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Developing strongly luminescent platinum(IV) complexes: facile synthesis of bis-cyclometalated neutral emitters†

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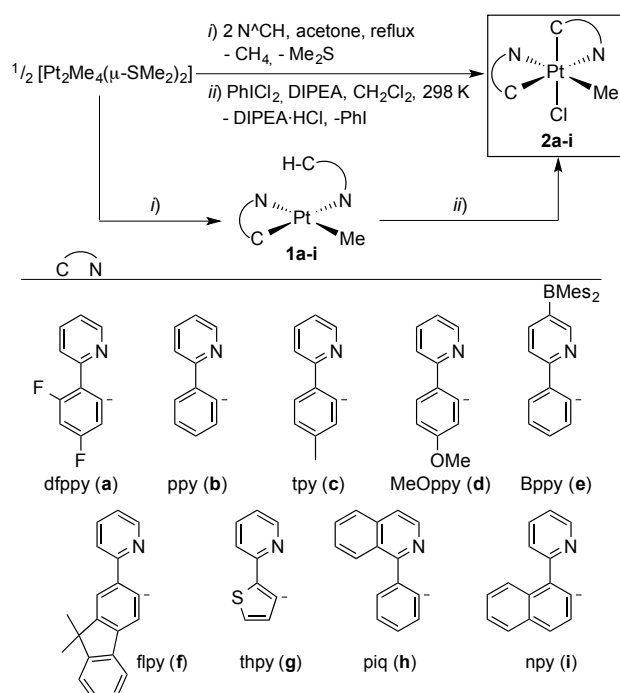
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A straightforward, one-pot procedure has been developed for the synthesis of bis-cyclometalated chloro(methyl)platinum(IV) complexes with a wide variety of heteroaromatic ligands of the 2-arylpiperidine type. The new compounds exhibit phosphorescent emissions in the blue to orange colour range and represent the most efficient Pt(IV) emitters reported to date, with quantum yields up to 0.81 in fluid solutions at room temperature.

Luminescent transition-metal complexes have been exhaustively studied for their rich photochemistry and wide applicability in optical technologies.¹ Thus, they are employed as electroluminescent materials,² chemosensors,³ photocatalysts,⁴ probes for bioimaging,⁵ and photosensitizers for dye-sensitized solar cells⁶ and singlet-oxygen generation and photodynamic chemotherapy.⁷ The majority of studies concentrate on complexes of d^6 [mainly Ru(II), Os(II) and Ir(III)], d^8 [Pt(II), Au(III)] and d^{10} [Cu(I)] ions with polypyridyls or cyclometalated arylpyridine ligands.¹ The quest for stable complexes that exhibit highly efficient triplet emissions, relatively long excited-state lifetimes and tunable colours has been a constant in this field, associated with the need to improve the performance and reliability of specific applications; in this regard, research on cyclometalated Pt(II)⁸ and Ir(III)^{2a,9} complexes has been particularly intense, since these systems are highly versatile and can reach very high quantum yields.

In stark contrast with the numerous photophysical studies on complexes of other d^6 ions, related works on Pt(IV) complexes are scarce and appear to have been overshadowed by the strong focus on Pt(II).^{8f} Bis-cyclometalated complexes of the type [Pt(C[^]N)₂(R)Cl] [C[^]N = *ortho*-deprotonated 2-phenylpyridine (ppy) or 2-thienylpyridine (thpy); R = CH₂Cl, CHCl₂] were the first luminescent Pt(IV) complexes, with reported quantum yields in the range 0.05–0.15.¹⁰ Later works have described weakly emissive Pt(IV) complexes.¹¹ Recently, we undertook the development of highly efficient Pt(IV)

emitters and described a family of cationic homoleptic tris-cyclometalated complexes *fac*-[Pt(C[^]N)₃]⁺ that exhibit high-energy (blue) emissions with quantum yields up to 0.49 and very long lifetimes.¹² We then extended the study to heteroleptic derivatives *mer*-[Pt(C[^]N)₂(C[^]N')]⁺ that display lower emission energies.¹³ These complexes emit from essentially ligand-centred triplet excited states (³LC) with a very low but critical metal-to-ligand charge-transfer (MLCT) character, which facilitates the formation of the triplet emitting state because of the spin-orbit coupling effect induced by the metal. Here we present a series of phosphorescent bis-cyclometalated Pt(IV) complexes of the type [Pt(C[^]N)₂(Me)Cl] (**2a-i**; Scheme 1), characterized by a high stability, tunable emission energies and generally high quantum yields, which make them very attractive as triplet emitters.



Scheme 1 One-pot synthesis of **2a-i**. DIPEA = *N,N*-diisopropylethylamine; Mes = mesityl.

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Compounds **2a-i** were prepared following a one-pot, two-step procedure (Scheme 1). The first step is the reaction of $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]^{14}$ with the $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ compound in 0.5:2 molar ratio in refluxing acetone, which leads to the cyclometalation of one $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ molecule and the coordination of a second one through the N atom to give the monocyclometalated Pt(II) complexes **1a-i**. This result is consistent with the known reactivity of the binuclear precursor, which reacts with $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ compounds to give cyclometalated complexes of the type $[\text{PtMe}(\text{C}^{\wedge}\text{N})(\text{SMe}_2)]$ and methane, while substitution of the labile Me_2S ligand allows further derivatization.¹⁵ Treatment of the intermediate derivatives **1a-i** with PhICl_2 at room temperature resulted in the oxidation to Pt(IV) and subsequent metalation of the pendant aryl moiety of the coordinated $\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ ligand to give complexes **2a-i**. Similar metalations upon oxidation with PhICl_2 have been reported for complexes of the type $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{N}^{\wedge}\text{C}^{\wedge}\text{H})\text{Cl}]$ ($\text{N}^{\wedge}\text{C}^{\wedge}\text{H}$ *trans* to N).¹⁶ The metalation reaction produces HCl, which must be trapped by adding a base; otherwise, it rapidly reacts with complexes **1a-i**, resulting in the substitution of the methyl ligand for a chloride (see the ESI† for details). The whole synthesis can be carried out without isolating the intermediate complexes **1a-i** under atmospheric conditions and the final products can be obtained in moderate to excellent yields (57-89%). It is worth emphasising that this method allows to prepare a wide range of derivatives from an easy-to-synthesize common precursor under mild conditions, typically consuming less than 6 hours.

The crystal structures of **2a**, **2b**, **2d** and **2f**· CH_2Cl_2 were solved by X-ray crystal diffraction studies.¹⁷ The molecular structure of **2b** is depicted in Fig. 1 and the other are included in the ESI† along with selected bond distances and angles. The Pt-N bond distances are rather long (range 2.121-2.156 Å) since the pyridyls are in *trans* to an aryl group or a methyl ligand, which exert very high *trans* influences. The Pt-Cl distances (2.423-2.446 Å) are similar to those found in other Pt(IV) complexes with a chloride ligand in *trans* to an aryl.^{16b} Correspondingly, the Pt-C distances are very short (1.996-2.011 Å), owing to the low *trans* influences of the pyridyl groups or the chloride ligand.

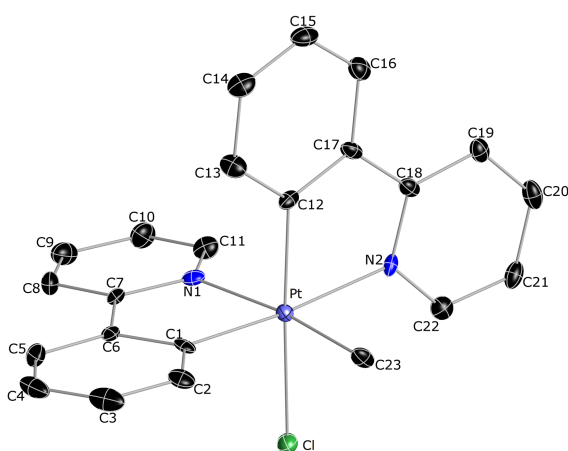


Fig. 1 Thermal ellipsoid representation (50% probability) of the crystal structure of **2b**. Hydrogen atoms are omitted for clarity.

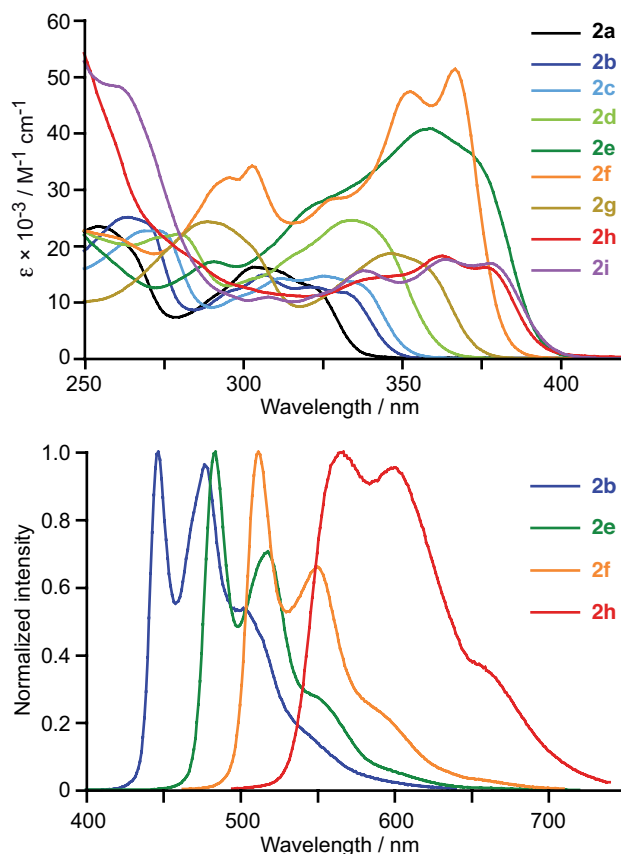


Fig. 2 Absorption spectra of compounds **2a-i** (top) and selected emission spectra (bottom) in CH_2Cl_2 solution at 298 K.

The absorption spectra of **2a-i** in CH_2Cl_2 solution at 298 K display intense structured bands in the 250-400 nm region (Fig. 2), which are similar in energy and shape to those found for the previously reported cyclometalated Pt(IV) complexes¹²⁻¹³ and can be ascribed to essentially ^1LC transitions within the $\text{C}^{\wedge}\text{N}$ ligands with little MLCT character. The lowest-energy band shifts from 322 to 378 nm along the sequence **2a**→**2i**, in line with the expected decreasing $\pi\text{-}\pi^*$ transition energies. This band has a significantly higher absorptivity for **2e** and **2f** (40600 or 51500 $\text{M}^{-1}\text{cm}^{-1}$, respectively), compared to the rest of derivatives. Such intense absorptions are highly desirable for certain applications, such as bioimaging or photocatalysis.

The excitation and emission spectra of **2a-i** were registered in deaerated CH_2Cl_2 solutions at 298 K and butyronitrile (PrCN) glasses at 77 K. The emission data are summarized in Table 1 and selected emission spectra at 298 K are shown in Fig. 2. The room-temperature emission spectra are vibrationally structured in all cases and the corresponding excitation spectra match the absorption profiles. Lifetimes are in the order of tens or hundreds of microseconds and Stokes shifts are in the range 6000-9000 cm^{-1} . The emission energies decrease on going from **2a** to **2i**, in accord with the $\pi\text{-}\pi^*$ transition energies of the $\text{C}^{\wedge}\text{N}$ ligands, and the associated emission colours range from blue to orange. The vibrational structure becomes better resolved in frozen glasses at 77 K and lifetimes increase as a consequence of the partial suppression of non-radiative processes. The mentioned characteristics are indicative of an essentially ^3LC emitting state, as found for the previously

Table 1 Emission data of complexes **2a-i**.

Complex	298 K ^a					77 K ^b	
	λ_{em}^c/nm	Φ^d	$\tau^e/\mu s$	$k_r^f \times 10^{-3}/s^{-1}$	$k_{nr}^g \times 10^{-3}/s^{-1}$	λ_{em}^c/nm	$\tau^e/\mu s$
2a	435	0.57	154	3.70	2.79	430	267
2b	447	0.60	99.7	6.02	4.01	442	215
2c	453	0.51	98.0	5.20	5.00	447	258
2d	458	0.28	74.3	3.77	9.69	451	478
2e	484	0.81	193	4.20	0.98	481	254
2f	512	0.20	110	1.82	7.27	504	450
2g	514	0.22	81.8	2.69	9.53	508	289
2h	565	0.05	17.2	2.91	55.23	553	65.6
2i	585	0.04	14.9	2.68	64.43	558	121

^a In deaerated CH₂Cl₂ solution (ca. 5×10^{-6} M). ^b In deaerated PrCN. ^c Highest-energy emission peak. ^d Absolute quantum yield. ^e Emission lifetime. ^f Radiative rate constant, $k_r = \Phi/\tau$. ^g Nonradiative rate constant, $k_{nr} = (1 - \Phi)/\tau$.

reported tris-cyclometalated Pt(IV) complexes.¹²⁻¹³ In fact, the emission spectra of **2b** and *fac*-[Pt(ppy)₃]⁺ are practically identical (Fig. S6, ESI[†]).

The new compounds are very bright emitters in CH₂Cl₂ solutions at room temperature, showing quantum yields (Φ) higher than 0.20, with the exception of **2h** and **2i**. An inspection of radiative and non-radiative rate constants (k_r and k_{nr} , respectively) shows that, while k_r values remain within the same order of magnitude along the series, k_{nr} values are significantly higher for **2h** and **2i**, indicating that non-radiative processes are more effective in these cases; reasonably, this behaviour can be ascribed to the lower energy of the emitting state in these derivatives, which leads to a more significant deactivation through vibrational coupling to the ground state.¹⁸ Both k_r and k_{nr} are higher in complexes **2** than in the respective tris-cyclometalated complexes *fac*-[Pt(C^{^A}N)₃]⁺ or *mer*-[Pt(ppy)₂(C^{^A}N')]⁺ bearing the same C^{^A}N or C^{^A}N' ligand in all the studied cases (C^{^A}N = dfppy, ppy, tpy; C^{^A}N' = thpy, piq).¹²⁻¹³ Notwithstanding, the new compounds exhibit higher quantum yields because the relative increase is much higher in k_r than in k_{nr} . This fact suggests a significantly higher MLCT contribution to the emitting ³LC state, which is known to accelerate the radiative transition to the ground state.^{9c,19} In turn, the higher MLCT character is attributable to the strong electron-donating ability of the methyl ligand and the uncharged nature of complexes **2**, which must necessarily correlate with a higher energy of the occupied metal d orbitals relative to the cationic tris-cyclometalated complexes and an increased contribution of these orbitals to the HOMO. The Bppy complex **2e** shows an impressive quantum yield of 0.81, comparable to the best Pt(II) and Ir(III) emitters^{8f,19-20} and represents the most efficient Pt(IV) complex ever reported. The excellent phosphorescent efficiency of metal complexes with the Bppy ligand has been previously ascribed to the enhancement of MLCT character in the excited state, which increases k_r ,²¹ in addition, this effect combines with an important decrease in k_{nr} owing to the presence of the bulky BMes₂ substituent.

The emission spectra of **2b** were also registered at concentrations in the range 10^{-5} - 10^{-3} M in CH₂Cl₂ at 298 K to probe possible concentration effects (Fig. S8, ESI[†]). Although the emission profile did not change, a dramatic decrease in intensity was observed at high concentrations, indicating intermolecular quenching. A similar effect has been observed for tris-cyclometalated Pt(IV) derivatives¹² and other octahedral emitters,²² most probably due to triplet-triplet annihilation.²³

Additional insight into the electronic properties of the new complexes was gathered by comparing the electrochemical data of **2b**, obtained using cyclic voltammetry in MeCN solution, with those of *fac*-[Pt(ppy)₃]⁺¹³ (Table 2). The cyclic voltammogram of **2b** (Fig. S9, ESI[†]) shows several irreversible reduction peaks that resemble those observed for *fac*-[Pt(ppy)₃]⁺; the first of them corresponds a one-electron process and occurs at almost the same potential, indicating that the LUMO is based on the ppy ligand. However, while the oxidation of the tris-cyclometalated complex falls outside the solvent discharge limit, the oxidation of **2b** occurs at a less positive potential and can be observed, which implies a significantly higher HOMO energy and is consistent with the above-discussed higher metal orbital involvement.

Photostability is an important issue in compounds designed for optical or photochemical applications. We have previously observed that tris-cyclometalated Pt(IV) complexes containing one thpy or piq ligand were not stable upon exposure to UV light.¹³ In contrast, derivatives **2g** and **2h**, which bear these ligands, remained unaltered upon irradiation with a 36 W UVB lamp in CD₂Cl₂ solution for 4 hours (Fig. S10 and S11, ESI[†]).

Table 2 Electrochemical data^a and HOMO/LUMO energy estimations^b for complex **2b** compared with *fac*-[Pt(ppy)₃]⁺OTf.

Complex	E_{pa}^c	E_{pc}^d	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO-LUMO}$
2b	1.93	-1.83	-6.50	-2.97	3.53
<i>fac</i> -[Pt(ppy) ₃] ⁺	— ^e	-1.80	—	-2.71	—

^a In V relative to SCE, measured in 0.1 M (Bu₄N)PF₆ anhydrous MeCN solution at 100 mV s⁻¹. ^b In eV. ^c Irreversible anodic peak potential. ^d First irreversible cathodic peak potential. ^e Outside solvent window.

In summary, we report the one-pot method for the synthesis of luminescent bis-cyclometalated chloro(methyl)platinum(IV) complexes featuring long excited-state lifetimes and remarkably high quantum yields that can reach the level of the best Pt(II) and Ir(III) emitters. Their easier synthesis, wider tunability and higher efficiencies with respect to the previously reported Pt(IV) emitters make them an attractive alternative for diverse applications, including photocatalysis, bioimaging or chemosensing.

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