

## Platinum Complexes of 4-Hydroxy-1,5-naphthyridines as Emitting Dyes

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4-Hydroxy-1,5-naphthyridines (HNt) are derivatives of 8-hydroxyquinolines, yet possess a wider HOMO and LUMO band gap than the latter. The cyclometalated complex of platinum(II) with Nt exists in a square planar geometry, and has a high tendency to aggregate in condensed media. Such a phenomenon was verified by examining its photo-luminescence spectra in different concentrations. In a dilute solution, it exhibits a yellow phosphorescence centered at 530~555 nm, yet red-shifted to ~660 nm in a concentrated solution or in the solid state. This series of compounds can be used as emitting dyes in light-emitting diodes (LED). The LED devices with a configuration ITO/NPB/dye (6%) in CBP/BCP/AlQ<sub>3</sub> or TPBI/LiF/Al displayed a yellow to red color, where NPB, CBP, BCP, AlQ<sub>3</sub> and TPBI denote 4,4'-bis[N-(1-naphthyl),N-phenylamino]biphenyl, 4,4'-bis(carbazol-9-yl)biphenyl, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, tris(8-hydroxyquinolinato)aluminium, and 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl-1H-benzimidazole), respectively. The maximal light intensity exceeds  $2.6 \times 10^4$  cd/m<sup>2</sup> with an external quantum efficiency up to 5.8%.

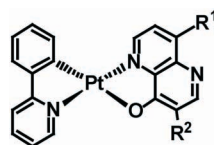
**Keywords:** Platinum complexes; 4-Hydroxy-1,5-naphthyridines; Phosphorescence; OLED; Broad band emission.

## INTRODUCTION

The high triplet emission of platinum complexes has been used effectively in the fabrication of light-emitting diodes (LEDs).<sup>1,2</sup> The platinum complexes form a square planar geometry around the metallic center, that renders them easier to stack together in condense media. Upon photo-excitation, the emissions of both the monomer and the aggregate display together forming a broad band spectrum. Forrest and Thompson *et al.* have taken advantage of the broad band emission of platinum complexes for the fabrication of white light LED devices. These type of devices may find useful applications on illumination.

Platinum complexes coordinated to either a phenylpyridine (PPy) ligand or a 8-hydroxyquinoline (HQ) ligand have been known for some time.<sup>3,4</sup> The emission from complex Pt(PPy)Q (679 nm) displayed a red color due to the quinoline ligand. By replacing the C(4) atom of HQ with a nitrogen, the HOMO-LUMO band gap of 4-hydroxy-1,5-naphthyridine (HNt) is substantially increased. The emission maximum of Pt(PPy)Nt (**1a**) (555 nm, Fig. 1) is blue-

shifted 124 nm with respect to that of Pt(PPy)Q. The emission colors of these materials, i.e., **1a**~**d**, are variable depending on the doping concentrations. Their characteristics are investigated in this report.



- 1a)** R<sup>1</sup> = R<sup>2</sup> = H  
**b)** R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H  
**c)** R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  
**d)** R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>

## EXPERIMENTAL

## Instrumentation

Absorption spectra were taken on a Hewlett-Packard 8453 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. Infrared spectra were taken on a Perkin-Elmer L118-F000 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX400 super-conducting FT NMR spectrometers. The signals of tetramethylsilane at δ 0.00 ppm was used as an internal standard for both <sup>1</sup>H and <sup>13</sup>C NMR spectra. Mass

Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

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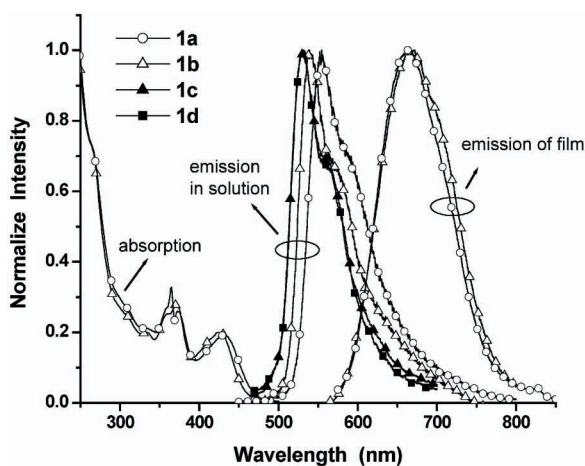


Fig. 1. Absorption (left), phosphorescence spectra in degassed dichloromethane solutions (center) and as solid films (right) of complexes **1a** (—○—), **1b** (—△—), **1c** (—▲—), and **1d** (—■—).

spectra were taken on a Jeol JMS-700 double focusing spectrometer with a resolution of 8000 (5% valley definition). For fast atom bombardment (FAB) spectra, the source accelerating voltage was operated at 10 kV with a Xe gun and using 3-nitrobenzyl alcohol as the matrix. Microanalyses were completed on a Perkin-Elmer 2400 elemental analyzer. Melting points of compounds were uncorrected. X-Ray diffraction analyses were done on a Bruker AXS X8APEX spectrometer. Differential scanning calorimetry was done on a Perkin-Elmer DCS-7 instrument. Cyclic voltammetry measurements were carried out on a BAS 100B electrochemical analyzer equipped with a conventional three-electrodes system, *i.e.*, glassy carbon, platinum wire and Ag/AgCl as working, counter, and reference electrodes respectively. Degassed dichloromethane solution with 0.1 M tetra-*n*-butylammonium hexafluorophosphate was used as electrolyte.  $E_{ox}$ ,  $E_{red}$  data were measured with reference to ferrocene (Fc) internal standard which was calibrated to +350 mV against to a Ag/AgCl reference electrode. Measurements were taken at a scan rate of 100  $mV \cdot s^{-1}$ .

#### Device Fabrication

A glass coated with indium-tin oxide (ITO) with sheet resistance of  $<50 \Omega/\square$  was used as substrate. The substrate was pre-patterned by photolithography to give an effective device size of  $3.14 \text{ mm}^2$ . Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. Thermal evaporation of organic materials was carried out using

ULVAC cryogenics at a chamber pressure of  $10^{-6}$  Torr. Typical devices were configured as ITO/NPB (40 nm)/dye (6%) doped in CBP (10 nm)/BCP(6 nm)/AlQ<sub>3</sub> or TPBI (40 nm)/LiF (1 nm)/Al (150 nm), where NPB, CBP, BCP, AlQ<sub>3</sub> and TPBI are 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl, 4,4'-bis(carbazol-9-yl)biphenyl, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, tris(8-hydroxyquinolato)-aluminium, and 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl-1*H*-benzimidazole), respectively. After the deposition of the electron-transporting layer, a thin film of LiF was followed. The devices were then capped with a thick layer of aluminum, which was served as cathode. Current voltage and light intensity measurements were done on a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with a Newport 818-ST silicon photodiode, respectively. All measurements were completed under ambient conditions.

#### (4-Hydroxy-1,5-naphthyridine)(2-phenylpyridine)platinum (**1a**)

To a two-necked round bottom flask (250 mL) containing sodium carbonate (4.35 g) in 2-ethoxyethanol (100 mL) were added compound **6a** (1.20 g, 8.22 mmol) and [(2-phenylpyridyl)PtCl]<sub>2</sub> (3.00 g, 3.90 mmol) under a nitrogen atmosphere. It was heated at 90 °C for 16 h, while the solution turned reddish brown. To the cooled solution was added distilled water, which was then extracted with dichloromethane. The combined organic solution was washed with brine, dried over anhydrous magnesium sulfate and dried *in vacuo*. The product was purified by a silica gel column chromatography eluted with dichloromethane/methanol (50/1) to yield complex **1a** (2.36 g) in 61% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.27 (d,  $J = 5$  Hz, 1H), 9.16 (d,  $J = 5$  Hz, 1H), 8.48-8.45 (m, 2H), 7.89-7.87 (m, 1H), 7.69-7.64 (m, 2H), 7.54 (t,  $J = 8$  Hz, 2H), 7.28-7.14 (m, 3H), 6.82 (d,  $J = 5$  Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, H-decoupled)  $\delta$  173.6, 166.7, 154.1, 149.3, 146.9, 146.8, 146.7, 146.1, 139.8, 138.9, 137.3, 131.5, 129.3, 124.2, 123.8, 123.6, 121.8, 118.3, 112.2. IR (KBr) 3046, 1583, 1553, 1494, 1384, 1262, 1196, 1196, 916, 823, 753, 720  $cm^{-1}$ . HRMS calcd for C<sub>19</sub>H<sub>13</sub>N<sub>3</sub>O<sup>+</sup>: 494.0785 (M+H)<sup>+</sup>, found: 495.0782.

#### (4-Hydroxy-8-methyl-1,5-naphthyridine)(2-phenylpyridine)platinum (**1b**)

The procedure was similar to that for the preparation of **1a**. Complex **1b** was obtained as yellow solids in 74% yield. Calcd for C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>O<sup>+</sup>: C, 47.25; H, 2.97; N, 8.26%.

Found: C, 47.04; H, 2.98; N, 8.06%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.26 (d,  $J = 5$  Hz, 1H), 8.99 (d,  $J = 5$  Hz, 1H), 8.44 (d,  $J = 5$  Hz, 1H), 7.87 (t,  $J = 8$  Hz, 1H), 7.67 (d,  $J = 8$  Hz, 1H), 7.56-7.49 (m, 3H), 7.25-7.13 (m, 3H), 6.81 (d,  $J = 5$  Hz, 1H), 2.75 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, H-decoupled)  $\delta$  173.8, 166.6, 152.8, 150.9, 149.2, 146.1, 145.7, 138.7, 137.7, 131.4, 129.2, 124.3, 123.7, 123.4, 121.7, 118.2, 112.0, 17.6 (two carbon nuclei could not be observed or resolved). IR (KBr) 3040, 1561, 1509, 1476, 1402, 1240, 934, 838, 823, 753, 728, 683, 628  $\text{cm}^{-1}$ . HRMS calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_4\text{Pt}$ : 509.0943 ( $\text{M}+\text{H}$ ) $^+$ , found: 509.0932.

**(3-Carboethoxy-4-hydroxy-8-methyl-1,5-naphthyridine)(2-phenylpyridine)platinum (1c)**

To a two-necked round bottom flask (250 mL) containing sodium carbonate (2.37 g) in ethanol (120 mL) were added compound **4b** (1.65 g, 7.11 mmol) and [(2-phenylpyridyl)PtCl] $_2$  (1.00 g, 1.30 mmol) under a nitrogen atmosphere. It was heated to reflux for 16 h, while the solution turned to reddish brown. The solution was cooled to ambient temperature, to it was then added distilled water and was extracted a few times with dichloromethane. The combined organic solution was washed with brine, dried over anhydrous magnesium sulfate and dried *in vacuo*. The product was purified by a silica gel column chromatography eluted with dichloromethane/methanol (50/1) to yield complex **1c** as orange solids (1.82 g, 3.14 mmol) in 44% yield, mp 254 °C. Calcd for  $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_3\text{Pt}$ : C, 48.08; H, 3.71; N, 6.73%. Found: C, 48.29; H, 3.50; N, 6.52%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.29 (br, 1H), 9.01 (br, 1H), 8.87 (d,  $J = 5.4$  Hz, 1H), 7.79-7.75 (m, 1H), 7.51 (d,  $J = 8.0$  Hz, 1H), 7.40-7.35 (m, 3H), 7.17-7.07 (m, 3H), 4.45 (q,  $J = 7.1$  Hz, 2H), 2.73 (s, 3H), 1.50 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.92, 166.51, 165.84, 155.09, 150.89, 149.50, 147.00, 146.83, 146.66, 146.11, 138.66, 137.12, 131.25, 129.29, 125.82, 123.75, 123.65, 121.68, 118.00, 113.49, 60.24, 17.94, 14.42. IR (KBr) 3046, 2979, 1678, 1561, 1517, 1241, 1199, 1166  $\text{cm}^{-1}$ . MS (FAB)  $m/z$  581.11 ( $\text{M}+\text{H}$ ) $^+$ .

**(3-Ethoxyethoxycarbonyl-4-hydroxy-8-methyl-1,5-naphthyridine)(2-phenylpyridine)platinum (1d)**

To a two-necked round bottom flask (250 mL) containing sodium carbonate (4.35 g) in 2-ethoxyethanol (100 mL) were added compound **4b** (3.04 g, 13.1 mmol) and [(2-phenylpyridyl)PtCl] $_2$  (1.84 g, 2.39 mmol) under a nitrogen atmosphere. It was heated at 80~100 °C for 16 h, while the solution turned reddish brown. To the cooled so-

lution was added distilled water, which was then extracted with dichloromethane. The combined organic solution was washed with brine, dried over anhydrous magnesium sulfate and dried *in vacuo*. The product was purified by a silica gel column chromatography eluted with dichloromethane/methanol (50/1) to yield complex **1d** as orange solids (3.69 g, 5.85 mmol) in 45% yield, mp 193 °C. Calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_4\text{Pt}$ : C, 47.59; H, 3.30; N, 7.24%. Found: C, 47.74; H, 3.12; N, 7.11%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.27 (br, 1H), 8.99 (br, 1H), 8.88 (d,  $J = 5.4$  Hz, 1H), 7.76-7.74 (m, 1H), 7.48 (d,  $J = 8.0$  Hz, 1H), 7.39-7.32 (m, 3H), 7.16-7.07 (m, 3H), 4.53 (t,  $J = 5.0$  Hz, 2H), 3.87 (t,  $J = 5$  Hz, 2H), 3.65 (q,  $J = 7.0$  Hz, 2H), 2.71 (s, 3H), 1.26 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.08, 166.25, 165.84, 165.33, 154.87, 150.68, 149.66, 146.69, 146.65, 146.01, 138.57, 131.16, 129.18, 125.90, 123.64, 123.53, 121.87, 117.85, 113.16, 68.63, 66.68, 63.43, 17.95, 15.31, 14.40. IR (KBr) 3047, 2974, 1684, 1561, 1516, 1242, 1199, 1163  $\text{cm}^{-1}$ . MS (FAB)  $m/z$  625.14 ( $\text{M}+\text{H}$ ) $^+$ .

**Diethyl (3-pyridyl)aminomethylenemalonate (3a)**

To a three-necked round bottom flask fitted with a condenser and a magnetic stirrer was charged with 3-aminopyridine (**2a**) (3.45 g, 37 mmol) and diethyl ethoxymethylenemalonate (8.87 g, 41 mmol). The mixture was stirred and heated to 150 °C, at which temperature ethanol was evolved. It was then stirred for a few hours until gas evolution was ceased. The product was cooled and purified by silica gel column chromatography eluted with ethyl acetate/hexane (1:4) to afford **3a** as white solids (9.57 g, 98% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.0 (d,  $J = 13$  Hz, 1H), 8.50 (s, 1H), 8.48 (d,  $J = 13$  Hz, 1H), 8.42-8.40 (m, 1H), 7.49-7.46 (m, 1H), 7.34-7.26 (m, 1H), 4.32 (q,  $J = 7$  Hz, 2H), 4.26 (q,  $J = 7$  Hz, 2H), 1.38 (t,  $J = 7$  Hz, 3H), 1.33 (t,  $J = 7$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , H-decoupled)  $\delta$  169.0, 165.4, 151.5, 146.1, 139.9, 136.0, 124.2, 123.7, 95.6, 60.7, 60.4, 14.5, 14.3; IR (KBr) 3448, 3254, 3188, 2986, 2900, 1682, 1638, 1605, 1576, 1458, 1409, 1343, 1257, 1100, 1019, 982, 923, 794, 698, 621, 573  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  264 ( $\text{M}^+$ , 96%), 218 (100), 175 (12), 162 (83), 145 (50) and 118 (20).

**Diethyl (4-methyl-3-pyridyl)aminomethylenemalonate (3b)**

The procedure was similar to that for the preparation of **3a**, starting from 3-amino-4-methylpyridine (**2b**). Compound **3b** was obtained as white powder in 98% yield. Calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 60.64; H, 6.18; N, 10.10%.

Found: C, 60.32; H, 6.42; N, 9.81%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.05 (d,  $J = 13$  Hz, 1H), 8.53 (s, 1H), 8.52 (d,  $J = 13$  Hz, 1H), 8.31 (d,  $J = 5$  Hz, 1H), 7.16 (d,  $J = 5$  Hz, 1H), 4.33 (q,  $J = 7$  Hz, 2H), 4.25 (q,  $J = 7$  Hz, 2H), 2.38 (s, 3H), 1.39 (t,  $J = 7$  Hz, 3H), 1.31 (t,  $J = 7$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , H-decoupled)  $\delta$  169.3, 165.3, 152.3, 146.2, 138.2, 136.4, 135.4, 125.6, 95.2, 60.7, 60.3, 17.0, 14.5, 14.4; IR (KBr) 3151, 3062, 2988, 1697, 1603, 1472, 1413, 1384, 1262, 1109, 1005, 919, 827, 602  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  278.1270 ( $\text{M}^+$ ,  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4$  requires 278.1267, 78%), 232 (100), 176 (12), 159 (43), 131 (23) and 119 (23).

### 3-Carboethoxy-4-hydroxy-1,5-naphthyridine (4a)

To a round bottom flask fitted with a condenser were added diphenyl ether (15 mL) and compound **3a** (1.00 g, 3.8 mmol). The solution was heated to reflux (258 °C) for 1 h, while the solution turned brownish and in which precipitates formed. It was filtered and the solids were washed repeatedly with hexane. Compound **4a** was collected as dark brown solids (0.67 g, 82%); IR (KBr) 3594, 3520, 3070, 2988, 2738, 1686, 1620, 1579, 1517, 1458, 1362, 1306, 1166, 1023, 908, 868, 812, 761, 750, 687, 588, 532  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  218 ( $\text{M}^+$ , 52%), 173 (62) and 146 (100).

### 3-Carboethoxy-4-hydroxy-8-methyl-1,5-naphthyridine (4b)

The procedure was similar to that for the preparation of **4a**, starting from 3-amino-4-methylpyridine (**3b**). Compound **4b** was obtained as dark brown solids in 74% yield. Calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ : C, 62.06; H, 5.21; N, 12.06%. Found: C, 62.17; H, 5.16; N, 12.02%. IR (KBr) 3614, 3143, 2981, 1690, 1623, 1576, 1531, 1476, 1435, 1292, 1229, 1159, 1026, 956, 919, 846, 816, 757, 687, 624  $\text{cm}^{-1}$ ;  $m/z$  (EI) 232.0844 ( $\text{M}^+$ ,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$  requires 232.0848).

### 3-Carboxy-4-hydroxy-1,5-naphthyridine (5a)

In a round bottom flask compound **4a** (3.0 g, 13 mmol) was heated with 10% sodium hydroxide (5.0 mL) to reflux for 16 h. Distilled water was added to the mixture, then the solution was filtered. The filtrate was acidified to pH 3, while solids were precipitated. The solids were filtered off, washed with water, and dried at 110 °C. Compound **5a** was collected (1.83 g, 70%) as brownish power; IR (KBr) 3675, 3647, 3091, 3036, 2969, 1624, 1578, 1555, 1482, 1456, 1428, 1391, 1338, 1312, 1207, 895, 820, 764, 737, 648, 584  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  190 ( $\text{M}^+$ , 6%), 172 (7), 146 (100) and 118 (45).

### 3-Carboxy-4-hydroxy-8-methyl-1,5-naphthyridine (5b)

The procedure was similar to that for the preparation

of **5a**, starting from 3-amino-4-methylpyridine (**4b**). Compound **5b** was obtained as brownish powder in 68% yield. Calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3$ : C, 58.82; H, 3.95; N, 13.72%. Found: C, 58.36; H, 4.00; N, 13.16%. IR (KBr) 3610, 3099, 3025, 1738, 1572, 1524, 1450, 1301, 1270, 1200, 1152, 846, 801, 761, 709  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  204.0534 ( $\text{M}^+$ ,  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3$  requires 204.0535).

### 4-Hydroxy-1,5-naphthyridine (6a)

In a round bottom flask compound **5a** (20.0 g, 105 mmol) was heated in mineral oil (500 mL) to 330 °C. Carbon dioxide gas evolved vigorously during the heating. Heating and stirring was continued for 30 min, then it was cooled and the precipitates were filtered off. It was washed with hexane to remove mineral oil and then recrystallized from 95% ethanol. Compound **6a**<sup>1</sup> was collected as yellow power (10.8 g, 70%); IR (KBr) 3651, 3062, 2915, 1623, 1576, 1502, 1192, 1085, 812, 787  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (d,  $J = 4$  Hz, 1H), 8.07 (d,  $J = 8$  Hz, 1H), 8.04 (d,  $J = 7$  Hz, 1H), 7.70 (dd,  $J = 7$  & 8 Hz, 1H), 6.52 (d,  $J = 7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , H-decoupled)  $\delta$  179.8, 148.6, 141.9, 141.2, 138.4, 129.2, 128.3; MS (EI)  $m/e$  146.0483 ( $\text{M}^+$ ,  $\text{C}_8\text{H}_6\text{N}_2\text{O}$  requires 146.0480, 100%) and 118 (40).

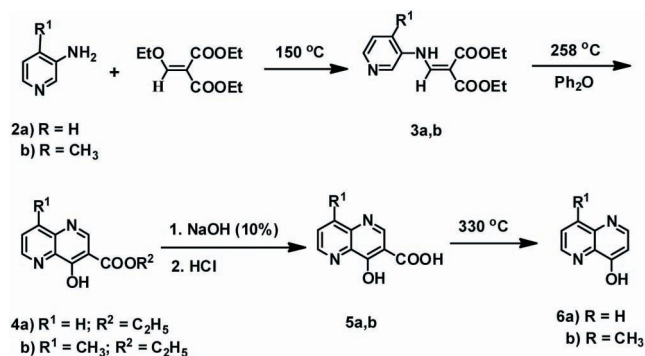
### 4-Hydroxy-8-methyl-1,5-naphthyridine (6b)

The procedure was similar to that for the preparation of **1a**, starting from 3-amino-4-methylpyridine (**5b**). Compound **6b** was obtained as brownish powder in 69% yield.  $\text{C}_9\text{H}_8\text{N}_2\text{O}$ : C, 67.49; H, 5.03; N, 17.49%. Found: C, 67.19; H, 5.03; N, 17.20%. IR (KBr) 3129, 3084, 2811, 1922, 1572, 1424, 1402, 1306, 1247, 1207, 1166, 1085, 1026, 964, 816, 672  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (d,  $J = 4$  Hz, 1H), 7.99 (d,  $J = 7$  Hz, 1H), 7.56 (d,  $J = 4$  Hz, 1H), 6.51 (d,  $J = 7$  Hz, 1H), 2.61 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , H-decoupled)  $\delta$  178.4, 146.4, 140.0, 139.4, 138.1, 136.4, 127.3, 111.0, 15.6; MS (EI)  $m/z$  160.0634 ( $\text{M}^+$ ,  $\text{C}_9\text{H}_8\text{N}_2\text{O}$  requires 160.0637, 100%), 132 (38).

## RESULTS AND DISCUSSION

### Syntheses and physical properties

The preparation of the HNt ligands were accomplished starting from 3-aminopyridine (**2a,b**) according to a published procedure (Scheme I).<sup>5</sup> Condensations of **2a,b** with diethyl 2-(ethoxymethylene)malonate were achieved by a thermal reaction at 150 °C. Heating the purified product **3a,b** at 250 °C induced a ring cyclization to yield the fused 1,5-naphthyridine skeleton of **4a** and **4b**. The car-

**Scheme 1** The synthesis of 4-hydroxy-1,5-naphthyridine and its 8-methyl derivative

boxylate substituents at C(3) were extruded by first converting **4a,b** to the acids **5a,b**, followed by thermal extrusions of CO<sub>2</sub>. The solubility of both structures **4a,b** and **5a,b** was very low in organic solvents, therefore their structures were confirmed mainly by elemental analyses. Thermal fragmentations of **5a,b** were accomplished by heating at 330 °C, while **6a,b** were obtained in *ca.* 70% yield.

The platinum complexes **1a** and **1b** were prepared in 61% and 74% yields from **6a** and **6b**, respectively, by heating with [(2-phenylpyridyl)PtCl]<sub>2</sub> in 2-ethoxyethanol. Complex **1d** was collected through the same procedure, however a nucleophilic substitution at the carboxylate moiety happened simultaneously accompanying the reaction. The ethoxyl group was replaced by a 2-ethoxyethoxyl group via solvation, so that **1d** was produced in 45% yield as an unexpected side product. Nevertheless this compound was considered also as a usable material, therefore its chemistry was explored along with other compounds. The ethoxycarbonyl derivative **1c** can be made by simply changing the solvent to ethanol. After heated to reflux in ethanol for 16 hours, compounds **1c** can be isolated in 44% yield. All products **1a~1d** were purified to form orange sol-

ids, which were stable under ambient condition and can be sublimed in vacuum chamber to condensed into thin films during OLED fabrications.

### Absorption and Emission Spectra

The absorption spectra of **1a,b** and the emission spectra of **1a~1d** are shown in Figure 1. A major absorption maximum of **1a** appeared at 247 nm, which was assigned to the <sup>1</sup>(π-π\*) transition of the ligands. The broad absorption region at longer wavelengths of 350~460 nm are derived from charge transfer transitions associated with the metal.<sup>6-8</sup> Photoexcitation of **1a~1d** in deoxygenated dichloromethane at 426 nm yielded emission bands at λ<sub>max</sub> 530~555 nm. Mild blue shifts were observed in the emissions of **1b** and **1c**, compared with those of **1a**. Adding an electron-withdrawing carboxylate group to the phenolic ring has an effect of reducing the potential level of HOMO, so that the band gap is broadened. The emission spectra of **1a,b** in the solid state were distinctively different. The maxima of emission was red shifted about 110 nm, from 555 nm to 666 nm, along with a significantly band broadening. The full width at half maximum (fwhm) expanded from *ca.* 70 nm to 100 nm. This low energy broad emission is believed to have derived from aggregates in the solid state.

### Redox Potentials

Their oxidation potentials were measured by cyclic voltammetry (CV) in degassed dichloromethane. Compounds **1a~1d** showed reversible anodic waves at 0.46~0.57 V separated by 320 mV in an oxidative sweep (Table 1). In a reductive sweep of **1a~1d**, quasi-irreversible waves appeared at -1.47~-1.61 V with peaks separated by *ca.* 110 mV. The band gaps, estimated by the difference between *E*<sub>ox</sub> and *E*<sub>red</sub>, were defined as the energy difference between HOMO and LUMO. The band gaps values can also be estimated by the 0-0 absorption energies in their UV spectra, which were measured at the position of interception be-

Table 1. Absorption energy, oxidation and reductive potentials of compounds **1a~1d**

	λ <sub>max</sub> <sup>a</sup> (nm)	Φ <sup>b</sup>	λ <sub>0-0</sub> <sup>c</sup> (nm)	<i>E</i> <sub>0-0</sub> <sup>c</sup> (eV)	<i>E</i> <sub>ox</sub> <sup>d</sup> (V)	<i>E</i> <sub>red</sub> <sup>d</sup> (V)	Band gap <sup>e</sup> (eV)	HOMO <sup>f</sup> (eV)	LUMO <sup>g</sup> (eV)
<b>1a</b>	553, 666 <sup>h</sup>	0.07	475	2.61	0.46	-1.47	1.93	-4.86	-2.25
<b>1b</b>	540, 663 <sup>h</sup>	0.06	485	2.56	0.53	-1.59	2.12	-4.93	-2.37
<b>1c</b>	532	0.10	466	2.66	0.57	-1.61	2.18	-4.97	-2.31
<b>1d</b>	532	0.11	467	2.65	0.54	-1.60	2.14	-4.94	-2.29

<sup>a</sup> Emission wavelength in dichloromethane, unless otherwise notified. <sup>b</sup> Quantum yield in dichloromethane. <sup>c</sup> Taken at the crossing point of absorption and emission spectra. <sup>d</sup> Fc/Fc<sup>+</sup> at 0.35 V against Ag/AgCl as internal reference. <sup>e</sup> Gap between *E*<sub>ox</sub> and *E*<sub>red</sub>. <sup>f</sup> Calculated as -(*E*<sub>ox</sub> + 4.40). <sup>g</sup> Calculated as (HOMO + λ<sub>0-0</sub>). <sup>h</sup> Emission wavelength of solid films.

Table 2. Working parameters of OLED devices. Typical configuration is ITO/NPB (40 nm)/dye (6%) doped in CBP (10 nm)/BCP (6 nm)/ETL (40 nm)/LiF (1 nm)/Al (150 nm), unless otherwise indicated. The parameters are quoted at 20 mA/cm<sup>2</sup> current density wherever applicable

Phosphorescent emitter	<b>1a</b>		<b>1b</b>			<b>1c</b>	<b>1d</b>
	A	B	A	B	B <sup>a</sup>	B	B
Wavelength maximum (nm)	652	646	548	550	668	532	532
Turn on voltage (V)	6.2	6.0	6.5	5.8	6.5	5.5	5.5
Maximum intensity (Cd/m <sup>2</sup> )	7450	15410	14620	26790	12060	7799	11118
Intensity (Cd/m <sup>2</sup> ) at 20 mA/cm <sup>2</sup>	620	660	3300	3680	650	1810	3220
Voltage (V) at 20 mA/cm <sup>2</sup>	10.5	8.7	13.7	11.5	9.7	11.3	11.1
External quantum efficiency (%)	2.5	2.4	5.3	5.8	5.2	4.0	5.2
Luminescence efficiency (Cd/A)	3.08	3.35	16.55	18.40	3.30	9.1	16.1
Power efficiency (lm/W)	1.0	1.2	3.8	5.0	1.1	2.5	4.6
FWHM (nm) <sup>b</sup>	182	174	76	76	142	160	60
CIE <sup>c</sup>	0.57, 0.43	0.56, 0.43	0.45, 0.54	0.45, 0.54	0.63, 0.37	0.45, 0.53	0.38, 0.58

NPB layer deposited in 30 nm. <sup>a</sup> 20% doped in CBP. <sup>b</sup> Full width at half maximum. <sup>c</sup> Commission Internationale de l'Éclairage 1931.

tween the absorption and emission spectra. The HOMO levels can be calculated according to the equation  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.40)$  eV.<sup>9</sup>

### Electrophosphorescence Devices

Two standard types of devices were made with the following configurations: (i) device A: ITO/NPB (40 nm)/dye (6%) doped in CBP (10 nm)/BCP (6 nm)/AlQ<sub>3</sub> (40 nm)/LiF (1 nm)/Al (150 nm), and (ii) device B: ITO/NPB (40 nm)/dye (6%) doped in CBP (10 nm)/BCP (6 nm)/TPBI (40 nm)/LiF (1 nm)/Al (150 nm). In these devices NPB worked as a hole transporter (HT), while BCP coupled with either AlQ<sub>3</sub> or TPBI as electron transporters (ET). All dyes were doped 6% in CBP host matrix as the emitting mediums, except in one case compound **1b** was doped in 20%. The two kinds of devices differed from each other on the ET materials used, *i.e.* AlQ<sub>3</sub> and TPBI, where the HOMO levels of AlQ<sub>3</sub> (5.7 eV) is higher than that of TPBI (6.2 eV). In device B, a higher energy barrier retards the migration of holes across the film boundary between the emitting layer and ET.<sup>10</sup> The parameters of all devices are listed in Table 2.

There is no clear distinction between the performance of devices type A and type B. In both type of devices, a layer of BCP served as an effective electron transporter as well as hole blocker, so that the influence of either AlQ<sub>3</sub> or TPBI was minimized. A noticeable feature was that the devices made of **1a** displayed a much broader spectrum than those made with **1b** (Fig. 2). The methyl substituent of **1b** increased the steric hindrance between adjacent molecules,

therefore reduced the degree of aggregation.

Plots of intensity versus voltage for the devices made with **1a**–**1d** are shown in Fig. 3. The turn-on voltages of the devices were at about 5.5–6.5 V, whilst at high voltages the

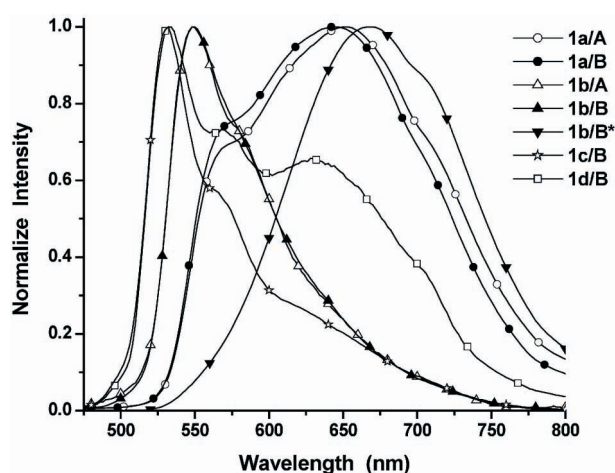


Fig. 2. Electrophosphorescence spectra of devices, using complexes **1a** (–○– and –●–), **1b** (–△–, –▲– and –▼–), **1c** (–☆–), and **1d** (–□–) as emitting materials. The devices were configured differently in type A (–○– and –△–) and type B (–●–, –▲– and –▼–). The short wavelength bands (~550 nm) were derived from the emissions of the monomers, while the long wavelength bands (~670 nm) were derived from aggregates. Excimer emission became predominant while the doping concentration of **1b** was increased to 20% (–▼–), whereas a highly intensive red color device was obtained.

maximal intensity can exceed 26000 Cd/m<sup>2</sup>. The external quantum efficiencies of devices **1b**~**1d** were in a range of 4~6% at 20 mA/cm<sup>2</sup> (Fig. 4 and Table 2). These values may be further improved, since the fabrication processes have not yet been extensively optimized. The EL spectra of these compounds exhibited broad band emissions due to molecular aggregation. The emission maxima can be adjusted by

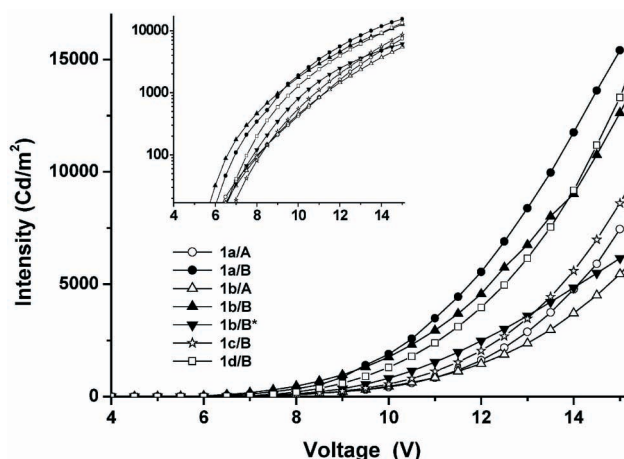


Fig. 3. Intensity vs. voltage plots for the devices made with complexes **1a** (—○— and —●—), **1b** (—△—, —▲—, and —▼—), **1c** (—☆—), and **1d** (—□—) as emitting materials. The devices were configured differently in type A (—○— and —△— in 6% doping), type B (—●— and —▲— in 6% doping) and B\* (—▼— in 20% doping). Turn-on voltages can be seen better in the inset.

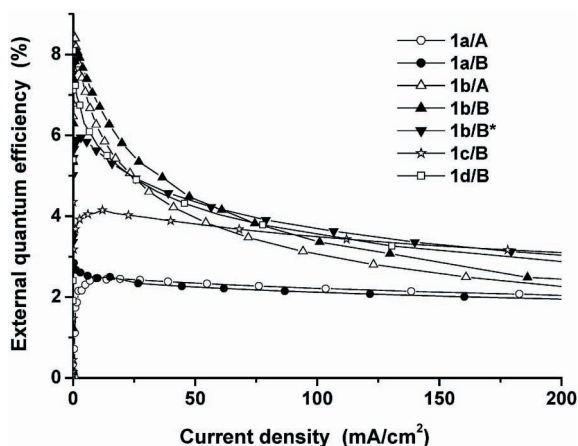


Fig. 4. External quantum efficiency of the devices made of complexes **1a** (—○— and —●—), **1b** (—△—, —▲—, and —▼—), **1c** (—□—), and **1d** (—☆—) as emitting materials. The devices were configured differently in type A (—○— and —△— in 6% doping), type B (—●— and —▲— in 6% doping) and B\* (—▼— in 20% doping).

changing the doping concentrations. For example, the emission maximum of **1b** was 550 nm at 6% doping, yet red-shifted to 660 nm at 20% doping (Fig. 2). The visual colors of the devices were distinctively different, i.e., the former was yellow and the latter red.

## CONCLUSIONS

The coordination compounds of 4-hydroxy-1,5-naphthyridine (HNt) with platinum ions have proven to be effective phosphorescent materials for the fabrication of LED devices. These complexes exhibited broad band emissions covering the region from 550 to 750 nm. The maximal external quantum yield can reach to a level of ~6% with the highest intensity exceeding 26000 Cd/m<sup>2</sup> at 18V, while doped 6% in CBP. The color of these devices can be tuned from yellow to red by adjusting the doping concentrations. At 20% doping in CBP, a highly intensive red color was produced.

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