

Synthesis and Luminescence Properties of [Pt{4-(*o*-MeC₆H₄)-pzbipy}Cl]SbF₆ [pzbipy = 6-2''-pyrazinyl)-2,2'-bipyridine]

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This paper is dedicated to our good friend and colleague, Helgard G. Raubenheimer, on the occasion of his 65th birthday

The synthesis and characterisation of the 4-(*o*-R-C₆H₄)pzbipy [R = H, CH₃ or CF₃; pzbipy = 6-(2''-pyrazinyl)-2,2'-bipyridyl] ligands are described. Reaction of the 4-(*o*-MeC₆H₄)pzbipy ligand with [Pt(PhCN)₂Cl₂] in the presence of AgSbF₆ affords [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ as a maroon-coloured microcrystalline solid. The [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]⁺ cation exhibits low intensity photoluminescence in dichloromethane that maximises at 543 nm and which is assigned to a ³MLCT excited state ($\tau = 20$ ns). The emission spectrum of the cation was also recorded in a frozen DME {1 : 5:5 (v/v) DMF / MeOH / EtOH} glass; a highly structured band is observed with vibrational spacings of *ca.* 1400 cm⁻¹, indicating emission from an intraligand ³ π - π^* state ($\tau = 11$ μ s). Variable temperature solid emission spectra show maxima that occur at significantly lower energies than is observed in fluid solution and that shift to the red when the temperature is lowered; specifically, $\lambda(\text{em})_{\text{max}}$ is 674 nm at 280 K ($\tau = 80$ ns) and 723 nm at 80 K ($\tau = 1.3$ μ s). Emission behaviour of this type is typical of emission from a metal-metal-ligand charge transfer (MMLCT) excited state that has its origins in $d_{z^2}(\text{Pt})$ - $d_{z^2}(\text{Pt})$ orbital interactions in the crystal.

Key words: Pyrazinylbipyridyl Ligand, Platinum Complex, Luminescence

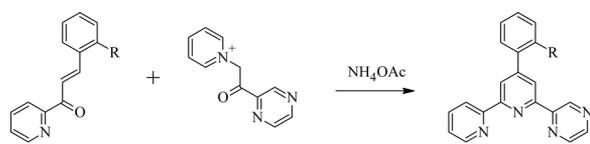
Introduction

Polypyridine ligands, especially 2,2'-bipyridine (bipy) and 2,2' : 6',2''-terpyridine (trpy), have been extensively used to confer desirable photophysical properties on complexes of ruthenium(II) [1] and platinum(II) [2–18]. Their attraction derives from the presence of a delocalised π -system that allows for facile electron transfer from the metal to the ligand, thus giving rise to easily accessible metal-to-ligand charge-transfer (MLCT) excited states. Less studied are polypyridine ligands that incorporate a pyrazine ring, this despite the fact that it has been shown that substituting pyrazine for pyridine can have a dramatic effect on the photophysical properties of a complex [19, 20]. Pyrazine is a poorer σ -donor and better π -acceptor ligand than pyridine [19, 21]. It is also distinguished from pyridine by the presence of *two* nitrogen donor atoms, a property that has been used to advantage by Lever and coworkers [22]. Of particular

relevance is their synthesis of the 4-*p*-tolyl-2,6-di(2-pyrazinyl)pyridyl ligand, where both the outer pyridine rings of the 2,2' : 6',2''-terpyridyl moiety have been replaced by a pyrazine ring [23]. Here we report the synthesis of the closely related 4-(2'''-R-phenyl)-6-(2''-pyrazinyl)bipyridyl [4-(*o*-R-C₆H₄)pzbipy with R = H, CH₃, or CF₃] ligands, where just one of the outer pyridine rings in 2,2' : 6',2''-terpyridine has been replaced by a pyrazine ring. As will be shown, this simple change has a marked effect on the solid state emission properties of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ as compared to that previously reported for [Pt{4'-(*o*-MeC₆H₄)trpy}Cl]SbF₆ [13].

Results and Discussion

The synthesis of the 4-(*o*-R-C₆H₄)pzbipy ligands followed the Kröhnke method [24] and is illustrated in Scheme 1. The pyrazine ring was introduced *via* the enolate with the synthesis of *N*-{1-pyrazinyl-1-oxo-2-



R = H, CH₃, or CF₃
Scheme 1.

ethyl}pyridinium iodide (PZPI) by adaptation of the method for the assembly of the well known *N*-{1-(2'-pyridyl)-1-oxo-2-ethyl}pyridinium iodide [24]. Reaction of the enones [1-(2'-pyridyl)-3-(2''-R-phenyl)prop-2-en-1-one (R = H, CH₃, or CF₃)] with PZPI in refluxing ethanolic ammonium acetate, affords a product that is isolated as a pale-yellow crystalline material in yields of 21–43%. A similar approach was used by Drew and coworkers for the synthesis of the closely related 6'-pyrazin-2-yl-4'-(4-heptyloxyphenyl)-2,2'-bipyridine ligand, the only difference being that the pyrazinyl moiety was incorporated *via* the enone rather than the enolate [25]. Details of the spectroscopic characterisation of the new ligands are given in the Experimental Section.

In order to synthesise [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆, the same approach was used as that previously employed for the synthesis of the trpy analogue [13]. Thus [Pt(PhCN)₂Cl₂] was first reacted with AgSbF₆ in refluxing acetonitrile, the AgCl that formed filtered-off, and the 4-(*o*-MeC₆H₄)pzbipy ligand added to the reaction mixture, finally affording the product as a maroon-coloured microcrystalline solid in a yield of 50%. Characterisation of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ was by means of elemental analysis for C, H and N, as well as by infrared and ¹H NMR spectroscopy. Unfortunately, despite repeated attempts, it was not possible to grow single crystals suitable for an X-ray diffraction study.

Photophysical properties of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆

The electronic absorption spectrum of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ measured in acetonitrile is shown in Fig. 1. The intense high energy peak at 285 nm and the vibrationally structured band in the 290–375 nm region are assigned to π - π^* absorptions localised on the conjugated ligand. At longer wavelengths weaker absorptions are observed that comprise a shoulder at 387 nm and a broad peak centred at 408 nm; these are assigned to MLCT absorptions. This pattern of absorption bands is typical of ter-

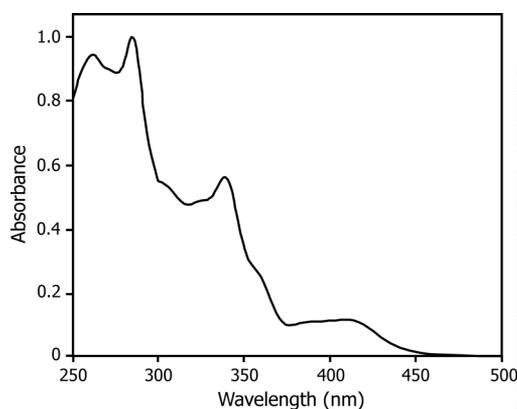


Fig. 1. Absorption spectrum of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ in acetonitrile solution.

pyridyl ligand complexes of platinum(II) [4–18]. Of particular interest is the effect on the positions of the MLCT absorption bands of replacing an outer pyridine of the trpy ligand with a pyrazine ring. In this regard we note that the corresponding MLCT absorption bands recorded in acetonitrile for [Pt{4-(*o*-MeC₆H₄)trpy}Cl]SbF₆ occur at 380 and 399 nm [13] *i. e.*, at a slightly higher energy than for the pyrazinylbipyridyl ligand complex. This is consistent with the stronger π -acceptor ability of the 4-(*o*-MeC₆H₄)pzbipy ligand as compared to the 4'-(*o*-MeC₆H₄)trpy ligand [19, 21].

The [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ complex exhibits low intensity photoluminescence in dichloromethane but not in acetonitrile. As shown in Fig. 2, the spectrum comprises a broad band centred at 543 nm with a barely discernible shoulder at 565 nm. Charge-transfer emission from platinum(II) terpyridines is characterised by an envelope of vibronic structure that shows a monotonically decreasing intensity with an increase in wavelength *i. e.*, the highest energy transition in the progression is the most intense and is attributable to the zero-zero band [4, 10, 18]. Though the band in Fig. 2 is poorly resolved, in this respect it does appear to show features typical of ³MLCT emission. Also, consistent with an ³MLCT assignment is the absence of any emission signal in acetonitrile, since emissions from planar complexes of platinum(II) tend to be quenched in a coordinating solvent, like acetonitrile [12]. The emission spectrum of the trpy analogue of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ has not been measured in fluid solution. However, it has been measured in dichloromethane for the closely related 4'-(Ph)trpy ligand complex, [Pt{4'-(Ph)trpy}Cl]TFPB where TFPB is tetrakis-[3,5-bis(tri-

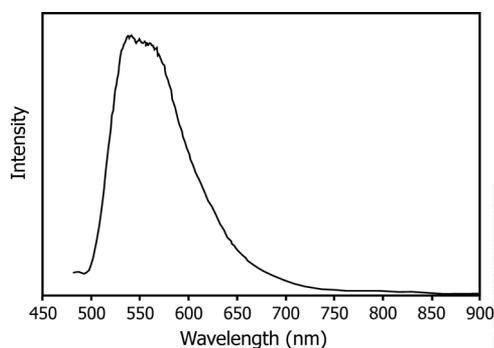


Fig. 2. Emission spectrum of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ in dichloromethane solution ($\lambda_{\text{ex}} = 405$ nm).

fluoromethyl)phenyl]borate; the spectrum exhibits a weakly resolved vibronic structure with the zero-zero band at 535 nm ($\tau = 85$ ns) and is assigned as ³MLCT in origin [10]. In order to make a direct comparison we have synthesised and measured the emission spectrum of [Pt{4-(Ph)pzbipy}Cl]BF₄ in dichloromethane. The spectrum is very similar to that shown in Fig. 2; the emission maximises at 550 nm and the shoulder appears at *ca.* 580 nm *i. e.*, it shifts to lower energies as compared to that for the trpy analogue. We conclude that the HOMO-LUMO energy gap in the pyrazinylbipyridyl complex is narrower than in the terpyridyl analogue due to the better π -acceptor ability of the pyrazine unit, and that this results in a lower energy for the emission. Somewhat surprisingly the lifetime of 96 ns measured for [Pt{4'-(Ph)pzbipy}Cl]BF₄ in dichloromethane is longer than that of 85 ns measured for [Pt{4-(Ph)trpy}Cl]TFPB in the same solvent; the energy gap law predicts an opposite trend [26].

The emission spectrum at 77 K of a 20 μM DME glass solution of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ is shown in Fig. 3. A highly structured band is observed with the zero-zero transition at 501 nm and further progressions at 539, 580, and 620 nm. The vibrational spacings are of the order 1300–1400 cm^{-1} which is typical of a C–C or C–N stretching motion of a terpyridine and, presumably, a pyrazinylbipyridyl framework. Other evidence in deciding the nature of the emitting state is, (i) a Huang-Rhys ratio (I_{0-1}/I_{0-0}) of *ca.* 0.95 that is close to 1.0 [4, 10, 14, 18], (ii) an energy for the zero-zero transition that is somewhat higher than that observed in dichloromethane solution (*cf.* Figs. 2 and 3) and (iii) a relatively long emission lifetime of 11 μs . Taken together the evidence suggests that the emitting state is an admixture of ³MLCT and ³ π - π^* character, with the latter differentially sta-

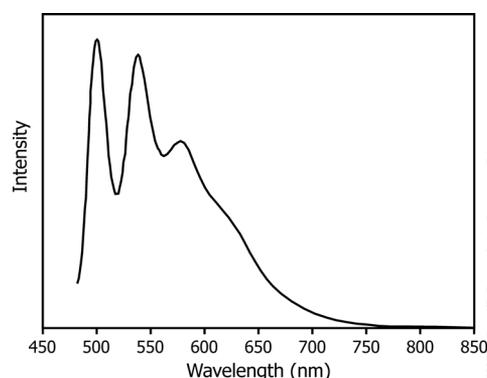


Fig. 3. Emission spectrum of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ in a DME glass at 77 K ($\lambda_{\text{ex}} = 405$ nm).

bilised due to the formation of the rigid matrix [10, 18]. The frozen DME glass emission spectrum obtained for the trpy analogue, [Pt{4'-(*o*-MeC₆H₄)trpy}Cl]SbF₆, is very similar in profile, the only significant difference being that the emission is shifted to somewhat higher energies as reflected in a zero-zero transition at 478 nm [13]. As discussed above this is consistent with a narrowing of the HOMO-LUMO energy gap in the pyrazinylbipyridyl complex, due to the better π -acceptor properties of pyrazine as compared to pyridine [19, 21].

Emission spectra have been recorded on a maroon-coloured microcrystalline sample of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ at 40 K intervals over the temperature range 80–280 K, see Fig. 4. At 280 K a structureless, narrow and asymmetric band that maximises at 674 nm is observed ($\tau = 80$ ns). Lowering the temperature causes a systematic red shift in the emission maximum, as well as a further narrowing of the band such that at 80 K the emission maximum occurs at 723 nm and the full-width-at-half-maximum (fwhm) is *ca.* 1200 cm^{-1} ($\tau = 1.3$ μs). The response of the emission to lowering the temperature as well as its profile is diagnostic for ³MMLCT emission *i. e.*, $d_{z^2}(\text{Pt})$ - $d_{z^2}(\text{Pt})$ orbital interactions are present in the crystal and these interactions increase as the temperature is lowered [3, 4, 13, 16]. A direct comparison can be made with the variable temperature solid emission spectra recorded for the red trpy analogue, [Pt{4'-(*o*-MeC₆H₄)trpy}Cl]SbF₆ [13]. In this case ³MMLCT emission that shifts to the red as the temperature is lowered is also observed, but at shorter wavelengths *i. e.*, $\lambda(\text{em})_{\text{max}}$ is 616 nm at 280 K and 673 nm at 80 K [13]. Note that a crystal structure determination of [Pt{4'-(*o*-MeC₆H₄)trpy}Cl]SbF₆

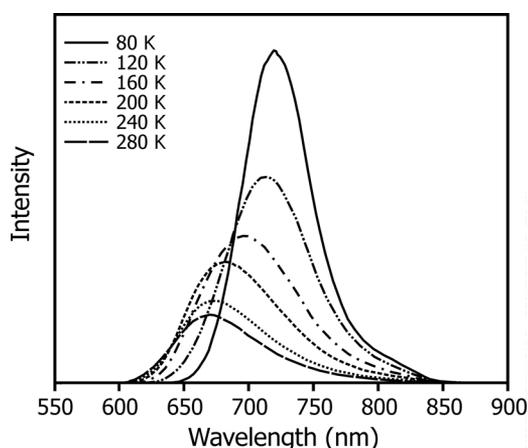


Fig. 4. Emission spectra of solid [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ measured at 40 K intervals from 80–280 K ($\lambda_{\text{ex}} = 575 \text{ nm}$).

at r.t. confirms that the platinum atoms define a linear chain structure and that the Pt...Pt distance of 3.368 Å is significantly shorter than 3.5 Å, the upper distance limit for effective $d_{z^2}(\text{Pt})$ - $d_{z^2}(\text{Pt})$ orbital interactions [27]. We assume that the crystal structure of the pyrazinylbipyridyl analogue also possesses a linear chain of closely-spaced platinum atoms, given the similar colour (maroon *vs.* red) and the same emission response to temperature for the two compounds. If this is indeed the case, the implication is that the $d_{z^2}(\text{Pt})$ - $d_{z^2}(\text{Pt})$ orbital interactions in solid [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ are stronger than in [Pt{4'-(*o*-CH₃-Ph)trpy}Cl]SbF₆ since the ³MMLCT emission occurs at lower energies for the former complex. This view is consistent with the argument that, because the pzbipy ligand is a better π -acceptor than the trpy ligand, electron density on the metal centre will be reduced in the pzbipy complex, thereby promoting close Pt...Pt contacts as the intermetallic repulsions are reduced. Whatever the explanation, it is clear that the simple change of a pyridine for a pyrazine in the trpy ligand has a dramatic effect on the energy of the solid emission.

Concluding Remarks

In conclusion we note how remarkably varied the excited state properties of the [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ system are. Thus, in fluid solution the cation exhibits ³MLCT emission that is subject to exciplex quenching, in a frozen glass the emission is predominantly intraligand in character and, finally, tem-

perature dependent ³MMLCT emission is observed in the solid state.

Experimental Section

General

The organic solvents used in the syntheses were from Aldrich and used as received except for acetonitrile that was distilled by a literature method [28]. The Acetylpyrazine was obtained from Aldrich and used as received, while the following organic reagents were also obtained from Aldrich and distilled prior to use: 2-Acetylpyridine, benzaldehyde, 2-tolualdehyde and α, α, α -trifluoromethyltolualdehyde. The ammonium acetate was dried in a vacuum desiccator over P₂O₅ for several days prior to use. [Pt(PhCN)₂Cl₂], AgSbF₆ and AgBF₄ were obtained from Strem Chemicals and also used as received. The 2-R-1-{3-(2-pyridyl)-3-oxopropenyl}benzene (R = H, CH₃ or CF₃) was prepared as described previously [13].

Instrumentation

Microanalyses for % C, H and N were performed in the Microanalytical Laboratory at the University of Natal, Pietermaritzburg. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 spectrometer at 25 °C with chemical shifts in ppm referenced to TMS. Infrared spectra were recorded as KBr discs on a Perkin Elmer Spectrum One FTIR spectrometer. UV/vis absorption spectra were recorded at 22 °C using a Shimadzu-2101PC scanning spectrophotometer and the spectrofluorimeter was a SLM Aminco SPF500C. A finger-Dewar filled with liquid nitrogen permitted measurements in a frozen DME glass. For the variable temperature emission measurements the cryostat was an Oxford Instruments DN1704 liquid-nitrogen-cooled system complete with an Oxford Instruments temperature controller. See previous work for a description of the nitrogen-pumped dye laser and associated equipment used for lifetime determinations [29]. The method for determining lifetimes has been described previously [30].

Syntheses

N-[1-pyrazinyl-1-oxo-2-ethyl]pyridinium iodide (PZPI): Acetylpyrazine (4.76 g, 39 mmol) was added to a suspension of iodine (5.0 g, 39 mmol) in pyridine (15 mL). The mixture was refluxed for 90 min, allowed to cool, and the black precipitate filtered off, washed with a small amount of cold pyridine and dried *in vacuo*. The crude product was purified by refluxing in a minimum volume of ethanol in the presence of deactivated charcoal (*ca.* 1–2% by weight) and filtered through Celite®. The desired product precipitated as golden flakes upon cooling. Yield: 6.12 g (48%). – IR: $\nu(\text{CO}) = 1705 \text{ cm}^{-1}$. – Anal. calcd. for C₁₁H₁₀N₃OI: C 40.4, H 3.1, N 12.8; found: C 40.1, H 2.9, N 12.7.

4-(2'''-*R*-phenyl)-6-(2''-pyrazinyl)bipyridine (*R* = *H*, CH₃, CF₃): Ammonium acetate (10 g, excess) was added to a suspension of 2-*R*-1-{3-(2-pyridyl)-3-oxopropenyl}benzene (2.0 mmol) and *N*-{1-pyrazinyl-1-oxo-2-ethyl}pyridinium iodide (0.72 g, 2.2 mmol) in absolute ethanol (8 mL). The mixture was heated to reflux for 90 min (25 min in the *R* = CH₃ case) and allowed to cool. The impure ligand precipitated as a grey solid which was recrystallised from ethanol (95 %) to produce off-white blocks of analytically pure ligand that was dried *in vacuo*.

For 4-phenyl-6-(2''-pyrazinyl)bipyridine: Yield: 0.27 g (43 %). – M. p. 217–219 °C. – Anal. calcd. for C₂₀H₁₄N₄: C 77.4, H 4.5, N 18.1; found: C 77.6, H 4.4, N 17.7. – ¹H NMR (200 MHz, CDCl₃): δ = 9.86 (d, 1H, H_{3''}) 8.78 (d, 1H, H₅) 8.71 (m, 1H, H_{6'}) 8.66 (m, 1H, H₃) 8.65 (m, 1H, H_{3'}) 8.62 (m, 2H, H_{5''}, 6'') 7.81–7.92 (m, 2H, phenyl H's) 7.85 (m, 1H, H_{4'}) 7.44–7.55 (m, 3H, phenyl H's) 7.35 (qd, 1H, H_{5'}). – ¹³C NMR (50 MHz, CDCl₃): δ = 150.5–156.2 (5C, ps, pyridyl and pyrazinyl quat. C's) 149.1 (s, 1C, C_{6'}) 143.5–144.5 (ts, 3C, pyrazinyl CH's) 138.1 (s, 1C, phenyl quat. C) 137.0 (s, 1C, C_{4'}) 127.2–129.3 (ts, 5C, phenyl CH's) 124.0 (s, 1C, C_{5'}) 121.4 (s, 1C, C_{3'}) 119.5 (s, 1C, C₅) 119.2 (s, 1C, C₃).

For 4-(2'''-CH₃-phenyl)-6-(2''-pyrazinyl)bipyridine: Yield: 0.23 g (35 %). – M. p. 174–176 °C. – Anal. calcd. for C₂₁H₁₆N₄: C 77.8, H 5.0, N 17.3; found: C 77.7, H 4.9, N 17.2. – ¹H NMR (200 MHz, CDCl₃): δ = 9.86 (d, 1H, H_{3''}) 8.65 (m, 1H, H_{6'}) 8.64 (m, 1H, H_{3'}) 8.57 (d, 2H, H_{5''}, 6'') 8.51 (d, 1H, H₅) 8.39 (d, 1H, H₃) 7.84 (td, 1H, H_{4'}) 7.20–7.40 (m, 5H, H_{5'} and phenyl H's) 2.34 (s, 3H, methyl H's). – ¹³C NMR (50 MHz, CDCl₃): δ = 151.0–155.6 (ps, 5C, pyridyl and pyrazinyl quat. C's) 149.1 (s, 1C, C_{6'}) 144.3 (s, 1C, pyrazinyl CH) 143.5 (ss, 2C, pyrazinyl CH's) 139.1 (s, 1C, phenyl quat. C) 136.8 (s, 1C, C_{4'}) 135.0 (s, 1C, phenyl quat. C) 125.9–130.5 (qs, 4C, phenyl CH's) 123.9 (s, 1C, C_{5'}) 122.1 (s, 1C, C₅) 121.8 (s, 1C, C₃) 121.2 (s, 1C, C_{3'}) 20.3 (s, 1C, CH₃).

For 4-(2'''-CF₃-phenyl)-6-(2''-pyrazinyl)bipyridine: Yield: 0.16 g (21 %). – M. p. 298–301 °C. – Anal. calcd. for C₂₁H₁₃N₄F₃: C 66.7, H 3.5, N 14.8; found: C 66.9, H 3.3, N 14.7. – ¹H NMR (200 MHz, CDCl₃): δ = 9.88 (d, 1H, H_{3''}) 8.67 (m, 2H, H_{3'}, 6') 8.60 (m, 2H, H_{5''}, 6'') 8.40–8.53 (dm, 2H, H_{3,5}) 7.88 (m, 1H, H_{4'}) 7.40–7.85 (m, 4H, phenyl H's) 7.34 (qd, 1H, H_{5'}). – ¹³C NMR (50 MHz, CDCl₃): δ = 150.0–155.5 (ps, 5C, pyridyl and pyrazinyl quat. C's) 149.2 (s, 1C, C_{6'}) 143.5–144.6 (ts, 3C, pyrazinyl CH's) 138.6 (s (low intensity), 1C, C_{1'''}) 137.0 (s, 1C, C_{4'}) 128.4–131.6 (ts, 3C, phenyl CH's) 128.2 (q, ²J_{C–F} = 30.6 Hz, 1C, C_{2'''}) 126.2 (q, ³J_{C–F} = 5.3 Hz, 1C, C_{3'''}) 124.1 (s, 1C, C_{5'}) 124.0 (q, ¹J_{C–F} = 273.9 Hz, 1C, CF₃) 121.5–122.0 (ss, 2C, C_{3,5}) 121.4 (s, 1C, C_{3'}).

[Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆: Silver hexafluoroantimonate (73 mg, 0.21 mmol) was dissolved in acetonitrile

(5 mL) and added to a suspension of [Pt(PhCN)₂Cl₂] (100 mg, 0.21 mmol) in acetonitrile (100 mL). The mixture was refluxed overnight under an inert atmosphere after which the precipitate of AgCl that had formed was removed by filtration. An approximately equimolar amount of 4-(2'''-CH₃-phenyl)-6-(2''-pyrazinyl)bipyridine (65 mg, 0.21 mmol) was added as a solid and the mixture refluxed for a further 24 h. After this period the solution was filtered while still hot and the solvent partially removed under reduced pressure resulting in the precipitation of [Pt{4-(*o*-MeC₆H₄)pzbipy}Cl]SbF₆ as a maroon-coloured solid. The product was washed on a frit with copious amounts of diethyl ether and then with smaller amounts of acetonitrile. The resulting powder was recrystallised from hot acetonitrile. Yield: 79 mg (50 %). – Anal. calcd. for C₂₁H₁₆ClF₆N₄PtSb: C 31.90, H 2.04, N 7.09; found: C 31.81, H 1.84, N 7.04. – ¹H NMR ([D₆]DMSO): δ = 9.89 (d, 1H, H_{3''}) 9.11 (d, 1H, H_{6''}) 8.85 (s, 1H, H₅) 8.83 (d, 1H, H_{5''}) 8.79 (s, 1H, H₃) 8.76 (m, 1H, H_{6'}) 8.71 (m, 1H, H_{3'}) 8.44 (td, 1H, H_{4'}) 7.86 (m, 1H, H_{5'}) 7.40–7.90 (m, 4H, phenyl H's) 2.45 (s, 3H, CH₃). – IR (KBr, cm⁻¹): ν[4-(*o*-MeC₆H₄)pzbipy] = 1610s, 1560w, 1473m, 1420m, 889w, 768s; ν(SbF₆⁻) = 662vs. – UV/vis (50 μM in MeCN): λ_{max} (ε) = 262 (2.8 × 10⁴), 285 (3.0 × 10⁴), 308sh (1.7 × 10⁴), 325sh (1.5 × 10⁴), 338 (1.7 × 10⁴), 356sh (8.0 × 10³), 387sh (3.3 × 10³), 408 nm (3.6 × 10³).

[Pt{4-(*Ph*)pzbipy}Cl]BF₄: Silver tetrafluoroborate (41 mg, 0.21 mmol) was dissolved in acetonitrile (5 mL) and added to a suspension of [Pt(PhCN)₂Cl₂] (100 mg, 0.21 mmol) in acetonitrile (100 mL). The mixture was refluxed overnight under an inert atmosphere after which the precipitate of AgCl that had formed was removed by filtration. An approximately equimolar amount of 4-phenyl-6-(2''-pyrazinyl)bipyridine (62 mg, 0.21 mmol) was added as a solid and the mixture refluxed for a further 24 h. After this period the solution was filtered while still hot and the solvent partially removed under reduced pressure resulting in the precipitation of [Pt{4-(*Ph*)pzbipy}Cl]BF₄ as a yellow solid. The product was washed on a frit with copious amounts of diethyl ether and then with smaller amounts of acetonitrile. The resulting powder was recrystallised from hot acetonitrile. Yield: 60 mg (48 %). – Anal. calcd. for C₂₀H₁₄BClF₄N₄Pt: C 38.27, H 2.25, N 8.93; found: C 38.62, H 2.17, N 8.50. – ¹H NMR ([D₆]DMSO): δ = 9.92 (d, 1H, H_{3''}) 9.10 (d, 1H, H_{6''}) 9.02 (s, 1H, H₅) 8.92 (s, 1H, H₃) 8.76 (d, 1H, H_{5''}) 8.70 (m, 1H, H_{3'}) 8.66 (m, 1H, H_{6'}) 8.44 (td, 1H, H_{4'}) 8.06–8.18 (m, 2H, H_{2'''}, 6''') 7.82 (qd, 1H, H_{5'}) 7.64–7.73 (m, 3H, H_{3''}, 4'', 5''). – IR (KBr, cm⁻¹): ν[4-(*Ph*)pzbipy] = 1610s, 1560w, 1474m, 1418m, 889w, 791s; ν(BF₄⁻) = 1053vs. – UV/vis (50 μM in MeCN): λ_{max} (ε) = 262 (3.3 × 10⁴), 284 (3.4 × 10⁴), 306sh (2.4 × 10⁴), 321sh (2.1 × 10⁴), 334 (2.0 × 10⁴), 384sh (4.8 × 10³), 404 (6.0 × 10³).

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