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Water-soluble Ir(III) complexes of deprotonated N-methylbipyridinium ligands: Fluorine-free blue emitters

Benjamin J. Coe,* Madeleine Helliwell, Sergio Sánchez, Martyn K. Peers, and Nigel S. Scrutton

New blue or blue-green emitting iridium complexes have been synthesised with cyclometalating ligands derived from the 1-methyl-3-(2′-pyridyl)pyridinium cation. Efficient luminescence is observed in MeCN or aqueous solutions, with a large range of lifetimes in the μs region and relatively high quantum yields.

The creation of bright and stable blue emitting compounds is a major challenge in the development of light-emitting electrochemical cells and organic light-emitting diodes (OLEDs). A common structural type is [Ir(III)(C^N)₂(N^N)]⁺, where C^N is a cyclometalating ligand like deprotonated 2-phenylpyridine, and N^N is an α-diimine. A popular strategy to blue-shift the emission is to derivatise C^N with electron-withdrawing groups (often –F or –CF₃) and/or place electron donors on N^N. Avoiding the use of fluorine is desirable to maximise the stability of the complexes in devices, and from an environmental perspective. Hence, we present an alternative approach, creating new fluorine-free Ir(III) luminophores by using 1-methyl-3-(2′-pyridyl)pyridinium to generate C^N. The quaternised nitrogen opposite the cyclometalating carbon is key to blue-shifting the emission.

Ir(III) complexes of C^N ligands derived from pyridinium species are extremely scarce. Notably, these known complexes are not suitable for luminescence, but were prepared in the context of catalytic studies. Complexes with quaternary N units as part of N^N have been reported, but these groups are generally not strongly coupled electronically to the Ir(III) centre. Remote ammonium groups have been attached to C^N or acetylacetonate ancillary ligands. Using Ir(III) complexes in bio-sensing/imaging is often restricted by poor water solubility, so increased positive charge is beneficial. Given this context and our general interest in photoactive complexes with quaternised pyridinium moieties, we targeted unusual Ir(III) species combining attractive emission and solubility properties.

The new complexes 1–3 were synthesised by a standard approach, i.e. cleaving a cyclometalated chloride-bridged dimer with a N^N ligand (Scheme 1). The PF₆⁻ and Cl⁻ salts were characterised by ¹H NMR spectroscopy, electrospray mass spectrometry and elemental analyses (see ESI†). In addition, single-crystal X-ray structures have been solved for 1P·2MeCN and 3P·3Me₂CO (Tables S1 and S3, Figs. S1 and S2, ESI†). As expected, both complexes exhibit pseudo-octahedral coordination at Ir, with the pyridyl rings of the C^N ligands in a trans geometry (Fig. 1). Their chemical structures bear some resemblance to the widely studied complexes of N-heterocyclic carbenes derived from imidazolium species, although such complexes are typically neutral or only +1 charged.

Scheme 1 Synthesis of the complex salts 1P–3P; their chloride counterparts 1C–3C were prepared by treating purified 1P–3P with [nBu₄N]Cl in acetone.

Fig. 1. Representations of the molecular structures of the complex cations 1P·2MeCN and 3P·3Me₂CO, with the PF₆⁻ anions, solvent molecules and H atoms removed for clarity (50% probability ellipsoids).
UV–vis absorption spectroscopic data are shown in Table 1. These spectra are almost unaffected by changing the counter-ions and solvent. They are dominated by intense bands at λ < 320 nm (Figs. 1P and 2P) with little effects, and the excitation profiles remain constant in all cases while monitoring at all the emission maxima. The spectra are very similar for R = H or 1Bu (λem = 468–474 nm), but shifted significantly to lower energy when R = CF3 (λem = 494). The fact that replacing H with 1Bu has little effect while –CF3 groups give a red-shift suggests that the character of the emitting state varies. The almost identical spectra of S3 and S4, ESI† show an irreversible oxidation, formally assigned to a Ir IV/III couple. The reductive region includes multiple irreversible processes, and a sharp return peak is observed for 1P and 3P, indicating adsorption onto the electrode surface.

Excitation at 315–400 nm in deoxygenated and oxygenated MeCN or aqueous solutions leads to bright blue (1 and 3) or blue-green (2) luminescence (Table 1). The spectra show significant fine structure, indicating primarily ligand-centred emission. As for the absorption spectra, changing the counter-anion and solvent has only slight effects, and the excitation profiles remain constant in all cases while monitoring at all the emission maxima. The spectra are very similar for R = H or 1Bu (λem = 468–474 nm), but shifted significantly to lower energy when R = CF3 (λem = 494). The fact that replacing H with 1Bu has little effect while –CF3 groups give a red-shift suggests that the character of the emitting state varies. The almost identical spectra of 1 and 3 (Fig. 2) indicate mainly 1Lc emission involving CN ligands with little MLCT contribution. However, the red-shift for 2 suggests that the emission is associated with N=N. The quantum yields ϕ are not affected significantly by the counter-ions under deoxygenated conditions, but are substantially enhanced when R = CF3 or 1Bu (ϕ ≈ 42–45%) as opposed to H (ϕ ≈ 24–27%). In oxygenated conditions, 2 shows the largest ϕ values. All complexes have emission lifetimes τ in the μs region, covering a large range of values (ca. 1–12 μs), with monoexponential decay kinetics. 1C and 3C show relatively long τ values in water, considerably longer than for 2C (Fig. 3).

The observed blue emissions from the fluorine-free complexes 1 and 3 are remarkable since, as mentioned above, decorating the CN ligands with F or fluorinated groups is a common strategy to blue-shift the emission of this type of complex. The influence of the pyridinum fragment located para to the cyclometalating carbon is clearly shown by comparing the emission properties of 3P (λmax = 470 nm, ϕdeoxygen = 68%, τdeoxygen = 2.3 ms) with other reported complexes [Ir(3 CN)(4,4′-(Bu)2py)]. When using the heavily fluorinated cyclometalating ligand derived from 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, the emission in MeCN (λmax = 470 nm, ϕdeoxygen = 43%, τdeoxygen = 3.8 ms) with other reported complexes [Ir(3 CN)(4,4′-(Bu)2py)]. When using the heavily fluorinated cyclometalating ligand derived from 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, the emission in MeCN

### Table 1. Absorption and emission data at 298 K in solutions ca. 1.0 × 10−5–2.0 × 10−4 M. Luminescence data measured in the presence (ox) or absence (deoxygen) of oxygen.

| Complex salt | Absorption, λmax/nm (ε/10^4 M⁻¹ cm⁻¹) | Emission, λ/nm | τ/μs | ϕ(%)† |
|--------------|--------------------------------------|==============|------|------|
| 1P          | 237 (54.3), 255sh (48.4), 302 (25.9), 313 (24.5), 352sh (5.3) | 444, 474, 504, 548 | 1.2 | 24 |
| 1C          | 237 (48.3), 255sh (42.4), 302 (22.8), 312 (21.8), 353sh (4.8) | 442, 470, 504, 547 | 1.2 | 27 |
| 2P          | 236 (47.4), 257 (43.2), 308 (21.6), 316 (20.9), 350sh (5.4) | 466, 494, 525, 574 | 1.5 | 16 |
| 2C          | 237 (52.7), 259 (52.1), 308 (25.2), 317 (24.3), 350sh (5.8) | 462, 494, 529, 575 | 1.2 | 24 |
| 3P          | 236 (51.8), 259sh (44.9), 299 (23.9), 311 (23.2), 356sh (4.5) | 440, 470, 502, 546 | 1.2 | 11 |
| 3C          | 237 (58.0), 260 (49.9), 300 (25.4), 312 (25.9), 355sh (5.5) | 440, 468, 500, 547 | 2.5 | 14 |

† In MeCN. In water. Estimated experimental errors ±10%.
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The $T_1$ geometries resemble the $S_0$ ones, except that 1 and 3 now have unequal Ir–C (and chemically equivalent) Ir–N distances, while in 2, these pairs of distances are equal. The calculated emission energies (Table 2) follow the experimental trend ($1 \approx 3 > 2$). The spin densities for the $T_1$ state (Fig. 4) show mainly $\text{L}^1\text{C}$ involving one C$^N$ ligand with some $3\text{MLCT}$ contribution for 1 and 3. In contrast, for 2, the spin density is located on N$^N$ largely, indicating that the emission has $\text{L}^1\text{C}$ character with some $1\text{MLCT}$. Therefore, on excitation from the C$^N$/Ir-centred HOMO–2 to the C$^N$-centred LUMO (336 nm transition) in 2, there is efficient inter-ligand energy transfer to the emitting $\text{L}^1\text{C}$ excited state of N$^N$. Such energy transfer is expected if the $\text{L}^1\text{C}$ state lies below the $3\text{MLCT}$. In 2, the presence of the electron-withdrawing –CF$_3$ groups stabilises the n* orbitals of the N$^N$ ligand, lowering the energy of the $\text{L}^1\text{C}$ state.

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**Notes and references**


**Table 2.** Predicted and measured emission data in MeCN.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{exc}}$/eV (λ/nm)</th>
<th>$E_{\text{em}}$/eV (λ/nm)</th>
<th>$\lambda_{\text{max}}$/nm (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.91 (426)</td>
<td>2.46 (504)</td>
<td>474</td>
</tr>
<tr>
<td>2</td>
<td>2.76 (450)</td>
<td>2.28 (544)</td>
<td>494</td>
</tr>
<tr>
<td>3</td>
<td>2.91 (426)</td>
<td>2.47 (503)</td>
<td>470</td>
</tr>
</tbody>
</table>

$E_{\text{exc}}$ calculated by using the DFT-optimised geometries for $T_1$ and $S_0$. $E_{\text{em}}$ calculated by using the DFT-optimised $T_1$ geometry for both states (adiabatic electronic emission).

GRAPHICAL ABSTRACT

Using the cation 1-methyl-3-(2’-pyridyl)pyridinium to produce cyclometalating ligands gives novel Ir$^{III}$ complex salts that are water-soluble and emit efficiently blue or blue-green light.