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

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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-arylpyridine 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 d6 [mainly Ru(II), Os(II) and Ir(III)], d8 [Pt(II), Au(III)] and d10 [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) 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 d6 ions, related works on Pt(IV) complexes are scarce and appear to have been overshadowed by the strong focus on Pt(II).9 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, CHCl3] 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=C=N)]13 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

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

† Electronic supplementary information (ESI) available: Experimental details and characterization data. CCDC 1435571–1435574. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc09566b

Received 18th November 2015, Accepted 2nd December 2015
DOI: 10.1039/c5cc09566b
www.rsc.org/chemcomm
high stability, tunable emission energies and generally high quantum yields, which make them very attractive as triplet emitters.

Compounds 2a–i were prepared following a one-pot, two-step procedure (Scheme 1). The first step is the reaction of \([\text{Pt}_2\text{Me}_4(\mu-\text{SMe}_2)_2]\) with the \(\text{N}^+\text{CH}\) compound in 0.5 : 2 molar ratio in refluxing acetone, which leads to the cyclometalation of one \(\text{N}^+\text{CH}\) 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 \(\text{N}^+\text{CH}\) compounds to give cyclometalated complexes of the type \([\text{PtMe}(\text{C}^4\text{N})(\text{SMe}_2)]\) and methane, while substitution of the labile \(\text{Me}_2\text{S}\) 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 \(\text{N}^+\text{CH}\) ligand to give complexes 2a–i. Similar metalations upon oxidation with PhICl\(_2\) have been reported for complexes of the type \([\text{Pt}(\text{C}^4\text{N})(\text{N}^+\text{CH})\text{Cl}]\) (\(\text{N}^+\text{CH}\) 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\(_2\text{Cl}_2\) were solved by X-ray crystal diffraction studies.\(^{17}\) The molecular structure of 2b is depicted in Fig. 1 and the others 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.\(^{16}\) 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.

The absorption spectra of 2a–i in CH\(_2\text{Cl}_2\) 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) complexes and can be ascribed to essentially \(1\text{LC}\) transitions within the \(\text{C}^4\text{N}\) 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 \(\pi–\pi^*\) transition energies. This band has a significantly higher absorptivity for 2e and 2f (40 600 or 51 500 M\(^{-1}\) 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\(_2\text{Cl}_2\) 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
The emission spectra of 2b were also registered at concentrations in the range 10^{-5} to 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 intramolecular quenching. A similar effect has been observed for tris-cyclometalated Pt(n) 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]2+ (Table 2). The cyclic voltammogram of 2b (Fig. S9, ESI†) shows several irreversible reduction peaks that resemble those observed for fac-[Pt(ppy)3]2+; 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(n) 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†).

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

This work was supported by Ministerio de Economía y Competitividad, Spain (project CTQ2011-24016, with FEDER support, and FPU grant to F. J.) and Universidad de Murcia.

### Table 1 Emission data of complexes 2a–i

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{em} /nm</th>
<th>Φ /Φ</th>
<th>τ /µs</th>
<th>k_{r} /10^{-3} s^{-1}</th>
<th>k_{nr} /10^{-3} s^{-1}</th>
<th>λ_{em} /nm</th>
<th>τ /µs</th>
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</thead>
<tbody>
<tr>
<td>2a</td>
<td>435</td>
<td>0.57</td>
<td>154</td>
<td>3.70</td>
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<td>267</td>
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<tr>
<td>2b</td>
<td>447</td>
<td>0.60</td>
<td>99.7</td>
<td>6.02</td>
<td>4.01</td>
<td>442</td>
<td>215</td>
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<tr>
<td>2c</td>
<td>453</td>
<td>0.51</td>
<td>98.0</td>
<td>5.20</td>
<td>5.00</td>
<td>447</td>
<td>238</td>
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<tr>
<td>2d</td>
<td>458</td>
<td>0.28</td>
<td>74.3</td>
<td>3.77</td>
<td>6.99</td>
<td>451</td>
<td>478</td>
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<tr>
<td>2e</td>
<td>484</td>
<td>0.81</td>
<td>193</td>
<td>4.20</td>
<td>0.98</td>
<td>481</td>
<td>254</td>
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<tr>
<td>2f</td>
<td>512</td>
<td>0.20</td>
<td>110</td>
<td>1.82</td>
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<td>450</td>
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<tr>
<td>2g</td>
<td>514</td>
<td>0.22</td>
<td>81.8</td>
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<td>9.53</td>
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<tr>
<td>2h</td>
<td>565</td>
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</tr>
<tr>
<td>2i</td>
<td>585</td>
<td>0.14</td>
<td>14.9</td>
<td>2.68</td>
<td>9.53</td>
<td>538</td>
<td>121</td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{Pa} /V</th>
<th>E_{pc} /V</th>
<th>E_{HOMO} /eV</th>
<th>E_{LUMO} /eV</th>
<th>ΔE_{HOMO-LUMO} /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>1.93</td>
<td>-1.83</td>
<td>-6.50</td>
<td>-2.97</td>
<td>3.53</td>
</tr>
</tbody>
</table>

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 First irreversible anodic peak potential. d Outside solvent window.
Notes and references

17. CCDC 1435571–1435574.