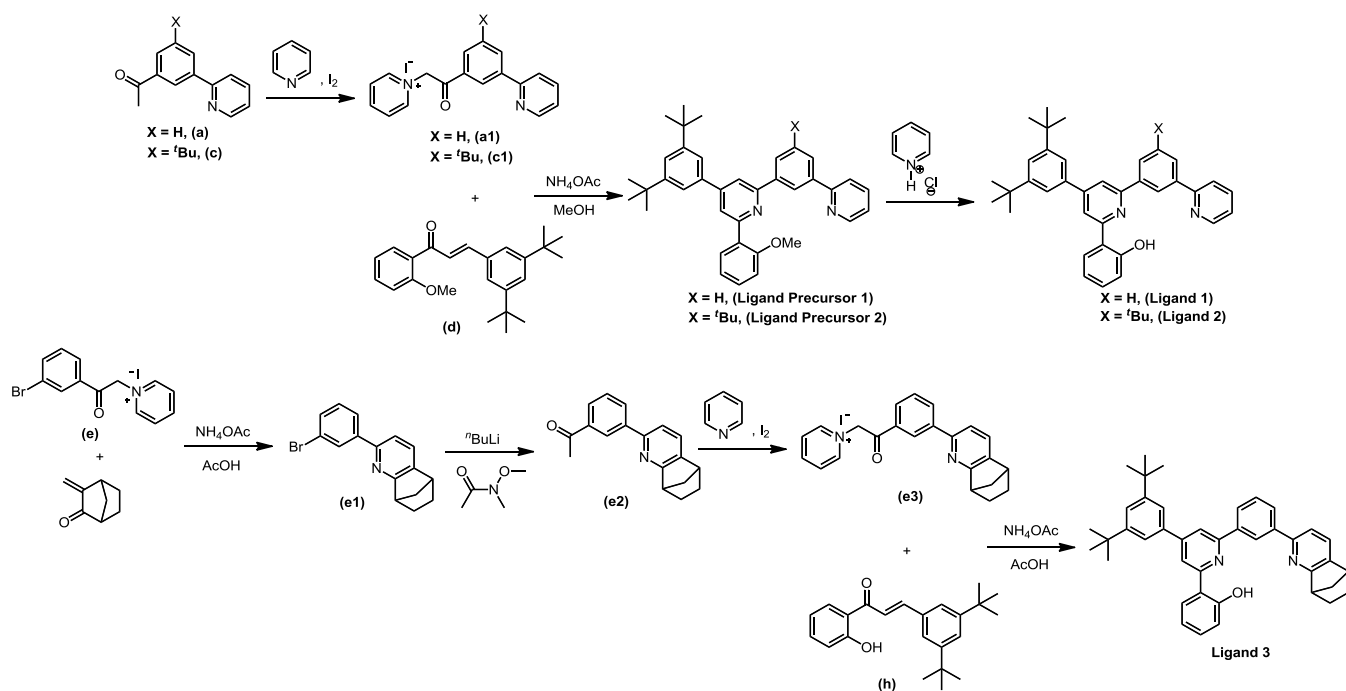


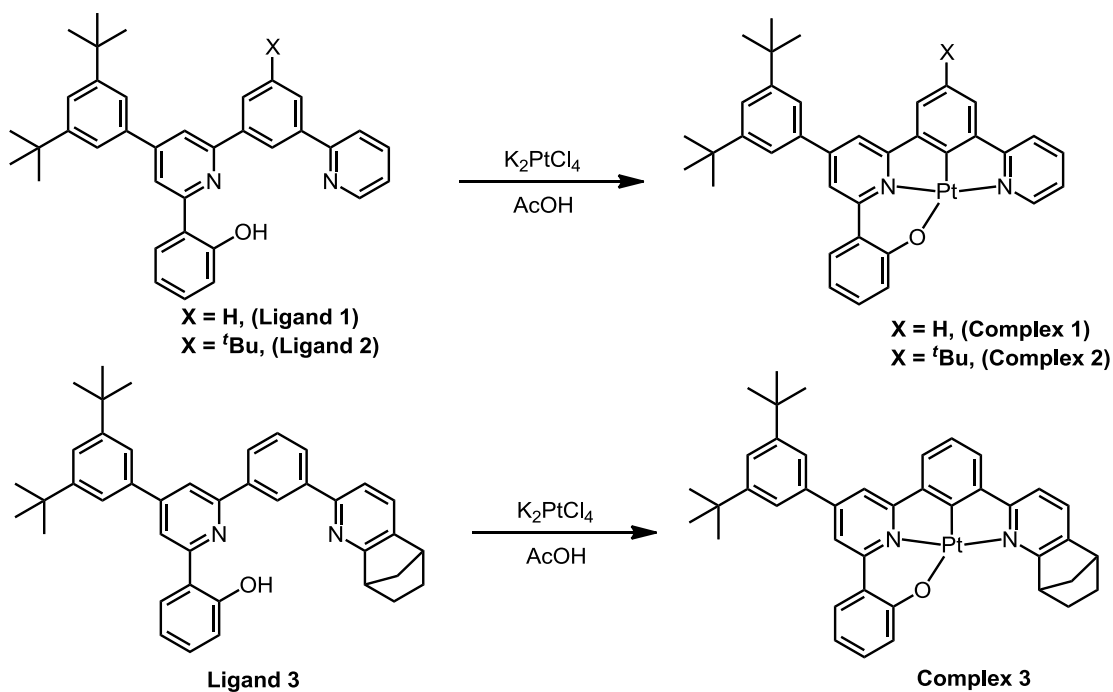
Figure S1. O[^]N[^]C[^]N platinum(II) complexes **1–3** studied in this work with the labeling scheme of the ligands.



Scheme S1. Retrosynthetic analysis of O[^]N[^]C[^]N ligands.



Scheme S2. Synthesis scheme for Ligands 1–3.

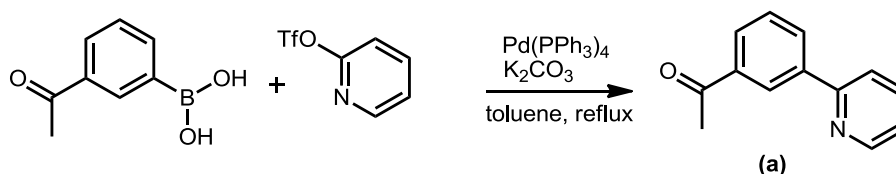


Scheme S3. Synthesis scheme for complexes 1–3.

(C) Synthetic procedure for complexes 1–3

(1) General procedure for starting materials (a), (b), (c), (e1), (e2)

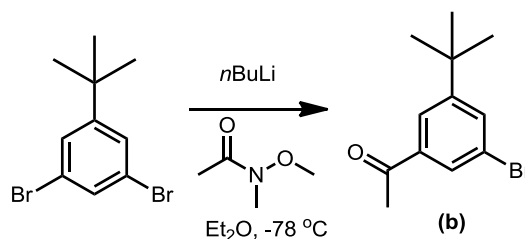
(i) Starting material (a)



Suzuki-Miyaura cross-coupling reaction was employed for the synthesis of (a). To a degassed solution of 3-acetylphenylboronic acid (10.0 g, 61.0 mmol), tetrakis(triphenylphosphine) palladium(0) (10 mol%) and pyridin-2-yl trifluoromethanesulfonate (13.9 g, 61.0 mmol) in toluene (100 mL), a solution of K₂CO₃ (2M, 10 mL) was added *via* a syringe. The reaction mixture was refluxed for 24 hours under nitrogen atmosphere. The solvent was then removed with reduced pressure and the crude product was extracted with dichloromethane (3 × 100 mL). The combined organic layer was dried over MgSO₄. After evaporation of the solvent, the residue was purified by silica gel flash chromatography on a silica gel column using *n*-hexane/EA (*v*:*v* = 4:1) as eluent to give (a) as off-white solid.

(a): Off-white solids. Yield: 90 %. ¹H NMR (400 MHz, CDCl₃): δ 2.69 (s, 3H), 7.27–7.31 (m, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.78–7.80 (m, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.59 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 1H). EI-MS (+ve, *m/z*): 197 [M⁺].

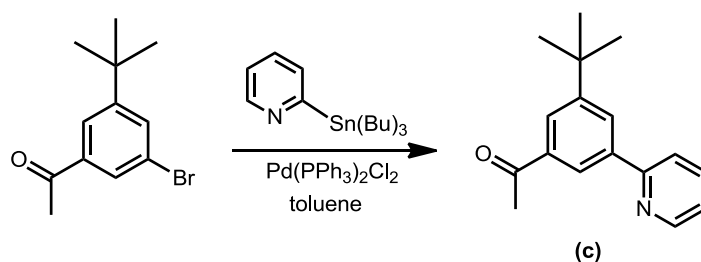
(ii) Starting material (b)



To a stirring solution of 1,3-dibromo-5-*tert*-butylbenzene (5.0 g, 17.0 mmol) in dry ether at -78 °C, *n*-Butyllithium (1.1 equiv.) was added dropwise. After stirring for 30 min under N₂ atmosphere, *N*-methoxy-*N*-methylacetamide (2.4 ml, 22.1 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After quenching with a saturated solution of ammonium chloride, water was added and the mixture was extracted with ether (2 × 150 ml). The combined organic extracts were washed with water (2 × 200 ml), dried with MgSO₄ and evaporated to give a crude product. Purification was done by silica gel flash column chromatography using ethyl acetate:*n*-hexane mixture (*v*:*v* = 1:28) as eluent to give (b) as pale yellow oil.

(b): Pale yellow oil. Yield: 82%. ¹H NMR (400 MHz, CDCl₃): δ 1.35 (s, 9H), 2.57 (s, 3H), 7.74 (s, 1H), 7.89 (s, 1H), 7.91 (s, 1H). EI-MS (+ve, *m/z*): 255 [M⁺].

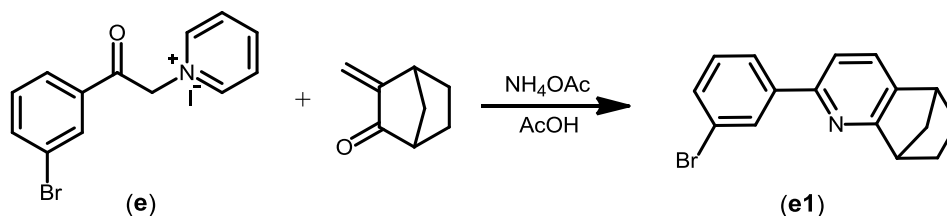
(iii) Starting material (c)



Stille coupling reaction was employed for synthesis of (c). A mixture of starting material (b) (3.0 g, 11.8 mmol), 2-(tributylstannyl)pyridine (5.0 ml, 15.3 mmol), [PdCl₂(PPh₃)₂] (10 mol %), was suspended in degassed toluene, and heated under reflux for 24 h. After cooling down to room temperature, aqueous NaOH (1 M, 40 mL) was added. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel flash column chromatography using ethyl acetate/hexane mixture (v:v = 1:9) as eluent to give (c) as yellow oil.

(c): yellow oil. Yield: 92%. ¹H NMR (400 MHz, CDCl₃): δ 1.43 (s, 9H), 2.69 (s, 3H), 7.26–7.31 (m, 1H), 7.78–7.79 (m, 2H), 8.07 (s, 1H), 8.26 (s, 1H), 8.36 (s, 1H), 8.73 (d, *J* = 4.8 Hz, 1H). EI-MS (+ve, *m/z*): 253 [M⁺].

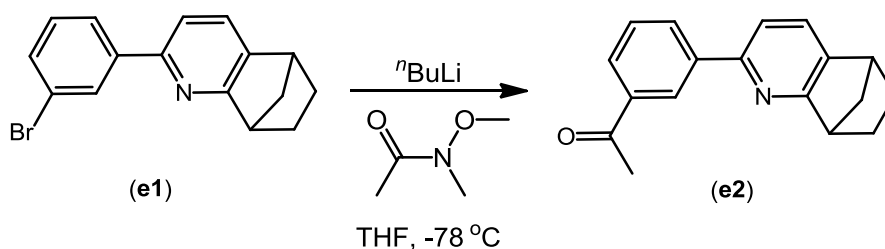
(iv) Starting material (e1)



Starting material (e1) was prepared by cyclization of the pyridine ring. A mixture of 3-methylene-2-norbornanone and pyridinium salt (e), and large excess (50 equiv.) of NH₄OAc in glacial acetic acid was refluxed for 12 hr. The reaction mixture was then poured into water and extracted with ethyl acetate (3 × 100 mL). The combined organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. Purification of the crude product was done by column chromatography on a silica gel flash column chromatography using *n*-hexane/Et₂O (9:1) as eluent to give starting material (e1) as pale yellow oil.

(e1): yellow oil. Yield: 69%. ¹H NMR (300 MHz, CDCl₃) δ 1.25 (m, 2H), 1.37 (t, *J* = 8.8 Hz, 1H), 1.61 (s, 1H), 1.89 (d, *J* = 9.1 Hz, 1H), 2.01 (m, 2H), 3.44 (s, 1H), 3.49 (s, 1H), 7.32 (m, 2H), 7.47 (m, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 8.11 (s, 1H).

(v) Starting material (e2)



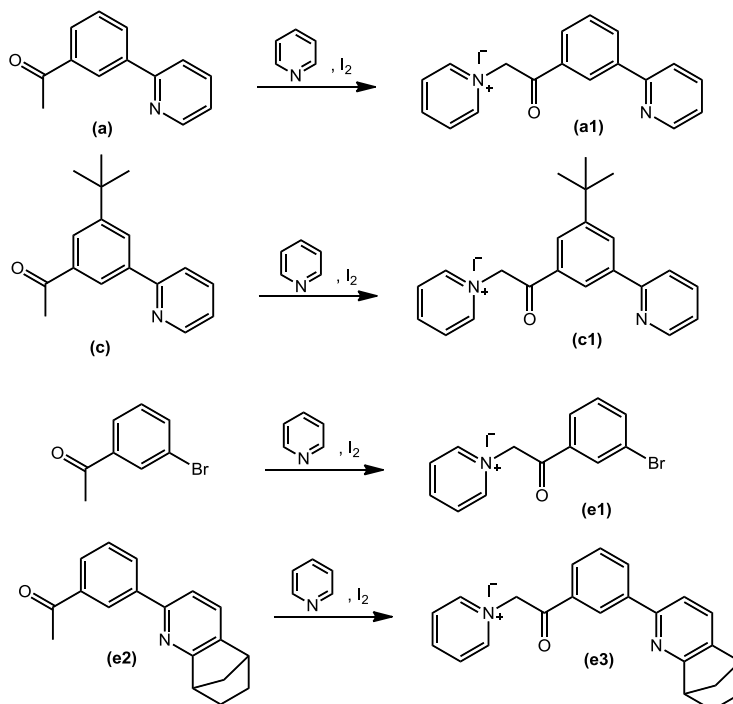
To a stirring solution of (e1) (1.0 g, 3.3 mmol) in 20 mL dry THF at $-78\text{ }^\circ\text{C}$, n -butyllithium (1.2 eq) was added dropwise under N_2 atmosphere. After stirring for 1 hr, N -methoxy- N -methylacetamide (1.5 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 hr. 1M HCl (2 eq.) was then added and the mixture was stirred vigorously for 4 hrs. The mixture was then extracted with ether (2×50 ml). The combined organic extracts were washed with brine (20 ml), dried with MgSO_4 and evaporated to give a crude product. Purification was done by silica gel flash column chromatography using ether: n -hexane mixture ($v:v = 1:9$) as eluent to give (e2) as pale yellow oil.

(e2): yellow oil. Yield: 68%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.25 (m, 1H), 1.38 (t, $J = 9.3$ Hz, 1H), 1.62 (d, $J = 9.1$ Hz, 1H), 1.88 (d, $J = 9.1$ Hz, 1H), 2.01 (m, 2H), 2.67 (s, 3H), 3.44 (s, 1H), 3.50 (s, 1H), 7.45 (q, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 8.14 (d, $J = 7.8$ Hz, 1H), 8.50 (s, 1H).

(2) General procedure for preparation of pyridinium salts (a1), (c1), (e), (e3)

A mixture of corresponding starting material (a), (c) and 3'-bromoacetophenone was heated with excess I₂ (1.2 equiv.) in pyridine (20 mL) for 2 h to produce (a1), (c1) and (e), respectively. The crude solid was filtered and washed with acetone or ethanol to give light brown crystalline solid (a1), (c1) and (e) respectively.

For pyridinium salt (e3), similar procedure was adopted using (e2) as starting material. After refluxing for 4 h, pyridine was evaporated in vacuo. Pyridinium salt (e3) was not isolated and the crude was used directly for further reaction without purification.

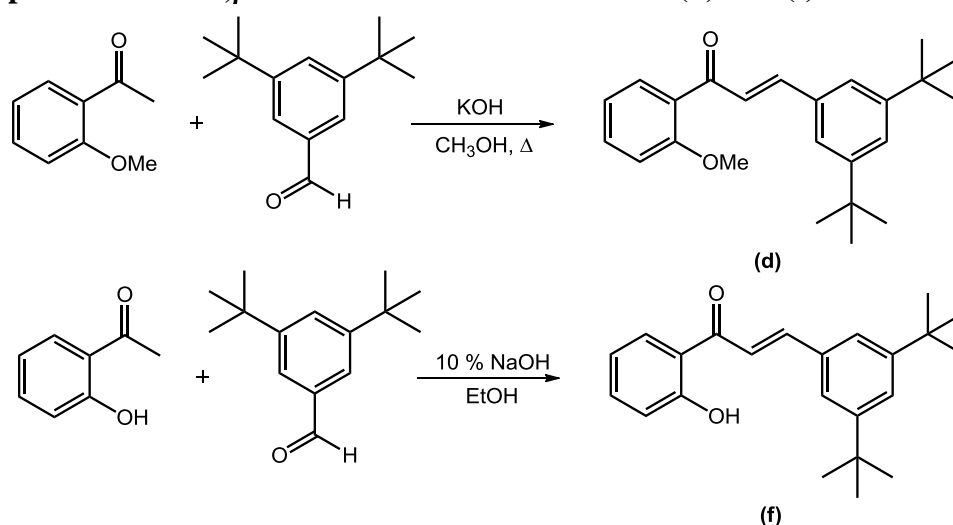


(a1): Brown solids. Yield: 90 %. ¹H NMR (400 MHz, d₆-DMSO): 6.56 (s, 2H), 7.43–7.46 (m, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.97 (t, *J* = 8.6 Hz, 1H), 8.12 (t, *J* = 7.5 Hz, 2H), 8.29 (t, *J* = 7.2 Hz, 2H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.72–8.77 (m, 3H), 8.99 (d, *J* = 5.5 Hz, 1H).

(c1): Brown solids. Yield: 95 %. ¹H NMR (400 MHz, d₆-DMSO): 1.41 (s, 9H), 6.59 (s, 2H), 7.44 (m, 1H), 7.97 (t, *J* = 6.4 Hz, 1H), 8.07 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.28 (t, *J* = 7.1 Hz, 2H), 8.48 (s, 1H), 8.58 (s, 1H), 8.72–8.77 (m, 4H).

(e1): Brown solids. Yield: 91 %. ¹H NMR (400 MHz, DMSO) δ 6.43 (s, 2H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 8.20 (s, 1H), 8.26 (m, 2H), 8.72 (t, *J* = 7.4 Hz, 1H), 8.93 (d, *J* = 6.1 Hz, 2H).

(3) General procedure for α,β -unsaturated ketone derivative (d) and (f)



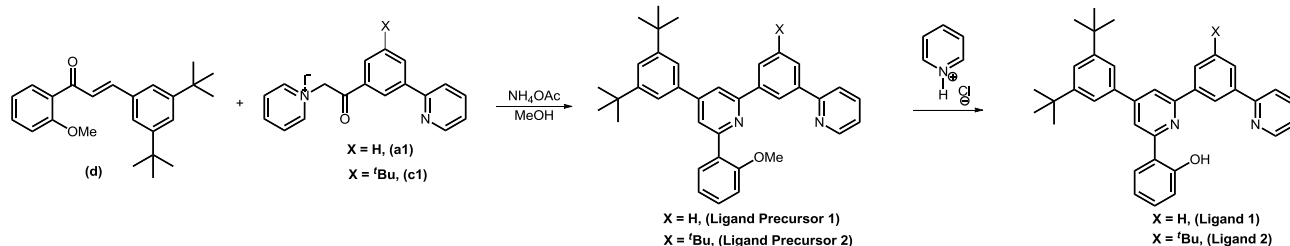
The α,β -unsaturated ketone derivative (d) and (f) was synthesized by aldol condensation between ketone and aldehyde under basic condition. A mixture of 1-(2-methoxyphenyl)ethanone (10.3 g, 68.7 mmol), 3,5-di-*tert*-butylbenzaldehyde (15.0 g, 68.7 mmol) and KOH (2.5 equiv.) in methanol was refluxed for 24 hr. The resulting solution was extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was washed with brine and dried over MgSO_4 , and concentrated to dryness in vacuo. Purification of the crude was done by silica gel flash column chromatography using *n*-hexane/EA (9:1) as eluent to give (d) as off-white solid.

3,5-di-*tert*-butylbenzaldehyde was dissolved in minimal amount of ethanol. 10% NaOH solution (2.5 eq) was added. 2'-hydroxyacetophenone (1.2 equiv.) was added slowly with stirring. The mixture was stirred at room temperature for 72 hr till the mixture changed from yellow to red. Acetic acid (3 equiv.) was then added and the reaction mixture was stored in refrigerator for 30 mins. The crude solid was collected, washed with water and cold ethanol to give (f) as yellow solid.

(d): Pale yellow oil. Yield: 88%. ^1H NMR (300 MHz, CDCl_3): 1.28 (s, 18H, *t*Bu), 3.83 (s, 3H, -OMe), 6.93–7.01 (m, 2H), 7.25 (d, $J = 15.9$ Hz, 1H), 7.35–7.44 (m, 4H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 15.9$ Hz, 1H). EI-MS (+ve, m/z): 350 [M^+].

(f): bright yellow solid. Yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ 1.38 (s, 18H), 6.97 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 1H), 7.45 – 7.58 (m, 4H), 7.63 (d, $J = 15.5$ Hz, 1H), 7.89 – 8.04 (m, 2H), 12.89 (s, 1H).

(4) General procedure for Ligands 1–2



The ligand precursors **1** and **2** were prepared by cyclization of the pyridine ring. A mixture of corresponding α,β -unsaturated ketone derivative (**g**), pyridinium salt (**a1** or **c1**), and large excess (10 equivalent) of NH_4OAc in MeOH solution was refluxed for 12 hr. The solvent was removed with reduced pressure. The crude was then washed with brine (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was dried over anhydrous MgSO_4 and concentrated in vacuo to obtain yellow or brown oil. Purification of the crude was done by Grace Reveleris® iES Flash Chromatography System on a Reveleris® Silica Flash Cartridge (Size 40 g, Davisil® silica) using *n*-hexane/ CH_2Cl_2 (4:1) as eluent to give **ligand precursors 1** and **2** as white solids and pale yellow oil respectively. Demethylation of **ligand precursors 1** and **2** were done in molten state pyridine hydrochloride under N_2 at 250°C for 12 hr, giving **Ligands 1** and **2** as off-white solids.

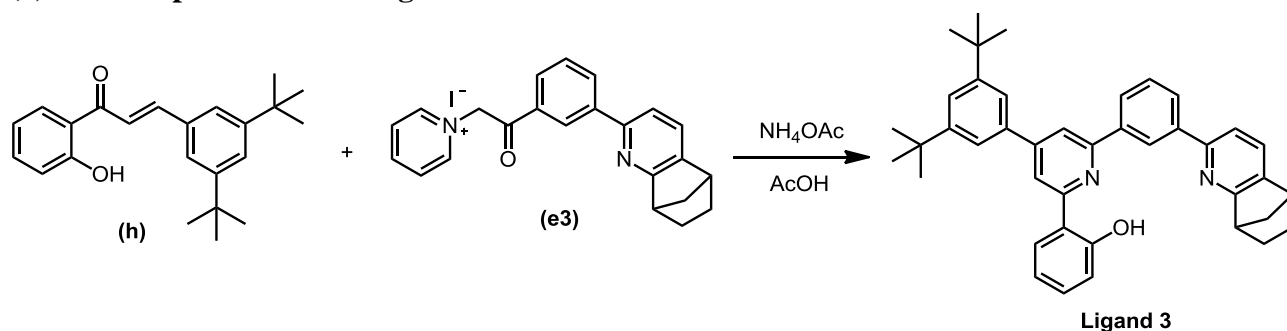
Ligand precursor 1: White solids. Yield: 83%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C): δ 1.41 (s, 18H, $t\text{Bu}$), 3.92 (s, 3H, -OMe), 7.06 (d, $J = 8.3$ Hz, 1H), 7.15 (t, $J = 8.2$ Hz, 1H), 7.25–7.28 (m, 1H), 7.42 (t, $J = 8.5$ Hz, 1H), 7.55 (s, 3H), 7.62 (t, $J = 7.7$ Hz, 1H), 7.76–7.86 (m, 2H), 7.91 (s, 1H), 8.04–8.09 (m, 3H), 8.21 (d, $J = 7.8$ Hz, 1H), 8.70 (s, 1H), 8.73 (d, $J = 4.2$ Hz, 1H). MS(EI, +ve): 527 (M^+).

Ligand 1: Off-white solids. Yield: 72%. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 1.43 (s, 18H, $t\text{Bu}$), 6.98 (t, $J = 8.1$ Hz, 1H, H^4), 7.08 (d, $J = 8.6$ Hz, 1H, H^2), 7.26–7.28 (m, 1H, H^{20}), 7.36 (t, $J = 8.4$ Hz, 1H, H^3), 7.53 (s, 2H, H^{24}), 7.60 (s, 1H, H^{26}), 7.67 (t, $J = 7.8$ Hz, 1H, H^{16}), 7.82 (t, $J = 7.2$ Hz, 1H, H^{21}), 7.85 (d, $J = 7.4$ Hz, 1H, H^{22}), 7.90 (s, 1H, H^{10}), 7.95 (d, $J = 8.1$ Hz, 1H, H^5), 8.04 (s, 1H, H^8), 8.07 (d, $J = 8.4$ Hz, 1H, H^{17}), 8.13 (d, $J = 7.8$ Hz, 1H, H^{15}), 8.59 (s, 1H, H^{13}), 8.73 (d, $J = 7.4$ Hz, 1H, H^{19}), 14.84 (s, 1H, -OH). MS(EI, +ve): 513 (M^+).

Ligand precursor 2: Pale-yellow oil. Yield: 77%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C): δ 1.41 (s, 18H, $t\text{Bu}$), 1.47 (s, 9H, $t\text{Bu}$), 3.92 (s, 3H, -OMe), 7.06 (d, $J = 8.4$ Hz, 1H), 7.17 (t, $J = 8.1$ Hz, 1H), 7.24–7.26 (m, 1H), 7.42 (t, $J = 8.4$ Hz, 1H), 7.54 (s, 3H), 7.76–7.84 (m, 2H), 7.87 (s, 1H), 8.04 (s, 1H), 8.07 (d, $J = 7.6$ Hz, 1H), 8.15 (s, 1H), 8.21 (s, 1H), 8.43 (s, 1H), 8.73 (d, $J = 4.2$ Hz, 1H). MS(EI, +ve): 583 (M^+).

Ligand 2: Off-white solid. Yield: 65%. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2 , 25°C): δ 1.43 (s, 18H, $t\text{Bu}$), 1.49 (s, 9H, $t\text{Bu}$), 6.98 (t, $J = 8.2$ Hz, 1H, H^4), 7.04 (d, $J = 9.3$ Hz, 1H, H^2), 7.29 (t, $J = 6.7$ Hz, 1H, H^{20}), 7.36 (t, $J = 8.5$ Hz, 1H, H^3), 7.58 (s, 2H, H^{24}), 7.62 (s, 1H, H^{26}), 7.83 (t, $J = 8.6$ Hz, 1H, H^{21}), 7.87 (d, $J = 8.0$ Hz, 1H, H^{22}), 7.94 (s, 1H, H^{10}), 8.01 (d, $J = 9.0$ Hz, 1H, H^5), 8.09 (s, 1H, H^8), 8.11 (s, 1H, H^{13}), 8.22 (s, 1H, H^{15}), 8.40 (s, 1H, H^{17}), 8.72 (d, $J = 6.4$ Hz, 1H, H^{19}), 14.76 (s, 1H, -OH). MS(EI, +ve): 569 (M^+).

(5) General procedure for Ligands 3



The ligand **3** was prepared by cyclization of the pyridine ring. A mixture of corresponding α,β -unsaturated ketone derivative (**h**), pyridinium salt (**e3** crude), and large excess (50 equivalent) of NH_4OAc in in glacial acetic acid was refluxed for 12 hr. Water was then added to the reaction mixture and was extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was dried over anhydrous MgSO_4 and concentrated in vacuo to obtain black oil. Purification of the crude was done by Grace Reveleris® iES Flash Chromatography System on a Reveleris® Silica Flash Cartridge (Size 40 g, Davisil® silica) using *n*-hexane/ether (19:1) as eluent to give **ligand 3** as off-white solid.

Ligand 3: Off-white solids. Yield: 32%. ^1H NMR (500 MHz, CDCl_3) δ 1.24–1.32 (m, 1H, $\text{H}^{28\text{b}}$), 1.39–1.50 (m, 19H, tBu , $\text{H}^{29\text{b}}$), 1.64 (d, $J = 9.0$ Hz, 1H, $\text{H}^{31\text{b}}$), 1.92 (d, $J = 9.0$ Hz, 1H, $\text{H}^{31\text{a}}$), 2.03 (m, 2H, $\text{H}^{28\text{a}}$, $\text{H}^{29\text{a}}$), 3.46 (s, 1H, H^{30}), 3.53 (s, 1H, H^{27}), 6.98 (t, $J = 7.5$ Hz, 1H, H^4), , 7.09 (d, $J = 8.2$ Hz, 1H, H^2), 7.36 (t, $J = 7.0$ Hz, 1H, H^3), 7.50 (s, 2H, H^{24}), 7.55 (d, $J = 1.7$ Hz, 2H, H^{21} , H^{22}), 7.59 - 7.68 (m, 2H, H^{16} , H^{26}), 7.92 (s, 1H, H^{10}), 7.96 (d, $J = 8.0$ Hz, 1H, H^5), 8.02 (d, $J = 7.8$ Hz, 1H, H^{17}), 8.04 (s, 1H, H^8), 8.07 (d, $J = 7.7$ Hz, 1H, H^{15}), 8.52 (s, 1H, H^{13}), 14.89 (s, 1H, -OH).

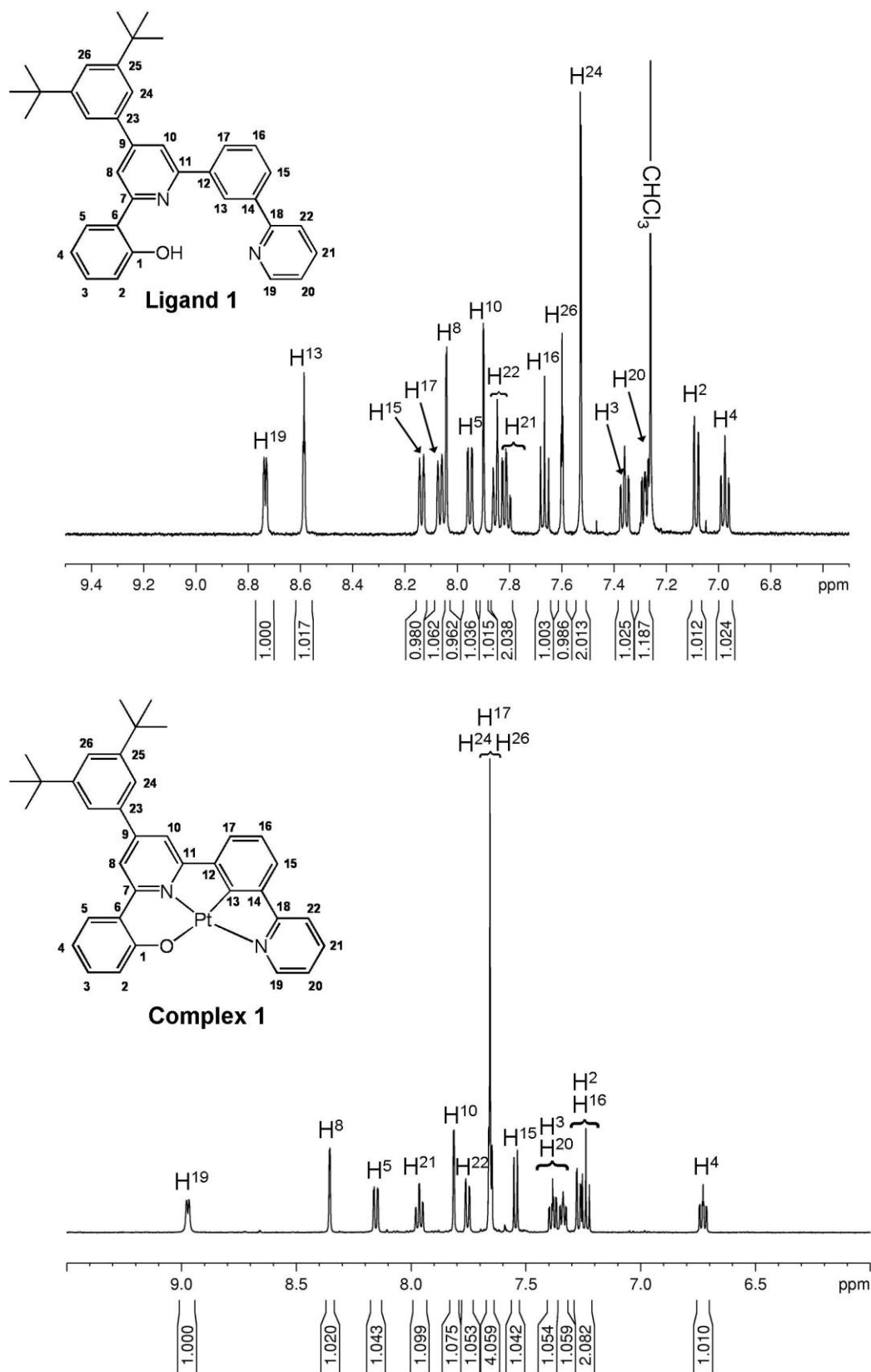
(6) [Pt(O[^]N[^]C[^]N)] 1–3

A mixture of K₂PtCl₄ (1.2 eq) and corresponding ligand (1.0 eq) in chloroform and glacial acetic acid mixture (v:v 1:9, 150 mL) was refluxed for 24 hours to give the crude as a yellowish-green solution. It was neutralized by a sodium carbonate solution and extracted by CH₂Cl₂ solution. Purification was done by alumina flash column chromatography using CH₂Cl₂ as eluent to yield yellow solids. Recrystallization was done by diffusion of Et₂O into the CHCl₃ solution of the solid to give the Pt(II) complex as yellow crystalline solids.

Complex 1: Yellow crystalline solids. Yield: 80%. ¹H NMR (500 MHz, CD₂Cl₂, 25 °C): δ 1.47 (s, 18H, ^tBu), 6.74 (t, *J* = 6.8 Hz, 1H, H⁴), 7.24–7.29 (m, 2H, H², H¹⁶), 7.34 (t, *J* = 6.5 Hz, 1H, H²⁰), 7.38 (t, *J* = 7.5 Hz, 1H, H³), 7.57 (d, *J* = 7.5 Hz, 1H, H¹⁵), 7.66–7.69 (m, 4H, H¹⁷, H²⁴, H²⁶), 7.78 (d, *J* = 7.4 Hz, 1H, H²²), 7.83 (s, 1H, H¹⁰), 7.97 (t, *J* = 7.8 Hz, 1H, H²¹), 8.17 (d, *J* = 8.5 Hz, 1H, H⁵), 8.37 (s, 1H, H⁸), 8.99 (d, *J* = 6.8 Hz, 1H, H¹⁹). MS(FAB, +ve): 706 (M⁺). Elemental analysis calcd (%) for C₃₆H₃₄N₂OPtEt₂O: C 61.60, H 5.69, N 3.59; found: C 61.54, H 5.43, N 3.56.

Complex 2: Yellow crystalline solids. Yield: 82%. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 1.45 (s, 27H, ^tBu), 6.75 (m, 1H, H⁴), 7.32 (t, *J* = 6.5 Hz, 1H, H²⁰), 7.40–7.43 (m, 2H, H², H³), 7.58 (s, 2H, H²⁴), 7.63 (s, 1H, H²⁶), 7.64 (s, 1H, H¹⁵), 7.69 (s, 1H, H¹⁷), 7.78 (s, 1H, H¹⁰), 7.80 (d, *J* = 8.0 Hz, 1H, H²²), 7.96 (t, *J* = 8.5 Hz, 1H, H²¹), 8.11 (d, *J* = 8.3 Hz, 1H, H⁵), 8.30 (s, 1H, H⁸), 9.07 (m, 1H, H¹⁹). MS(FAB, +ve): 762 (M⁺). Elemental analysis calcd (%) for C₄₀H₄₂N₂OPt: C 63.06, H 5.56, N 3.68; found: C 62.94, H 5.57, N 3.53.

Complex 3: Orange crystalline solids. Yield: 83%. ¹H NMR (500 MHz, CDCl₃) δ 1.31 (d, *J* = 10.6 Hz, 1H, H^{28b}), 1.45 (s, 18H, ^tBu), 1.54 (d, *J* = 7.0 Hz, 1H, H^{29b}), 1.76 (d, *J* = 9.3 Hz, 1H, H^{31b}), 2.03 (d, *J* = 9.3 Hz, 1H, H^{31a}), 2.10 (t, *J* = 11.2 Hz, 1H, H^{28a}), 2.24 (t, *J* = 11.5 Hz, 1H, H^{29a}), 3.50 (s, 1H, H²⁷), 5.38 (s, 1H, H³⁰), 6.74 (ddd, *J* = 8.2, 6.0, 2.1 Hz, 1H, H⁴), 7.21 (t, *J* = 7.6 Hz, 1H, H¹⁶), 7.40 (m, 2H, H², H³), 7.46 (m, 2H, H¹⁵, H²²), 7.61 (m, 5H, H¹⁷, H²¹, H²⁴, H²⁶), 7.81 (s, 1H, H¹⁰), 8.10 (d, *J* = 8.7 Hz, 1H, H⁵), 8.33 (s, 1H, H⁸). MS(FAB, +ve): 772 (M⁺). Elemental analysis calcd (%) for C₄₁H₄₀N₂OPt: C 63.80, H 5.22, N 3.63; found: C 63.52, H 5.23, N 3.50.



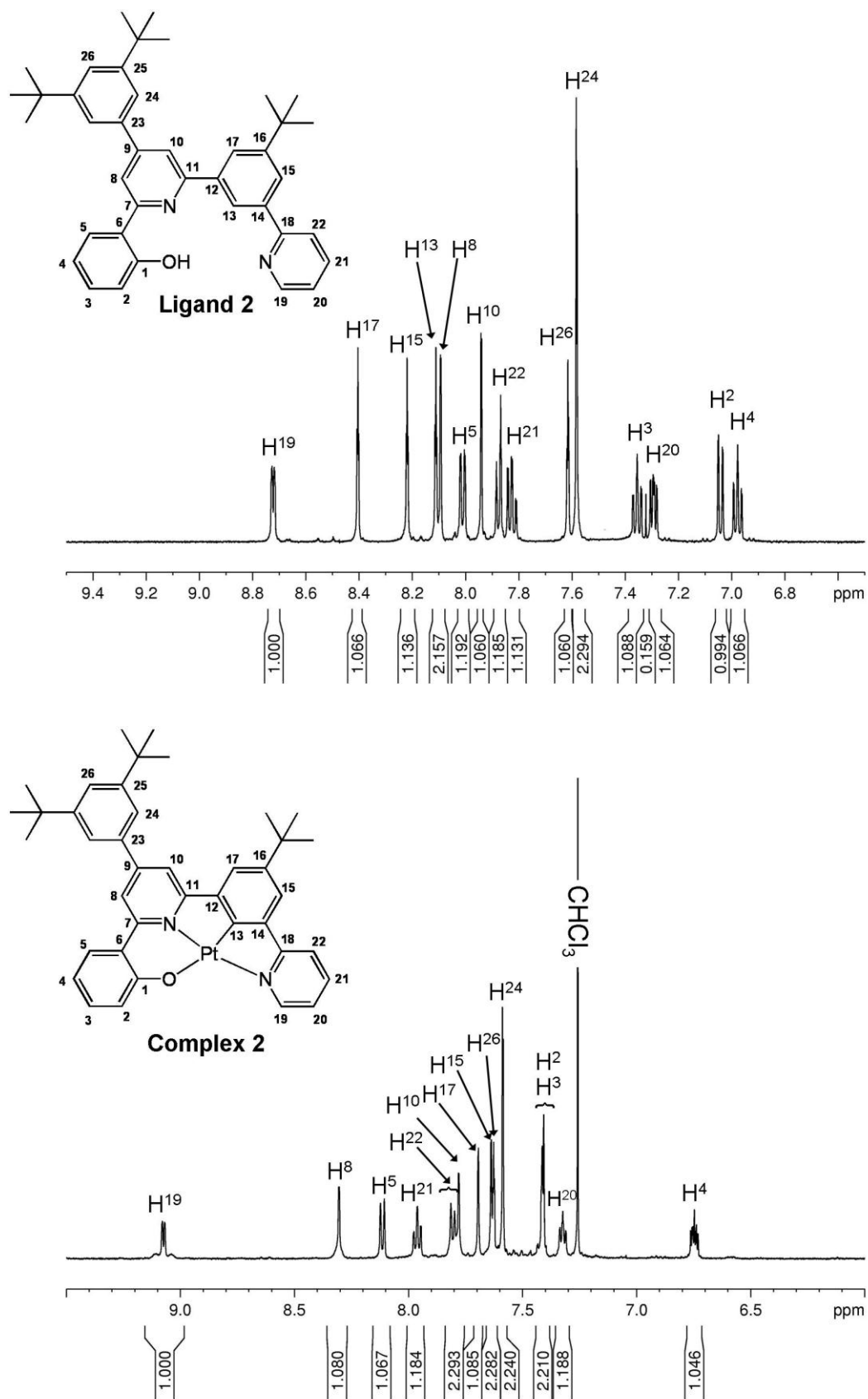


Figure S3. ¹H NMR spectra (aromatic region) of ligand **2** (CD₂Cl₂) and complex **2** (CDCl₃) at 298 K.

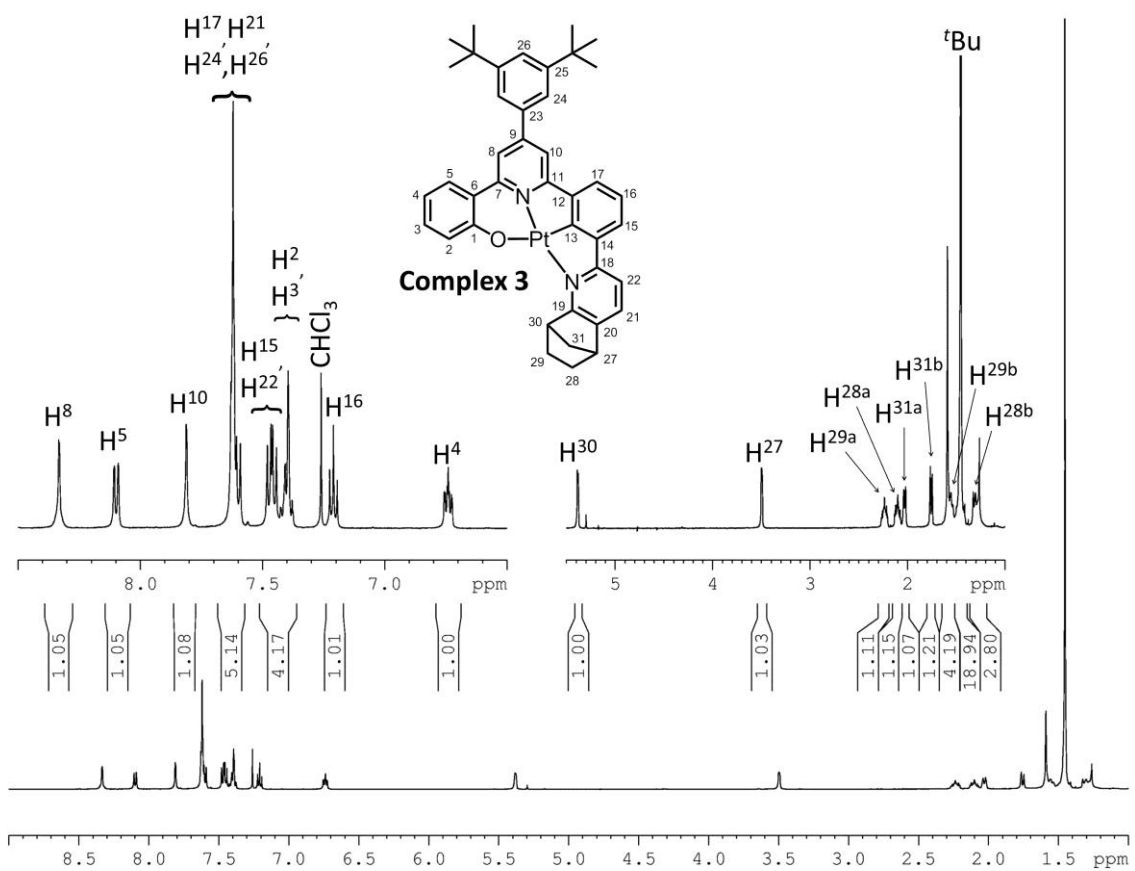
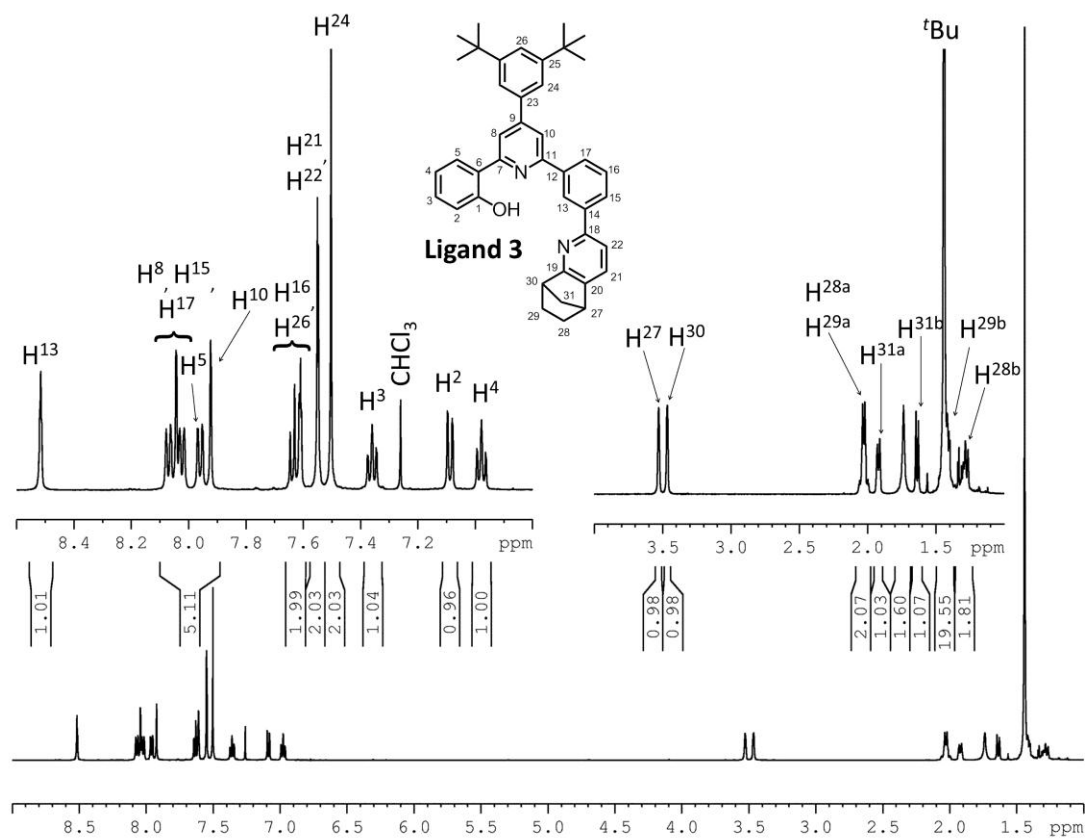


Figure S4. ¹H NMR spectra (aromatic region) of ligand **3** (CDCl₃) and complex **3** (CDCl₃) at 298 K.

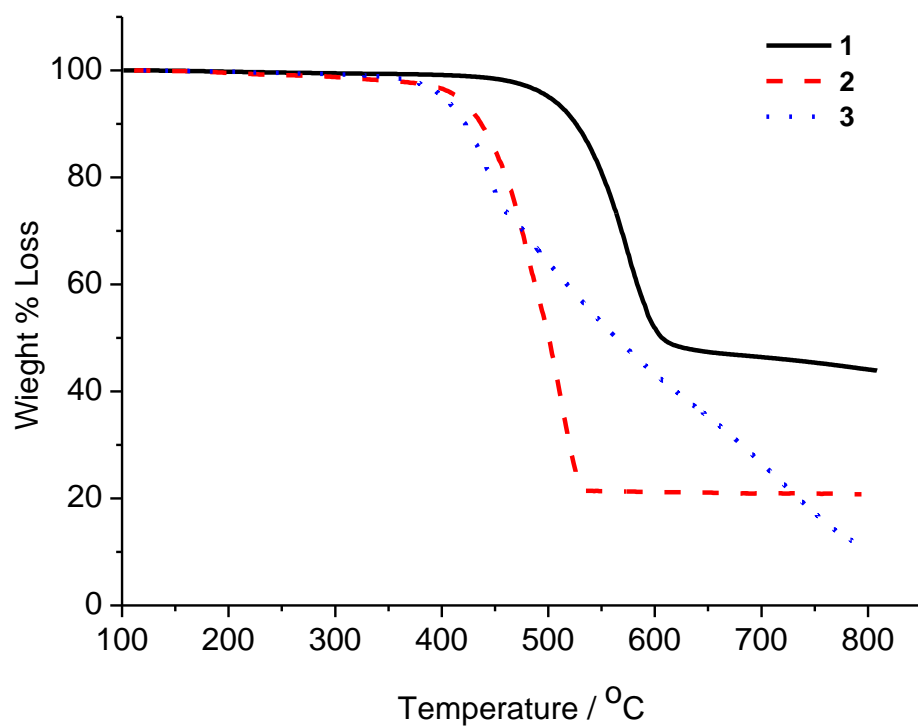


Figure S5. TGA thermograms of complexes 1–3.

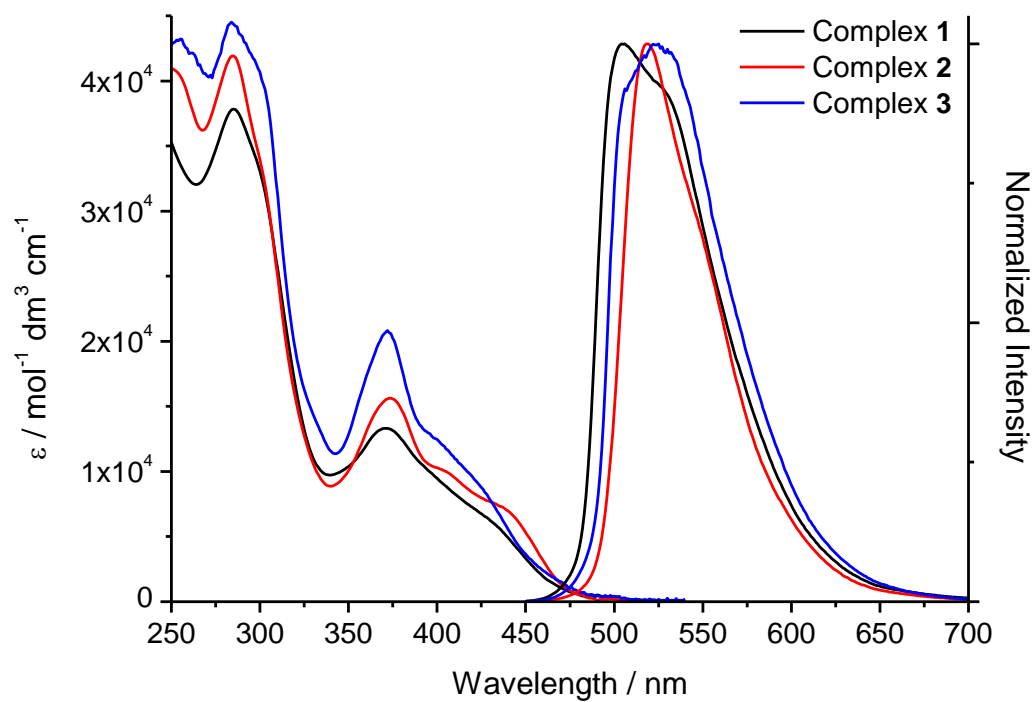


Figure S6. UV absorption spectra and emission spectra of 1–3 in CH_2Cl_2 ($2.0 \times 10^{-5} \text{ mol dm}^{-3}$).

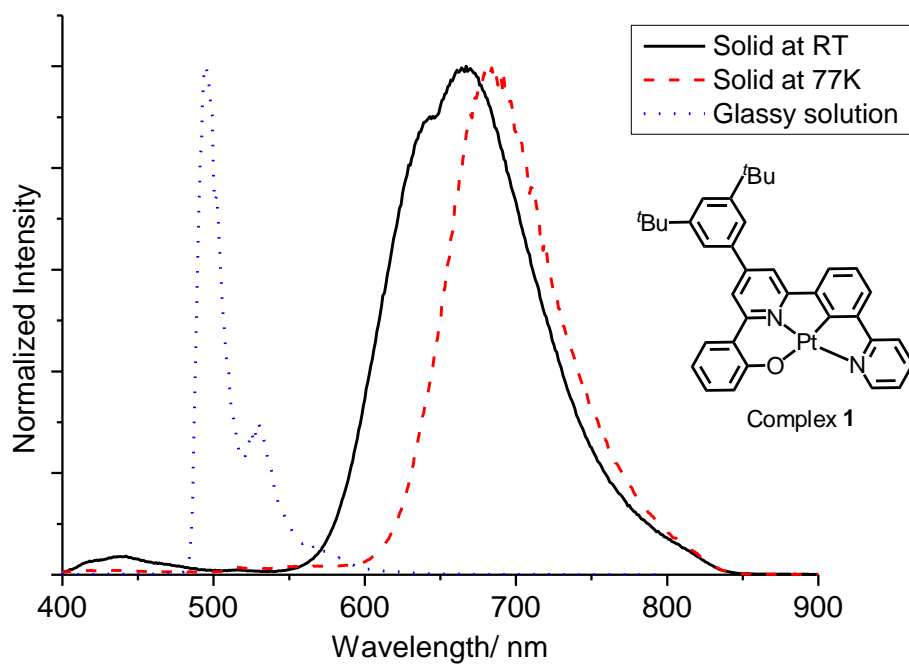


Figure S7. Solid state and glassy state emission spectra of complex **1** at room temperature or 77K.

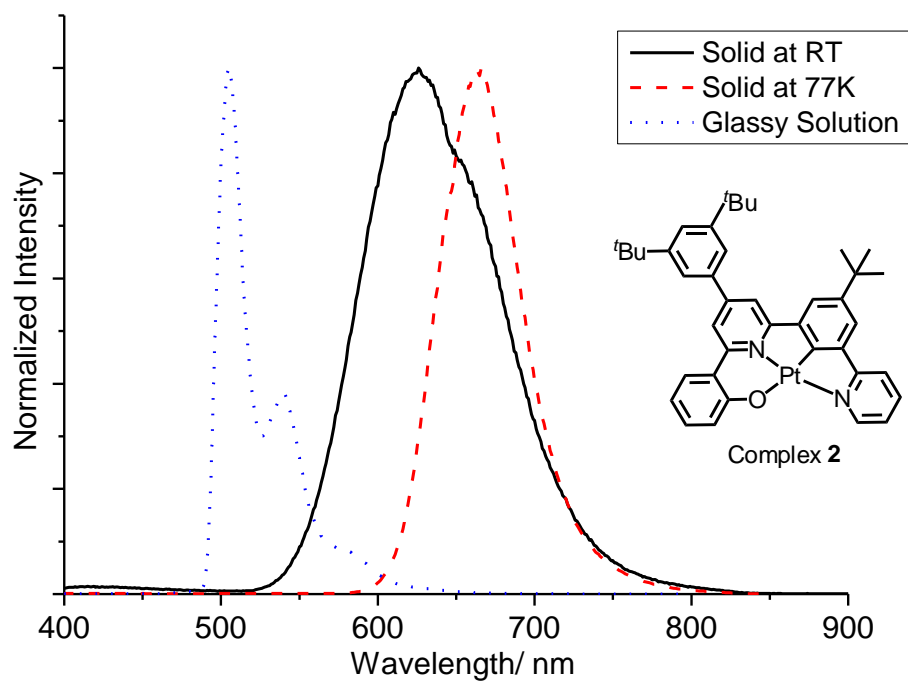


Figure S8. Solid state and glassy state emission spectra of complex **2** at room temperature or 77K.

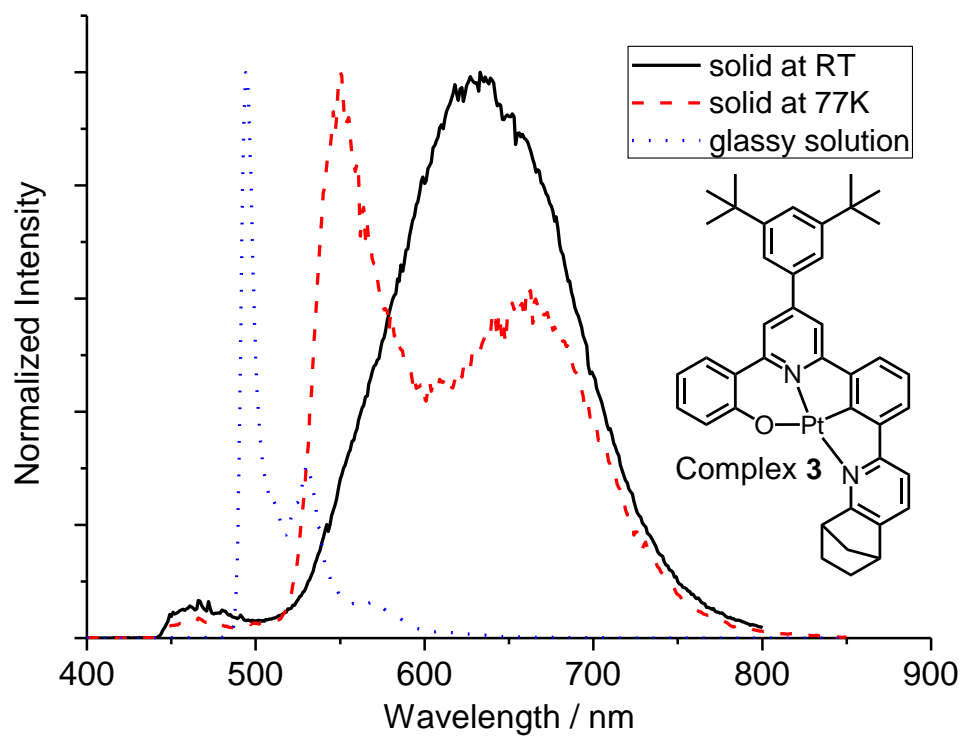


Figure S9. Solid state and glassy state emission spectra of complex 3 at room temperature or 77K.

Table S1. Photophysical Data of Complexes 1–3

Complex	UV-vis absorption ^a λ_{\max}/nm ($\epsilon/10^4 \text{mol}^{-1} \text{dm}^{-3} \text{cm}^{-1}$)	Photoluminescence Data					
		Solution ^a λ_{\max}/nm ($\tau/\mu\text{s}$)	Quenching Constant, k_q ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Quantum ^b Yield Φ	Solid-state, 298 K λ_{\max}/nm ($\tau/\mu\text{s}$)	Solid-state, 77 K λ_{\max}/nm ($\tau/\mu\text{s}$)	Glassy solution, 77 K ^c λ_{\max}/nm ($\tau/\mu\text{s}$)
1	284 (3.81), 371 (1.32), 426 (sh, 0.66)	503 (4.7)	2.08×10^9	0.73	666 (0.39)	684 (1.82)	495 (4.68), 530 (4.68), 567 (5.85)
2	285 (4.25), 374 (1.57), 404 (sh, 1.01), 438 (sh, 0.72)	518 (3.7)	1.79×10^9	0.82	626 (0.33), 654 (0.33)	665 (1.54)	505 (4.20), 540 (4.40), 576 (4.53)
3	284 (4.45), 372 (2.08), 420 (sh, 0.96)	525 (4.9)	8.82×10^7	0.90	633 (0.39)	550 (1.57), 662 (2.80)	494 (6.36), 531 (5.67) 568 (6.34)

[a] Determined in degassed dichloromethane solution. [b] Absolute emission quantum yield was measured by the optical dilute method with 9,10-bis(phenylethynyl)anthracene (BPEA) in benzene as standard ($\phi_r = 0.85$) and calculated by: $\phi_s = \phi_r (B_r/B_s)(n_s/n_r)^2 (D_s/D_r)$, where the subscripts s and r refer to sample and reference standard solution respectively, n is the refractive index of the solvents, D is the integrated intensity, and ϕ is the luminescence quantum yield. The excitation intensity B is calculated by: $B = 1 - 10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length ($L = 1$ cm in all cases). The refractive indices of the solvents at room temperature were taken from standard source. Errors for ϕ values ($\pm 10\%$) are estimated. [c] In DMF: MeOH: EtOH mixture (v:v:v = 1:1:4).

Table S2. Crystal data and structural refinement for **2** and **3**

	2	3
Empirical formula	C ₈₂ H ₉₀ Cl ₄ N ₄ O ₃ Pt ₂	C ₈₃ H ₈₂ Cl ₂ N ₄ O ₂ Pt ₂
Formula weight	1711.54	1628.61
Temperature K	100(2)	100(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	31.5586(14)	13.5492(19)
<i>b</i> (Å)	16.6386(8)	15.830(2)
<i>c</i> (Å)	13.6571(6)	17.648(2)
α (°)	90.00	95.117(3)
β (°)	90.00	110.674(3)
γ (°)	90.00	102.438(3)
Volume (Å ³)	7171.2(6)	3401.3(7)
Z	4	2
Density (g cm ⁻³)	1.585	1.590
Absorption coefficient (mm ⁻¹)	8.969	8.708
F(000)	3432	1628
Crystal size	0.08 × 0.06 × 0.02 mm	0.08 × 0.08 × 0.08 mm
Theta range for data collection (°)	2.8 to 66.1	3.6 to 66.06
Index ranges	-36 ≤ <i>h</i> ≤ 36 -19 ≤ <i>k</i> ≤ 18 -15 ≤ <i>l</i> ≤ 16	-15 ≤ <i>h</i> ≤ 15 -18 ≤ <i>k</i> ≤ 18 -20 ≤ <i>l</i> ≤ 20
Reflections collected	44156	39388
Independent reflections	6211 [R _{int} = 0.0655] full-matrix	11446 [R _{int} = 0.0478] full-matrix
Refinement method	least-squares refinement on <i>F</i> ²	least-squares refinement on <i>F</i> ²
Data/restraints/parameters	6211 / 0 / 442	11446 / 0 / 880
Goodness-of-fit indicator	1.087	1.053
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0481	0.0358
<i>wR</i> (<i>F</i> ²)	0.1433	0.0994
Δρ _{max} (e Å ⁻³)	1.96	1.38
Δρ _{min} (e Å ⁻³)	-2.60	-1.65

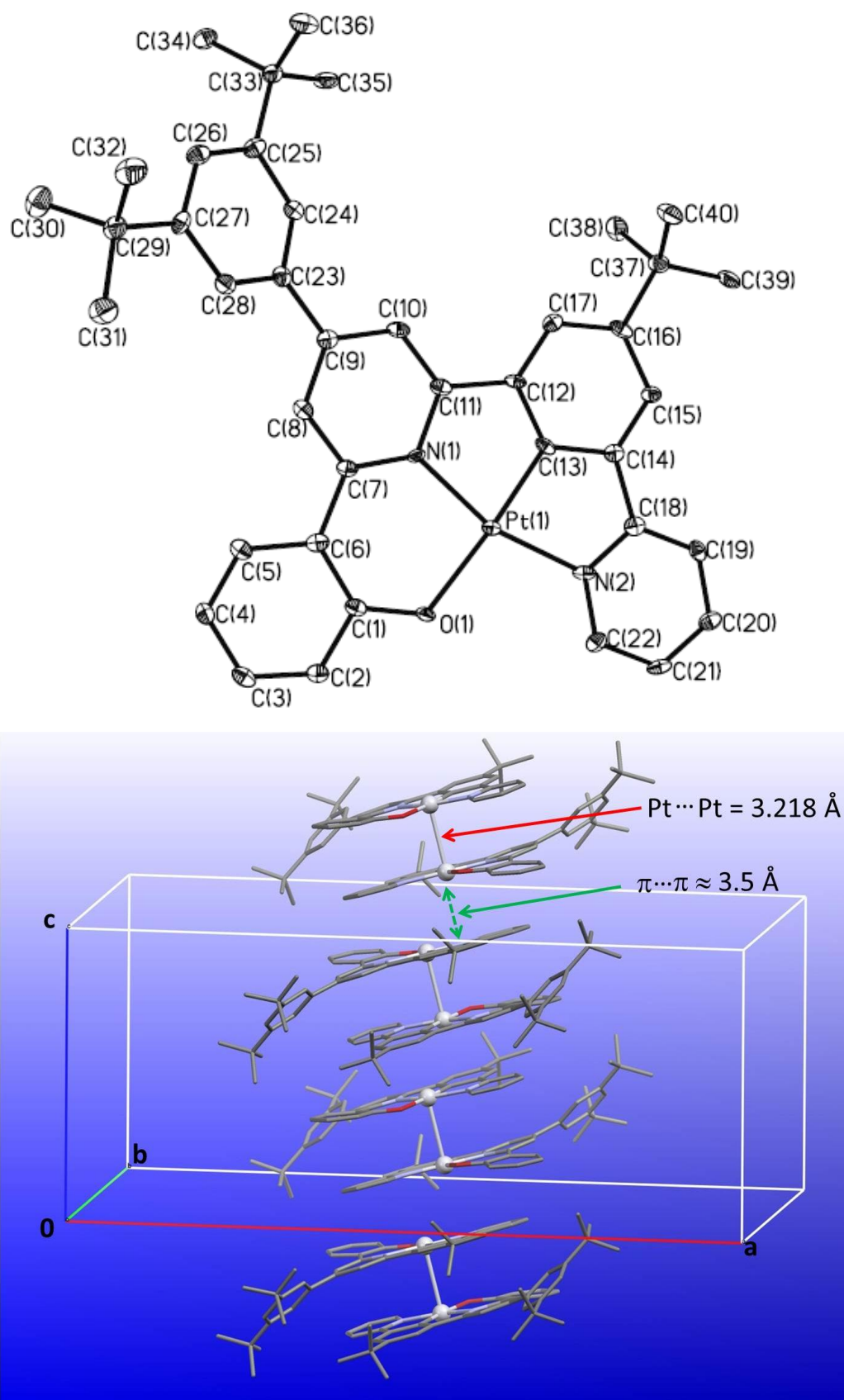


Figure S10. Perspective view (upper) and molecular packing (bottom) of complex **2** (all hydrogen atoms and solvent molecules are omitted for clarity).

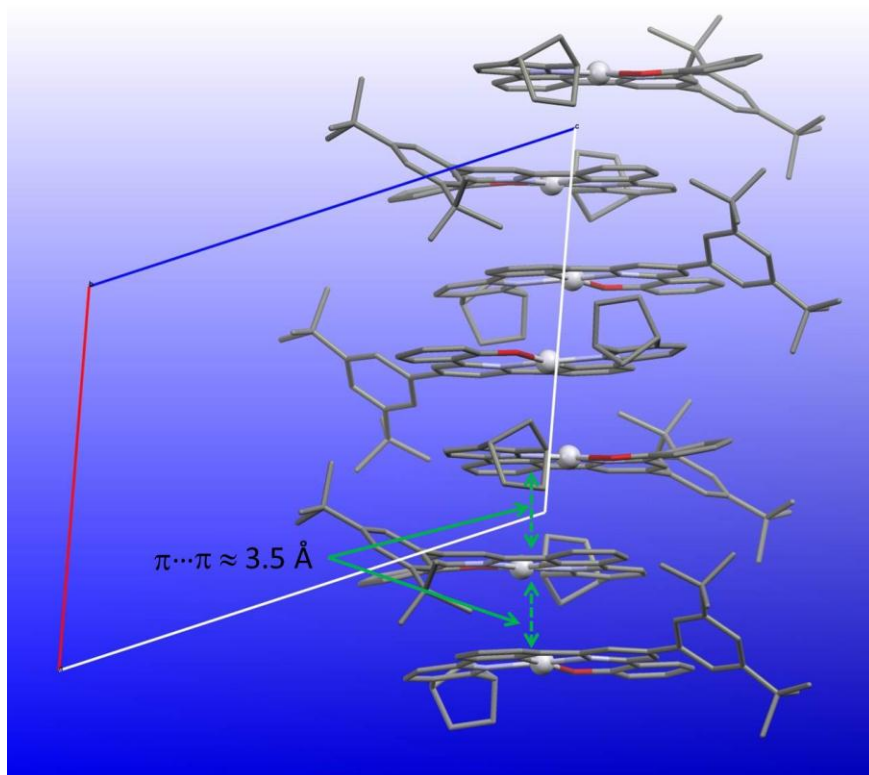
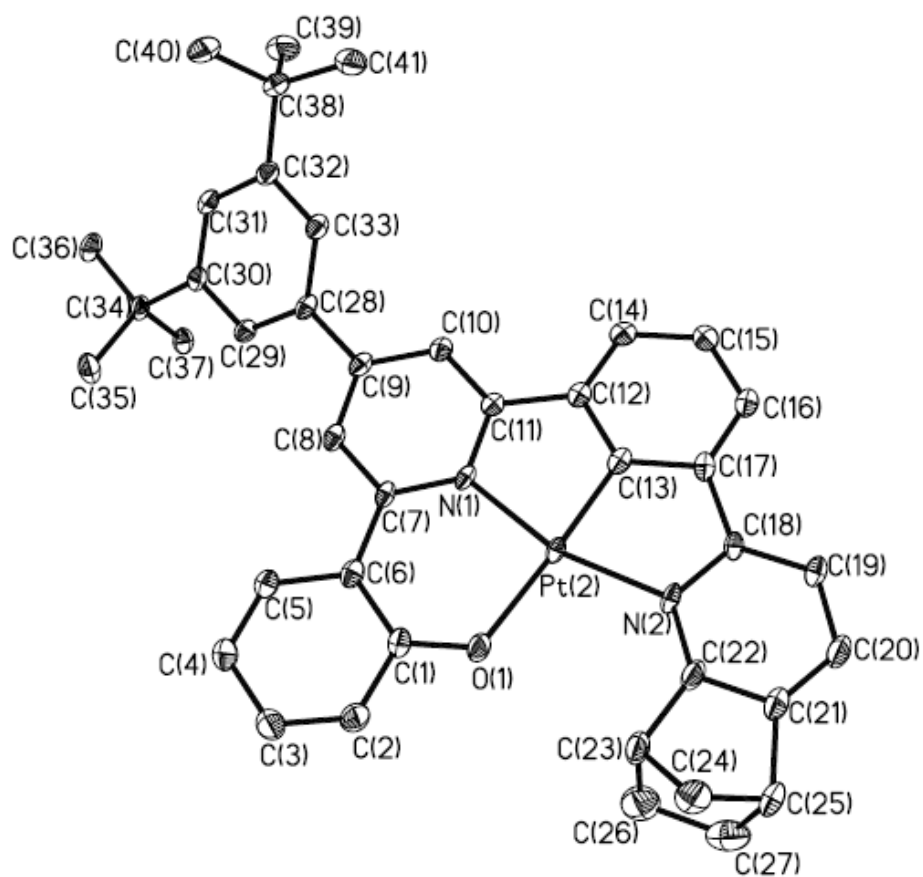


Figure S11. Perspective view (upper) and molecular packing (bottom) of complex **3** (all hydrogen atoms and solvent molecules are omitted for clarity).

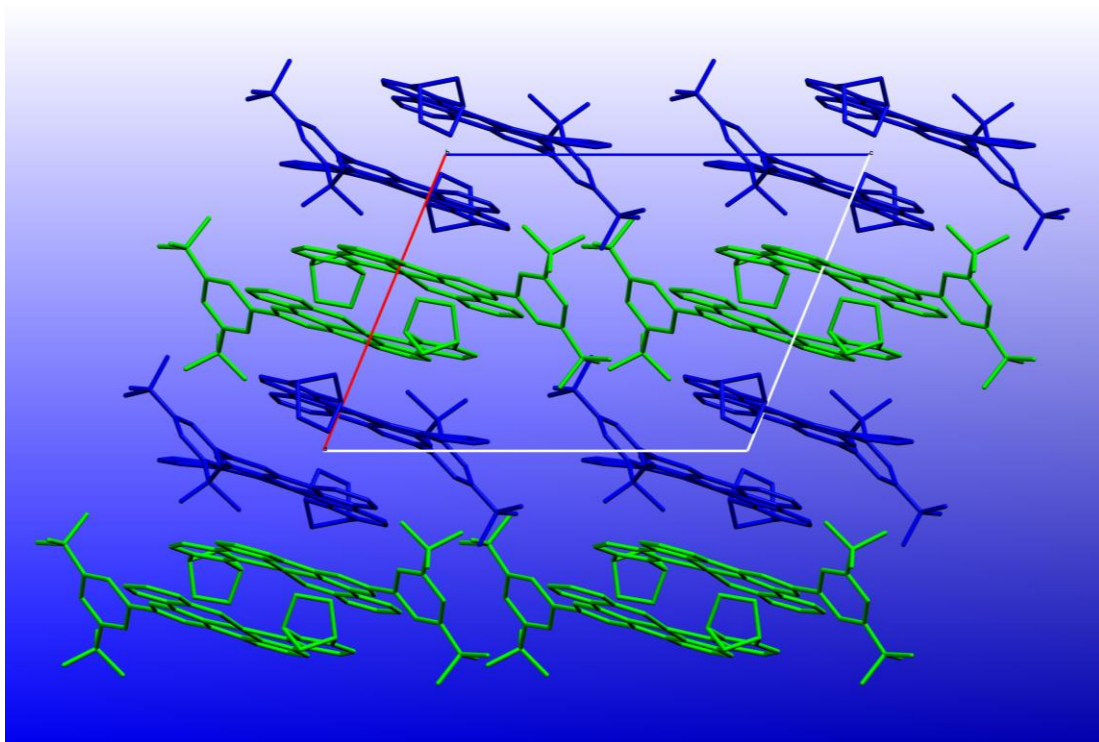


Figure S12. Molecular packing of complex **3** viewed along *b*-axis in which pairs of enantiomers are shown in different color (all hydrogen atoms and solvent molecules are omitted for clarity).

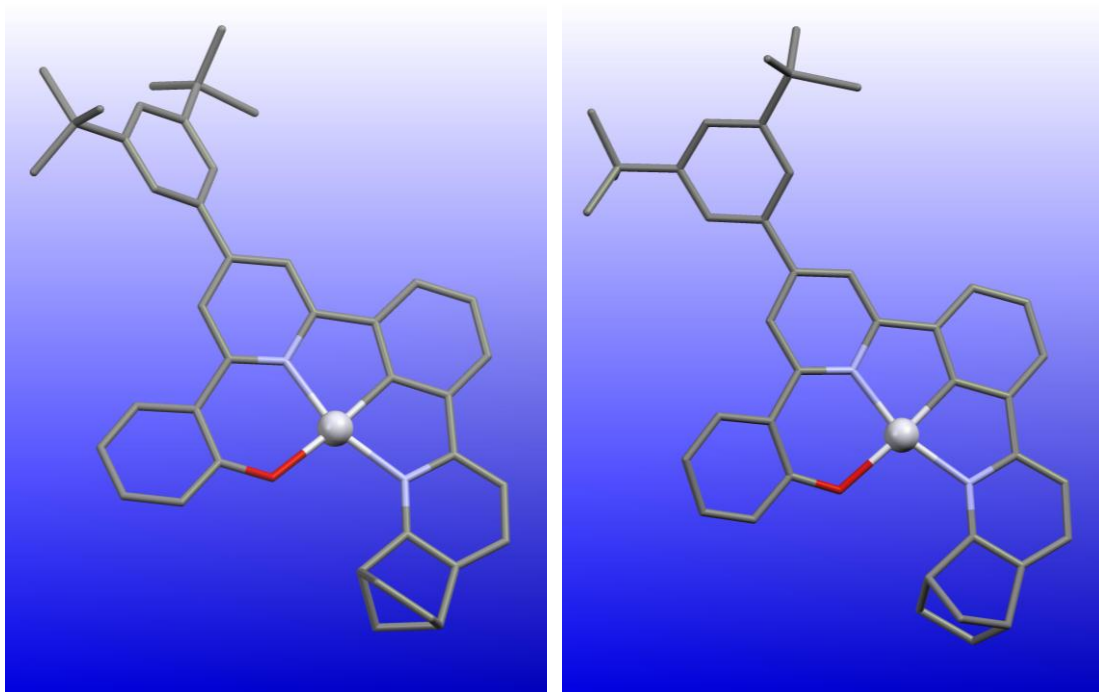


Figure S13. Perspective view of enantiomers of complex **3**.

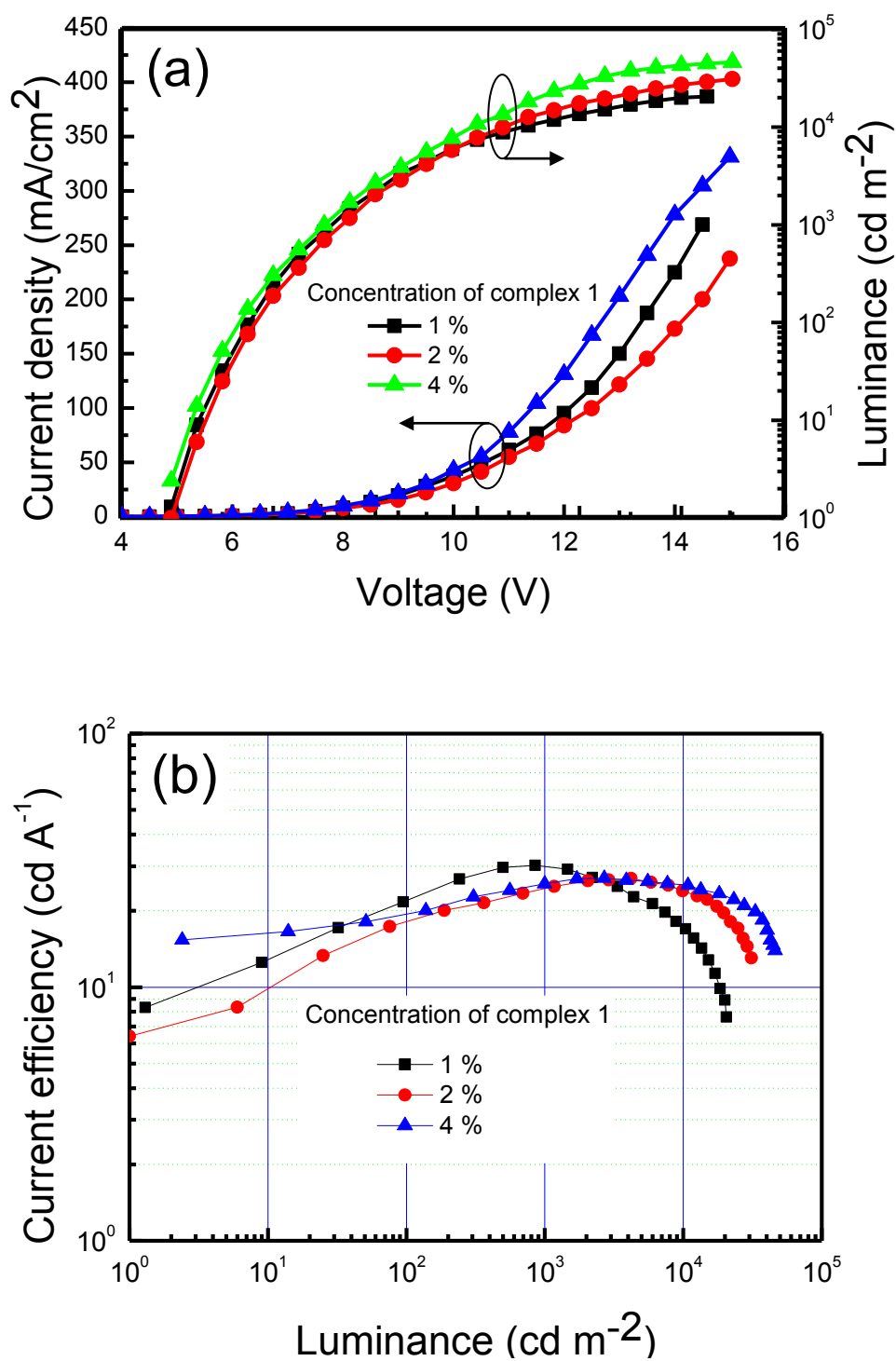


Figure S14. (a) *L-J-V* and (b) current efficiency-luminance characteristics of OLEDs with 1%, 2%, and 4% complex 1.

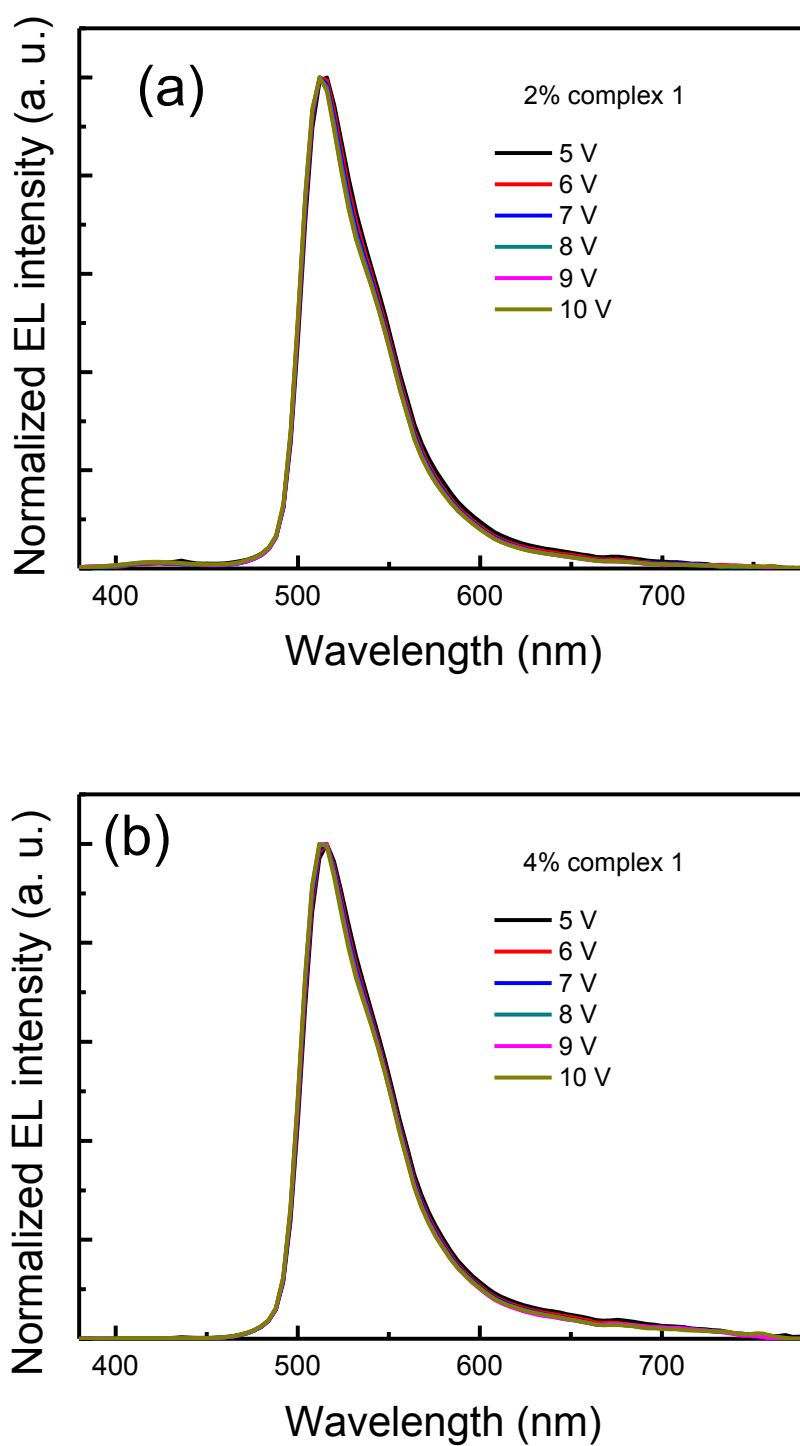


Figure S15. (a) Normalized EL spectra of the OLED with 2% complex **1** at various driving voltages. (b) Normalized EL spectra of the OLED with 4% complex **1** at various driving voltages.

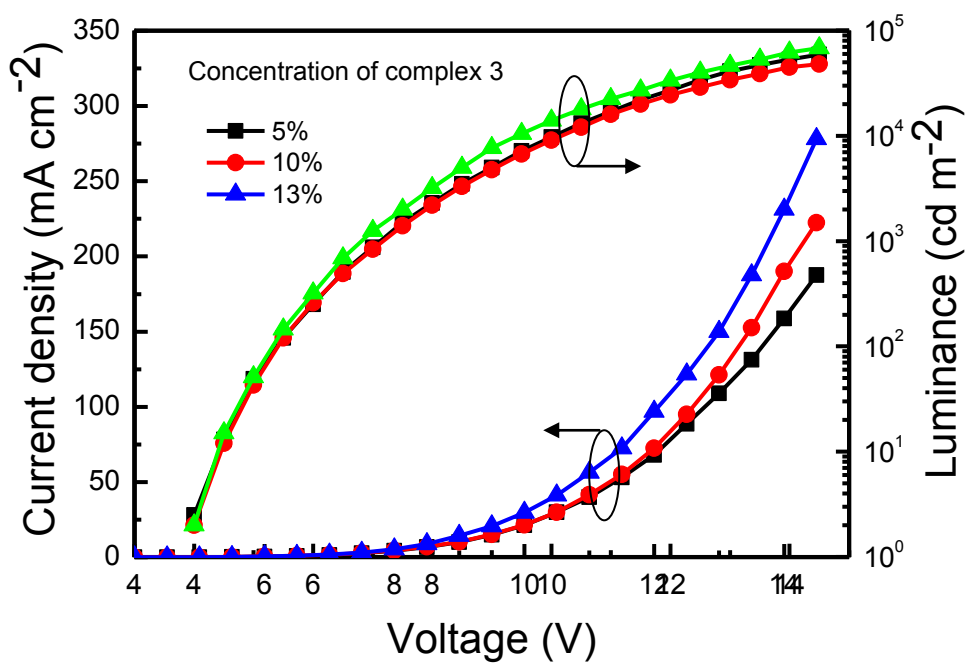


Figure S16. *L-J-V* characteristics of OLEDs with 5%, 10%, and 13% complex **3**.

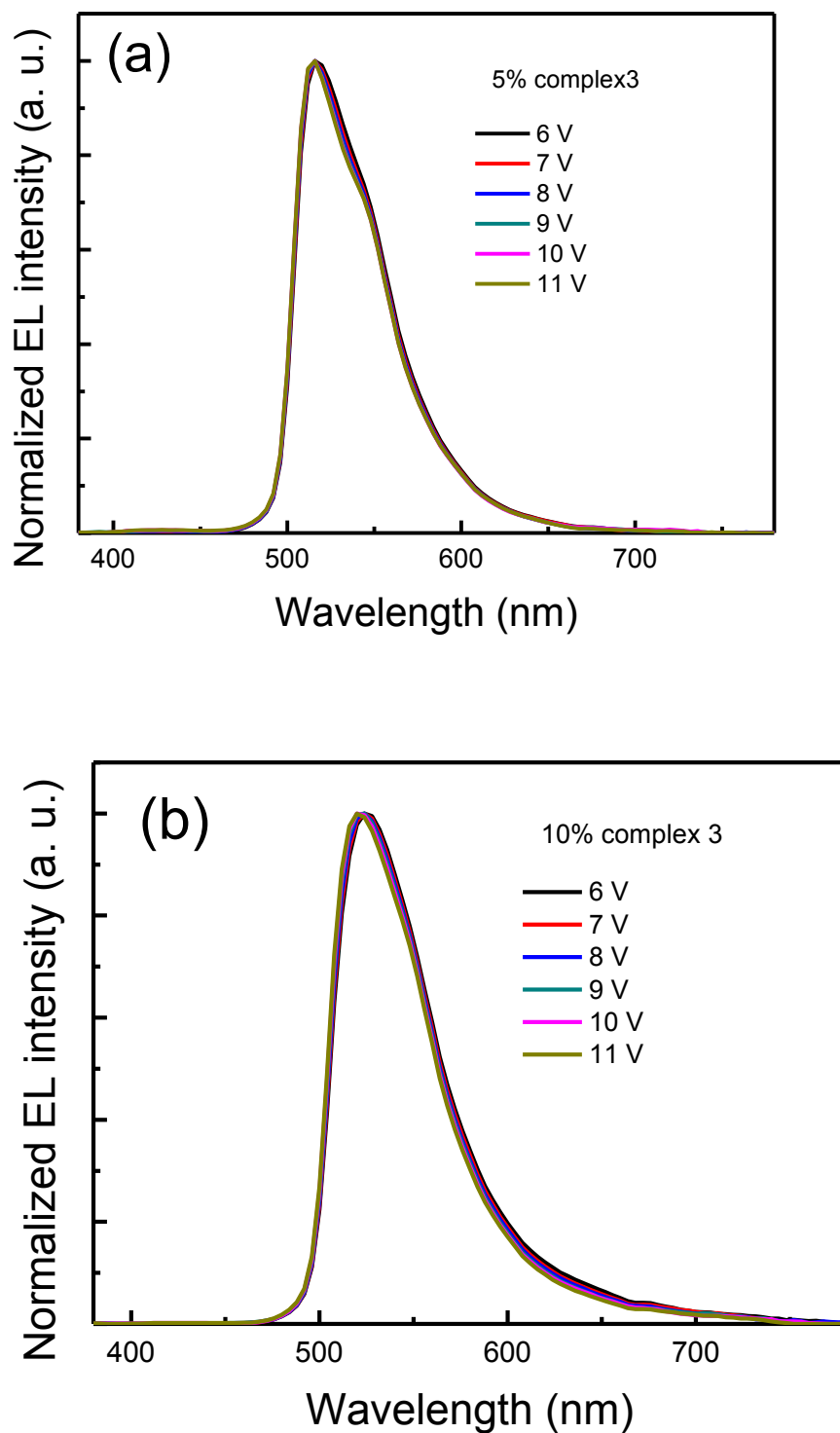


Figure S17. (a) Normalized EL spectra of the OLED with 5% complex **3** at various driving voltages. (b) Normalized EL spectra of the OLED with 10% complex **3** at various driving voltages.