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[Pt(topy)(Htopy)(ONO_2)] complex (Htopy = 2-*p*-tolylpyridine) and its analogs: ^{195}Pt NMR spectra and fabrication of light-emitting devices

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We report fast, high-yield syntheses of a series of [Pt(C^N)(HC^N)X] complexes, where HC^N is 2-phenylpyridine (Hppy) or 2-*p*-tolylpyridine (Htopy) and X^- is Cl^-, Br^-, I^-, ONO_2^-, NO_2^- or SCN^-. The structure of [Pt(topy)(Htopy)(ONO_2)] was analyzed by single-crystal X-ray diffraction. Substitution of Cl^- with Br^- or I^- in our complexes shifted the ^{195}Pt NMR peaks upfield in the order $Cl^- < Br^- < I^-$, but the magnitudes of their shifts were one-tenth those observed for non-cyclometalated platinum(II) complexes. As the two nitrato complexes showed strong emissions in acetonitrile solution – three to six times those of other complexes – they were used to fabricate OLEDs. Although their emissions were not particularly strong, devices fabricated with platinum(II) complexes containing bulky ligands emitted green light with a short lifetime (τ). Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: platinum(II); phenylpyridine; ^{195}Pt NMR; emission; OLEDs

Introduction

Recently, significant research has been conducted on the synthesis of cyclometalated iridium(III) complexes, with a focus on their use in the fabrication of organic light-emitting diodes (OLEDs).[1–5] Platinum(II) complexes show similar possibilities, but only a few reported mononuclear platinum(II) complexes are emissive at room temperature in solution, some of which have been used as luminescent centers in OLEDs.[6–13] The concept review article has been reported previously.[14] Platinum(II) species with aromatic chelating ligands such as bipyridine, phenanthroline, or 2-phenylpyridine emit in solution from excited states localized on the aromatic systems.

We studied ^{195}Pt NMR chemical shifts in previous work, and have reported the preparation and ^{195}Pt NMR chemical shifts of platinum(II) and platinum(IV) complexes with oligopeptides.[15–17] It is known that the ^{195}Pt NMR chemical shifts of platinum complexes depend on the particular set of coordinated ligand atoms; this is known as the additivity rule.[18–20] As far as we know, there have been few reports of ^{195}Pt NMR chemical shifts of cyclometalated platinum(II) complexes containing C^N,[21] and no reports of ^{195}Pt NMR chemical shifts of cyclometalated [Pt(C^N)(HC^N)Cl] complexes.

Several types of [Pt(C^N)(HC^N)Cl] complex, where C^N is a C,N-chelate ligand, have been investigated to elucidate their structures and photophysical properties.[22–24] A high-yield synthesis of [Pt(C^N)(HC^N)Cl] complexes was recently reported;[25] however, the synthesis had the disadvantage of being slow. We wished to develop a fast, high-yield synthesis of [Pt(C^N)(HC^N)X] complexes (Fig. 1), where X is Cl^-, Br^-, I^-, ONO_2^-, NO_2^- or SCN^-, and examine the relationship between their ^{195}Pt NMR chemical shifts and structures. To this end, we synthesized several platinum(II) complexes and used them to fabricate devices in order to investigate their electrophosphorescent properties. These were fabricated by spin coating rather than the more usual vapor deposition method in order to prevent decomposition of the Pt(II) complexes at high temperatures.

Experimental

Synthesis of [Pt(ppy)(Hppy)Cl] and [Pt(topy)(Htopy)Cl] Complexes

2-Phenylpyridine or 2-*p*-tolylpyridine (3.0 mmol) was added to a stirred solution of K_2PtCl_4 (0.415 g, 1.0 mmol) in ethylene glycol (10 ml). The solution was heated at 130 °C for 10 min and allowed to cool slowly to room temperature. The resulting yellow precipitate was collected by filtration and washed with water. The yellow solid was dissolved in chloroform and the solvent was evaporated to terminate the interaction of the complexes with ethylene glycol. Methanol was added to the residue and a yellow suspension was

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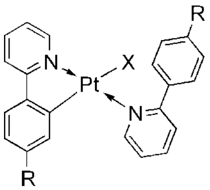

X	R = H	R = CH$_3$
Cl	**1a**	**2a**
ONO$_2$	**2a**	**2b**
NO$_2$	**3a**	**3b**
Br	**4a**	**4b**
I	**5a**	**5b**
SCN	**6a**	**6b**

Figure 1. [Pt(C^N)(HC^N)X] complexes.

formed. The resulting yellow precipitate was collected by filtration, washed with methanol, and dried to give a yellow solid.

[Pt(ppy)(Hppy)Cl] (**1a**) (yield: 75.0%). Anal. calcd for $C_{22}H_{17}N_2ClPt$: C, 48.94; H, 3.17; N, 5.19. Found: C, 48.97; H, 3.19; N, 5.19.
[Pt(topy)(Htopy)Cl] (**1b**) (yield: 86.6%). Anal. calcd for $C_{24}H_{21}N_2ClPt$: C, 50.75; H, 3.73; N, 4.93. Found: C, 50.46; H, 4.04; N, 4.78.

Synthesis of [Pt(ppy)(Hppy)(ONO$_2$)] and [Pt(topy)(Htopy)(ONO$_2$)] Complexes

To **1a** (1.46 mmol) or **1b** (1.46 mmol) in ethanol (50 ml) was added $AgNO_3$ (0.248 g, 1.46 mmol), and the reaction mixture was refluxed for 10 min. The resulting dark gray precipitate was removed from the yellow solution by filtration. The solution was evaporated and dried to give a light yellow solid.

[Pt(ppy)(Hppy)(ONO$_2$)] (**2a**) (yield: 93.6%). Anal. calcd for $C_{22}H_{17}N_3O_2Pt$: C, 48.00; H, 3.11; N, 7.63. Found: C, 47.95; H, 3.26; N, 7.62.
[Pt(topy)(Htopy)(ONO$_2$)] (**2b**) (yield: 93.3%). Anal. calcd for $C_{24}H_{21}N_3O_3Pt$: C, 48.49; H, 3.56; N, 7.07. Found: C, 48.75; H, 3.78; N, 6.67.

Synthesis of [Pt(ppy)(Hppy)X] and [Pt(topy)(Htopy)X] complexes where $X^- = Br^-, I^-, NO_2{}^-, SCN^-$

Compounds **2a** or **2b** (0.5 mmol) and $NaNO_2$ or KX ($X^- = Br^-, I^-, SCN^-$; 0.5 mmol) in ethanol (30 ml) were refluxed for 10 min, and the resulting yellow solution was evaporated. Water was added to the residue and a yellow precipitate was formed. The precipitate was collected by filtration, washed with water and methanol, and dried to give a yellow solid.

[Pt(ppy)(Hppy)(NO$_2$)] (**3a**) (yield: 96.6%). Anal. calcd for $C_{22}H_{17}N_3O_2Pt$: C, 48.00; H, 3.11; N, 7.63. Found: C, 47.95; H, 3.26; N, 7.62.
[Pt(topy)(Htopy)(NO$_2$)] (**3b**) (yield: 89.9%). Anal. calcd for $C_{24}H_{21}N_3O_2Pt$: C, 49.83; H, 3.66; N, 7.26. Found: C, 49.49; H, 3.74; N, 7.30.
[Pt(ppy)(Hppy)Br] (**4a**) (yield: 89.0%). Anal. calcd for $C_{22}H_{17}N_2BrPt$: C, 45.22; H, 2.93; N, 4.79. Found: C, 44.95; H, 3.00; N, 4.75.
[Pt(topy)(Htopy)Br] (**4b**) (yield: 93.4%). Anal. calcd for $C_{24}H_{21}N_2BrPt$: C, 47.07; H, 3.46; N, 4.57. Found: C, 47.05; H, 3.58; N, 4.78.
[Pt(ppy)(Hppy)I] (**5a**) (yield: 90.6%). Anal. calcd for $C_{22}H_{17}N_2IPt$: C, 41.85; H, 2.71; N, 4.44. Found: C, 41.39; H, 2.81; N, 4.41.
[Pt(topy)(Htopy)I] (**5b**) (yield: 86.1%). Anal. calcd for $C_{24}H_{21}N_2IPt$: C, 43.71; H, 3.21; N, 4.25. Found: C, 43.58; H, 3.29; N, 4.26.

Table 1. Crystallographic data for **2b**

	[Pt(topy)(Htopy)(ONO$_2$)] **2b**
Empirical formula	$C_{25}H_{23}Cl_2N_3O_3Pt$
Formula weight	679.45
Temperature	120 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 15.4525(3)$ Å $b = 11.4567(2)$ Å $c = 15.1794(3)$ Å $\beta = 116.4740(7)^\circ$
Volume	2405.48(8) Å^3
Z	4
Density (calculated)	1.876 mg/m^3
Absorption coefficient	6.088 mm^{-1}
$F(000)$	1320
Crystal size	$0.30 \times 0.27 \times 0.27$ mm^3
Theta range for data collection	3.00–30.50°.
Index ranges	$-22 \le h \le 19, -16 \le k \le 16, -21 \le l \le 21$
Reflections collected	29 369
Independent reflections	7288 [R(int) = 0.0588]
Completeness to theta = 30.03°	99.40%
Absorption correction	Numerical
Max. and min. transmission	0.4108 and 0.2646
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	7288/5/340
Goodness-of-fit on $F2$	1.069
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0256$, $wR(F^2) = 0.0620$
R indices (all data)	$R(F) = 0.0278$, $wR(F^2) = 0.0630$
Largest difference peak and hole	2.051 and −1.565 e.Å^{-3}

[Pt(ppy)(Hppy)(SCN)] (**6a**) (yield: 82.0%). Anal. calcd for $C_{23}H_{17}N_3SPt$: C, 49.11; H, 3.05; N, 7.47. Found: C, 49.27; H, 3.11; N, 7.63.
[Pt(topy)(Htopy)(SCN)] (**6b**) (yield: 70.2%). Anal. calcd for $C_{25}H_{21}N_3SPt$: C, 50.84; H, 3.58; N, 7.11. Found: C, 50.53; H, 3.61; N, 7.31.

Measurements

^{1}H and ^{195}Pt NMR spectra were recorded on a Jeol JNM-ECX-400 spectrometer. The sample concentration was 20 mg in 0.4 ml of $CDCl_3$ (diameter 5 mm NMR tube). ^{195}Pt NMR signals were referenced to $Na_2[PtCl_6]$ in D_2O (external standard, −1622 ppm for $K_2[PtCl_4]$ and −2998 ppm for K[Pt(DMSO)Cl$_3$] in D_2O). UV–vis absorption spectra were recorded on a Shimadzu UV-1200 UV–vis spectrophotometer. The concentration of the sample in acetonitrile was 10^{-5} M and the volume was 4 ml (10 mm path quartz cell). Luminescence spectra were recorded on a Jasco FP-6300 spectrofluorometer at room temperature. The concentration of the sample in acetonitrile was 10^{-5} M and the volume was 4 ml (10 mm path fluorescence rectangular cell). Elemental analyses were performed on a Yanaco CHN Corder MT-3. Block-shaped yellow crystals were grown from dichloromethane–diethyl ether–hexane solution. Diffraction data were collected on a Rigaku RAXIS-RAPID diffractometer. Measurement details are listed in Table 1. Crystallographic data were deposited in the

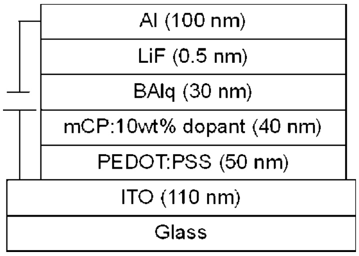

Figure 2. Multilayered device structure.

Cambridge Crystallographic Data Centre, deposition code CCDC 669 043. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request.

OLED Fabrication and Testing

The luminescence properties at short wavelengths and the strong luminescence intensity of **2a** and **2b** make them suitable candidates for emitters in high-efficiency OLEDs, which are general multilayered structures for electrophosphorescent devices (Fig. 2). In the devices fabricated in this study, indium-tin oxide (ITO)-coated glass served as an anode; 50 nm PEDOT : PSS [poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)] as a hole transport layer; a 40 nm layer containing mCP (3,5-dicarbazolylbenzene) and a dopant (10 wt% **2a** or **2b**) as the emitting layer; 30 nm BAlq [aluminum(III)bis(2-methyl-8-quinolinato)-4-phenylphenolate] as a hole blocking and electron transport layer; and 0.5 nm LiF/100 nm Al as a cathode. PEDOT : PSS and mCP were fabricated on ITO-coated glass via a spin coating method, and BAlq and LiF/Al were fabricated by vacuum deposition. When using a pure metal complex dopant that does not decompose at high temperatures, devices are usually fabricated by the vapor deposition method rather than the spin coating method. In this case, as the nitrato complexes **2a** and **2b** decomposed at 200 °C, mCP and the dopant (**2a** or **2b**), both in toluene, were spin-coated. A device was also fabricated using FIrpic [bis(4,6-difluorophenylpyridinato)(picolinato)iridium(III)][2,3] dopant (10 wt%) to allow comparison of emission properties.

Results and Discussion

Synthesis of [Pt(C^N)(HC^N)X] Complexes

When **1a** and [Pt(ppy)(L)Cl] complexes were synthesized from $K_2[PtCl_4]$ and the corresponding ligands, only *trans-N*,*N*-complexes were obtained, because the *cis-N*,*N*-complex isomerized to the *trans-N*,*N*-complex due to the strong kinetic trans effect of the σ-carbon ligand.[26,27] Craig *et al*. synthesized a **1a** complex using dichloro(1,5-cyclooctadiene)platinum(II) as a starting material in ethanol.[28] The reaction mixture was stirred for 48 h under a flow of nitrogen gas, and the product was obtained in 59% yield. Mdleleni *et al*. reacted $(Bu_4N)_2[PtCl_4]$ in CH_2Cl_2 with 2-phenylpyridine at 50 °C for 12 h to obtain a **1a** complex, albeit in low yield.[22] Recently, Cho *et al*. prepared a [Pt(C^N)(HC^N)Cl] complex in 77.3% yield by reacting $K_2[PtCl_4]$ with 2-arylpyridine in the presence of 3 : 1 2-ethoxyethanol/H_2O as solvent and a flow of nitrogen gas at 80 °C for 16 h.[25]

In this study, the reaction of $K_2[PtCl_4]$ with 2-phenylpyridine or 2-tolylpyridine in ethylene glycol at 130 °C for 10 min with no nitrogen gas flow produced [Pt(C^N)(HC^N)Cl] complexes with yields of 75.0% for **1a** and 86.6% for **1b**. This short synthesis, which was performed in air, had a high yield compared with the procedure of Cho *et al*. [Pt(C^N)(HC^N)(ONO_2)] complexes were obtained by adding $AgNO_3$ to [Pt(C^N)(HC^N)Cl] in ethanol solution. The reaction proceeded quantitatively and gave no by-products except for AgCl. [Pt(C^N)(HC^N)(ONO_2)] complexes are reactive in ethanol, and the addition of $NaNO_2$ or KX ($X^- = Br^-, I^-, SCN^-$) produced the corresponding [Pt(C^N)(HC^N)X] complexes with yields of greater than 70%.

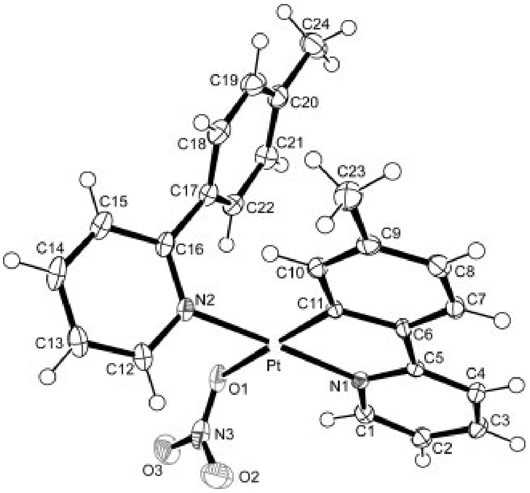

Figure 3. ORTEP drawing of **2b** at 50% probability level.

X-ray Crystal Structure of [Pt(topy)(Htopy)(ONO_2)] Complex

The molecular structure of the **2b** complex is shown in Fig. 3 and the geometric data are listed in Table 2. To our knowledge, X-ray crystal structures of cyclometalated platinum(II) complexes containing nitrato ligands have not yet been reported. The crystal contains one dichloromethane per unit complex. The Pt−O1 bond length of 2.1757(19) Å in **2b** is greater than those reported for [Pt(terpy)(ONO_2)][H(ONO_2)$_2$] [2.043(4) Å],[29] and *cis*- and *trans*-[Pt(pyridine)$_2$(ONO_2)$_2$] [2.010(6)−2.035(5) Å],[30] which demonstrates the strong trans effect of the coordinated C atom. The bond lengths Pt−C11 [1.977(2) Å], Pt−N1 [2.011(2) Å], and Pt−N2 [2.041(2) Å] in **2b** are similar to those of **1a** reported by Mdleleni *et al*.,[22] but the bond angles of 97.61(9)° for C11−Pt−N2 and 85.50(7)° for N2−Pt−O1 are, respectively, larger and smaller than those of **1a** [93.8(3)° for C11−Pt−N2 and 88.99(21)° for N2−Pt−Cl],[22] which shows that N2 is located fairly close to O1, compared with the distance between N2 and Cl in **1a**. The torsion angles of C11−Pt−N2−C12 and N2−C16−C17−C22 in **2b** are 106.94(18)° and 51.5(3)°, respectively, which are similar to those obtained for **1a** [95.5(6)° and 49.2(6)°, respectively].[22] This indicates that the monodentate 2-phenylpyridine ligand is almost perpendicular to the C11−Pt−N2 plane. Owing to steric hindrance between the two *p*-tolyl moieties, between H10 and H12, and between the monodentate 2-tolylpyridine and the nitrato group, rotation of monodentate 2-*p*-tolylpyridine around the Pt−N2 and C16−C17 bonds is fairly restricted. H10 is in the pyridine plane of monodentate 2-tolylpyridine, and H12 is in the nitrato plane. The O1−N3−O2, O1−N3−O3 and O2−N3−O3 bond angles of the nitrato moiety are 121.5(2)°, 117.7(2)° and 120.8(3)°, which means that O1, O2 and O3 are located in an equilateral triangle. The O1−N3, O2−N3 and O3−N3 bond lengths of the nitrato

Table 2. Selected bond lengths (Å) and angles (deg) and torsion angles (deg) of **2b**

[Pt(topy)(Htopy)(ONO$_2$)] **2b**			
Bond distance (Å)			
Pt–C11	1.977(2)	O1–N3	1.227(3)
Pt–N1	2.011(2)	O2–N3	1.248(3)
Pt–N2	2.041(2)	O3–N3	1.255(3)
Pt–O1	2.1757(19)		
Bond angle (deg)			
C11–Pt–N1	81.51(9)	N3–O1–Pt	119.61(16)
C11–Pt–N2	97.61(9)	O1–N3–O2	121.5(2)
N1–Pt–N2	177.17(8)	O1–N3–O3	117.7(2)
C11–Pt–O1	176.13(8)	O2–N3–O3	120.8(3)
N1–Pt–O1	95.49(8)		
N2–Pt–O1	85.50(7)		
Torsional angle (deg)			
C11–Pt–N2–C12	106.94(18)	N1–Pt–O1–N3	80.09(19)
N2–C16–C17–C22	51.5(3)	Pt–O1–N3–O2	5.3(3)

moiety are almost the same, at 1.227(3), 1.248 (3) and 1.255 (3) Å, respectively. This is in contrast to [Pt(terpy)(ONO$_2$)][H(ONO$_2$)$_2$], in which the bond length of O–N where O is coordinated to Pt is 1.318(7) Å, and the equivalent bond lengths in the absence of coordination to Pt are shorter.[29] It is also in contrast to *cis*- and *trans*-[Pt(pyridine)$_2$(ONO$_2$)$_2$], in which the average bond length of O1–N3 where O is coordinated to Pt is 1.311(11) Å,[30] which is longer than the equivalent O–N bonds without Pt coordination, and longer than those of the free ONO$_2{}^-$ ion. The torsional angles of Pt–O1–N3–O2 and N1–Pt–O1–N3 are 5.3(3) and 80.09(19)°, respectively, which indicates that the nitrato plane is perpendicular to the four-coordinated platinum plane (O1, N1, C11 and N2).

^{1}H NMR Spectra

The ^{1}H peaks were assigned on the basis of H–H COSY spectra of [Pt(C^N)(HC^N)X]. Selected chemical shifts and coupling constants of [Pt(C^N)(HC^N)X] are listed in Table 3, and the proton numbering followed that of the carbon atoms, as shown in Fig. 4. The chemical shifts and coupling constants of **1a** at 200 MHz have been reported previously.[22]

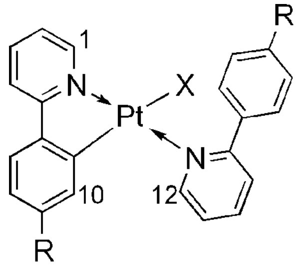

Figure 4. Proton numbering of [Pt(C^N)(HC^N)X].

The H1 peaks of **1a, 4a, 5a** and **1b, 4b, 5b** were shifted downfield by approximately 1 or 2 ppm compared with those of free Hppy or Htopy ligand. The order was X$^-$ = Cl$^-$ < Br$^-$ < I$^-$, reflecting the anisotropic effect of the Pt–X bond. The H10 peaks appeared at markedly higher fields than in the free ligands, which was thought to be due to the anisotropic effect of the monodentate 2-phenylpyridine or 2-*p*-tolylpyridine. The ^{1}H chemical shifts of monodentate 2-phenylpyridine and 2-*p*-tolylpyridine appeared at similar positions to those of the free ligands, except for those of H12, which is attached to a C atom adjacent to a N atom coordinated to Pt; these were shifted downfield compared with the signals of the free ligands. $^{3}J_{Pt-H}$ coupling constants were observed for the H1, H10 and H12 protons of [Pt(C^N)(HC^N)X], which showed that the atoms adjacent to these protons were coordinated to platinum.

^{195}Pt NMR spectra

The ^{195}Pt NMR chemical shifts of [Pt(C^N)(HC^N)X], measured in CDCl$_3$, are listed in Table 4. Chassot and von Zelewsky reported the ^{195}Pt NMR spectra of [Pt(ppy)$_2$] and its analog,[21] with chemical shifts of −3142 ppm for [Pt(ppy)$_2$], −3148 ppm for [Pt(thpy)$_2$] [thpy = 2-(2-thienyl)pyridinato] and −3224 ppm for [Pt(thpz)$_2$] [thpz = 1-(2-thienyl)pyrazolato]. All of the ^{195}Pt NMR peaks of

Table 3. ^{1}H NMR chemical shifts (δ ppm) and coupling constants (Hz) of [Pt(C^N)(HC^N)X] in CDCl$_3$

[Pt(ppy)(Hppy)X]	H1	H10	H12	[Pt(topy)(Htopy)X]	H1	H10	H12
Hppy δ (multi)	8.67 (d)	7.45 (t)	8.67 (d)	Htopy δ (multi)	8.65 (d)	7.25 (d)	8.65 (d)
J (Hz)	5.2	7.6	5.2	*J* (Hz)	4.8	8.0	4.8
1a	9.62	6.19	9.24 (dd)	**1b**	9.58 (dd)	6.00 (t)	9.23 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	4.0(18.2)	7.6(16.0)	6.0(20.0)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	6.0(13.2)	(23.6)	6.0(20.4)
2a	8.5	6.14	9.35 (dd)	**2b**	8.50 (dd)	5.95 (t)	9.30 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	5.2(16.4)	6.4(18.2)	4.8(17.2)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	4.8(10.2)	(22.4)	4.4(15.8)
3a	8.9	6.14	9.35 (dd)	**3b**	8.86 (dd)	5.92 (t)	9.33 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	5.2(18.0)	8.0(17.6)	5.2(18.8)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	5.6(16.4)	(16.8)	4.8(17.6)
4a	9.81	6.14	9.25 (dd)	**4b**	9.77 (dd)	5.95 (t)	9.23 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	5.6(16.6)	7.6(18.0)	4.8(19.8)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	4.8(16.6)	(23.6)	5.6(17.2)
5a	10.07	6.05	9.27 (dd)	**5b**	10.04 (dd)	5.86 (t)	9.26 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	6.0(17.4)	8.0(16.2)	6.0(19.8)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	6.0(17.2)	(24.8)	6.0(18.8)
6a	8.83	6.29	9.11 (dd)	**6b**	8.80 (dd)	6.10 (t)	9.08 (dd)
$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	6.0(23.2)	6.8(20.4)	4.4(22.8)	$^{3}J_{H-H}$ ($^{3}J_{Pt-H}$)	5.2(23.6)	(25.2)	4.4(18.8)

Table 4. ^{195}Pt NMR chemical shifts of [Pt(C^N)(HC^N)X] in $CDCl_3$

Complex	δ ppm	Complex	δ ppm	Complex	δ ppm
1a	−3201	**1b**	−3200	$\{PtCl[2,6\text{-}C_6H_3(CH_2NMe_2)_2]\}^a$	−3150
2a	−3224	**2b**	−3220	$\{PtBr[2,6\text{-}C_6H_3(CH_2NMe_2)_2]\}^a$	−3178
3a	−3214	**3b**	−3210	$\{PtI[2,6\text{-}C_6H_3(CH_2NMe_2)_2]\}^a$	−3212
4a	−3238	**4b**	−3237	$[Pt(ppy)_2]^b$	−3142
5a	−3289	**5b**	−3287	$[Pt(thpz)_2]^b$	−3224
6a	−3243	**6b**	−3242	$[Pt(thpy)_2]^b$	−3148

[a] Tessier and Rochon.[30] Solvent is benzene-d_6. External standard is $K_2[Pt(Cl)_4]$, $\delta_{Pt} = -1630$ ppm.
[b] Priqueler *et al.*[20] Solvent is $CHCl_3$. External standard is $[Pt(CN)_6]^{2-}$ in H_2O. These data were obtained by recalculating based on the ^{195}Pt NMR chemical shift of $[Pt(CN)_6]^{2-}$, −3863 ppm.

[Pt(C^N)(HC^N)X] also appeared at approximately −3200 ppm. Interestingly, the ^{195}Pt NMR peaks of most cyclometalated platinum(II) complexes appear over only a small region of the chemical shift range, although ^{195}Pt NMR chemical shifts are known to spread over 13 000 ppm.

Substitution of Cl^- with Br^- or I^- in our complexes shifted the ^{195}Pt NMR peaks upfield in the order $Cl^- < Br^- < I^-$. As the other elements coordinated to platinum(II) were the same or similar (i.e. C^N and N), the difference in chemical shift was attributed to the X ions. The chemical shift differences for **1a, 4a** and **5a** are $\delta(Br) - \delta(Cl) = 40$ ppm and $\delta(I) - \delta(Cl) = 90$ ppm. The chemical shift differences were one-tenth those of non-cyclometalated platinum(II) complexes, i.e. $\delta(Br) - \delta(Cl) = 250$ ppm and $\delta(I) - \delta(Cl) = 1000$ ppm.[15–18] This cannot be explained by replacement of the X ligands with solvent molecules, because the solvent used was inert $CDCl_3$. The presence of fold-overs is not likely, because ^{195}Pt NMR signals were referenced to $Na_2[PtCl_6]$ in D_2O {external standard, −1622 ppm for $K_2[PtCl_4]$ and −2998 ppm for $K[Pt(DMSO)Cl_3]$ in D_2O}. Similar small δ shifts due to halogen substitution have been reported previously.[31] Albrecht *et al.* reported ^{195}Pt NMR chemical shifts of [Pt(N^C^N)X] complexes in which N^C^N was a pincer ligand $[2,6\text{-}C_6H_3(CH_2NMe_2)_2]^-$ and X^- was Cl^-, Br^- or I^-; the chemical shifts were −3150 ppm for X = Cl, −3178 ppm for X = Br, and −3212 ppm for X = I.[31]

The ^{195}Pt NMR peaks of [Pt(C^N)(HC^N)X] were shifted upfield in the order $X^- = Cl^- < NO_2{}^- < ONO_2{}^- < Br^- < SCN^- < I^-$, which is different from the order observed for non-cyclometalated platinum(II) complexes ($X^- = ONO_2{}^- < Cl^- < NO_2{}^- < Br^- < SCN^- < I^-$).[19,20] As far as we know, the ^{195}Pt NMR chemical shifts of cyclometalated platinum(II) complexes containing $ONO_2{}^-$ ligands have not yet been reported. The order of the ^{195}Pt NMR chemical shifts of **2a** and **2b** is interesting, but the reason is not yet understood.

UV–vis Absorption and Emission Spectra

The UV–vis absorption spectra of [Pt(topy)(Htopy)X] are shown in Fig. 5, and the corresponding data are listed in Table 5. Four peaks – 250, 270 (sh), 320 and 350 nm – were observed in all UV–vis absorption spectra of [Pt(C^N)(HC^N)X]. The peak maxima in area 200 nm could be due to the coordinated ligands. Mdleleni *et al.* reported the UV–vis absorption spectra of $[Pt(ppy)Cl_2]^-$, [Pt(ppy)(CO)Cl] and **1a** complexes and assigned peaks from 250 to 350 nm as $\pi \rightarrow \pi^*$ transitions and those from 380 to 400 nm as MLCT transitions of the chelated C^N moiety.[22] The four peaks became sharper as the extinction coefficient increased. The absorption peaks at 360–380 nm of **1a, 4a, 5a** and **1b, 4b, 5b** were shifted to shorter wavelengths in the order $X^- = Cl^- < Br^- < I^-$. According to the spectrochemical series in coordination chemistry, peak maxima are expected to appear in the order $X^- = I^- < Br^- < Cl^- < SCN^- < ONO_2{}^- < NO_2{}^-$ at shorter wavelengths, and the fact that the order is reversed here may indicate that these peaks do not correspond to d–d transitions.

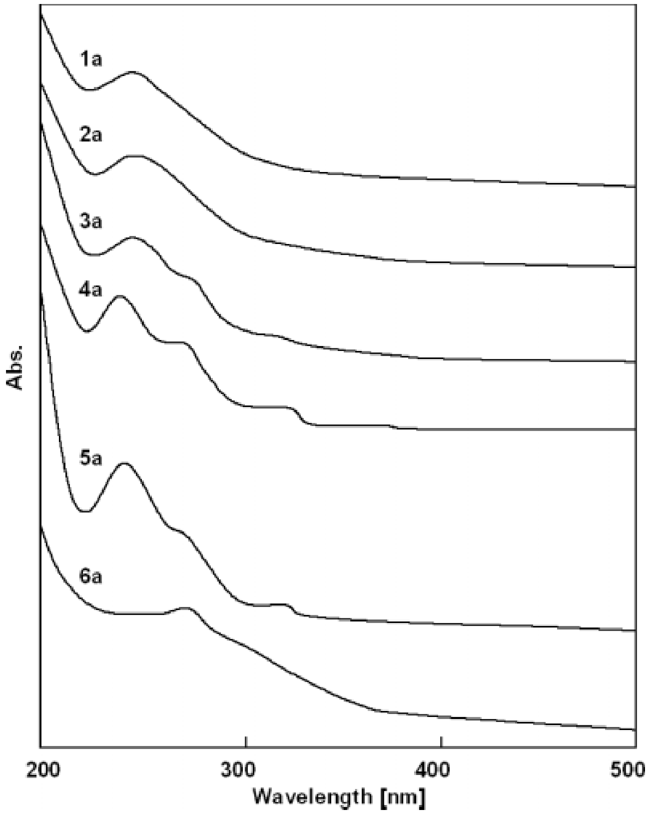

Figure 5. UV/vis spectra of [Pt(topy)(Htopy)X].

The emission spectra of [Pt(topy)(Htopy)X], measured in acetonitrile at room temperature, are shown in Fig. 6, and corresponding data are listed in Table 5. Two peaks near 480 nm and near 510 nm were observed in all emission spectra of [Pt(C^N)(HC^N)X]. Several results for maximum emissions of cyclometalated platinum(II) complexes have been reported previously: 489 nm for **1a** at 298 K in toluene;[22] 556 nm for [Pt(thpy)(Hthpy)Cl] at 298 K in CH_2Cl_2;[24] and 491 nm for *cis*-$[Pt(ppy)_2]$ and 570 nm for *cis*-

Table 5. UV–vis spectral and emission data of [Pt(C^N)(HC^N)X] in acetonitrile (10^{-5} M)

	UV–vis absorption	Emission (λ_{ex} 380 nm)
Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{max}/nm (Int.)
1a	250 (34200), 380 (2240)	481 (0.70), 510 (0.67)
2a	241 (39400), 313 (7690), 322 (7580), 356 (2800)	477 (3.90), 509 (3.60)
3a	224 (33200), 313 (7490), 322 (7250), 353 (2910)	476 (0.77), 509 (0.73)
4a	247 (37300), 374 (2320)	476 (1.39), 508 (1.28)
5a	244 (49600), 366 (2940)	477 (1.69), 510 (1.54)
6a	248 (26300), 350 (4100)	481 (3.66), 512 (3.22)
1b	256 (32000), 380 (2370)	485 (1.18), 516 (0.99)
2b	246 (31700), 314 (7240), 327 (6660), 361 (3210)	482 (3.74), 515 (3.33)
3b	211 (42600), 315 (7790), 326 (7330), 358 (2870)	482 (1.06), 514 (0.93)
4b	252 (34600), 377 (2520)	482 (1.69), 515 (1.49)
5b	247 (44000), 365 (3080)	484 (2.39), 516 (2.13)
6b	252 (33400), 351 (5300)	486 (3.34), 518 (2.27)

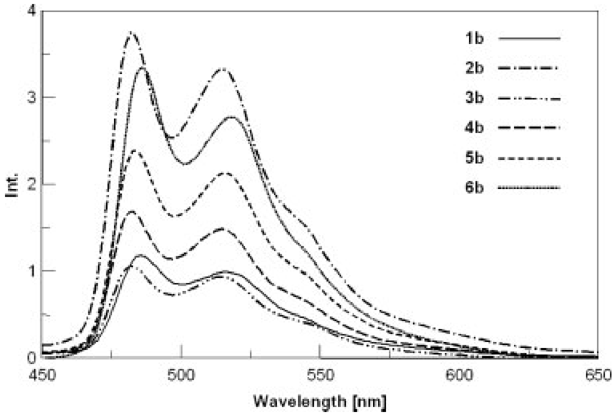

Figure 6. Emission spectra of [Pt(topy)(Htopy)X].

[Pt(thpy)$_2$] at 77 K in propionitrile-butyronitrile.[32] In [Pt(N^C^N)Cl] complexes, the maximum emission is 491 nm when N^C^N is 1,3-di(2-pyridyl)benzene, 481 nm when it is methyl-3,5-di(2-pyridyl)benzoate and 505 nm when it is 3,5-di(2-pyridyl)toluene, at 293 K in CH$_2$Cl$_2$.[33] The existence of a maximum emission at short wavelengths is important for the fabrication of blue OLEDs. The new [Pt(C^N)(HC^N)X] complexes prepared in this study showed maximum emissions at approximately 476 nm, which is shorter than previously reported maxima. [Pt(ppy)(Hppy)X] complexes showed maximum emissions at wavelengths approximately 6 nm shorter than those of [Pt(topy)(Htopy)X] complexes.

The emission was found to increase in the order $X^- = Cl^-$, $NO_2^- < Br^- < I^- < SCN^- < ONO_2^-$. To our surprise, the emission of **2a** and **2b** were three to six times greater than those of other [Pt(C^N)(HC^N)X] complexes.

Electroluminescent Devices

In previous reports, most devices fabricated using platinum complexes showed emission wavelengths longer than 500 nm and produced red, orange or white emissions. Examples include a red-emitting device containing (Pt{2,2-[1,2-phenylene-bis(nitrilomethylidyne)]bis(4,6-di-tert-butylphenolate)]}, which showed Commission Internationale de L'Eclairage (CIE) color coordinates of (0.68, 0.32) and λ_{max} of 645 nm;[6] an orange-emitting device containing {Pt[(9,9-diethyl-7-pyridin-2-ylfluoren-2-yl)diphenylamine](acac)}, which has CIE coordinates (0.55, 0.45) and λ_{max} 572 nm;[11] a white-emitting device containing {Pt[*N*, *N*′-bis(salicylidene)-1,2-ethylenediamine]}, with CIE coordinates (0.33, 0.35) and λ_{max} 448, 552 nm;[8] and a green-emitting device containing [Pt(pentafluorophenyl)$_2$(4,7-diphenylphenanthroline)], with CIE coordinates (0.329, 0.551) and λ_{max} 519 nm.[7] As **2a** and **2b** show luminescence at short wavelengths and strong luminescence intensity, they are suitable candidates for emitters in high-efficiency OLEDs. Table 6 shows the electroluminescence properties of devices using **2a, 2b** and FIrpic dopants, and Fig. 7 shows the current density vs applied voltage curves of **2a** and **2b**, and FIrpic-doped OLEDs, where the turn-on voltages of **2a** and **2b** were 6 V. Figure 8 shows the luminance vs applied voltage curves

Table 6. Performance of **2a, 2b**, and FIrpic-doped OLEDs

		2.5 mA/cm^2						
Dopant	*V* (V)	*L* (cd/m^2)	η_{ext} (%)	η_L (cd/A)	η_P (lm/W)	CIE (*x*, *y*)	λ_{max} (nm)	L_{max} [cd/m^2 (V)]
2a	8.5	13.1	0.2	0.5	0.2	0.24, 0.44	487, 521	371 (22.0)
2b	8.5	15.0	0.2	0.6	0.2	0.25, 0.45	488, 522	513 (22.0)
Firpic	7.4	83.8	1.6	3.4	1.4	0.16, 0.34	471, 498	5205 (12.0)

Values in parentheses for L_{max} are the applied driving voltage.
V, voltage; *L*, luminance; η_{ext}, external quantum efficiency; η_L, current efficiency; η_P, power efficiency; CIE, color coordinates; λ_{max}, emission peak maxima; L_{max}, maximum luminance.

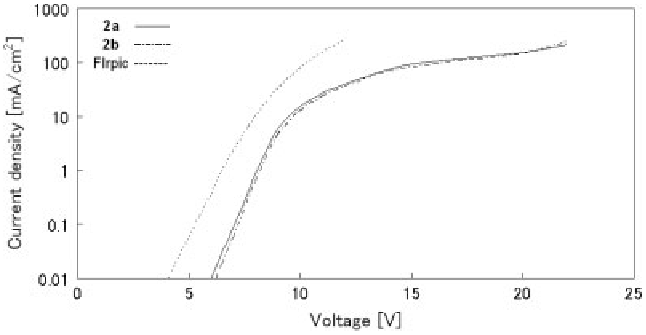

Figure 7. Current density vs. applied voltage of **2a**, **2b** and FIrpic-doped OLEDs.

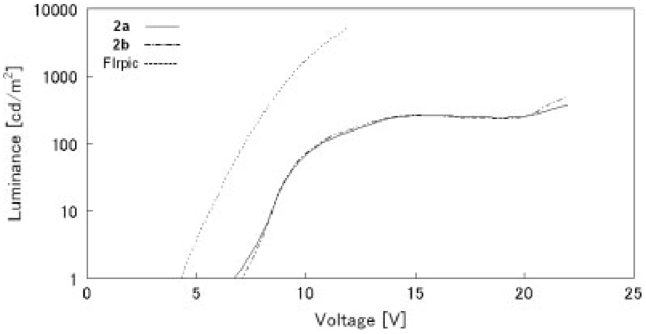

Figure 8. Luminance vs. applied voltage of **2a**, **2b** and FIrpic-doped OLEDs.

of **2a** and **2b,** and FIrpic-doped OLEDs. The emissions of **2a** and **2b** were observed at approximately 7 V.

The devices prepared here showed green emissions, and had the following maximum emission wavelengths: 487 and 521 nm for **2a**, and 488 and 522 nm for **2b**. The CIE coordinates of the devices were 0.24, 0.44 for **2a** and 0.25, 0.45 for **2b.** Figure 9 shows the external quantum efficiency vs. luminance curves of **2a, 2b,** and FIrpic-doped OLEDs. For **2a**, $L = 13.1$ cd/m^2, $\eta_{\mathrm{ext}} = 0.2\%$, $\eta_{\mathrm{L}} = 0.5$ cd/A, and $\eta_{\mathrm{P}} = 0.2$ l m/W, and for **2b**, $L = 15.0$ cd/m^2, $\eta_{\mathrm{ext}} = 0.2\%$, $\eta_{\mathrm{L}} = 0.6$ cd/A, and $\eta_{\mathrm{P}} = 0.2$ l m/W at 2.5 mA/m^2 (where L = luminance, η_{ext} = external quantum efficiency, η_{L} = current efficiency and η_{P} = power efficiency). These nitrato platinum devices showed maximum luminances of 371 cd/m^2 for **2a** and 513 cd/m^2 for **2b** at 22.0 V. The phosphorescence lifetimes at 77 K in acetonitrile were 4.0 µs for **2a** and 7.2 µs for **2b**; these are relatively short and are suitable for OLED devices.

When the values of L, η_{ext}, η_{L} and η_{P} for these nitrato platinum complexes were compared with those of FIrpic, the efficiency of the complexes was found to be lower. However, it is notable that the devices emitted light despite being fabricated by the spin coating method rather than the more commonly used vapor deposition method.

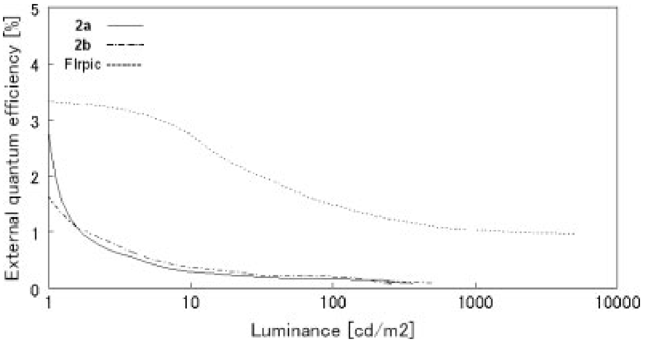

Figure 9. External quantum efficiency vs. luminance of **2a**, **2b** and FIrpic-doped OLEDs.

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