Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

Structurally robust phosphorescent [Pt(O^N^C^N)] emitters for high performance organic light-emitting devices with power efficiency up to 126 lm W^{-1} and external quantum efficiency over 20%

Gang Cheng,[a,b,d] Steven C. F. Kui,[a,d] Wai-Hung Ang,[a] Man-Ying Ko,[a] Pui-Keong Chow,[a] Chun-Lam Kwong,[a] Chi-Chung Kwok,[a,d] Chensheng Ma,[a] Xiangguo Guan,[a] Kam-Hung Low,[e] Shi-Jian Su[c] and Chi-Ming Che*[a,d]

[a] State Key Laboratory of Synthetic Chemistry, HKU-CAS Joint Laboratory on New Materials, and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China. E-mail: cmche@hku.hk

[b] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun130012, China.

[c] State Key Laboratory of Luminescent Materials and Devices (South China University of Technology) and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China.

[d] HKU Shenzhen Institute of Research and Innovation, Shenzhen 518053, China.

[e] GuangDong Aglaia Optoelectronic Materials Co., Ltd.

[f] School of Chemistry and Chemical engineering, Shenzhen University, Shenzhen, Guangdong, P. R. China, 518060.

Experimental

(A) General considerations

All materials were used as received. The solvents used for synthesis were of analytical grade. ^1H and ^{13}C 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. Thermogravimetric analyses were performed on Perkin Elmer TGA 7. Cyclic voltammetry was performed on Princeton Applied Research – Potentiostat/Galvanostat Model 273A. The reference electrode was $Ag/AgNO_3$ (0.1 M in acetonitrile), the working electrode was a glassy carbon electrode and a platinum wire was used as the counter electrode. Ferrocene was used as the internal reference.

(B) Emission and lifetime measurements

Steady-state excitation and emission spectra were obtained on a SPEX Fluorolog-3 spectrophotometer. All solutions for photophysical measurements were degassed with no less than three freeze-pump-thaw cycles prior to the measurements. 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, $\Phi_r = 0.85$) or acetonitrile solution of $Ru(bpy)_3(PF_6)_2$ ($\Phi_r = 0.062$) as a standard reference. Errors for λ values (± 1 nm), τ (± 10%), and Φ (± 10%) were estimated.

(C) X-ray diffraction

X-Ray diffraction data were collected on 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.

(D) Device fabrication and characterization

Glass slides with pre-patterned ITO electrode used as substrate 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 deionized water, acetone, and *iso*-propanol, and subsequently dried in an oven for 1 h. OLEDs were fabricated in a Kurt J. Lesker SPECTROS vacuum deposition system with a base pressure of 10^{-8} mBar. In the vacuum chamber, organic materials 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 technology. Afterwards, LiF (1.2 nm) and Al (150 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. 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 without encapsulation except for those for device stability investigation. UV-curable sealant, cover glass and desiccant were used to encapsulate the OLEDs for stability investigation. External quantum efficiency and power efficiency were calculated by assuming a Lambertian distribution.

(E) OLED materials used in this study

LiF was purchased from Sigma-Aldrich, MoO_3, TAPC, NPB, TCTA, 26DCZppy, mCBP, BAlq, and TmPyPb from Luminescence Technology Corp. All of these materials were used as received. Tm3PyBPZ was synthesized following the procedure described in Ref. 19 of the main text. The synthetic procedures of **1**−**6** are described in the following section and the synthetic procedure of **7** is reported in previous paper Ref. 9b. Tm3PyBPZ and **1**−**7** were purified by gradient sublimation before use.

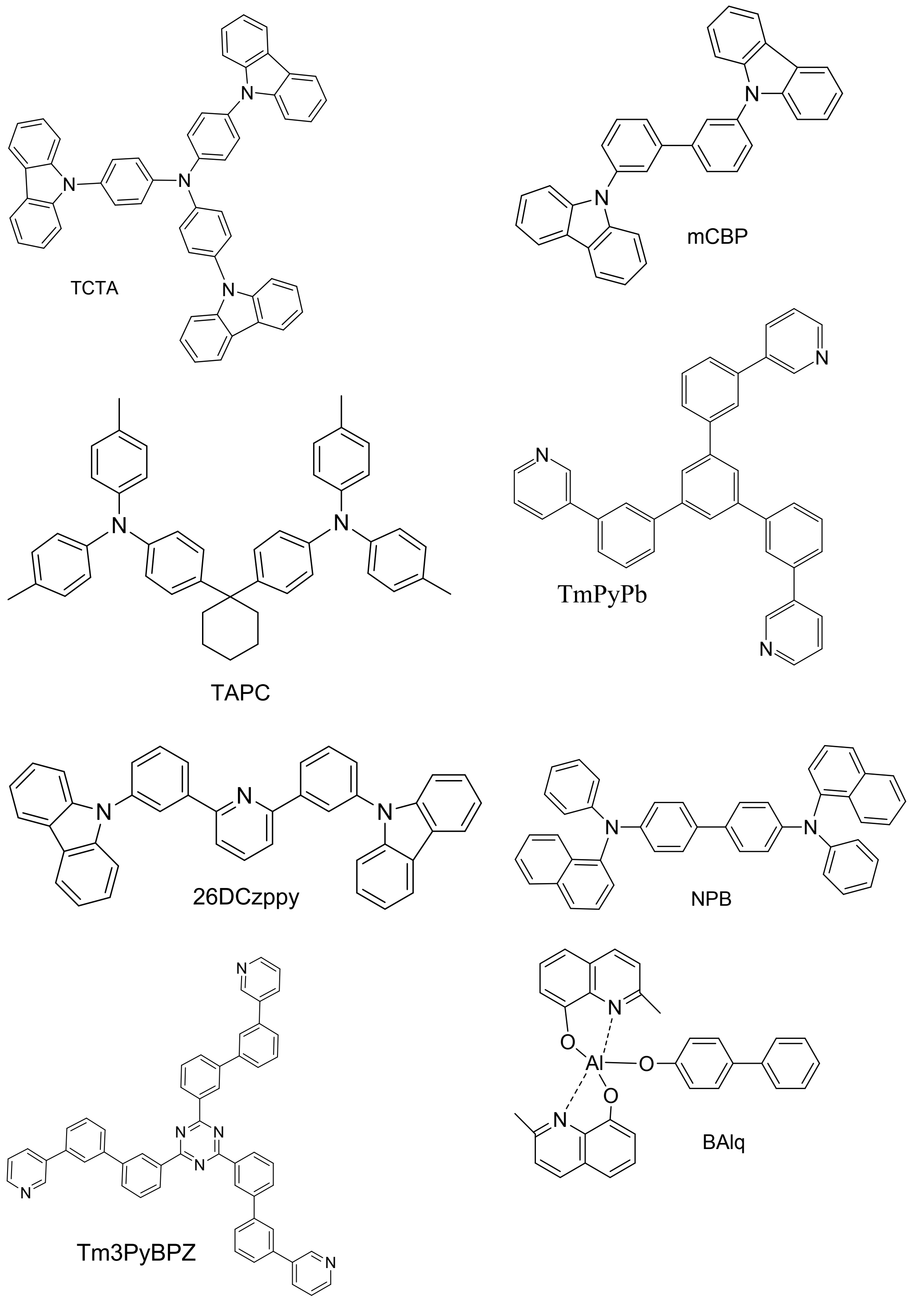


Chart S1. Chemical structures of organic materials used in this work.

(F) Synthetic scheme for O^N^C^N Pt(II) 1-6:

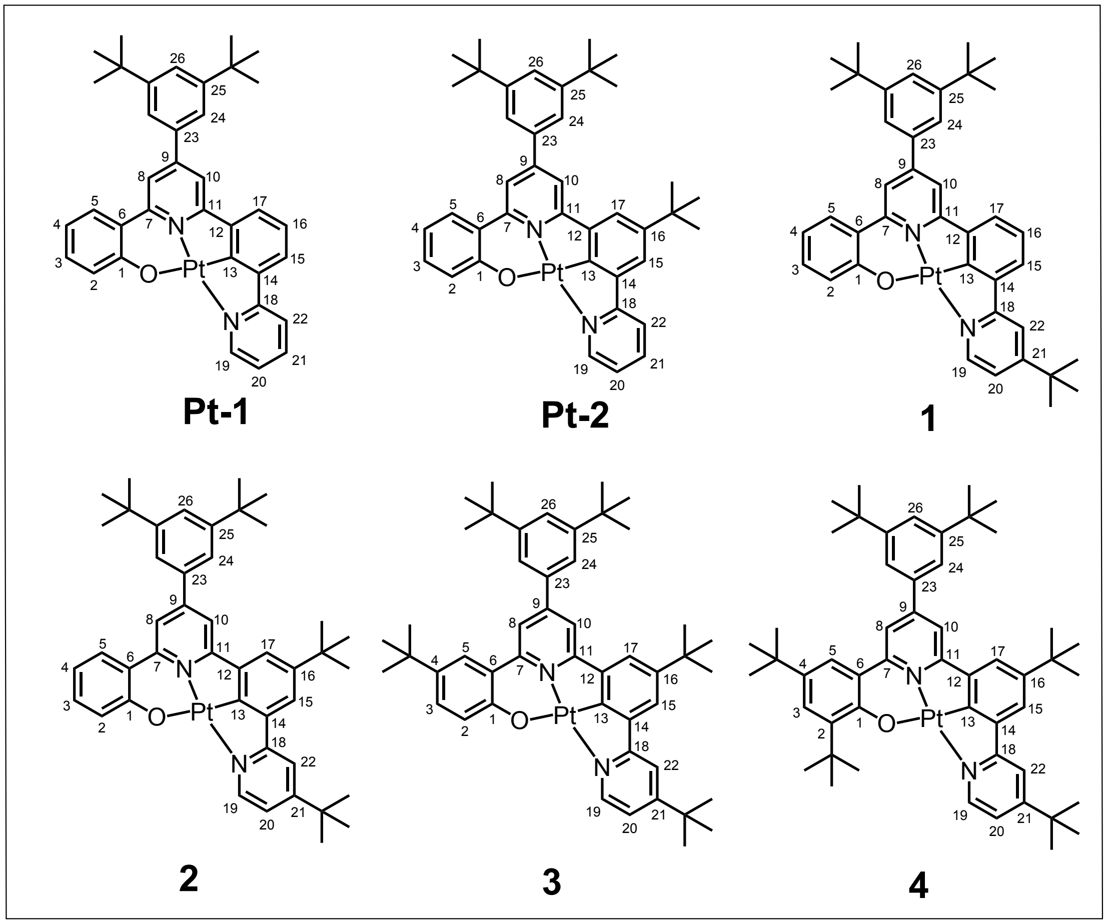


Fig. S1. O^N^C^N platinum(II) complexes **Pt-1**, **Pt-2**, and **1**–**4 s**tudied in this work with the labeling scheme of the ligands.

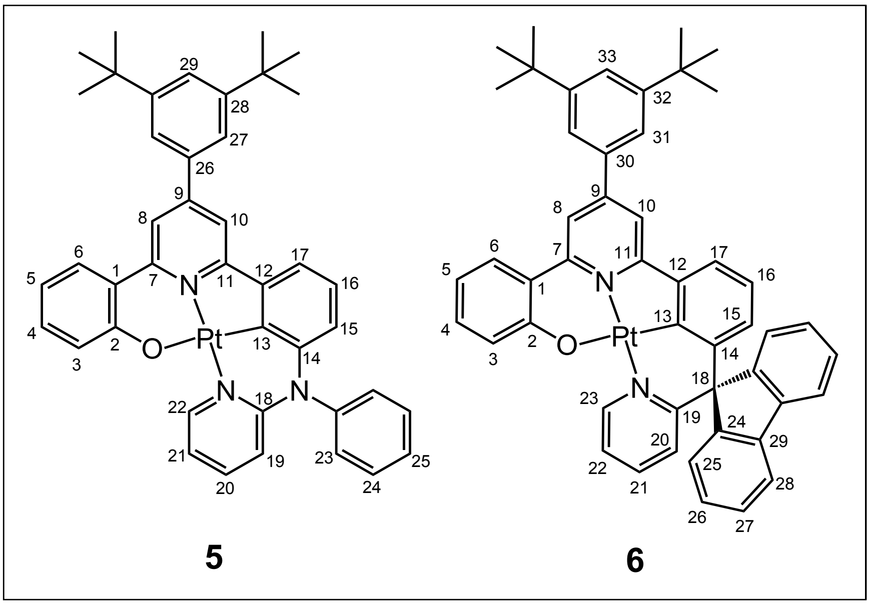
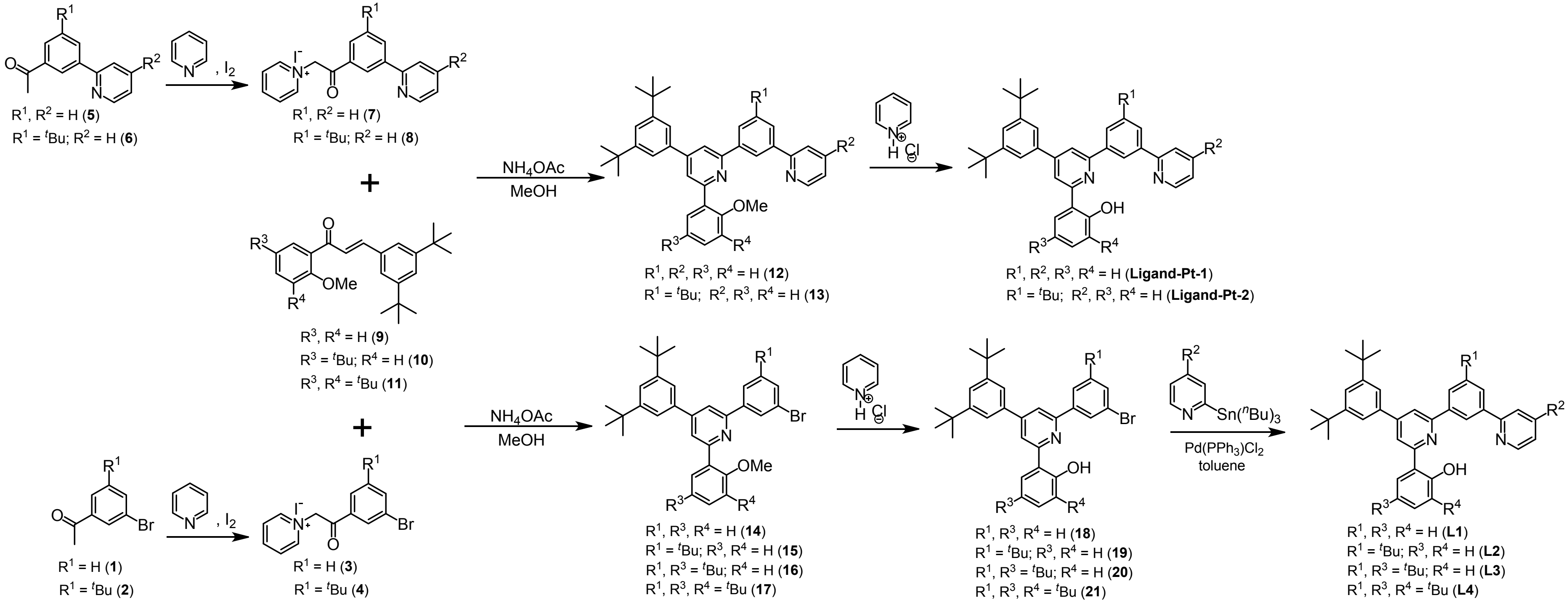
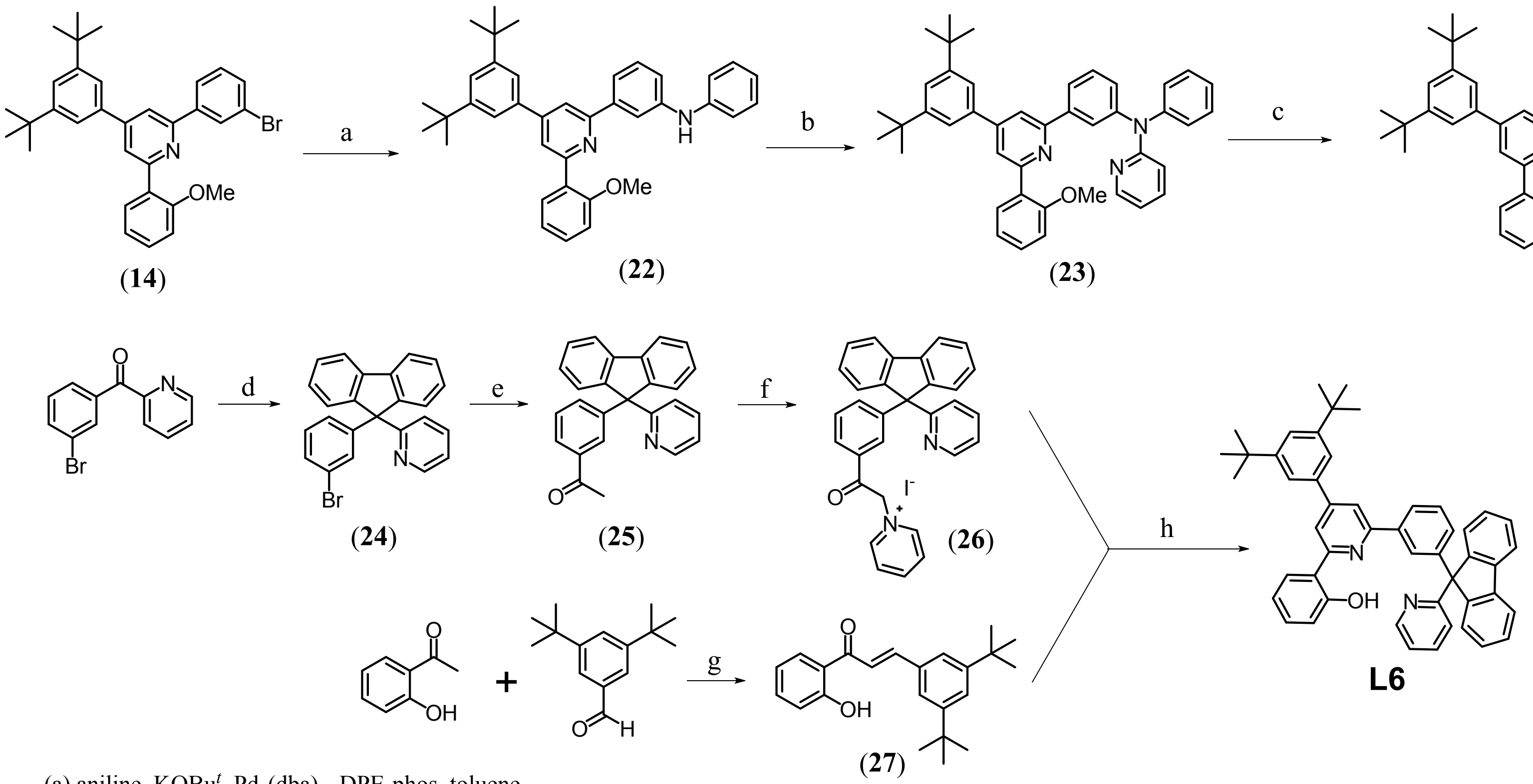


Fig. S2. O^N^C^N platinum(II) complexes **5**–**6 s**tudied in this work with the labeling scheme of the ligands.



Scheme S1. Synthesis scheme for **Ligand-Pt-1**, **Ligand-Pt-2** and **L1–L4**.



(a) aniline, KOBu^t, $Pd_2(dba)_3$, DPE-phos, toluene

(b) 2-iodopyridine, KOBu^t, $Pd_2(dba)_3$, DPE-phos, toluene

(c) PyHCl

(d) biphenyl-2-ylmagnesium iodide, THF, H_2SO_4, acetic anhydride;

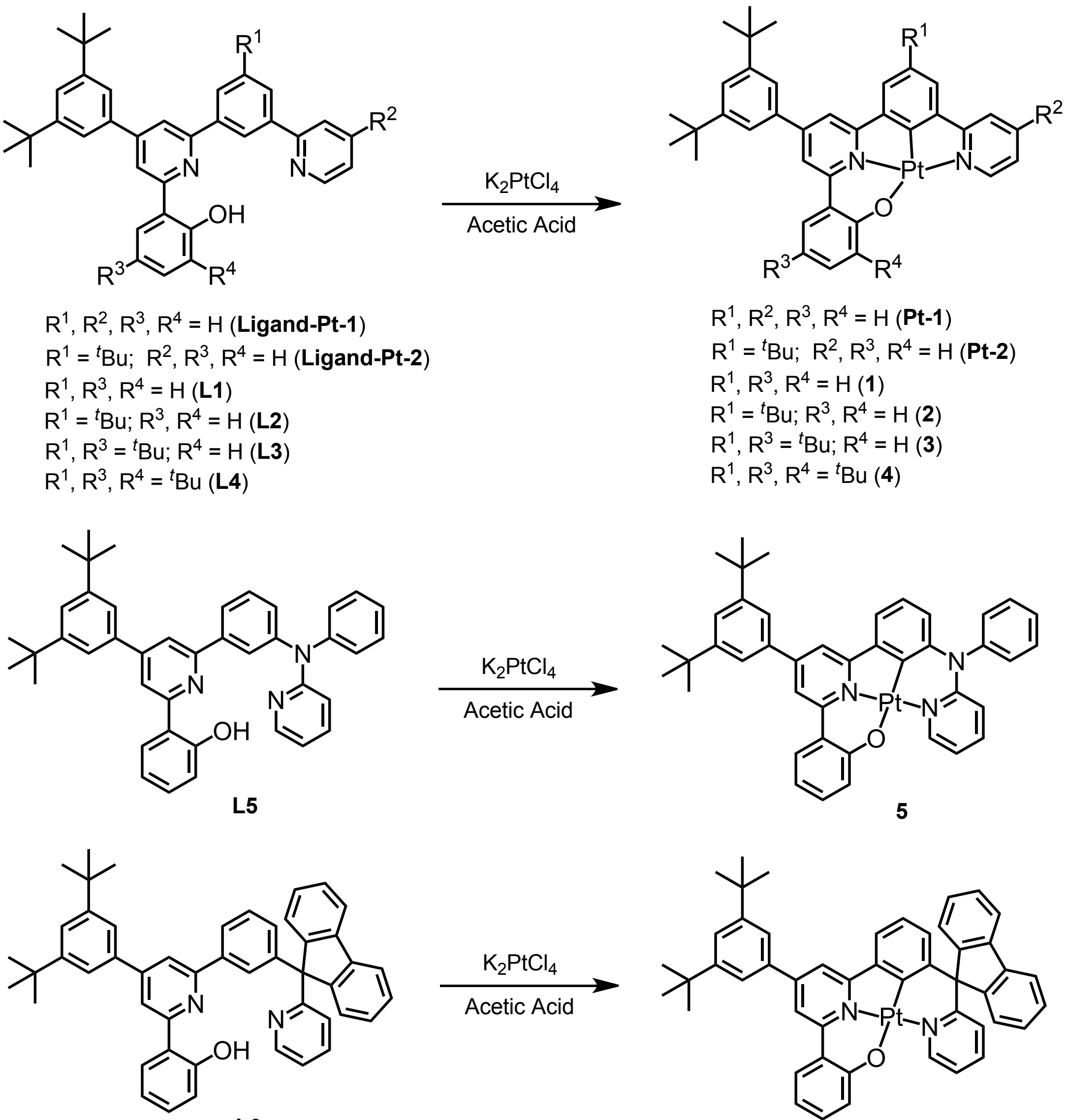
(e) tributyl(1-ethoxyvinyl)stannane, $Pd(PPh_3)_2Cl_2$, toluene;

(f) pyridine, I_2;

(g) NaOH, ethanol;

(h) AcOH, NH_4OAc

Scheme S2. Synthesis scheme for **L5–L6**.



R^1, R^2, R^3, R^4 = H (**Ligand-Pt-1**)
R^1 = ^{t}Bu; R^2, R^3, R^4 = H (**Ligand-Pt-2**)
R^1, R^3, R^4 = H (**L1**)
R^1 = ^{t}Bu; R^3, R^4 = H (**L2**)
R^1, R^3 = ^{t}Bu; R^4 = H (**L3**)
R^1, R^3, R^4 = ^{t}Bu (**L4**)

R^1, R^2, R^3, R^4 = H (**Pt-1**)
R^1 = ^{t}Bu; R^2, R^3, R^4 = H (**Pt-2**)
R^1, R^3, R^4 = H (**1**)
R^1 = ^{t}Bu; R^3, R^4 = H (**2**)
R^1, R^3 = ^{t}Bu; R^4 = H (**3**)
R^1, R^3, R^4 = ^{t}Bu (**4**)

L5

5

L6

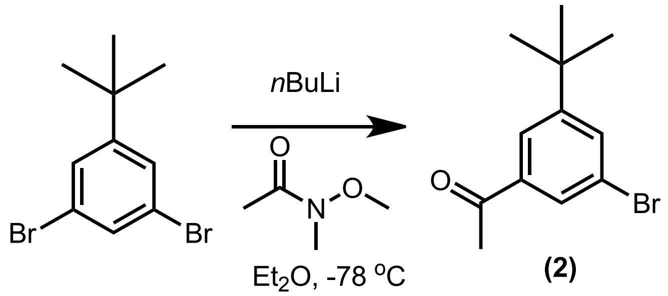
6

Scheme S3. Synthesis scheme for **Pt-1**, **Pt-2** and **1**–**6**.

(G) Synthetic procedure for complexes Pt-1, Pt-2 and 1–6.

(i) General procedure for starting materials (1)–(27)

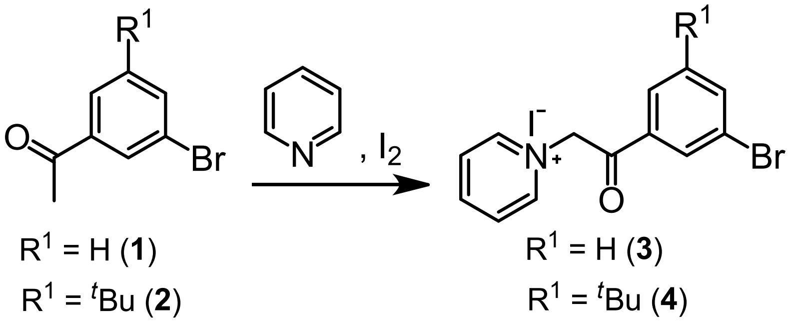
1) Starting material (2)



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 N_2 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 $MgSO_4$ and evaporated to give a crude product. Purification was done by silica gel flash column chromatography using *n*-hexane:EA mixture (*v*:*v* = 28:1) as eluent to give (**2**) as pale yellow oil.

(**2**): Pale yellow oil. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.89 (s, 1H), 7.74 (s, 1H), 2.57 (s, 3H), 1.35 (s, 9H). EI-MS (+ve, m/z): 255 [M^+].

2) Starting materials (3) and (4)

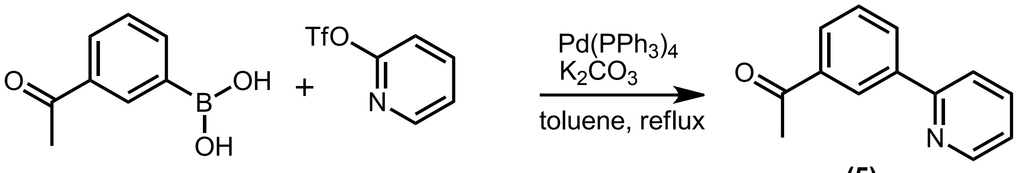


A mixture of corresponding starting material 3'-bromoacetophenone (**1**) and (**2**) was heated with excess I_2 (1.2 equiv.) in pyridine (20 ml) for 2 h to produce (**3**) and (**4**), respectively. The crude product was filtered and washed with acetone. The filtrate was then evaporated to dryness and recrystallized from methanol to give light brown crystalline solid (**3**) and (**4**), respectively.

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

(**4**): Brown solids. Yield: 80 %. ^{1}H NMR (400 MHz, DMSO): δ 9.09 (d, *J* = 6.1 Hz, 2H), 8.77 (t, *J* = 7.8 Hz, 1H), 8.28 (t, *J* = 7.0 Hz, 2H), 8.06 (s, 1H), 7.99 (s, 2H), 6.49 (s, 2H), 1.35 (s, 9H).

3) Starting material (5)

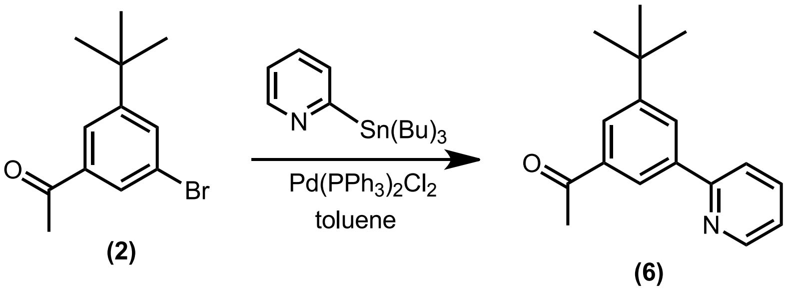


(5)

Suzuki-Miyanra cross-coupling reaction was employed for the synthesis of (**5**). 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 K_2CO_3 (2M, 10 ml) was added *via* a syringe. The reaction mixture was refluxed for 24 h 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 $MgSO_4$. 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 (**5**) as off-white solid.

(**5**): Off-white solids. Yield: 90 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1H), 8.59 (s, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.80–7.78 (m, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.31–7.27 (m, 1H), 2.69 (s, 3H). EI-MS (+ve, m/z): 197 [M$^+$].

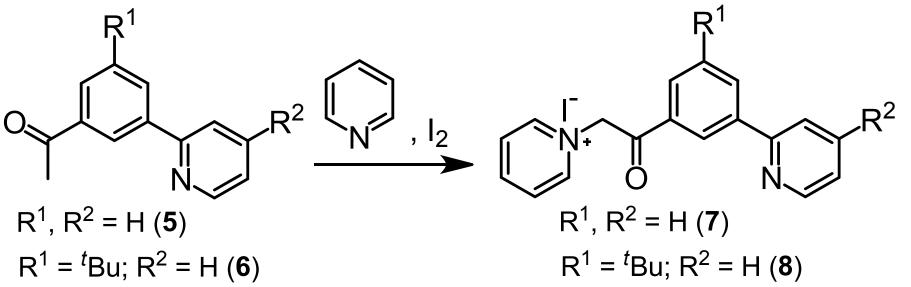
4) Starting material (6)



Stille coupling reaction was employed for synthesis of (**6**). A mixture of starting material (**2**) (3.0 g, 11.8 mmol), 2-(tributylstannyl)pyridine (5.0 ml, 15.3 mmol), [$PdCl_2(PPh_3)_2$] (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 CH_2Cl_2 (3 × 100 ml). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel flash column chromatography using *n*-hexane/EA mixture (*v*:*v* = 9:1) as eluent to give (**6**) as yellow oil.

(**6**): yellow oil. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.36 (s, 1H), 8.26 (s, 1H), 8.07 (s, 1H), 7.79–7.78 (m, 2H), 7.31–7.26 (m, 1H), 2.69 (s, 3H), 1.43 (s, 9H). EI-MS (+ve, m/z): 253 [M^+].

5) Starting materials (7) and (8)

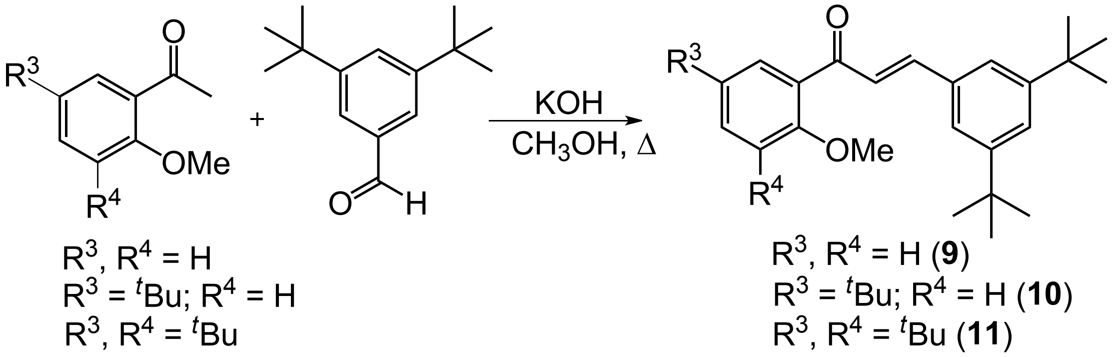


A mixture of corresponding starting material (**5**) and (**6**) was heated with excess I_2 (1.2 equiv.) in pyridine (20 ml) for 2 h to produce (**7**) and (**8**), respectively. The filtrate was then evaporated to dryness and recrystallized from methanol to give light brown crystalline solid (**7**) and (**8**), respectively.

(**7**): Brown solids. Yield: 90 %. ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.99 (d, *J* = 5.5 Hz, 1H), 8.77–8.72 (m, 3H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.29 (t, *J* = 7.2 Hz, 2H), 8.12 (t, *J* = 7.5 Hz, 2H), 7.97 (t, *J* = 8.6 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.46–7.43 (m, 1H), 6.56 (s, 2H).

(**8**): Brown solids. Yield: 95 %. ^{1}H NMR (400 MHz, d$_6$-DMSO): δ 8.77–8.72 (m, 4H), 8.58 (s, 1H), 8.48 (s, 1H), 8.28 (t, *J* = 7.1 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.97 (t, *J* = 6.4 Hz, 1H), 7.44 (m, 1H), 6.59 (s, 2H), 1.41 (s, 9H).

6) Starting materials (9)–(11)



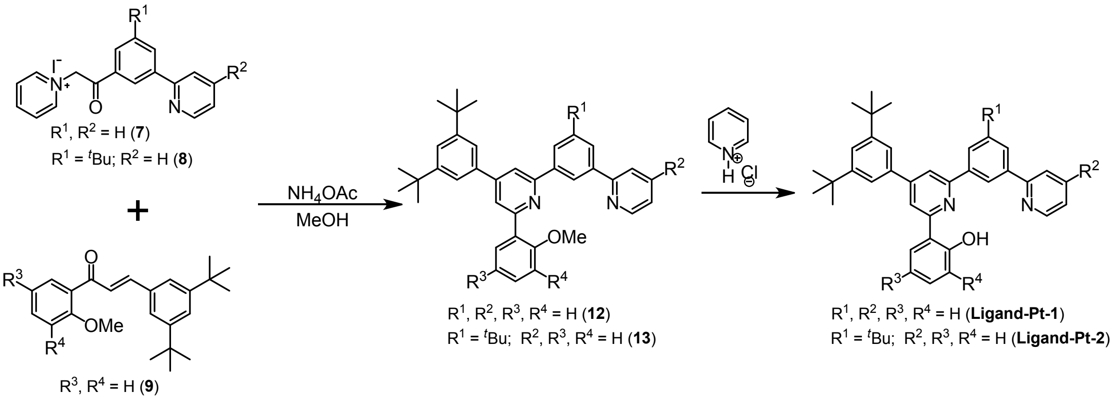
The α,β-unsaturated ketone derivative (**9**)–(**11**) was synthesized by aldol condensation between ketone and aldehyde under basic condition. A mixture of 1-(2-methoxyphenyl)ethanone) or 1-(5-*tert*-butyl-2-methoxyphenyl)ethanone or 1-(3,5-bis(*tert*-butyl)-2-methoxyphenyl)ethanone and 3,5-di-*tert*-butylbenzaldehyde (1 equiv.) and KOH (2.5 equiv.) in methanol was refluxed for 24 h. 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 mixture (v:v = 9:1) as eluent to give (**9**)–(**11**) as off-white solid.

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

(**10**): Pale yellow oil. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 2H), 7.51–7.47 (m, 2H), 7.44–7.43 (m, 2H), 7.35 (d, *J* = 15.9 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H, -OMe), 1.34 (s, 18H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu). EI-MS (+ve, m/z): 350 [M$^+$].

(**11**): Pale yellow oil. Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.49 (s, 1H), 7.49 (s, 1H), 7.43 (s, 1H), 7.42 (s, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.29 (s, 1H), 3.70 (s, 3H), 1.44 (s, 9H), 1.34 (s, 18H), 1.32 (s, 9H).

7) General procedure for Ligand-Pt-1 and Ligand-Pt-2



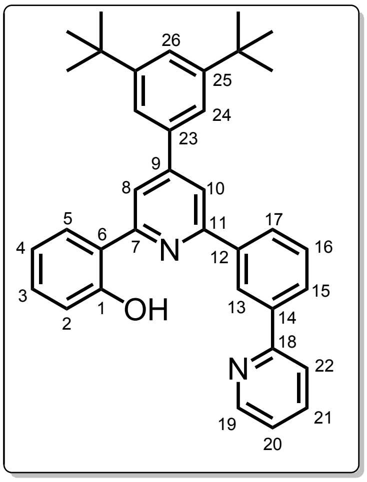
The ligand precursors (**12**) and (**13**) were prepared by cyclization of the pyridine ring. A mixture of corresponding α,β-unsaturated ketone derivative (**9**), pyridinium salt (**7** or **8**), and large excess (10 equiv.) of NH_4OAc in MeOH solution was refluxed for 12 h. The solvent was removed 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 (**12**) and (**13**) as white solids and pale yellow oil respectively.

Demethylation of ligand precursors (**12**) and (**13**) were done in molten state pyridine hydrochloride under N_2 at 250 °C for 12 h, giving **Ligand-Pt-1** and **Ligand-Pt-2** as off-white solids.

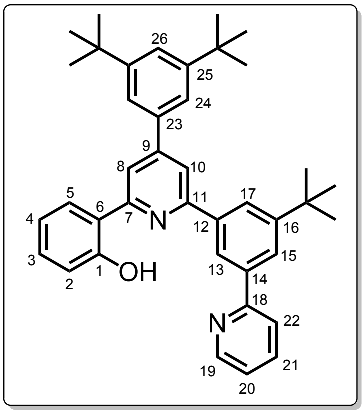
(**12**): White solids. Yield: 83%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.2 Hz, 1H), 8.70 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.09–8.04 (m, 3H), 7.91 (s, 1H), 7.86–7.76 (m, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.55 (s, 3H), 7.42 (t, *J* = 8.5 Hz, 1H), 7.28–7.25 (m, 1H), 7.15 (t, *J* = 8.2 Hz,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

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

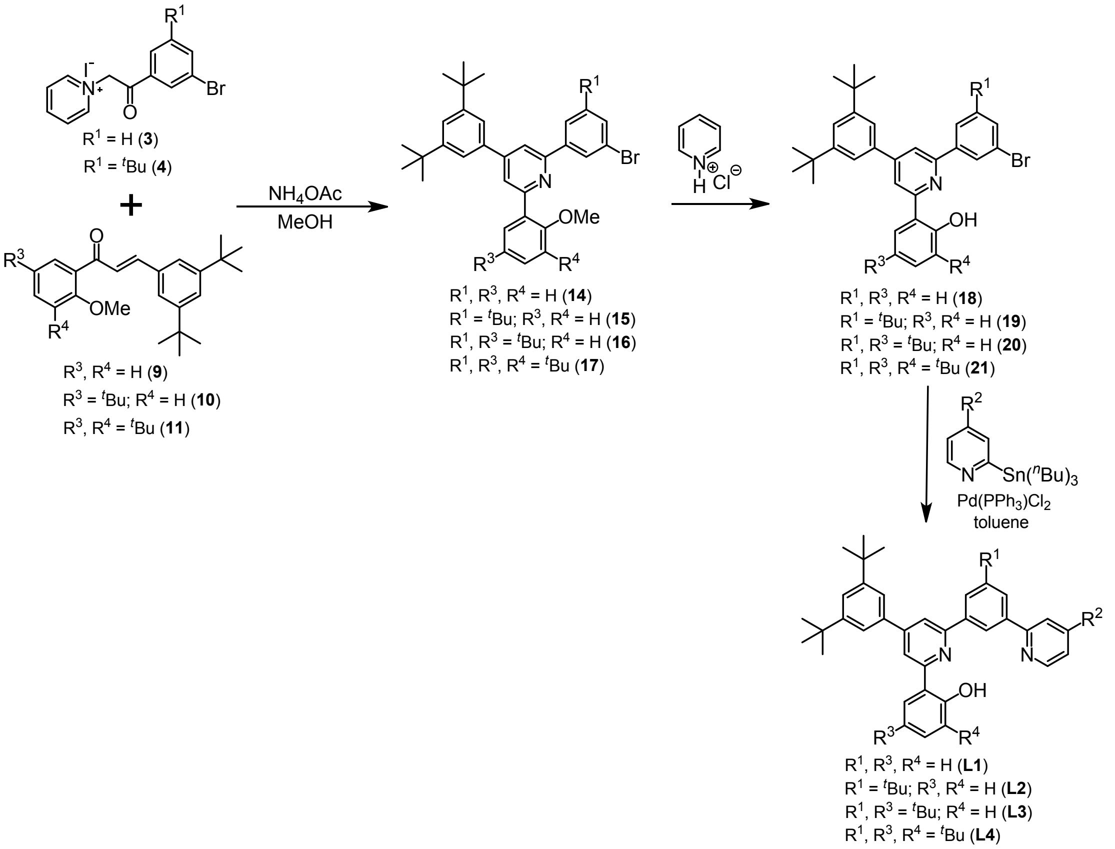
Ligand-Pt-1: Off-white solids. Yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.84 (s, 1H, -OH), 8.73 (d, *J* = 7.4 Hz, 1H, H^{19}), 8.59 (s, 1H, H^{13}), 8.13 (d, *J* = 7.8 Hz, 1H, H^{15}), 8.07 (d, *J* = 8.4 Hz, 1H, H^{17}), 8.04 (s, 1H, H^{8}), 7.95 (d, *J* = 8.1 Hz, 1H, H^{5}), 7.90 (s, 1H, H^{10}),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



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



8) General procedure for L1–L4



The starting materials (**14**)–(**17**) were prepared by cyclization of the pyridine ring. A mixture of corresponding α,β-unsaturated ketone derivative (**9**)–(**11**), pyridinium salt (**3** or **4**), and large excess (10 equiv.) of NH_4OAc in MeOH solution was refluxed for 12 h. 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 corresponding starting materials (**14**)–(**17**), respectively.

Ligand precursors (**18**)–(**21**) were obtained by demethylation of corresponding materials (**14**)–(**17**) in molten state pyridine hydrochloride under N_2 at 250 °C for 12 h. They were purified by column chromatography with CH_2Cl_2 as eluent. Ligand precursors (**18**)–(**21**) were obtained as off-white solids.

Stille coupling reaction was employed for synthesis of **L1–L4**. A mixture of corresponding ligand precursors (**18**)–(**21**), 2-(tributylstannyl)pyridine or 2-(tributylstannyl)-4-*tert*-buthylpyridine, $[PdCl_2(PPh_3)_2]$ (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 CH_2Cl_2 (3 × 100 ml). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. 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 **L1–L4** as off-white solids.

(**14**): Pale yellow solid. Yield: 88%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.09 – 8.03 (m, 2H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.59 – 7.53 (m, 2H), 7.52 (s, 2H), 7.42 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H), 1.46 – 1.37 (m, 18H).

(**15**): Off-white solid. Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.95 (t, *J* = 1.5 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.89 (t, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 1.1 Hz, 1H), 7.62 (dt, *J* = 13.9, 1.7 Hz, 2H), 7.50 (s, 2H), 7.42 – 7.28 (m, 1H), 7.09 (d, *J* = 8.2, 1H), 7.03 – 6.90 (m, 1H), 3.93 (s, 3H), 1.42 (s, 18H), 1.41 (s, 9H).

(**16**): Off-white solid. Yield: 62%. ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (t, *J* = 1.6 Hz, 1H), 8.11 (d, *J* = 2.6 Hz, 1H), 8.06 (d, *J* = 1.4 Hz, 1H), 8.04 (t, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.4 Hz, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 2H), 7.44 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H), 1.41 (s, 18H), 1.39 (s, 9H), 1.39 (s, 9H).

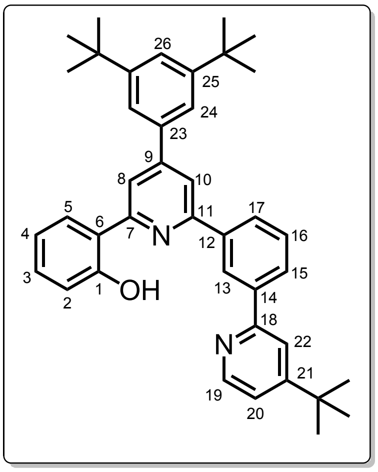
(**17**): Off-white solid. Yield: 69%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.08 (s, 1H), 7.98 (s, 1H), 7.77 (s, 1H), 7.74 (d, *J* = 2.5 Hz, 1H), 7.58 (s, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 1.6 Hz, 2H), 7.45 (d, *J* = 2.5 Hz, 1H), 3.44 (s, 3H), 1.46 (s, 9H), 1.40 (s, 18H), 1.39 (s, 18H).

(**18**): Off-white solid. Yield: 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 14.48 (s, 1H), 8.10 (s, 1H), 8.04 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.74 (s, 1H), 7.67 – 7.56 (m, 2H), 7.50 (s, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.0 Hz, 1H), 1.42 (s, 18H).

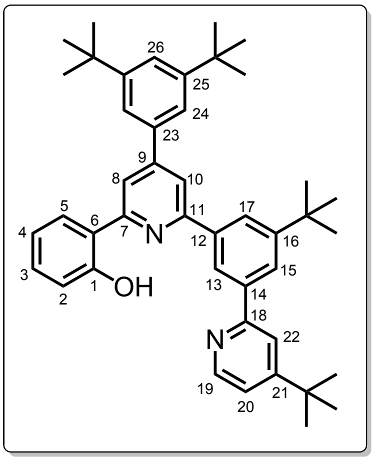
(**19**): Off-white solid. Yield: 74%. ^1H NMR (400 MHz, $CDCl_3$) δ 14.47 (s, 1H), 8.03 (s, 1H), 7.95 (t, *J* = 1.5 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.89 (t, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 1.1 Hz, 1H), 7.62 (dt, *J* = 13.9, 1.7 Hz, 2H), 7.50 (d, *J* = 1.7 Hz, 2H), 7.42 – 7.28 (m, 1H), 7.09 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.03 – 6.90 (m, 1H), 1.43 (s, 18H), 1.40 (s, 9H).

(**20**): Off-white solid. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.11 (s, 1H), 8.01 (s, 1H), 7.95 (t, *J* = 1.6 Hz, 1H), 7.88 (s, 2H), 7.70 (d, *J* = 1.1 Hz, 1H), 7.62 (dt, *J* = 5.1, 1.7 Hz, 2H), 7.51 (d, *J* = 1.7 Hz, 2H), 7.41 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 1.43 (s, 18H), 1.39 (s, 9H), 1.36 (s, 9H).

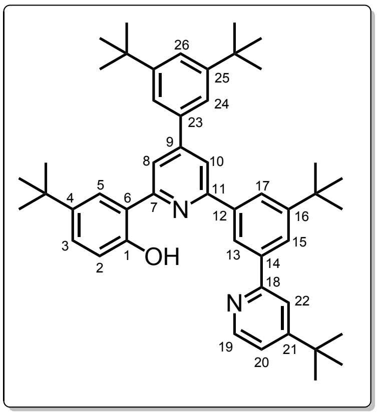
(**21**): Off-white solid. Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.56 (s, 1H), 8.04 (s, 2H), 7.99 (s, 1H), 7.89 (s, 1H), 7.73 (d, *J* = 2.2 Hz, 2H), 7.70 (s, 1H), 7.63 (s, 2H), 7.60 (s, 1H), 7.50 (d, *J* = 1.6 Hz, 2H), 7.44 (d, *J* = 2.2 Hz, 1H), 1.51 (s, 9H), 1.42 (s, 18H), 1.40 (s, 9H), 1.36 (s, 9H).



L1: Off-white solid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 14.87 (s, 1H, -OH), 8.63 (d, *J* = 5.2 Hz, 1H, H^{19}), 8.57 (s, 1H, H^{13}), 8.10 (d, *J* = 7.8 Hz, 1H, H^{15}), 8.07 (d, *J* = 8.1 Hz, 1H, H^{17}), 8.04 (s, 1H, H^8), 7.95 (d, *J* = 9.4 Hz, 1H, H^5), 7.92 (s, 1H, H^{10}), 7.83 (s, 1H, H^{22}), 7.66 (t, *J* = 7.8 Hz, 1H, H^{16}), 7.60 (s, 1H, H^{26}), 7.54 (s, 2H, H^{24}), 7.36 (t, *J* = 8.0 Hz, 1H, H^3), 7.29 (d, *J* = 7.0 Hz, 1H, H^{20}), 7.08 (d, *J* = 9.2 Hz, 1H, H^2), 6.97 (t, *J* = 8.2 Hz, 1H, H^4), 1.43 (s, ^{t}Bu, 18H), 1.41 (s, ^{t}Bu, 9H). MS(EI, +ve): 569 (M^+).



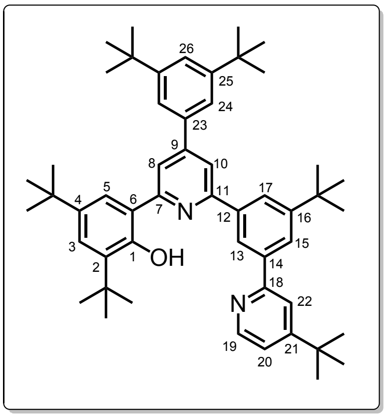
L2: Off-white solid. Yield: 82%. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C): δ14.78 (s, 1H, -OH), 8.62 (d, *J* = 5.8 Hz, 1H, H^{19}), 8.40 (s, 1H, H^{13}), 8.20 (s, 1H, H^{15}), 8.12 (s, 1H, H^{17}), 8.10 (s, 1H, H^8), 8.02 (d, *J* = 9.5 Hz, 1H, H^5), 7.96 (s, 1H, H^{10}), 7.85 (s, 1H, H^{22}), 7.62 (s, 1H, H^{26}), 7.60 (s, 2H, H^{24}), 7.36 (t, *J* = 8.5 Hz, 1H, H^3), 7.31 (d, *J* = 7.1 Hz, 1H, H^{20}), 7.04 (d, *J* = 9.4 Hz, 1H, H^2), 6.98 (t, *J* = 8.2 Hz, 1H, H^4), 1.50 (s, 9H, ^{t}Bu), 1.42 (s, 18H, ^{t}Bu), 1.41 (s, 9H, ^{t}Bu). MS(EI, +ve): 625 (M^+).



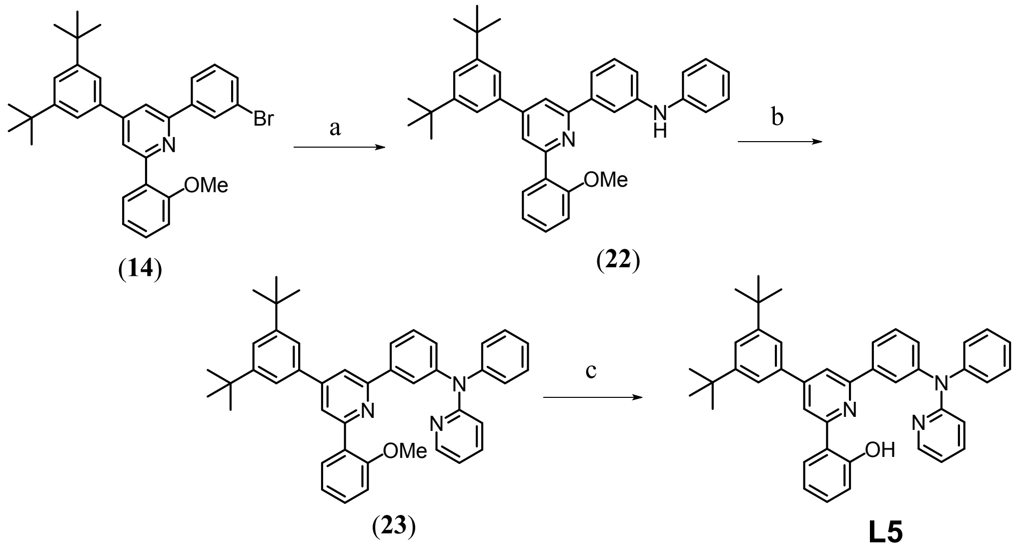
L3: Off-white solid. Yield: 88%. ^{1}H NMR (600 MHz,

CD_2Cl_2, 25 °C): δ 14.43 (s, 1H, -OH), 8.62 (d, *J* = 5.2 Hz, 1H, H^{19}), 8.37 (s, 1H, H^{13}), 8.19 (s, 1H, H^{15}), 8.12 (s, 1H, H^{17}), 8.09 (s, 1H, H^{8}), 7.96 (s, 1H, H^{5}), 7.94 (s, 1H, H^{10}), 7.85 (s, 1H, H^{22}), 7.62 (s, 1H, H^{26}), 7.59 (s, 2H, H^{24}), 7.41 (d, *J* = 8.5 Hz, 1H, H^{3}), 7.31 (d, *J* = 6.8 Hz, 1H, H^{20}), 6.98 (d, *J* = 8.6 Hz, 1H, H^{2}), 1.49 (s, 9H, ^{t}Bu), 1.42 (s, 18H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 1.38 (s, 9H, ^{t}Bu). MS(EI, +ve): 684 (M^+).

L4: Off-white solid. Yield: 76%. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C): δ 15.04 (s, 1H, -OH), 8.61 (d, *J* = 5.2 Hz, 1H, H^{19}), 8.38 (s, 1H, H^{13}), 8.26 (s, 1H, H^{15}), 8.15 (s, 1H, H^{17}), 8.08 (s, 1H, H^{8}), 7.94 (s, 1H, H^{10}), 7.89 (s, 1H, H^{22}), 7.82 (s, 1H, H^{5}), 7.61 (s, 1H, H^{26}), 7.59 (s, 2H, H^{24}), 7.44 (s, 1H, H^{3}), 7.31 (d, *J* = 5.1 Hz, 1H, H^{20}), 1.51 (s, 9H, ^{t}Bu), 1.49 (s, 9H, ^{t}Bu), 1.42 (s, 18H, ^{t}Bu), 1.40 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu). MS(EI, +ve): 737 (M^+).



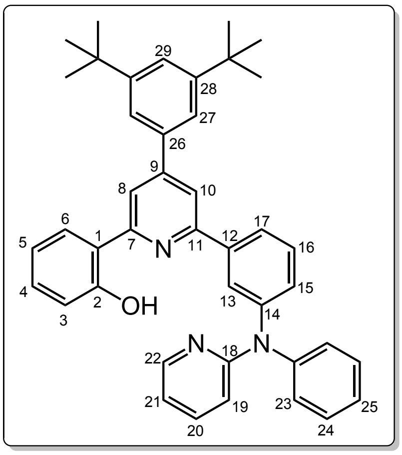
9) Procedure for L5



(a) aniline, KOBu^t, $Pd_2(dba)_3$, DPE-phos, toluene
(b) 2-iodopyridine, KOBu^t, $Pd_2(dba)_3$, DPE-phos, toluene
(c) PyHCl

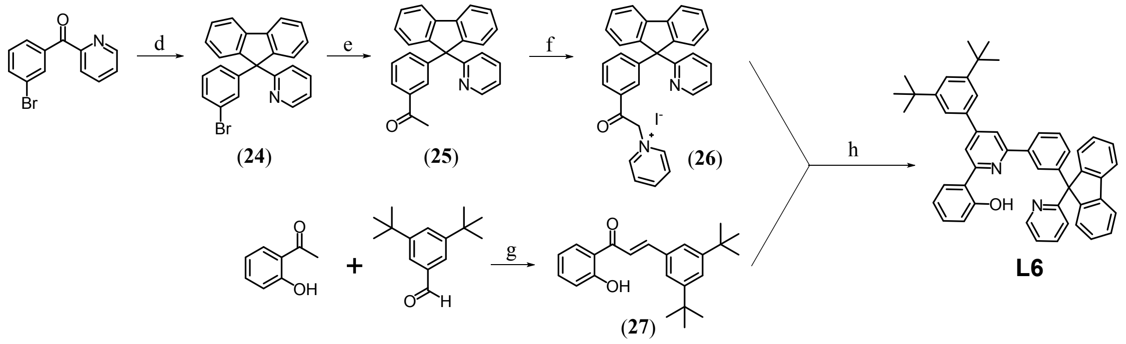
(**22**): A mixture of 1.44 g of (**14**), 0.25 g aniline, 0.42 g potassium *tert*-butoxide, 0.25 g $Pd_2(dba)_3$ and 0.29 g DPE-phos in 40 ml of anhydrous toluene was refluxed for 24 h under nitrogen. The resulting solution was extracted with water and ethyl acetate (3 × 50 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to dryness. The crude product (**22**) was then purified by column chromatography on silica gel using *n*-hexane/EA (9:1) as eluent to afford the desired product as yellow solid. Yield: 1.31 g (90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (s, 2H), 7.88 (s, 1H), 7.79 (s, 1H),7.62 (m, 1H), 7.53 (s, 3H), 7.42 – 7.39 (m, 2H), 7.38 – 7.36 (m, 1H), 7.30 – 7.28 (m, 2H), 7.13 – 7.11 (m, 2H), 7.05 – 7.03 (m, 2H), 6.93 (m, 1H), 5.86 (s, 1H), 3.89 (s, 3H), 1.40 (s, 18H).

(**23**): A mixture of 1.31 g (**22**), 0.50 g 2-iodopyridine, 0.33 g potassium *tert*-butoxide, 0.22 g $Pd_2(dba)_3$ and 0.26 g DPE-phos in 40 ml of anhydrous toluene was refluxed for 24 hours under nitrogen. The resulting solution was extracted with water and ethyl acetate (3 × 50 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to dryness. The crude product (**23**) was then purified by column chromatography on silica gel using *n*-hexane/EA (9:1) as eluent to afford the desired product as yellow solid. Yield: 1.29 g (87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (m, 1H), 8.01 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.69 (s, 1H), 7.52 – 7.48 (m, 3H), 7.45 – 7.23 (m, 8H), 7.11 (q, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.78 (m, 1H), 3.86 (s, 3H), 1.38 (s, 18H).



L5: A mixture of 1.31 g (**23**) and 5 g pyridine hydrochloride was refluxed for 24 h under nitrogen. The resulting solution was extracted with water and CH_2Cl_2 (3 × 50 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to dryness. The crude product was then purified by column chromatography on silica gel using *n*-hexane/EA (9:1) as eluent to afford the desired product as yellow solid. Yield: 1.20 g (95%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 14.37 (s, 1H, -OH), 8.22 (d, $J = 4.9$ Hz, 1H, H^{22}), 8.05 (s, 1H, H^{13}), 7.96 (d, $J = 8.1$ Hz, 1H, H^8), 7.78 (s, 1H, H^{15}), 7.75 (d, $J = 7.7$ Hz, 1H, H^{10}), 7.72 (s, 1H, H^{29}), 7.58 (s, 1H, H^6), 7.52 – 7.48 (m, 4H, H^{20}, H^{25}, H^{27}), 7.38 – 7.31 (m, 3H, H^{16}, H^{24}), 7.28 – 7.24 (m, 3H, H^{19}, H^{23}), 7.19 (t, $J = 5.8$ Hz, 1H, H^4), 6.99 (d, $J = 8.3$ Hz, 1H, H^{17}), 6.95 (t, $J = 7.5$ Hz, 1H, H^5), 6.86 – 6.82 (m, 2H, H^3, H^{21}), 1.39 (s, 18H, -tBu). MS(FAB, +ve): 604.1 (M^+).

10) Procedure for L6



(d) biphenyl-2-ylmagnesium iodide, THF, H_2SO_4, acetic anhydride;
(e) tributyl(1-ethoxyvinyl)stannane, $Pd(PPh_3)_2Cl_2$, toluene;
(f) pyridine, I_2;
(g) NaOH, ethanol;
(h) AcOH, NH_4OAc;

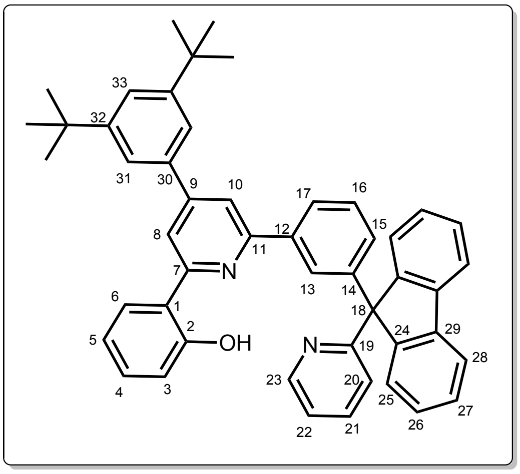
(**24**): Grignard reaction was employed for synthesizing compound (**24**). To a solution of magnesium (3.3 g, 137 mmol, 1.2 equiv.) and 40 ml of anhydrous diethyl ether was slowly added 2-iodobiphenyl (41.5 ml, 137 mmol, 1.2 equiv.) *via* dropping funnel under nitrogen atmosphere. The Grignard reagent was formed after stirring at reflux for 3 h. A solution of 2-(3-bromobenzoyl)pyridine (30.0 g, 114 mmol, 1.0 equiv.) in anhydrous THF (30 ml) was slowly added to the above Grignard reagent at room temperature under nitrogen atmosphere. After complete addition, the reaction mixture was stirred at reflux for 12 h. The mixture was poured into a solution containing 5 ml of concentrated H_2SO_4, 5 ml of acetic anhydride and 90 ml of acetic acid. The reaction mixture was stirred at 150 °C for 6 h. The mixture was poured into methanol. After filtration and washing with cool methanol twice, the compound **(24)** was obtained as pale brown solid (29.0 g, 65 %). ^1H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 5.1 Hz, 1H), 8.22 (t, *J* = 1.8 Hz, 1H), 8.04 (m, 2H), 7.90 (dt, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 7.6 Hz, *J* = 4.8 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H).

(**25**): Stille coupling was employed for synthesizing compound (**25**). To a solution of compound (**24**) (29.0 g, 72.8 mmol, 1.0 equiv.), bis(triphenylphosphine)palladium(II) dichloride (5.1 g, 7.2 mmol, 10 mol%), and 80 ml of anhydrous toluene was added 1-ethoxyvinyl tributylstannane (39.3 ml, 101.9 mmol, 1.4 equiv.) under nitrogen atmosphere. The reaction mixture was refluxed for 24 h. After cooling, HCl (100 ml, 12 M) was poured into the mixture, and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with H_2O (3 x 100 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude compound was purified by column chromatography on SiO_2 using ethyl acetate/hexane mixture (1:9) as eluent to afford (**25**) as light yellow solid (17.1 g, 66 %). ^1H NMR (300 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.1 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 3H), 7.70 (s, 1H), 7.56 (d, *J*

= 7.6 Hz, 2H), 7.48 – 7.21 (m, 8H), 7.13 (t, *J* = 5.2, 1H), 7.00 (d, *J* = 7.9Hz, 1H), 2.55 (s, 3H).

(**26**): A reaction mixture containing compound (**25**) (16.8 g, 46.4 mmol, 1 equiv.), iodine (17.7 g, 69.6 mmol, 1.5 equiv.) and pyridine (30 ml) was stirred at 150 ºC for 2 h. The mixture was concentrated under reduced pressure and washed with water twice. The compound (**26**) was allowed to re-crystallize in water/methanol mixture and obtained as pale brown solid (13.4 g, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, *J* = 5.8 Hz, 2H), 8.68 (t, *J* = 7.8 Hz, 1H), 8.60 (d, *J* = 4.6 Hz, 1H), 8.21 (t, *J* = 6.7 Hz, 2H), 7.99 – 7.93 (m, 3H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 4H), 7.47 – 7.42 (m, 3H), 7.37 – 7.29 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.30 (s, 2H).

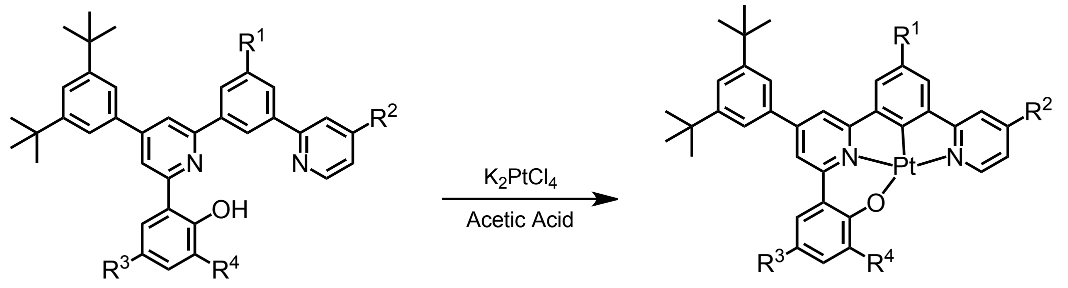
(**27**): To a solution of 3,5-di-*tert*-butylbenzaldehyde (9.1 g, 41.5 mmol, 1 equiv.), 2-hydroxyacetophenone (5 ml, 41.5 mmol, 1 equiv.) in 30 ml of ethanol, NaOH was added (2.5 equiv., 10 M). The resultant mixture was stirred at room temperature for 48 h. After neutralization by acetic acid, the crude product was filtered and washed with cold ethanol (3 x 20 ml) to afford (**27**) as yellow solid (10.2 g, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.87 (s, 1H), 7.99 – 7.94 (m, 2H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.54 – 7.50 (m, 4H), 7.04 (s, 1H), 6.97 (s, 1H), 1.38 (s, 18H).



L6: The reaction mixture containing compound (**27**) (10.4 g, 30.8 mmol, 1.2 equiv.), compound (**26**) (14.6 g, 25.7 mmol, 1.0 equiv.), ammomium acetate (19.8 g, 257 mmol, 10 equiv.) in glacial acetic acid (100 ml) was heated to reflux for 24 h. The crude mixture was extracted with dichloromethane (3 x 60 ml). The combined organic phases were washed with H_2O (3 x 50 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude compound was purified by column chromatography on SiO_2 using ethyl acetate/hexane mixture (1:10) as eluent to afford **Ligand 6** as light yellow solid (4 g, 23%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 14.63 (s, 1H, -OH), 8.70 (s, 1H, H^{23}), 7.96 (s, 1H, H^8), 7.88 (m, 2H, H^6, H^{17}), 7.80 (d, *J* = 7.6 Hz, 2H, H^{25}), 7.73 (d, *J* = 7.6 Hz, 3H, H^{26}, H^{13}), 7.56 (s, 2H, H^{10}, H^{33}), 7.48, (t, *J* = 7.8 Hz, 1H, H^{22}), 7.44 (s, 2H, H^{31}), 7.39 (q, *J* = 7.9 Hz, 3H, H^{16}, H^{23}, H^{25}), 7.32 (t, *J* = 7.0 Hz, 3H, H^4,

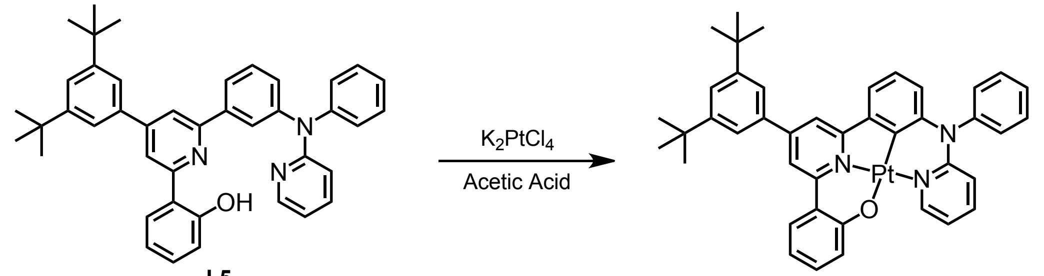
H^{27}), 7.17 (d, *J* = 8.0 Hz, 1H, H^{20}), 7.13 (t, *J* = 5.6 Hz, 1H, H^{21}), 7.08 (d, *J* = 8.0 Hz, 1H, H^{15}), 7.04 (d, *J* = 7.4 Hz, 1H, H^{3}), 6.92 (t, *J* = 7.6 Hz, 1H, H^{5}), 1.40 (s, 18 H, -CH_3).

11) Complexes Pt-1, Pt-2 and 1–6.

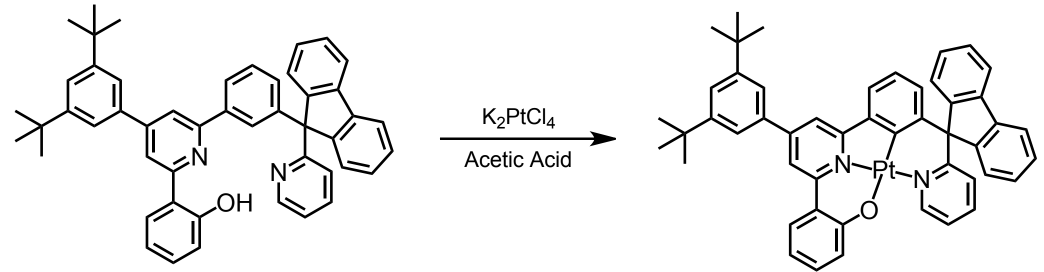


R^1, R^2, R^3, R^4 = H (**Ligand-Pt-1**)
R^1 = ^{t}Bu; R^2, R^3, R^4 = H (**Ligand-Pt-2**)
R^1, R^3, R^4 = H (**L1**)
R^1 = ^{t}Bu; R^3, R^4 = H (**L2**)
R^1, R^3 = ^{t}Bu; R^4 = H (**L3**)
R^1, R^3, R^4 = ^{t}Bu (**L4**)

R^1, R^2, R^3, R^4 = H (**Pt-1**)
R^1 = ^{t}Bu; R^2, R^3, R^4 = H (**Pt-2**)
R^1, R^3, R^4 = H (**1**)
R^1 = ^{t}Bu; R^3, R^4 = H (**2**)
R^1, R^3 = ^{t}Bu; R^4 = H (**3**)
R^1, R^3, R^4 = ^{t}Bu (**4**)

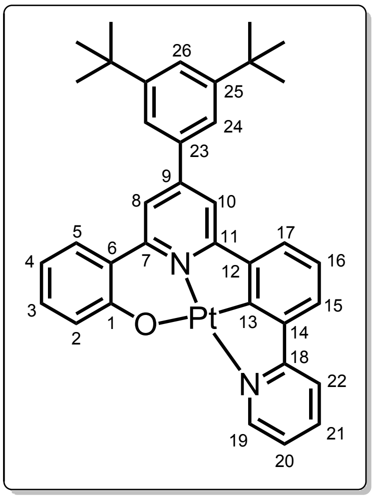


L5 **5**



L6 **6**

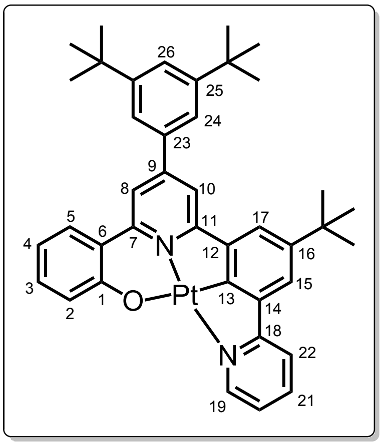
A mixture of K$_2$PtCl$_4$ (1.2 equiv.) and corresponding ligand (1.0 equiv.) in chloroform and glacial acetic acid mixture (v:v = 1:9, 150 ml) was refluxed for 24 h to give the crude as an yellowish-green solution. It was neutralized by a sodium carbonate solution and extracted by CH$_2$Cl$_2$ solution. Purification was done by silica gel column chromatography using hexane/ethyl acetate (v:v = 3:1) mixture as eluent to yield yellow solids. Recrystallization was done by diffusion of Et$_2$O into the CHCl$_3$ solution of the solid to give the Pt(II) complex **Pt-1**, **Pt-2** and **1–6** as yellow crystalline solids.



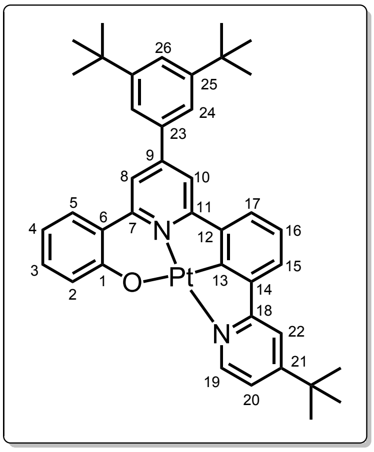
Pt-1: Yellow crystalline solids. Yield: 80%. ^{1}H NMR

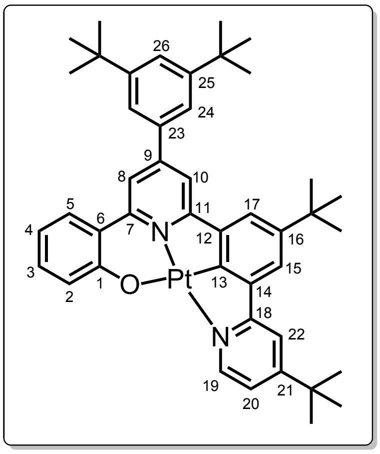
(500 MHz, CD_2Cl_2, 25 ^{o}C): δ 8.99 (d, J = 6.8 Hz, 1H, H^{19}), 8.37 (s, 1H, H^{8}), 8.17 (d, J = 8.5 Hz, 1H, H^{5}), 7.97 (t, J = 7.8 Hz, 1H, H^{21}), 7.83 (s, 1H, H^{10}), 7.78 (d, J = 7.4 Hz, 1H, H^{22}), 7.69–7.66 (m, 4H, H^{17}, H^{24}, H^{26}), 7.57 (d, J = 7.5 Hz, 1H, H^{15}), 7.38 (t, J = 7.5 Hz, 1H, H^{3}), 7.34 (t, J = 6.5 Hz, 1H, H^{20}), 7.29–7.24 (m, 2H, H^{2}, H^{16}), 6.74 (t, J = 6.8 Hz, 1H, H^{4}), 1.47 (s, 18H, ^{t}Bu). MS(FAB, +ve): 706 (M^+). Elemental analysis calcd (%) for $C_{36}H_{34}N_2OPt{\cdot}Et_2O$: C 61.60, H 5.69, N 3.59; found: C 61.54, H 5.43, N 3.56.

Pt-2: Yellow crystalline solids. Yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ 9.07 (m, 1H, H^{19}), 8.30 (s, 1H, H^{8}), 8.11 (d, J = 8.3 Hz, 1H, H^{5}), 7.96 (t, J = 8.5 Hz, 1H, H^{21}), 7.80 (d, J = 8.0 Hz, 1H, H^{22}), 7.78 (s, 1H, H^{10}), 7.69 (s, 1H, H^{17}), 7.64 (s, 1H, H^{15}), 7.63 (s, 1H, H^{26}), 7.58 (s, 2H, H^{24}), 7.43–7.40 (m, 2H, H^{2}, H^{3}), 7.32 (t, J = 6.5 Hz, 1H, H^{20}), 6.75 (m, 1H, H^{4}), 1.45 (s, 27H, ^{t}Bu). MS(FAB, +ve): 762 (M^+). Elemental analysis calcd (%) for $C_{40}H_{42}N_2OPt$: C 63.06, H 5.56, N 3.68; found: C 62.94, H 5.57, N 3.53.



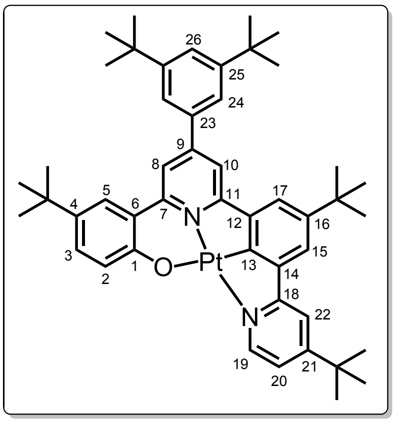
1: Yellow crystalline solids. Yield: 80%. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.83 (d, J = 5.5 Hz, 1H, H^{19}), 8.33 (s, 1H, H^{8}), 8.14 (d, J = 7.8 Hz, 1H, H^{5}), 7.80 (s, 1H, H^{10}), 7.75 (d, J = 1.5 Hz, 1H, H^{22}), 7.66 (m, 3H, H^{24}, H^{26}), 7.64 (d, J = 7.7 Hz, 1H, H^{17}), 7.56 (d, J = 7.5 Hz, 1H, H^{15}), 7.38 (t, J = 8.0 Hz, 1H, H^{3}), 7.34 (d, J = 4.1 Hz, 1H, H^{20}), 7.27 (d, J = 8.2 Hz, 1H, H^{2}), 7.24 (t, J = 7.6 Hz, 1H, H^{16}), 6.72 (t, J = 7.3 Hz, 1H, H^{4}), 1.46 (s, 18H, ^{t}Bu), 1.44 (s, 9H, ^{t}Bu). MS(FAB, +ve): 762 (M^+). Elemental analysis calcd (%) for $C_{40}H_{42}N_2OPt$: C 63.06, H 5.56, N 3.68, O 2.10, Pt 25.61; found: C 63.06, H 5.70, N 3.56.



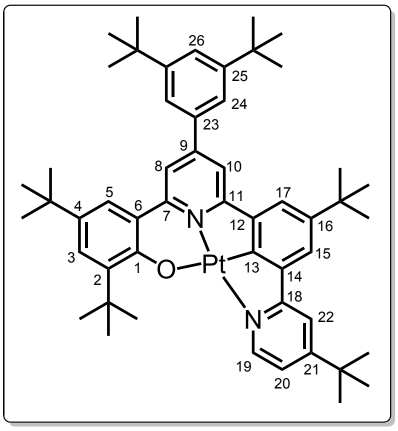


2: Yellow crystalline solids. Yield: 85%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.87 (d, J = 5.9 Hz, 1H, H^{19}), 8.34 (s, 1H, H^{8}), 8.15 (d, J = 10.1 Hz, 1H, H^{5}), 7.85 (s, 1H, H^{10}), 7.82 (s, 1H, H^{22}), 7.76 (s, 1H, H^{17}), 7.70 (s, 1H, H^{15}), 7.65 (s, 3H, H^{24}, H^{26}), 7.42 – 7.34 (m, 2H, H^{3}, H^{20}), 7.30 (d, $J = 9.8$ Hz, 1H, H^{2}), 6.72 (t, $J = 8.2$ Hz, 1H, H^{4}), 1.48 (s, 9H), 1.47 (s, 9H), 1.45 (s, 18H). MS(FAB, +ve): 818 (M^{+}). Elemental analysis calcd (%) for $\mathrm{C_{44}H_{50}N_{2}OPt}$: C 64.61, H 6.16, N 3.42, O 1.96, Pt 23.85; found: C 64.12, H 6.12, N 3.43.

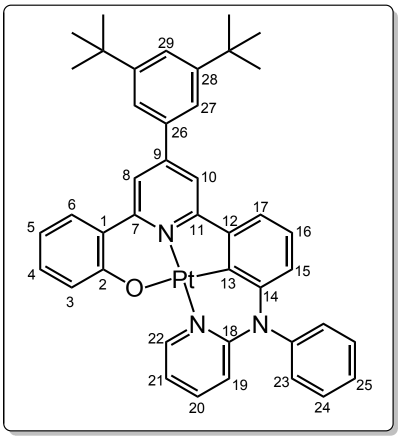
3: Yellow crystalline solids. Yield: 90%. ^{1}H NMR (600 MHz, $\mathrm{CD_2Cl_2}$) δ 8.88 (d, $J = 6.0$ Hz, 1H, H^{19}), 8.37 (s, 1H, H^{8}), 8.09 (s, 1H, H^{5}), 7.87 (s, 1H, H^{10}), 7.82 (s, 1H, H^{22}), 7.78 (s, 1H, H^{17}), 7.73 – 7.67 (m, 3H, H^{15}, H^{24}), 7.66 (s, 1H, H^{26}), 7.48 (d, $J = 11.1$ Hz, 1H, H^{3}), 7.38 (d, $J = 7.8$ Hz, 1H, H^{20}), 7.25 (d, $J = 8.8$ Hz, 1H, H^{2}), 1.49 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 1.46 (s, 18H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu). MS(FAB, +ve): 874 (M^{+}). Elemental analysis calcd (%) for $\mathrm{C_{48}H_{58}N_{2}OPt}$: C 65.96, H 6.69, N 3.20, O 1.83, Pt 22.32; found: C 64.34, H 6.49, N 3.02.



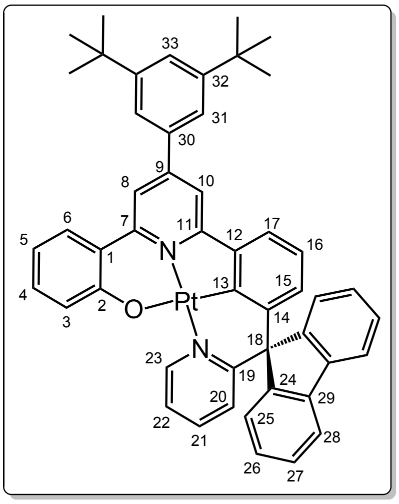
4: Yellow crystalline solids. Yield: 82%. ^{1}H NMR (600 MHz, $\mathrm{CD_2Cl_2}$) δ 8.94 (d, $J = 6.0$ Hz, 1H, H^{19}), 8.33 (s, 1H, H^{8}), 7.94 (s, 1H, H^{5}), 7.86 (s, 1H, H^{22}), 7.85 (s, 1H, H^{10}), 7.80 (s, 1H, H^{15}), 7.74 (s, 1H, H^{17}), 7.69 (m, 2H, H^{24}), 7.64 (s, 1H, H^{26}), 7.56 (s, 1H, H^{3}), 7.42 (d, $J = 8.0$ Hz, 1H, H^{20}), 1.68 (s, 9H, ^{t}Bu), 1.50 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 1.45 (s, 18H, ^{t}Bu), 1.39 (s, 9H, ^{t}Bu). MS(FAB, +ve): 930 (M^{+}). Elemental analysis calcd (%) for $\mathrm{C_{52}H_{66}N_{2}OPt}$: C 67.14, H 7.15, N 3.01, O 1.72, Pt 20.97; found: C 68.66, H 7.31, N 3.09.



5: Orange crystalline solids. Yield: 90 %. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz): δ 10.18 (d, $J = 6.3$ Hz, 1H, H^{22}), 8.23 (s, 1H, H^{8}), 7.99 (d, $J = 8.4$ Hz, 1H, H^{6}), 7.90 (s , 1H, H^{10}), 7.72 – 7.69 (m, 2H, H^{24}), 7.64 – 7.59 (m, 4H, H^{25}, H^{27}, H^{29}), 7.54 – 7.51 (m, 2H, H^{17}, H^{20}),



7.39 – 7.44 (m, 3H, H^{4}, H^{23}), 7.25 (d, J = 8.4 Hz, 1H, H^{3}), 6.98 (t, J = 7.9 Hz, 1H, H^{16}), 6.85 (t, J = 6.6 Hz, 1H, H^{21}), 6.72 (t, J = 7.5 Hz, 1H, H^{5}), 6.41 (d, J = 8.7 Hz, 1H, H^{19}), 6.14 (d, J = 8.3 Hz, 1H, H^{15}), 1.43 (s, 18H, -^{t}Bu). MS(FAB, +ve) : 797.3 (M^{+}). Anal. Calcd for $C_{49}H_{42}N_{2}OPt$: C 67.65, H 4.87, N 3.22. Found: C 67.07, H 4.99, N 3.06.



6: Light yellow solids. Yield: 31 %. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.40 (s, 1H, H^{23}), 8.21 (s, 1H, H^{8}), 8.09 (d, J = 7.7 Hz, 2H, H^{25}), 8.02 (d, J = 7.5 Hz, 1H, H^{6}), 7.89 (s, 1H, H^{10}), 7.84 (d, J = 7.6 Hz, 2H, H^{28}), 7.65 (s, 2H, H^{31}), 7.64 – 7.60 (m, 3H, H^{17}, H^{21}, H^{33}), 7.45 – 7.38 (m, 4H, H^{4}, H^{22}, H^{27}), 7.30 – 7.28 (m, 3H, H^{3}, H^{26}), 6.92 (d, J = 8.3 Hz, 1H, H^{20}), 6.85 (t, J = 7.7 Hz, 1H, H^{16}), 6.78 (t, J = 6.9 Hz, 1H, H^{5}), 6.36 (d, J = 7.9 Hz, 1H, H^{15}), 1.43 (s, 18H, -^{t}Bu). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.13, 164.54, 160.97, 153.30, 152.00, 151.79, 150.74, 150.44, 145.50, 140.64, 139.96, 139.01, 137.97, 137.88, 131.42, 130.38, 128.50, 128.20, 126.62, 126.27, 125.05, 123.84, 123.80, 123.48, 122.95, 122.80, 122.69, 121.45, 120.47, 118.80, 114.84, 113.52. MS (FAB): 867.29[M^{+}]. Anal. Calcd for $C_{49}H_{42}N_{2}OPt$: C 67.65, H 4.87, N 3.22. Found: C 67.07, H 4.99, N 3.06.

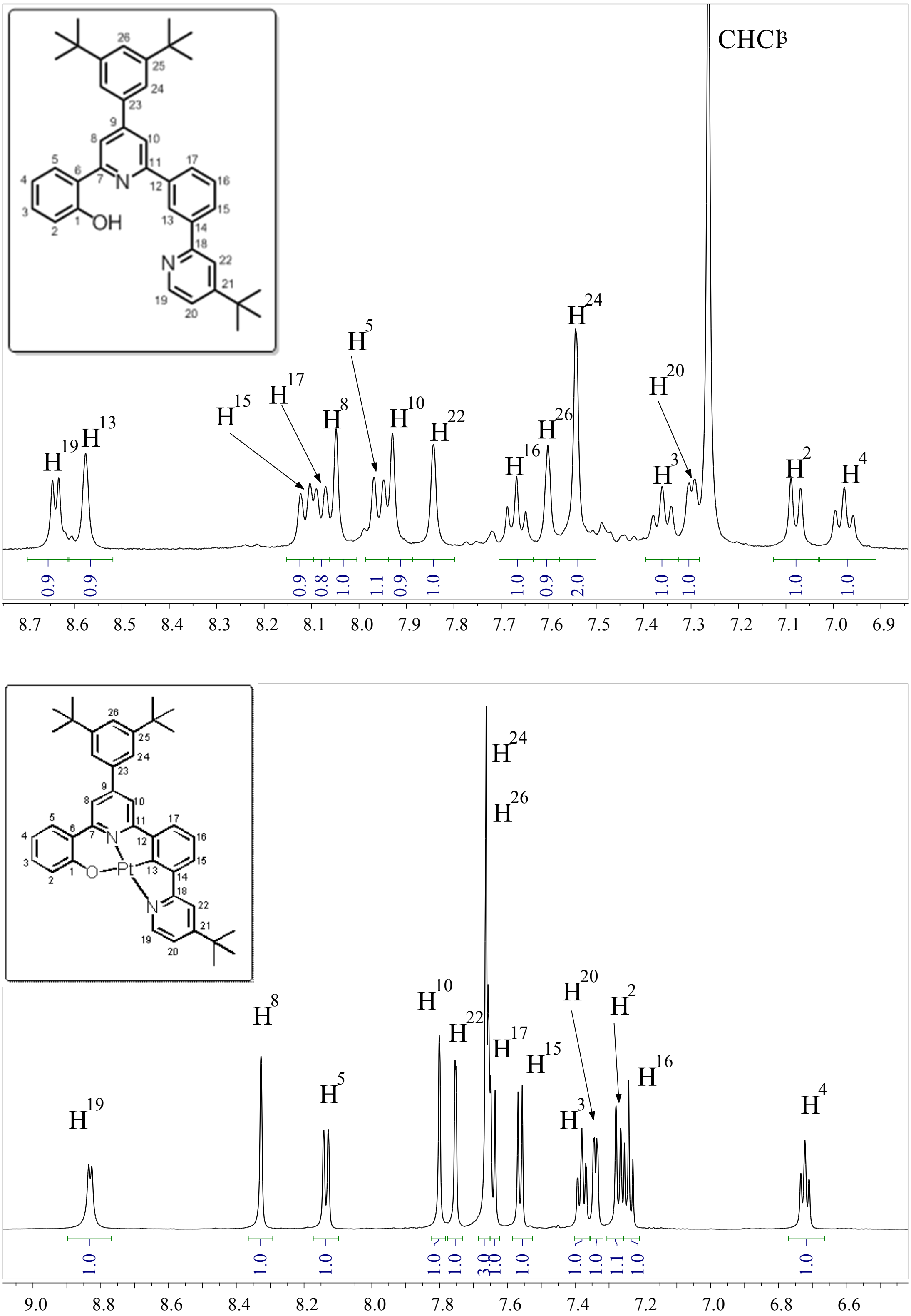


Fig. S3. ^{1}H NMR spectra of **L1** (upper) and **1** (bottom) (aromatic region).

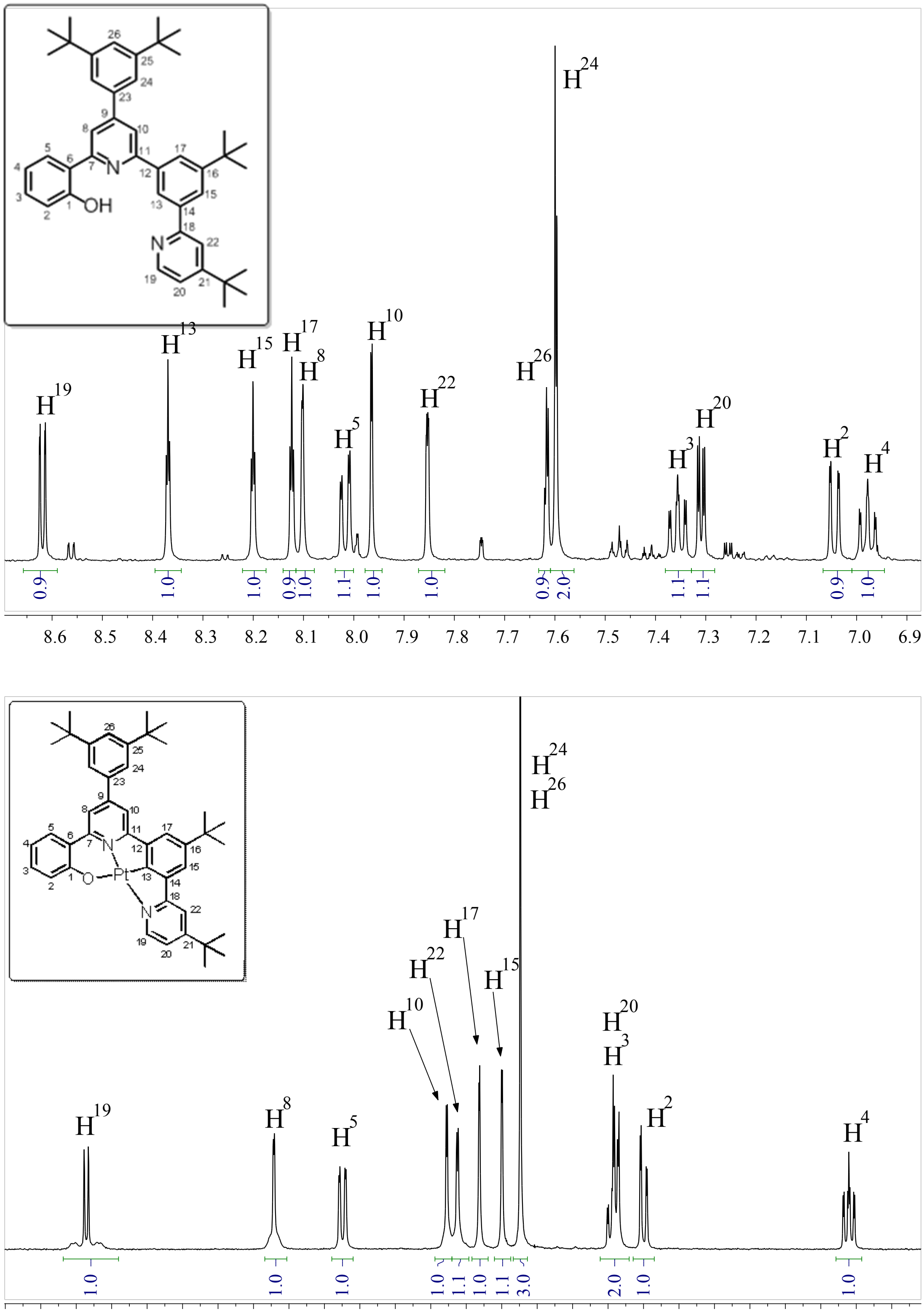


Fig. S4. ^{1}H NMR spectra of **L2** (upper) and **2** (bottom) (aromatic region).

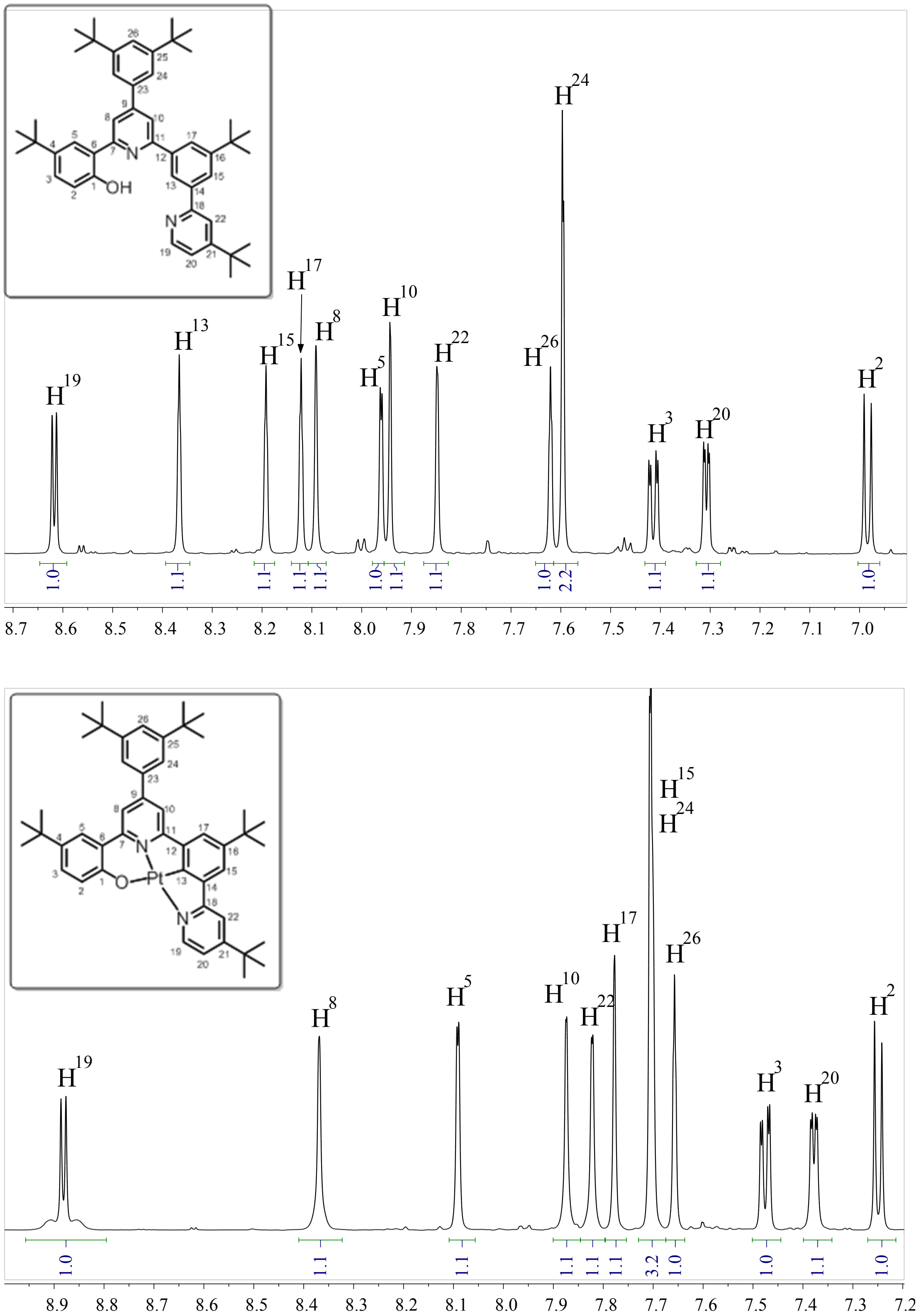


Fig. S5. ^{1}H NMR spectra of **L3** (upper) and **3** (bottom) (aromatic region).

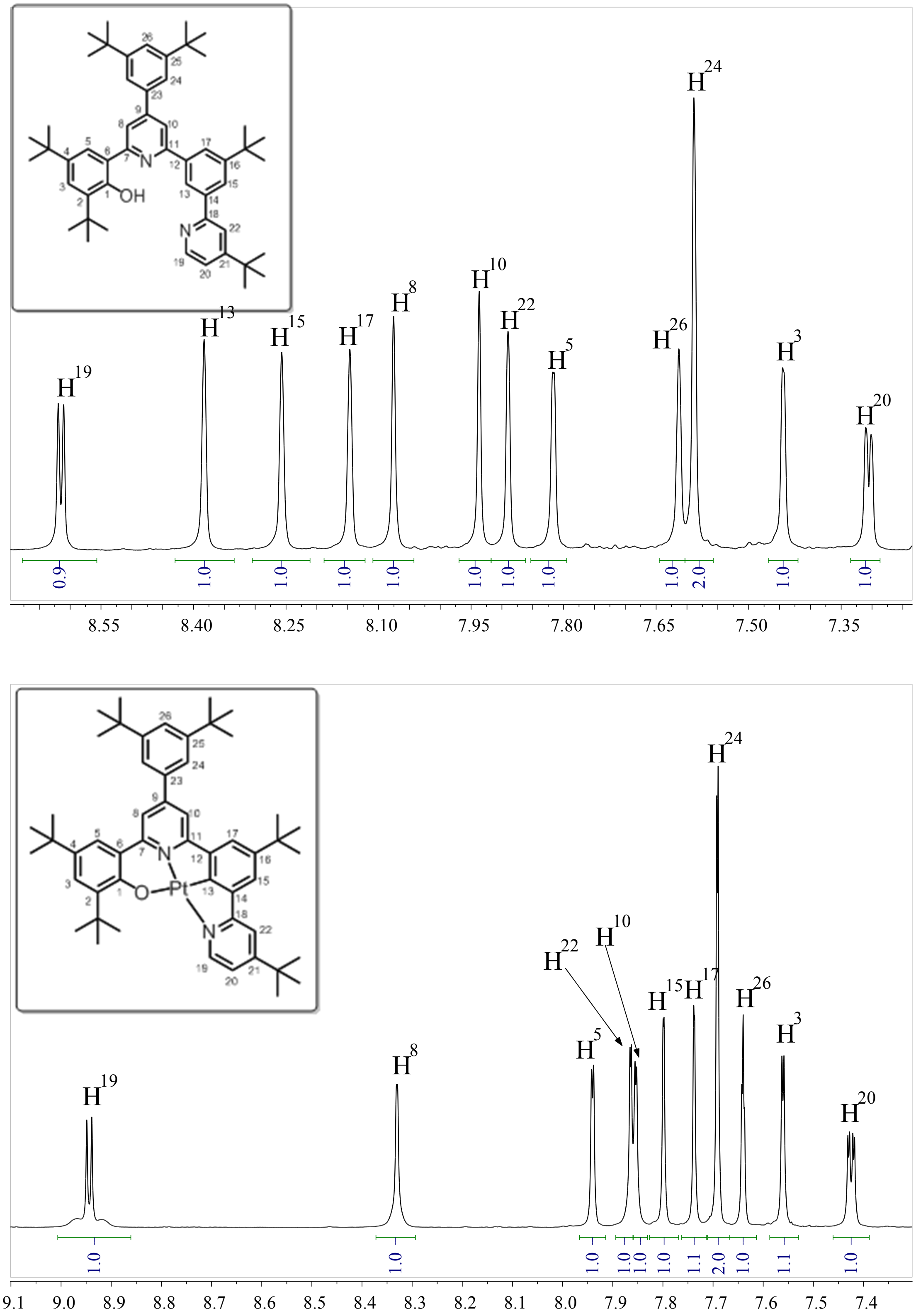


Fig. S6. ^{1}H NMR spectra of **L4** (upper) and **4** (bottom) (aromatic region).

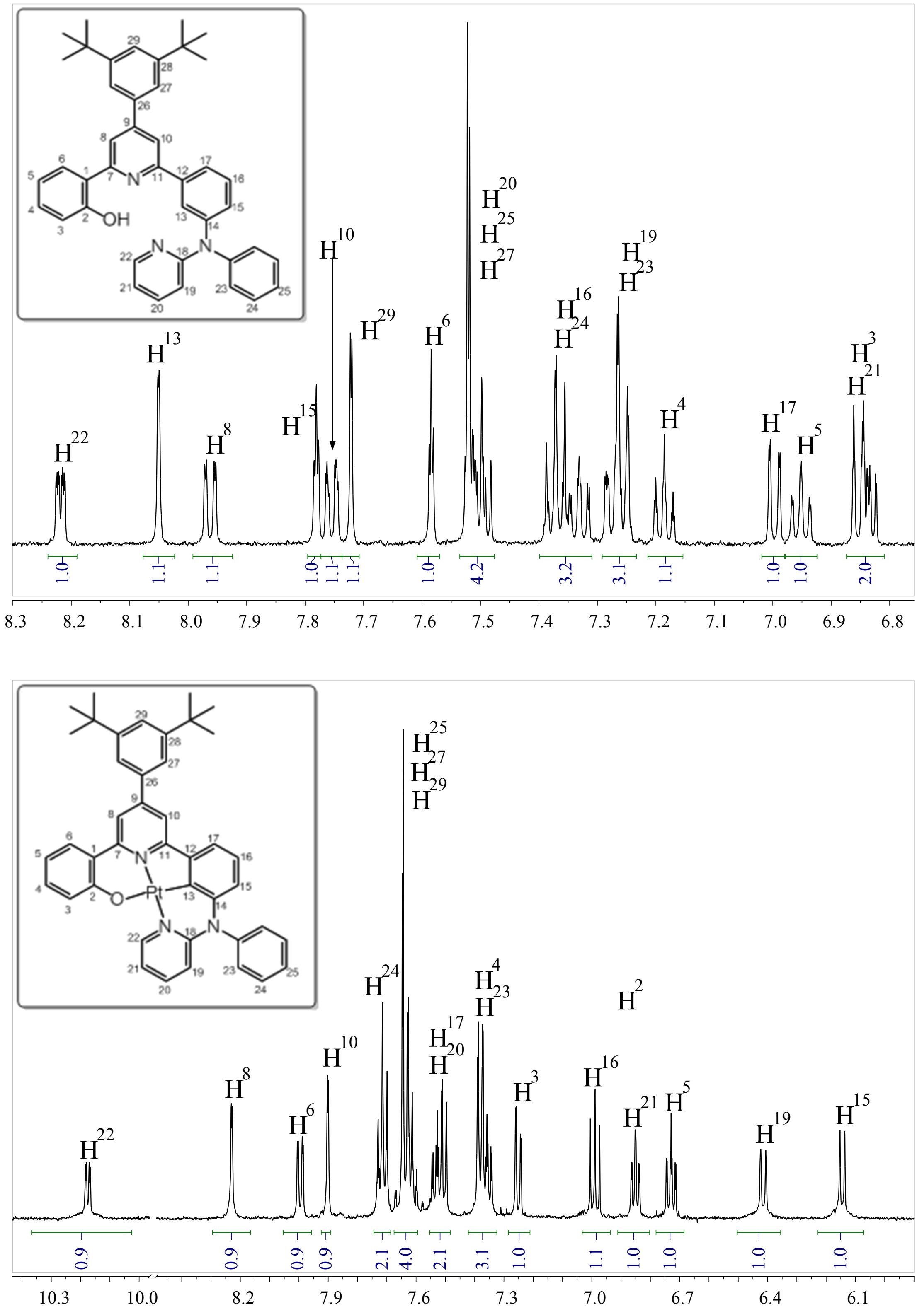


Fig. S7. ^{1}H NMR spectra of **L5** (upper) and **5** (bottom) (aromatic region).

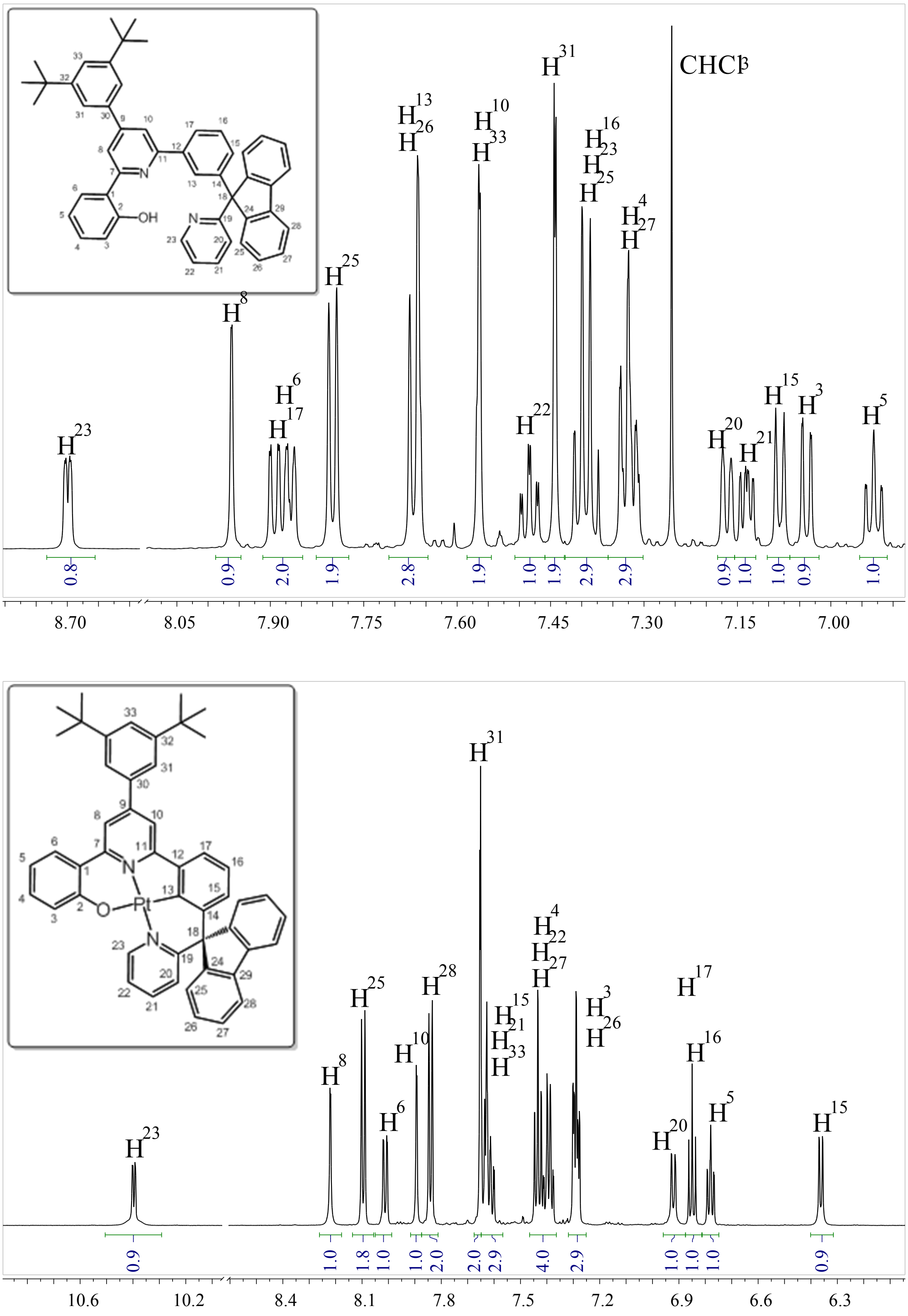


Fig. S8. ^{1}H NMR spectra of **L6** (upper) and **6** (bottom) (aromatic region).

(H). X-ray crystallography data of 6

Table S1. Crystal data and structural refinement data for **6**.

Formula	$C_{49}H_{42}N_2OPt$
Temperature, K	100
Formula weight	869.29
Crystal system	triclinic
Space group	P -1
a, Å	12.4607(5)
b, Å	12.7920(5)
c, Å	14.1587(6)
α, deg	67.97(1)
β, deg	85.66(1)
γ, deg	68.67(1)
Cell volume, $Å^3$	1944.0(14)
Z	□1
Density, calculated, g/cm^3	1.588
μ, mm^{-1}	8.013
Index ranges	h = -14→13
	k = -15→15
	i = -16→15
F(000)	930
Theta range, deg	3.4–66.1
R_1	0.0439
wR_2	0.1182
GoF	1.097
largest diff. peak/hole [e $Å^{-3}$]	2.46/-1.42

Note : $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

(I). Photophysical data of Pt-1, Pt-2, Pt-3 and 1–6 in solid and glassy state

Table S2. Photophysical data of **Pt-1**, **Pt-2**, **Pt-3** and **1–6** in solid and glassy state.

Complex	Emission λ_{max}[nm] (τ [µs])		
	Solid (298K)	Solid (77K)	Glassy[a]
Pt-1	666 (0.39)	684 (1.8)	495 (4.7), 530 (4.7), 567 (5.8)
Pt-2	626 (0.33), 654 (0.33)	665 (1.5)	505 (4.2), 540 (4.4), 576 (4.5)
Pt-3	633 (0.39)	550 (1.6), 662 (2.8)	494 (6.4), 531 (5.7), 568 (6.3)
1	683 (0.28)	719 (--)[b]	489 (5.2), 526 (5.2), 566 (5.2)
2	619 (0.85)	631 (1.8)	502 (4.6), 538 (4.8)
3	519 (--)[c], 557sh	533 (0.15), 575(0.15)	502 (4.4), 537 (4.4)
4	542 (--)[c], 579sh	542 (4.0), 580sh	521 (5.2), 564 (5.2)
5	546, 576 (0.74)	553, 599 (3.4)	555, 592 (0.38)
6	499, 533 (1.9)	497, 510, 533 (4.9)	497, 532 (6.1)

[a] In DMF: MeOH: EtOH mixture (v:v:v = 1:1:4). [b] Emission intensity was too low for lifetime measurement. [c] Lifetime was too short that cannot be measured due to instrument limitation.

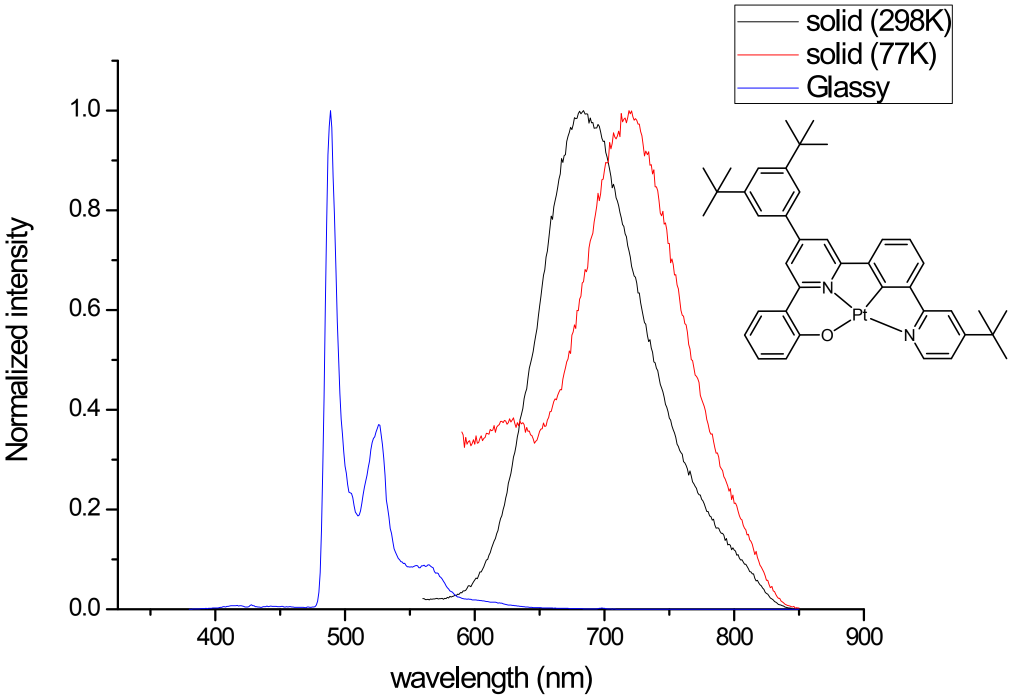


Fig. S9. Emission spectra of **1** in their solid state (room temperature and 77 K) and glassy state (77 K).

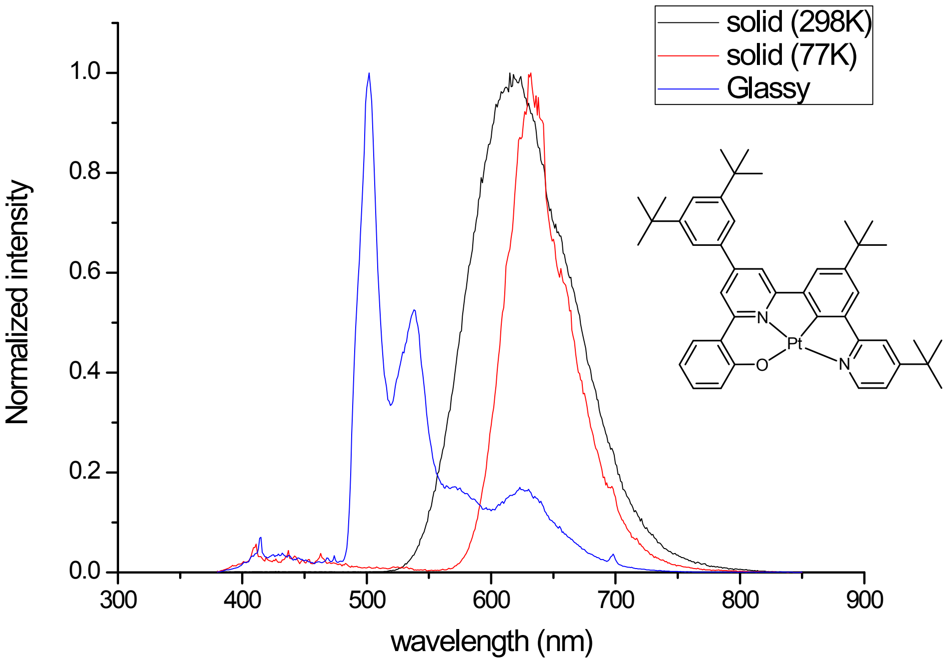


Fig. S10. Emission spectra of **2** in their solid state (room temperature and 77 K) and glassy state (77 K).

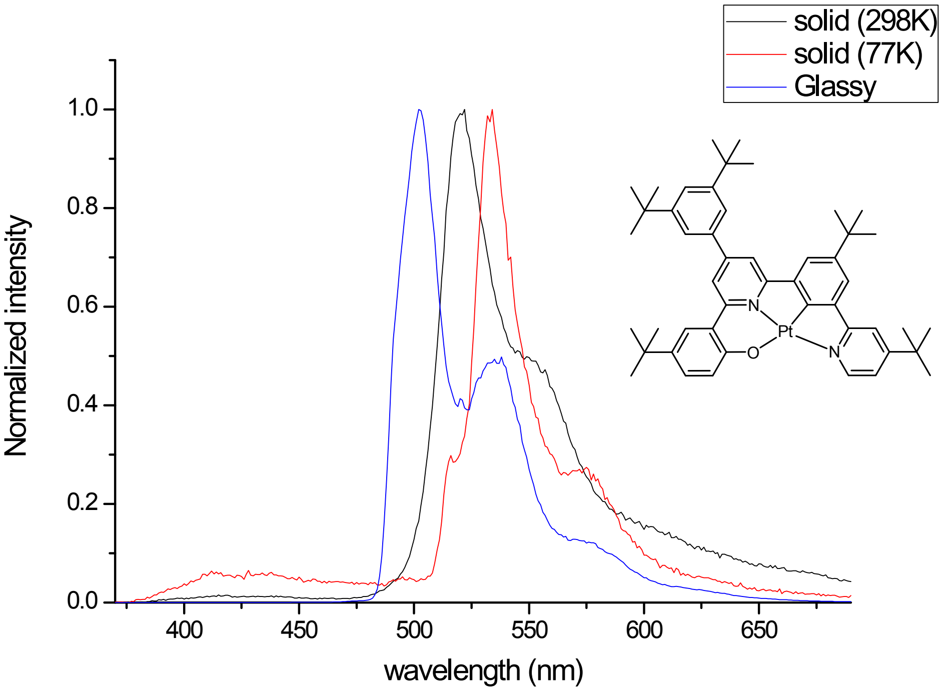


Fig. S11. Emission spectra of **3** in their solid state (room temperature and 77 K) and glassy state (77 K).

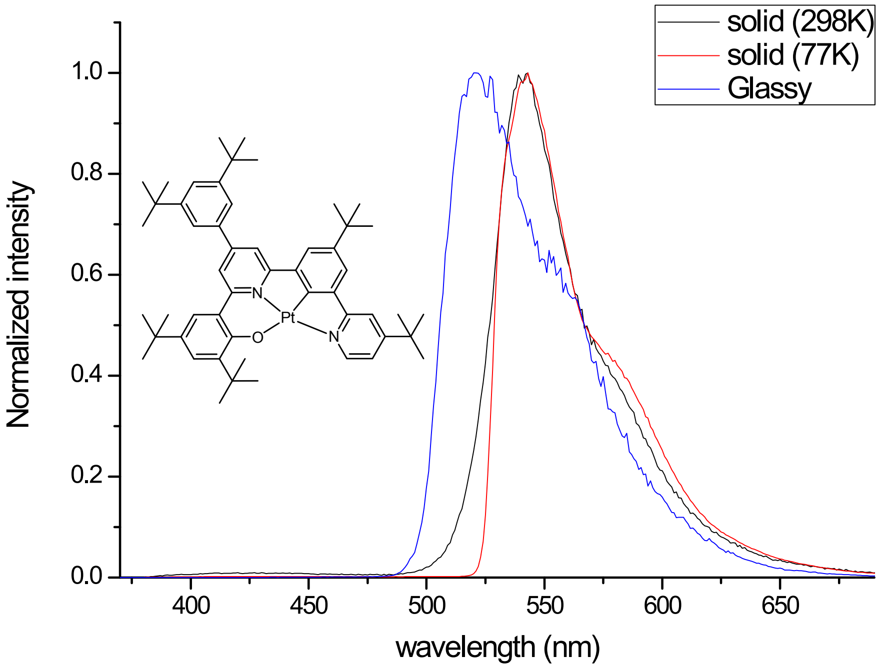


Fig. S12. Emission spectra of **4** in their solid state (room temperature and 77 K) and glassy state (77 K).

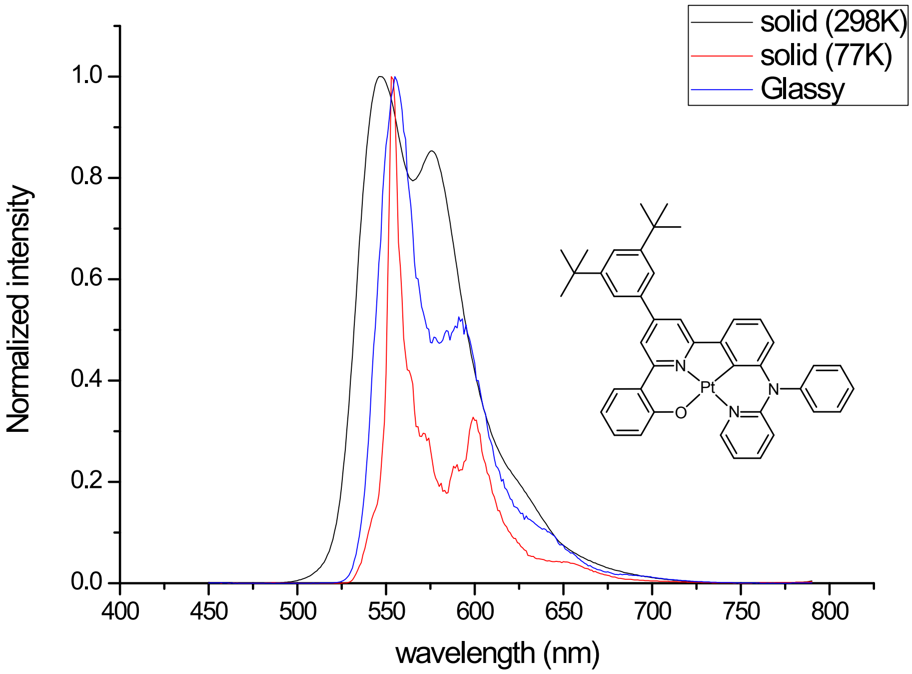


Fig. S13. Emission spectra of **5** in their solid state (room temperature and 77 K) and glassy state (77 K).

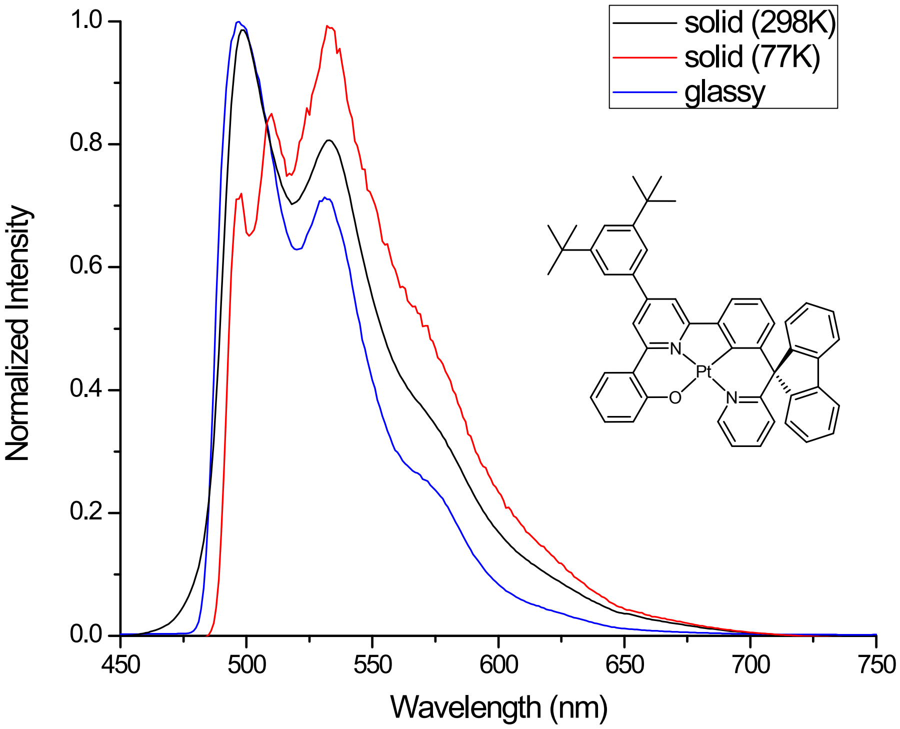


Fig. S14. Emission spectra of **6** in their solid state (room temperature and 77 K) and glassy state (77 K).

(J) Cyclic voltammetry

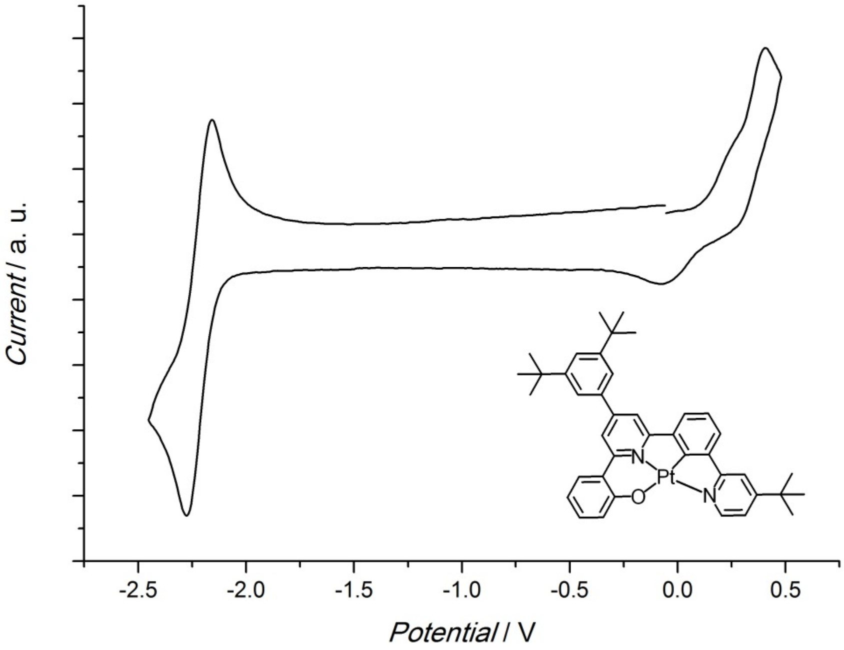


Fig. S15. Cyclic voltammogram of **1** in DMF at 298 K.

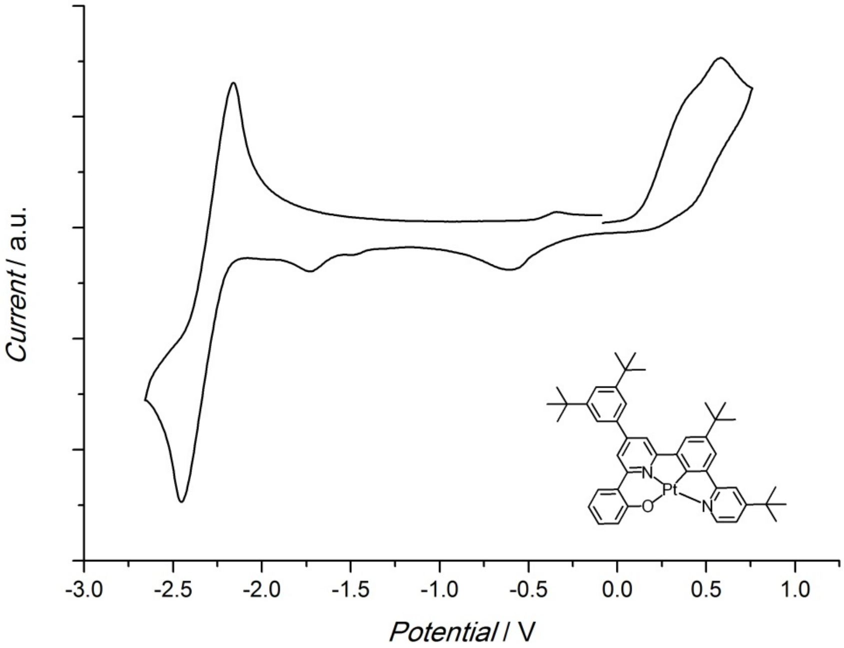


Fig. S16. Cyclic voltammogram of **2** in DMF at 298 K.

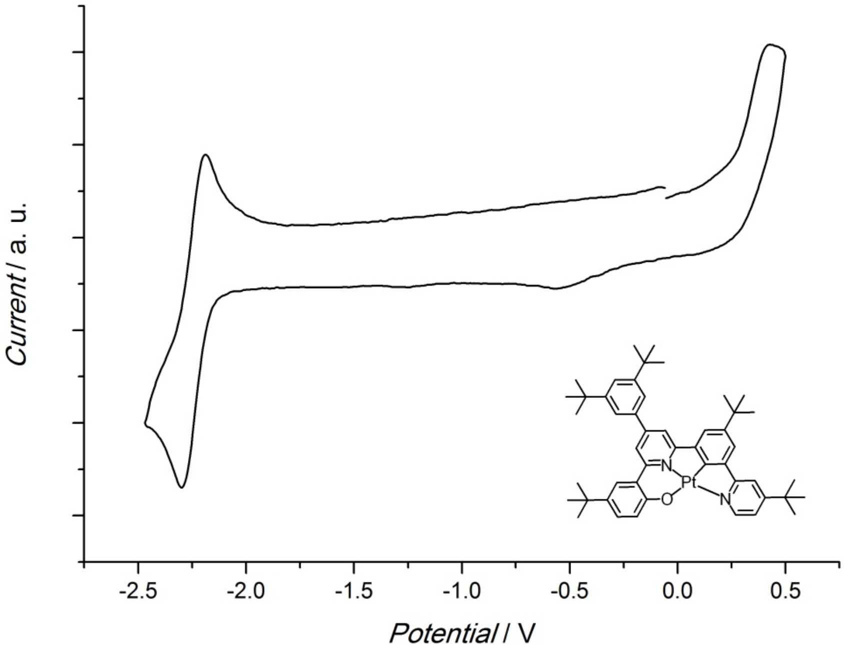


Fig. S17. Cyclic voltammogram of **3** in DMF at 298 K.

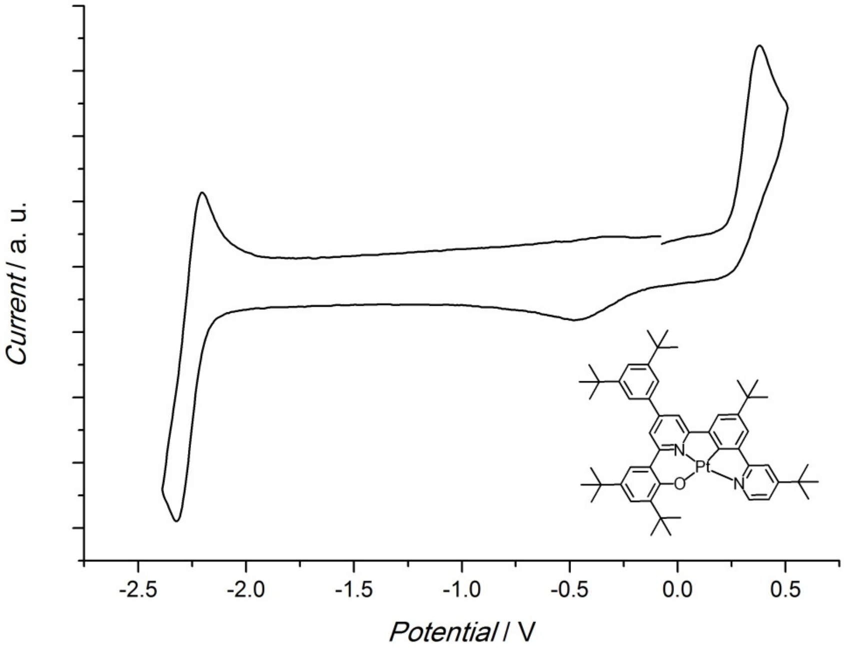


Fig. S18. Cyclic voltammogram of **4** in DMF at 298 K.

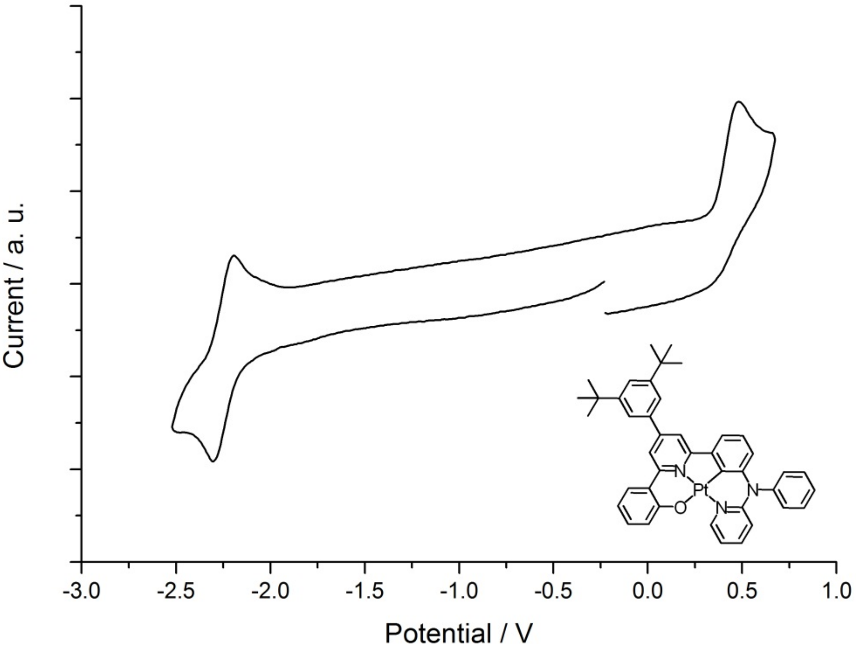


Fig. S19. Cyclic voltammogram of **5** in DMF at 298 K.

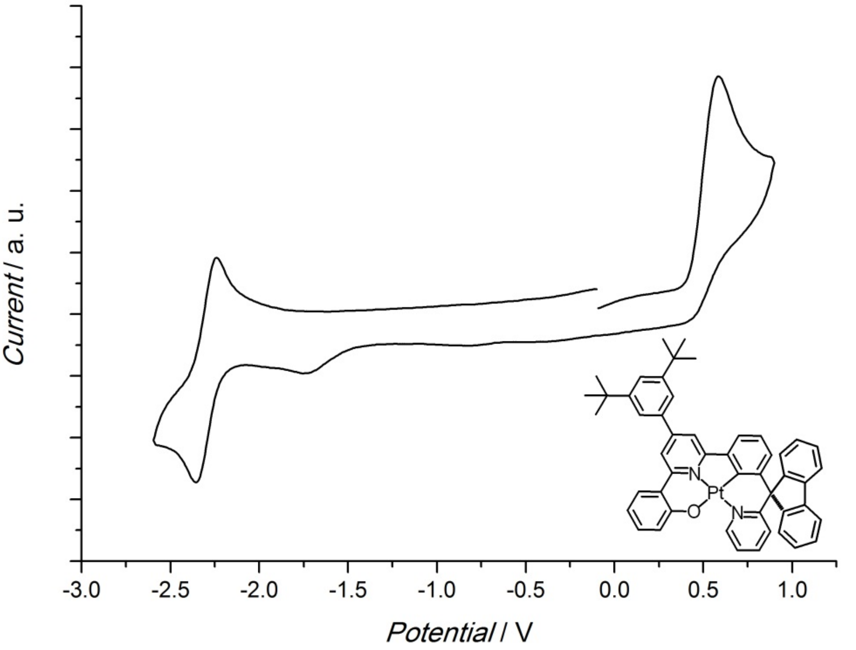


Fig. S20. Cyclic voltammogram of **6** in DMF at 298 K.

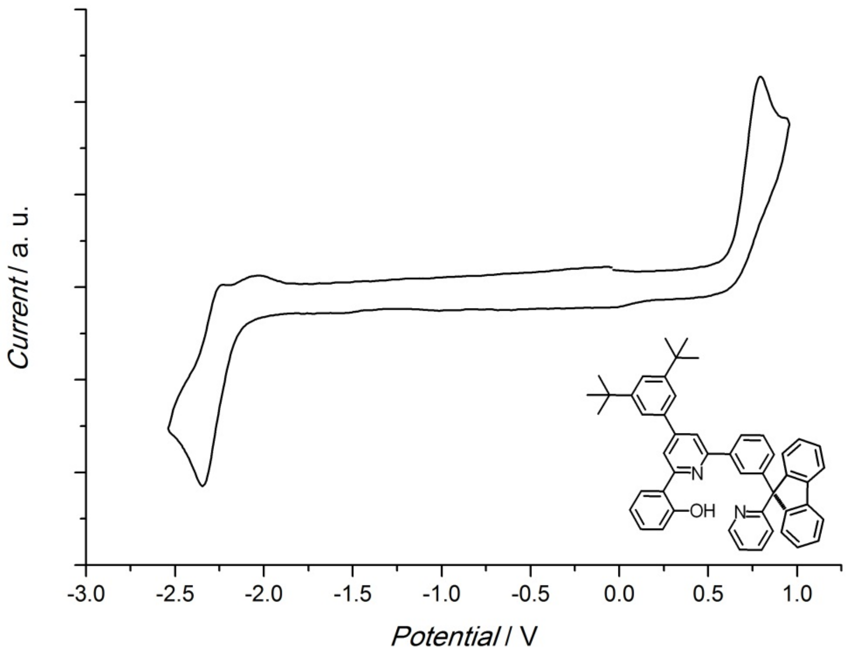
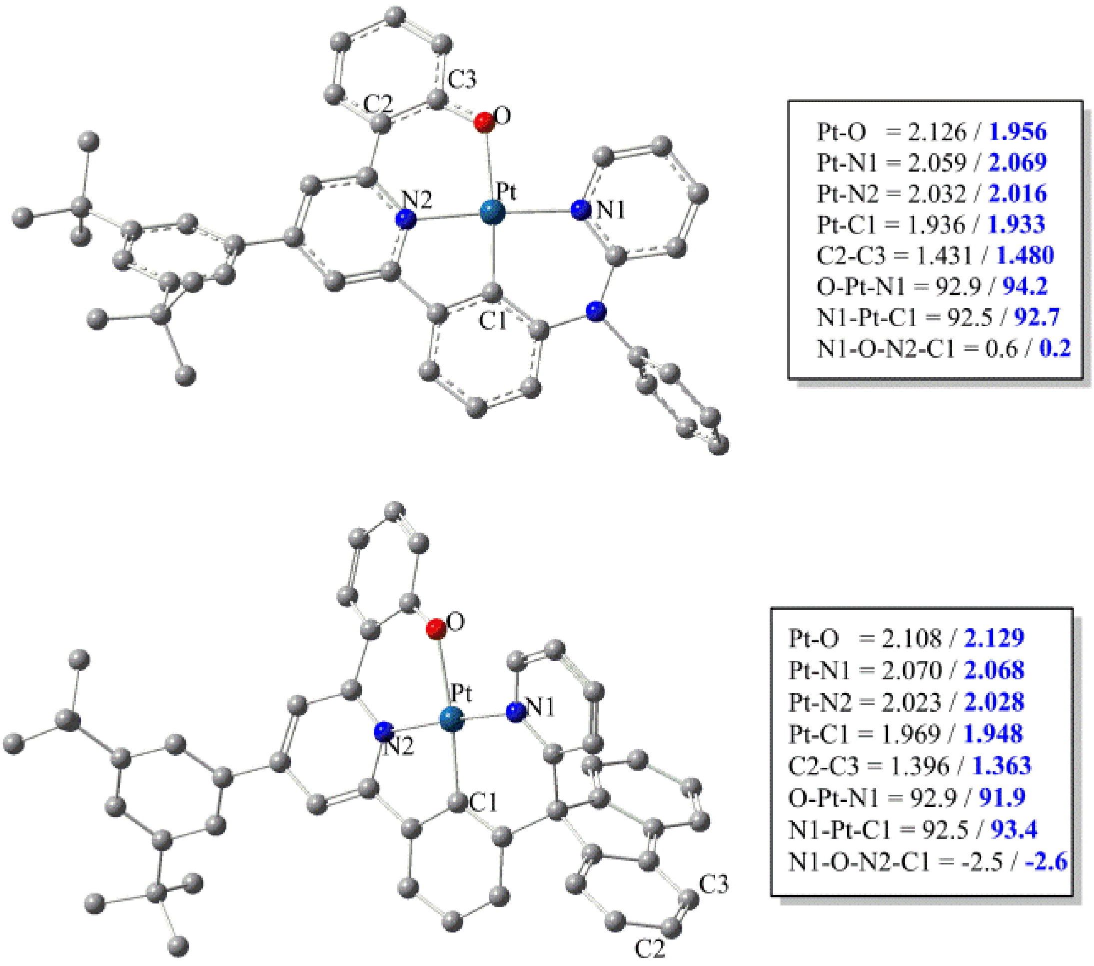


Fig. S21. Cyclic voltammogram of **L6** in DMF at 298 K.

(K) DFT calculations



Pt-O = 2.126 / **1.956**
Pt-N1 = 2.059 / **2.069**
Pt-N2 = 2.032 / **2.016**
Pt-C1 = 1.936 / **1.933**
C2-C3 = 1.431 / **1.480**
O-Pt-N1 = 92.9 / **94.2**
N1-Pt-C1 = 92.5 / **92.7**
N1-O-N2-C1 = 0.6 / **0.2**

Pt-O = 2.108 / **2.129**
Pt-N1 = 2.070 / **2.068**
Pt-N2 = 2.023 / **2.028**
Pt-C1 = 1.969 / **1.948**
C2-C3 = 1.396 / **1.363**
O-Pt-N1 = 92.9 / **91.9**
N1-Pt-C1 = 92.5 / **93.4**
N1-O-N2-C1 = -2.5 / **-2.6**

Fig. S22. Comparison of the changes of key geometrical parameters of triplet state (T_1) with respect to the corresponding ground state (S_0) of **5** and **6**. (Ground states in black, triplet states in blue).

(L) Fs-time-resolved fluorescence of 5 and 6

Briefly, the fs-TRF measurement was performed based on a commercial Ti:Sapphire regenerative amplifier laser system (800 nm, 40 fs, 1 kHz, and 3.5 mJ/pulse). The 350 nm pump pulse was generated from TOPAS-C pumped by the 800 nm fundamental laser pulse. The fs-TRF was measured by using the Kerr-gate technique.[S1] A Kerr device composed of Kerr medium (a quartz plate of 1 mm thick) equipped within a crossed polarizer pair was driven by the 800 nm laser to function as an ultrafast optical shutter to sample transient fluorescence spectra at various selected pump/probe delays. The temporal delay of probe to pump pulse was controlled by an optical delay line. To eliminate the effect of rotational diffusion, the polarization direction of pump laser was set at the magic angle in relative to that of the first polarizer in the Kerr device. The fs-TRF signals were collected by a monochromator and detected with a liquid nitrogen cooled CCD detector. The instrument response function (IRF) of fs-TRF is wavelength-dependent. The IRF varies from ~0.3 to ~1 ps as detection wavelength changes from 600 to 280 nm. The measurement was done at room temperature and atmospheric pressure with the samples of ~15 ml flowed in a cell with 0.5 mm path length. The samples were monitored by UV-Vis absorption and revealed no degradation after the fs-TRF measurement.

S1. (*a*) W.-M. Kwok, C. Ma and D. L. Phillips, *J. Am. Chem. Soc.*, 2006, **128**, 11894; (*b*) W.-M. Kwok, C. Ma and D. L. Phillips, *J. Am. Chem. Soc.*, 2008, **130**, 5131; (*c*) P. Matousek, M. Towrie, C. Ma, W.-M. Kwok, D. Phillips, W. T. Toner and A. W. Parker, *J. Raman Spectrosc.*, 2001, **32**, 983; (*d*) P. Matousek, M. Towrie, A. Stanley and A. W. Parker, *Appl. Spectrosc.*, 1999, **53**, 1485.

(M) OLED data

Table S3. Detailed performances of OLEDs with **1**–**4**.

	V (V)		PE (lm W^{-1})			CE (cd A^{-1})			EQE (%)		
Complex (C)	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}
1 (2 wt%)	2.9	3.5	90.8	88.9	74.3	78.0	82.3	82.5	22.8	24.1	24.2
1 (6 wt%)	3.0	3.8	24.9	24.8	20.5	20.6	23.6	25.5	10.9	12.6	13.4
1 (12 wt%)	3.4	4.7	6.1	6.5	6.7	5.4	7.1	9.9	5.3	7.0	9.8
2 (4 wt%)	3.3	3.9	52.5	58.2	53.6	50.0	61.1	67.1	13.7	16.7	18.3
2 (8 wt%)	3.3	3.9	39.4	51.3	59.3	37.5	54.0	74.0	10.2	14.7	20.1
2 (16 wt%)	3.2	4.0	48.6	45.2	39.7	41.7	46.4	51.0	16.6	18.5	20.2
3 (2 wt%)	3.1	3.7	97.5	92.7	75.8	90.0	92.7	88.9	22.8	23.6	22.5
3 (10 wt%)	2.9	3.5	89.3	92.1	81.7	82.5	86.9	89.4	22.7	23.6	24.6
3 (15 wt%)	2.9	3.5	56.8	60.2	65.2	52.5	56.2	72.3	15.7	15.9	21.7
4 (4 wt%)	3.4	4.0	81.4	77.3	63.3	81.3	83.5	81.0	21.4	22.0	21.4
4 (10 wt%)	3.2	3.7	84.7	85.8	82.1	80.0	88.5	98.0	21.6	23.8	26.3
4 (16 wt%)	3.2	3.7	91.0	83.6	74.5	84.0	84.8	88.5	23.5	23.7	24.8

Table S4. Detailed performances of OLEDs with **5**–**6**.

	V (V)		PE (lm W^{-1})			CE (cd A^{-1})			EQE (%)		
Complex (C)	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}	at 1 cd m^{-2}	at 10 cd m^{-2}	at 100 cd m^{-2}
5 (2 wt%)[h]	3.0	3.6	102.9	100.0	83.4	95.0	95.9	96.4	25.3	25.6	25.7
5 (10 wt%)[h]	3.2	3.9	105.4	95.9	81.4	94.0	96.9	99.8	24.4	25.3	26.0
5 (16 wt%)[h]	3.2	3.8	101.0	95.4	79.6	90.0	96.4	96.5	23.9	25.7	25.6
5 (30 wt%)[h]	3.1	3.8	80.7	78.2	66.8	72.0	76.6	81.2	21.5	22.8	24.4
6 (2 wt%)[h]	3.1	3.7	99.5	92.8	75.5	91.7	90.1	87.2	24.8	24.5	23.6
6 (6 wt%)[h]	3.0	3.6	106.6	105.6	89.2	100.0	100.3	100.9	26.6	26.6	26.8
6 (10 wt%)[h]	2.9	3.5	103.7	106.3	92.8	88.9	98.3	100.8	23.5	26.0	26.7
6 (30 wt%)[h]	3.1	3.6	95.6	92.2	75.1	85.3	90.0	87.1	22.6	23.8	23.2
5 (10 wt%)[i]	2.5	2.9	116.6	115.6	96.5	89.1	94.1	91.9	23.8	25.2	24.6
6 (10 wt%)[i]	2.5	2.8	125.9	119.9	107.5	96.3	97.8	97.8	25.7	26.1	26.0

(1). EL properties of OLEDs with 1–4

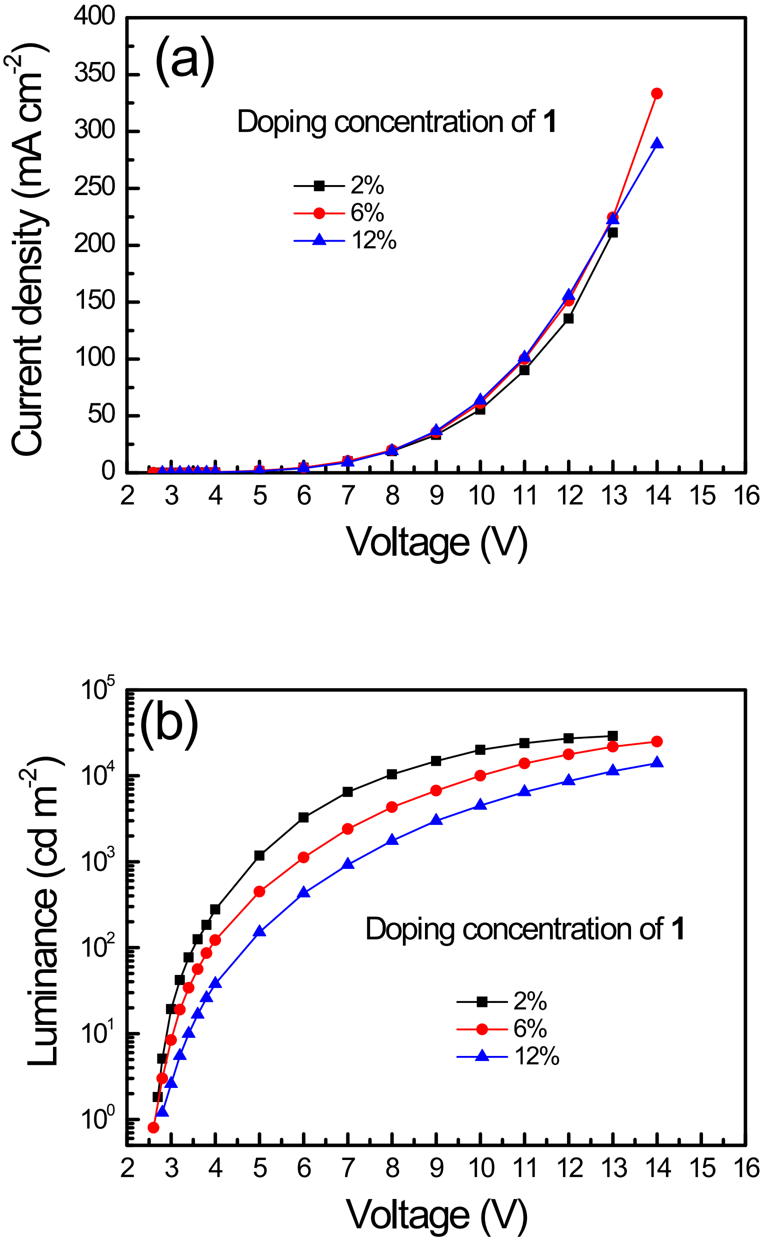


Fig. S23. (a) Current density-voltage and (b) luminance-voltage characteristics of OLEDs based on **1** with different concentrations.

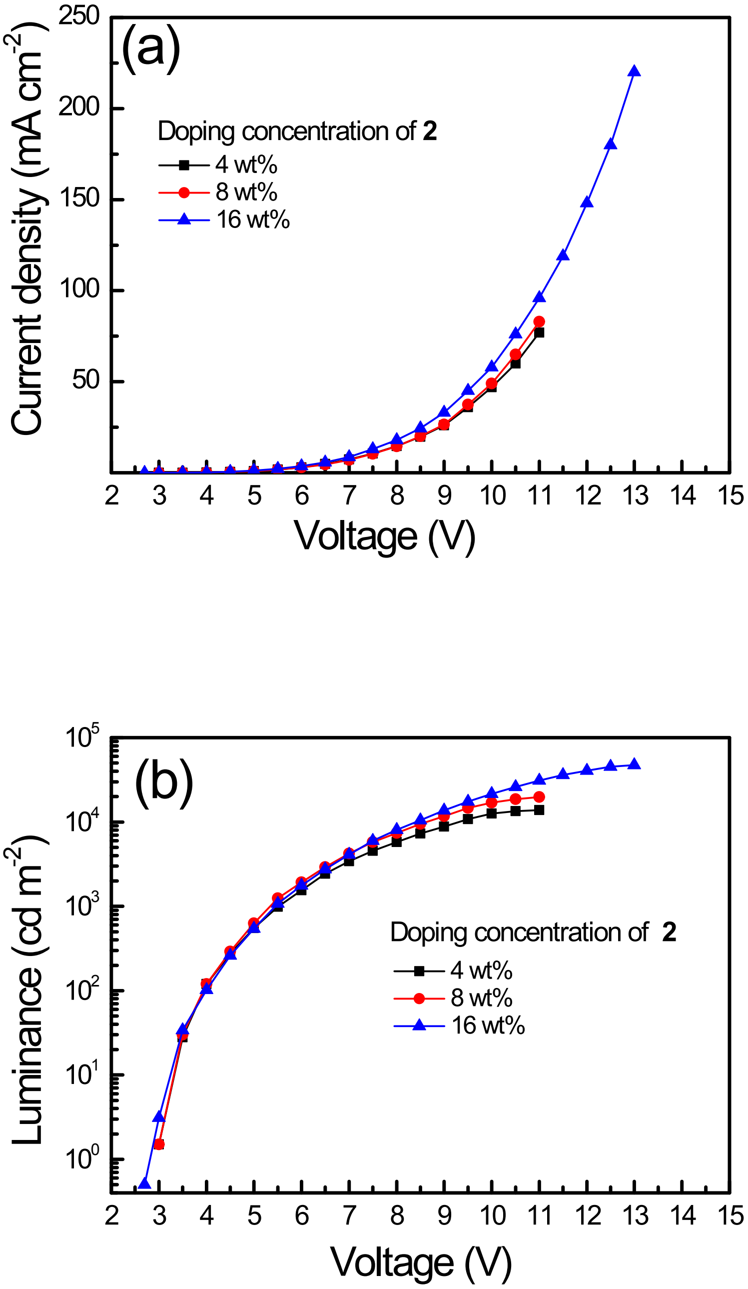


Fig. S24. (a) Current density-voltage and (b) luminance-voltage characteristics of OLEDs based on **2** with different concentrations.

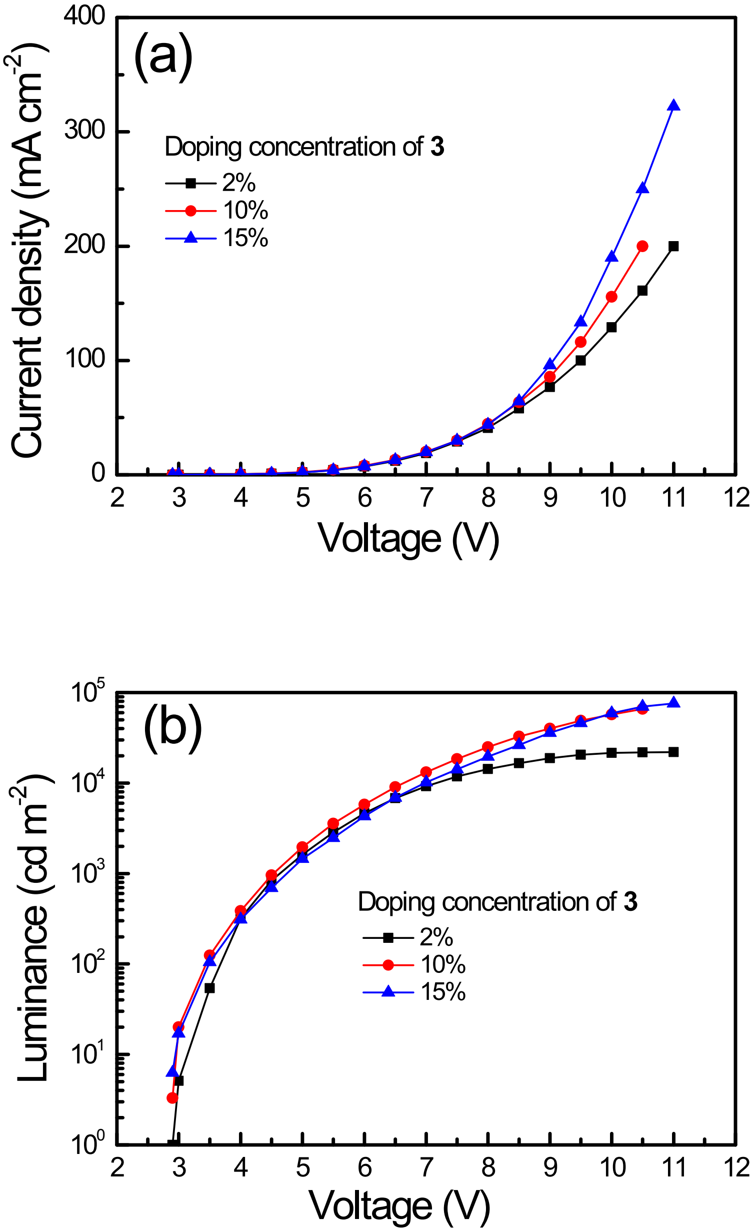


Fig. S25. (a) Current density-voltage and (b) luminance-voltage characteristics of OLEDs based on **3** with different concentrations.

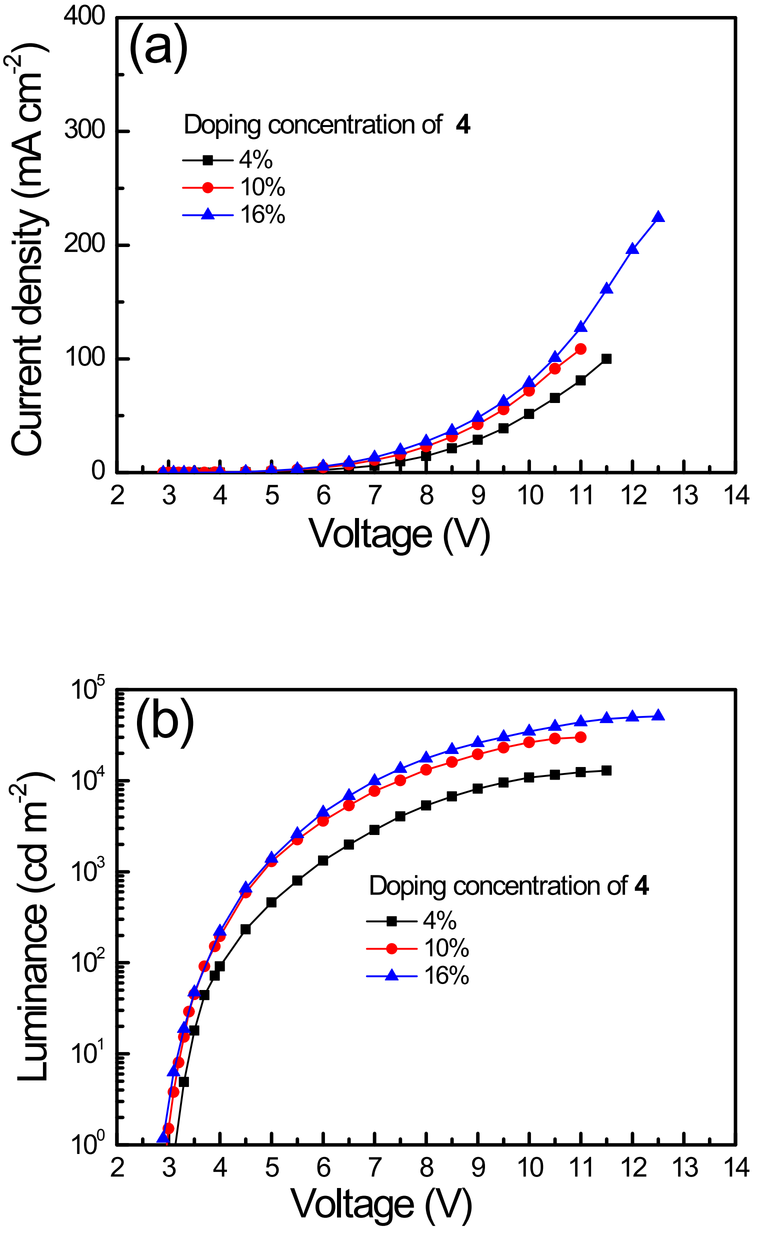


Fig. S26. (a) Current density-voltage and (b) luminance-voltage characteristics of OLEDs based on **4** with different concentrations.

(2). EL properties of TmPyPb-OLEDs with 5 or 6

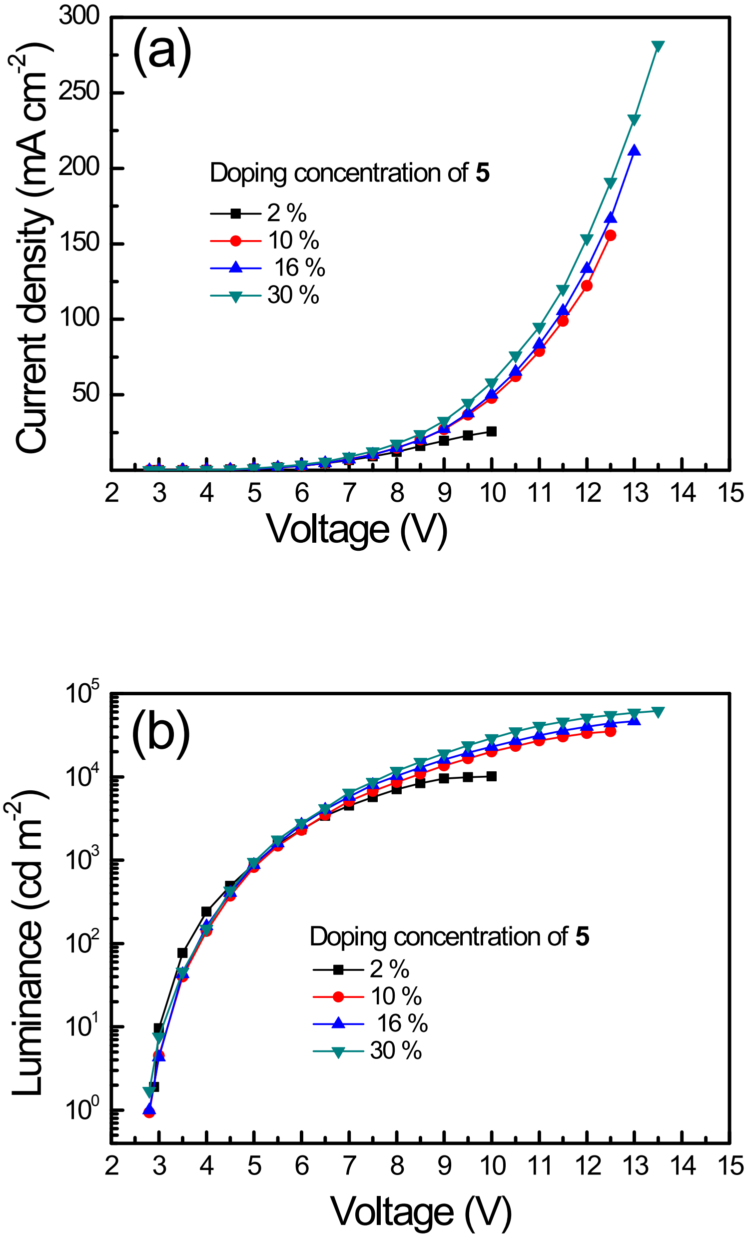


Fig. S27. (a) Current density-voltage and (b) luminance-voltage characteristics of TmPyPb-OLEDs based on **5** with different concentrations.

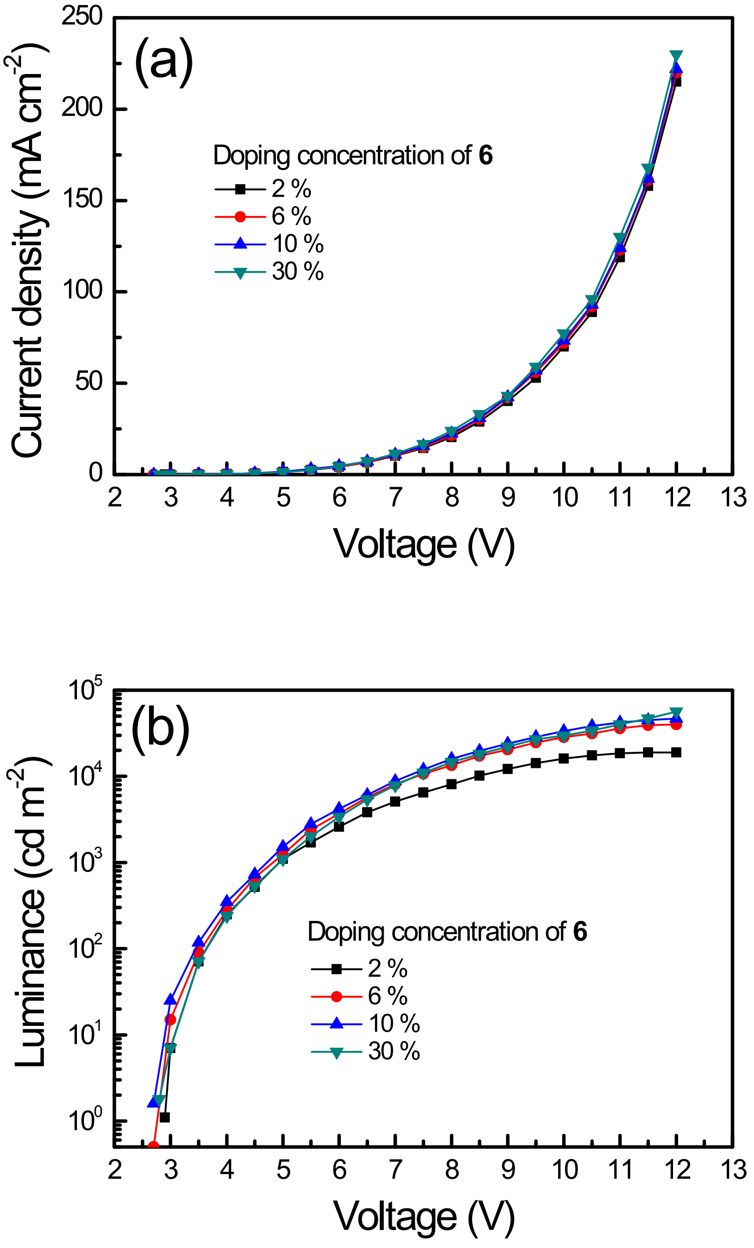
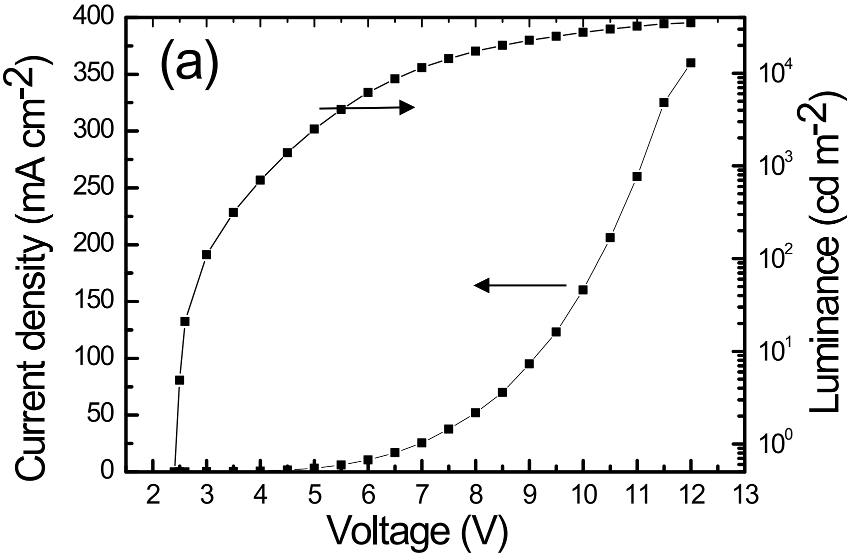


Fig. S28. (a) Current density-voltage and (b) luminance-voltage characteristics of TmPyPb-OLEDs based on **6** with different concentrations.

(3). EL properties of Tm3PyBPZ-OLEDs with 5 or 6



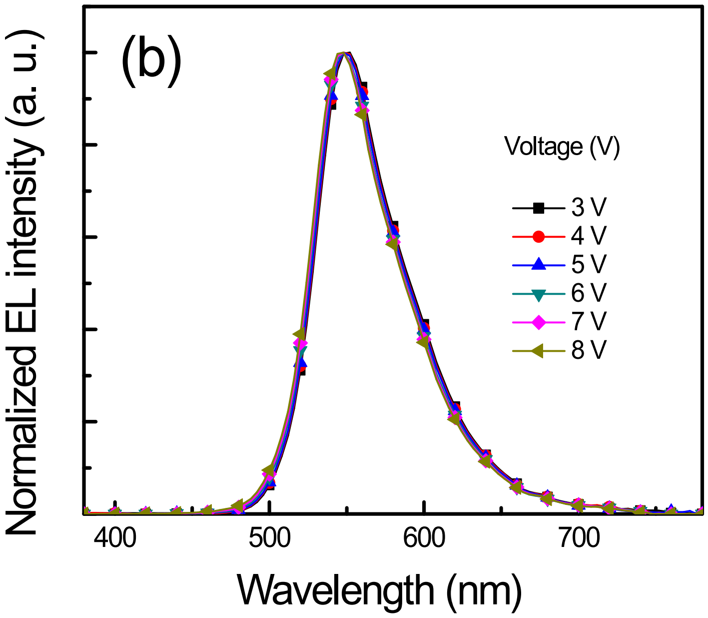
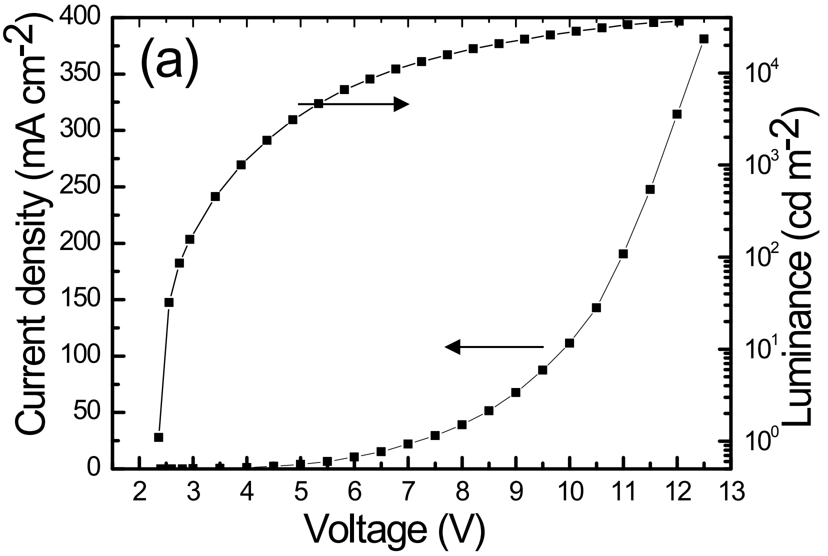


Fig. S29. (a) Current density-luminance-voltage characteristics and (b) normalized EL spectra of the Tm3PyBPZ-OLED with 10 wt% **5**.



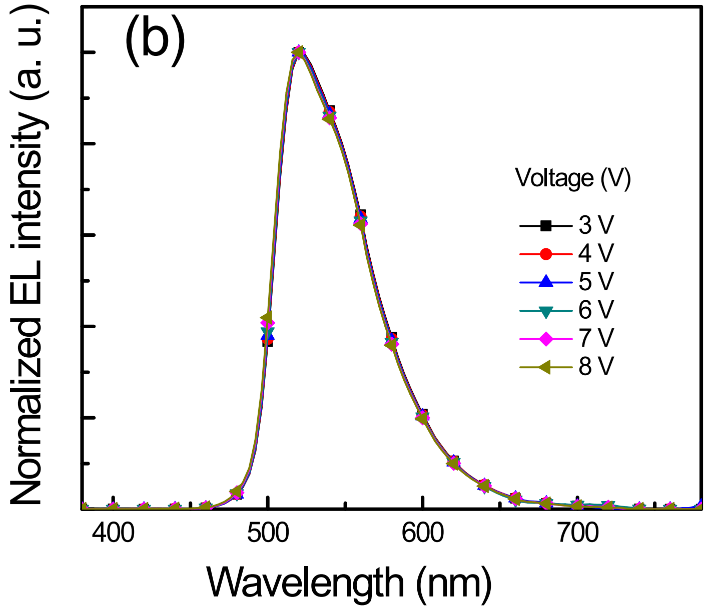


Fig. S30. (a) Current density-luminance-voltage characteristics and (b) normalized EL spectra of the Tm3PyBPZ-OLED with 10 wt% **6**.

(4). EL properties of the white OLEDs with 7

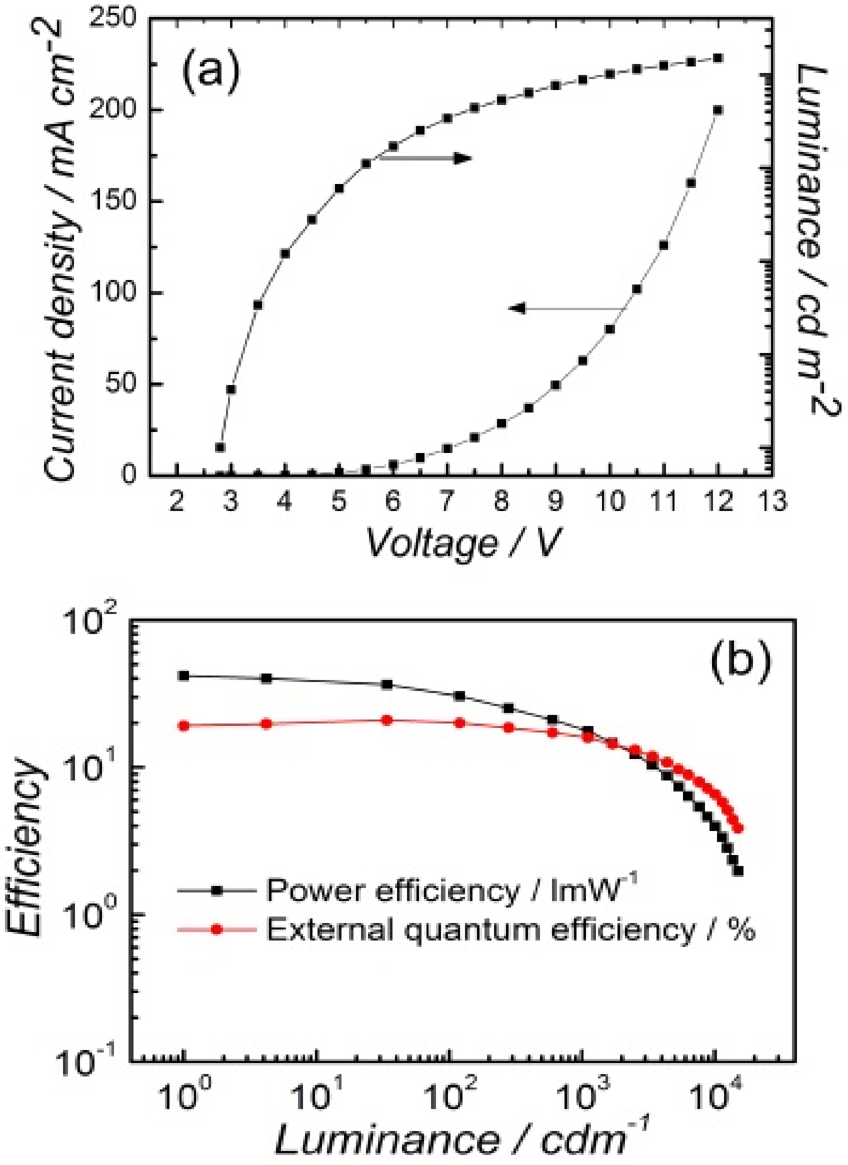


Fig. S31. (a) Current density-luminance-voltage characteristics and (b) power efficiency-external quantum efficiency-luminance curves spectra of the white OLED based on **7** with TCTA as host and TmPyPb as ETL.

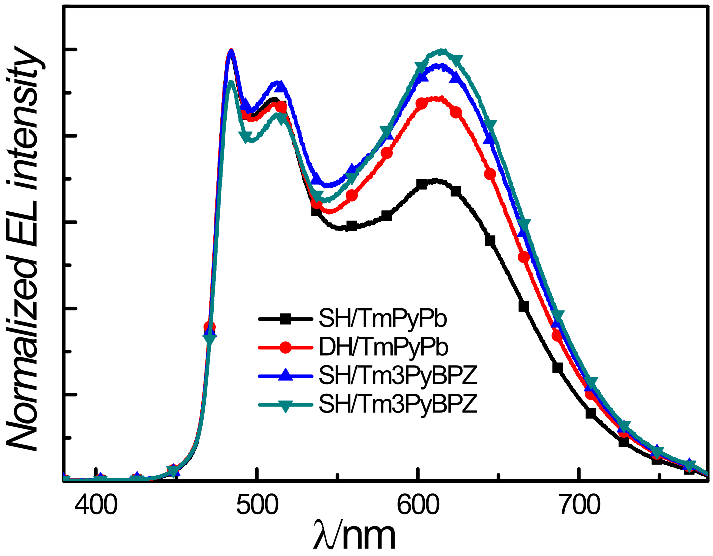


Fig. S32. Normalized EL spectra of OLEDs with **7** having different device structures.

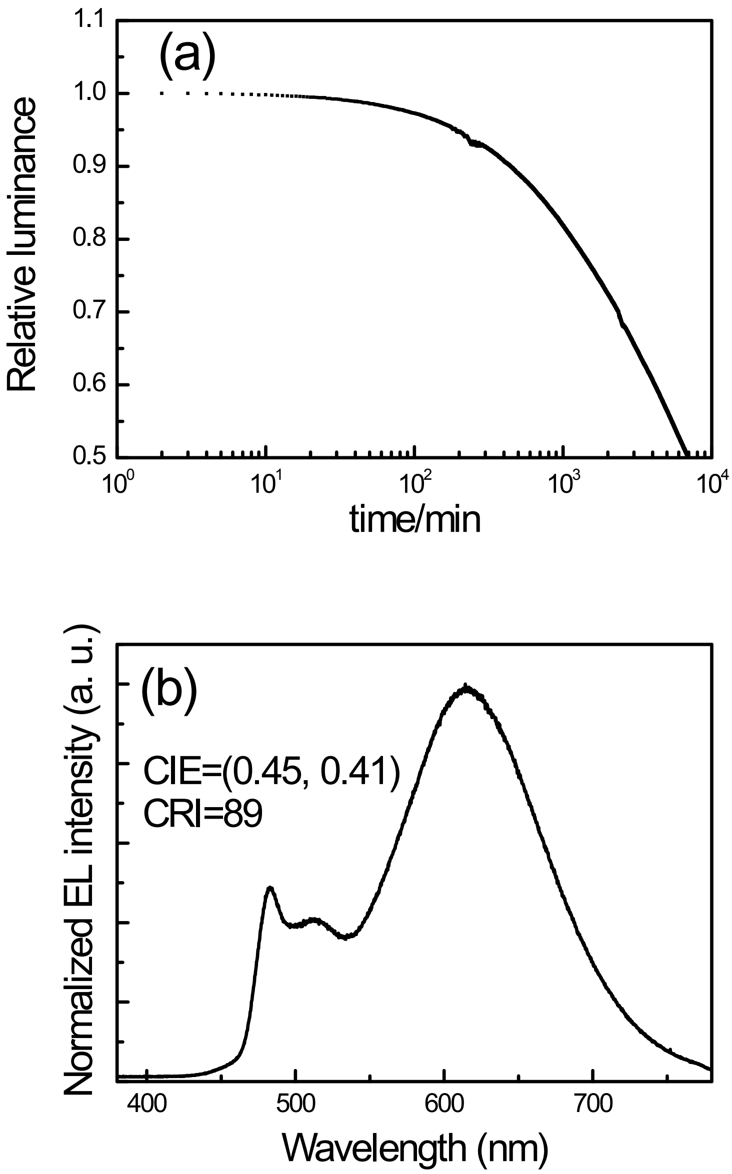


Fig. S33. (a) Operation lifetime of the white OLED with **7** operated at a constant current density of 1.3 mA cm^{-2} with an initial luminance of 1630 cd m^{-2}. The dots represent experimental data that measured every minute; (b) EL spectrum of the white OLED at 10 V.

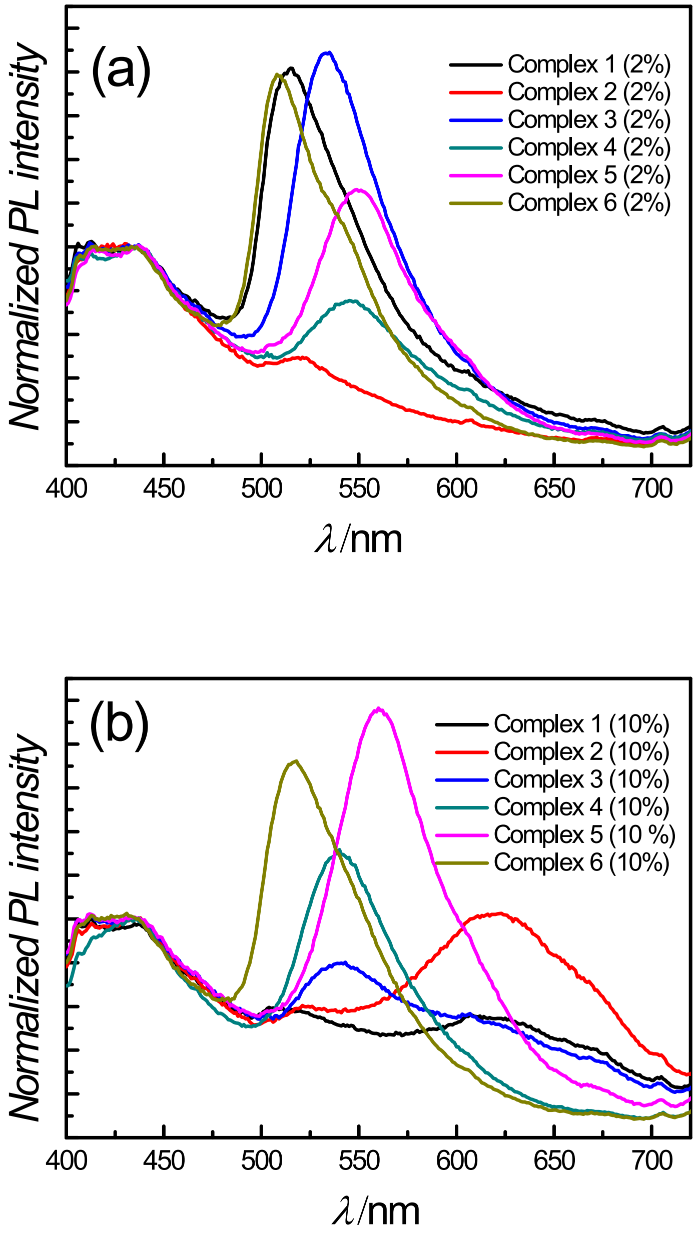


Fig. S34. PL spectra of **1**–**6** in TCTA with concentrations of (a) 2 wt% and (b) 10 wt%. The excitation wavelength for all samples was 370 nm.