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

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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 μ s region and relatively high quantum yields.

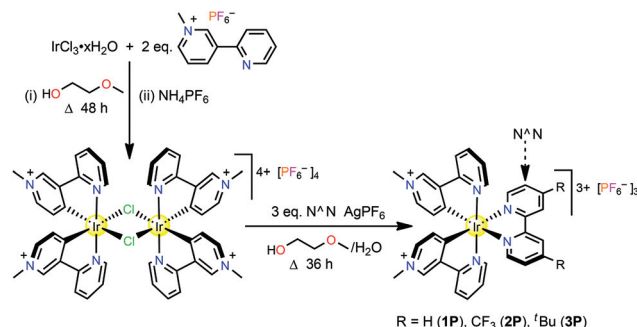
The creation of bright and stable blue emitting compounds is a major challenge in the development of light-emitting electrochemical cells and organic light-emitting diodes (OLEDs).^{1,2} Iridium complexes have been investigated extensively due to their widely tunable and efficient luminescence.^{2–12} A common structural type is $[\text{Ir}^{\text{III}}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$, where $\text{C}^{\wedge}\text{N}$ is a cyclometalating ligand like deprotonated 2-phenylpyridine, and $\text{N}^{\wedge}\text{N}$ is an α -diimine. A popular strategy to blue-shift the emission is to derivatise $\text{C}^{\wedge}\text{N}$ with electron-withdrawing groups (often $-\text{F}$ or $-\text{CF}_3$) and/or place electron donors on $\text{N}^{\wedge}\text{N}$. 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 $\text{C}^{\wedge}\text{N}$. The quaternised nitrogen opposite the cyclometalating carbon is key to blue-shifting the emission.

Ir^{III} complexes of $\text{C}^{\wedge}\text{N}$ ligands derived from pyridinium species are extremely scarce.¹³ 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 $\text{N}^{\wedge}\text{N}$ have been reported, but these groups are generally not strongly coupled electronically to the Ir^{III} centre.^{14–17} Remote ammonium groups have been attached to $\text{C}^{\wedge}\text{N}$ ¹⁸ or acetylacetonate¹⁹ ancillary ligands. Using Ir^{III}

complexes in bio-sensing/imaging²⁰ is often restricted by poor water solubility,²¹ so increased positive charge is beneficial. Given this context and our general interest in photoactive complexes with quaternised pyridinium moieties,²² 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 $\text{N}^{\wedge}\text{N}$ ligand (Scheme 1). The PF_6^- 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, Fig. S1 and S2, ESI†). As expected, both complexes exhibit pseudooctahedral coordination at Ir, with the pyridyl rings of the $\text{C}^{\wedge}\text{N}$ 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.^{23–26}

UV–vis absorption spectroscopic data are shown in Table 1. These spectra are almost unaffected by changing the counter-anions and solvent. They are dominated by intense bands at $\lambda < 320$ nm (Fig. S3 and S4, ESI†), assigned to $\pi \rightarrow \pi^*$ and high



Scheme 1 Synthesis of the complex salts 1P–3P; their chloride counterparts 1C–3C were prepared by treating purified 1P–3P with [$t\text{Bu}_4\text{N}$]Cl in acetone.

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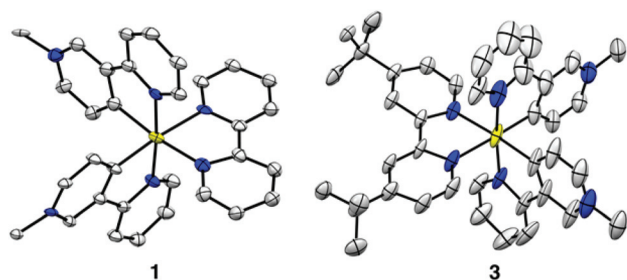


Fig. 1 Representations of the molecular structures of the complexations in **1P**-2MeCN and **3P**-3PMe₂CO, with the PF₆[−] anions, solvent molecules and H atoms removed for clarity (50% probability ellipsoids).

energy metal-to-ligand charge-transfer (MLCT) transitions, involving both the C[^]N and N[^]N ligands. Weaker bands ($\lambda_{\text{max}} \approx 350\text{--}356\text{ nm}$) are observed also. Cyclic voltammograms of **1P**-**3P** in MeCN (Fig. S5, Table S2, 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 ^tBu ($\lambda_{\text{em}} = 468\text{--}474\text{ nm}$), but shifted significantly to lower energy when R = CF₃ ($\lambda_{\text{em}} = 494$). The fact that replacing H with ^tBu 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 ³LC emission involving C[^]N with little ³MLCT 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-anions under deoxygenated conditions, but are substantially enhanced when R = CF₃ or ^tBu ($\phi \approx 42\text{--}45\%$) as opposed to H ($\phi \approx 24\text{--}27\%$). In oxygenated conditions, **2** shows the largest ϕ values. All complexes have

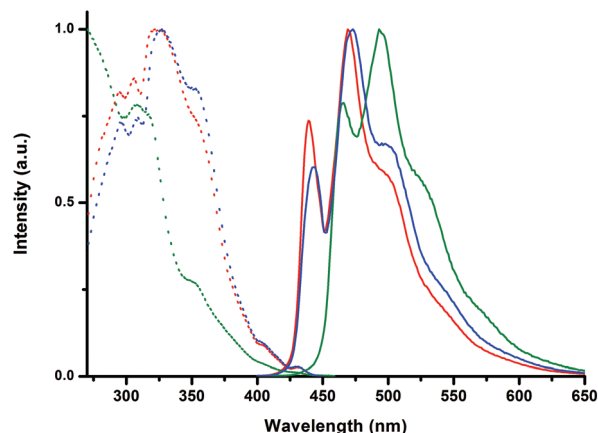


Fig. 2 Emission spectra of **1P** (blue), **2P** (green) and **3P** (red) with excitation at 350 nm in MeCN.

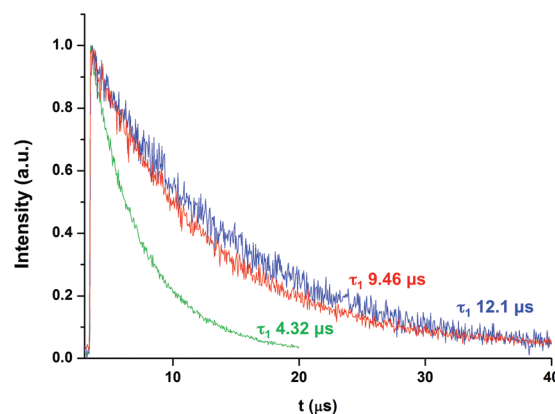


Fig. 3 Emission decay traces in water of **1C** (blue), **2C** (green) and **3C** (red) following 375 nm excitation with a ps pulsed diode laser.

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).

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 (deox) of oxygen

Complex salt	Absorption, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3\text{ M}^{-1}\text{ cm}^{-1}$)	Emission, λ/nm	$\tau^c/\mu\text{s}$		ϕ^c (%)	
			deox	ox	deox	ox
1P ^a	237 (54.3), 255sh (48.5), 302 (25.9), 313 (24.5), 352sh (5.3)	444, 474 _{max} , 504, 548	3.5	1.2	24	4.7
1C ^b	237 (48.3), 255sh (42.4), 302 (22.8), 312 (21.8), 353sh (4.8)	442, 470 _{max} , 504, 547	12.1	3.9	27	9.7
2P ^a	236 (47.4), 257 (43.2), 308 (21.6), 316 (20.9), 350sh (5.4)	466, 494 _{max} , 525, 574	3.8	1.5	43	16
2C ^b	237 (52.7), 259 (52.1), 308 (25.2), 317 (24.3), 350sh (5.8)	462, 494 _{max} , 529, 575	4.3	2.6	42	24
3P ^a	236 (51.8), 259sh (44.9), 299 (23.9), 311 (23.2), 356sh (4.5)	440, 470 _{max} , 502, 546	3.8	1.2	43	11
3C ^b	237 (58.0), 260 (49.9), 300 (25.4), 312 (25.9), 355sh (5.5)	440, 468 _{max} , 500, 547	9.5	2.9	45	14

^a In MeCN. ^b In water. ^c Estimated experimental errors $\pm 10\%$.



The observed blue emissions from the fluorine-free complexes **1** and **3** are remarkable since, as mentioned above, decorating the C[^]N ligands with F or fluorinated groups is a common strategy to blue-shift the emission of this type of complex. The influence of the pyridinium fragment located *para* to the cyclometalating carbon is clearly shown by comparing the emission properties of **3P** ($\lambda_{\text{max}} = 470$ nm, $\phi_{\text{deox}} = 43\%$, $\tau_{\text{deox}} = 3.8$ ms) with other reported complexes $[\text{Ir}^{\text{III}}(\text{C}^{\wedge}\text{N})_2\{4,4'-(\text{tBu})_2\text{bpy}\}]^+$. When using the heavily fluorinated cyclometalating ligand derived from 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, the emission in MeCN ($\lambda_{\text{max}} = 470$ nm, $\phi_{\text{deox}} = 68\%$, $\tau_{\text{deox}} = 2.3$ ms) is similar to that of **3P**.²⁷ On the other hand, when C[^]N is deprotonated 2-phenylpyridine, the emission in MeCN is red-shifted strongly ($\lambda_{\text{max}} = 581$ nm) with a lower ϕ_{deox} (24%) and shorter τ_{deox} (0.56 ms).²⁸

The singlet ground (S_0) and lowest triplet excited (T_1) states of **1–3** were optimised by using density functional theory (DFT) (Fig. S6–S9, Tables S3–S8, ESI†). The calculated ground-state structures for **1** and **3** reproduce well the X-ray crystallographic ones. The LUMO is located on the C[^]N (69–90%) and N[^]N (6–27%) ligands. The HOMO is located at the Ir atom (50–55%) and the C[^]N ligands (40–46%), and is essentially invariant. Such relatively high C[^]N contributions are consistent with the irreversible oxidations observed by cyclic voltammetry (see above). The spectra simulated by time-dependent DFT agree relatively well with those measured. The weak low energy bands are due to a single transition for **1** and **3**, a mixture of HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1 (347 nm, **1**) or HOMO \rightarrow LUMO (348 nm, **3**). For **2**, transitions occur at 342 nm (HOMO \rightarrow LUMO+1) and 336 nm (HOMO–2 \rightarrow LUMO), with the latter being *ca.* 5-fold more intense. These results indicate ¹MLCT character with ¹ML/CT and also ¹LL/CT for **1** and **2** ($L = \text{C}^{\wedge}\text{N}$; $L' = \text{N}^{\wedge}\text{N}$).

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 ³LC involving one C[^]N ligand with some ³MLCT contribution for **1** and **3**. In contrast, for **2**, the spin density is located on N[^]N largely, indicating that the emission has ³L/C character with some ³ML/CT. 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

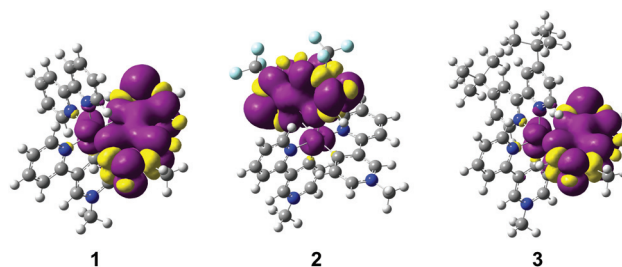


Fig. 4 M06/Def2-QZVP/SVP-calculated spin density plots for the T_1 state of complexes **1–3**.

the emitting ³L/C excited state of N[^]N. Such energy transfer is expected if the ³L/C state lies below the ³MLCT.²⁹ In **2**, the presence of the electron-withdrawing $-\text{CF}_3$ groups stabilises the π^* orbitals of the N[^]N ligand, lowering the energy of the ³L/C state.

To conclude, using 1-methyl-3-(2'-pyridyl)pyridinium to generate C[^]N affords new water-soluble Ir^{III} complexes. Their excited-state and emissive behaviour can be switched between two types by modifying N[^]N. The bright blue emission in MeCN and water of the fluorine-free complexes **1** and **3** suggests potential uses in highly efficient OLEDs or bio-imaging. The tunability of the emission properties is shown, not only by the emission maxima, but also in the range of quantum yields (*ca.* 5–45%) and lifetimes, from quite short (*ca.* 1 μs) to relatively long (*ca.* 12 μs). Much further scope exists for modifying properties, for example by using groups other than methyl on the quaternised N atom.

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Notes and references

- 1 X.-L. Yang, X.-B. Xu and G.-J. Zhou, *J. Mater. Chem. C*, 2015, **3**, 913–944.
- 2 Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2010, **39**, 638–655.
- 3 M. S. Lowry and S. Bernhard, *Chem. – Eur. J.*, 2006, **12**, 7970–7977.
- 4 J. A. G. Williams, A. J. Wilkinson and V. L. Whittle, *Dalton Trans.*, 2008, 2081–2099.
- 5 M. Mydlak, C. Bizzarri, D. Hartmann, W. Sarfert, G. Schmid and L. De Cola, *Adv. Funct. Mater.*, 2010, **20**, 1812–1820.
- 6 C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich and L. De Cola, *Chem. Mater.*, 2012, **24**, 3684–3695.
- 7 P. Brulatti, R. J. Gildea, J. A. K. Howard, V. Fattori, M. Cocchi and J. A. G. Williams, *Inorg. Chem.*, 2012, **51**, 3813–3826.

Table 2 Predicted and measured emission data in MeCN

Complex	$E_{0,0}/\text{eV}$ (λ/nm)	E_{AE}/eV (λ/nm)	$\lambda_{\text{max}}/\text{nm}$ (exp)
1	2.91 (426)	2.46 (504)	474
2	2.76 (450)	2.28 (544)	494
3	2.91 (426)	2.47 (503)	470

$E_{0,0}$ calculated by using the DFT-optimised geometries for T_1 and S_0 . E_{AE} calculated by using the DFT-optimised T_1 geometry for both states (adiabatic electronic emission).



- 8 N. Mohd Ali, V. L. MacLeod, P. Jennison, I. V. Sazanovich, C. A. Hunter, J. A. Weinstein and M. D. Ward, *Dalton Trans.*, 2012, **41**, 2408–2419.
- 9 N. M. Shavaleev, F. Monti, R. D. Costa, R. Scopelliti, H. J. Bolink, E. Ortí, G. Accorsi, N. Armaroli, E. Baranoff, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2012, **51**, 2263–2271.
- 10 E. Baggeley, D.-K. Cao, D. Sykes, S. W. Botchway, J. A. Weinstein and M. D. Ward, *Chem. – Eur. J.*, 2014, **20**, 8898–8903.
- 11 N. Darmawan, C.-H. Yang, M. Mauro, R. Fröhlich, L. De Cola, C.-H. Chang, Z.-J. Wu and C.-W. Tai, *J. Mater. Chem. C*, 2014, **2**, 2569–2582.
- 12 J.-B. Kim, S.-H. Han, K. Yang, S.-K. Kwon, J.-J. Kim and Y.-H. Kim, *Chem. Commun.*, 2015, **51**, 58–61.
- 13 G. Song, Y. Zhang, Y. Su, W. Deng, K. Han and X. Li, *Organometallics*, 2008, **27**, 6193–6201.
- 14 E. Zysman-Colman, J. D. Slinker, J. B. Parker, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2008, **20**, 388–396.
- 15 Y. Ma, S.-J. Liu, H.-R. Yang, Y.-Q. Wu, C.-J. Yang, X.-M. Liu, Q. Zhao, H.-Z. Wu, J.-C. Liang, F.-Y. Li and W. Huang, *J. Mater. Chem.*, 2011, **21**, 18974–18982.
- 16 F. Cucinotta, A. Guenet, C. Bizzarri, W. Mróz, C. Botta, B. Milián-Medina, J. Gierschner and L. De Cola, *ChemPlusChem*, 2014, **79**, 45–57.
- 17 H. Ahmad, A. Wragg, W. Cullen, C. Wombwell, A. J. H. M. Meijer and J. A. Thomas, *Chem. – Eur. J.*, 2014, **20**, 3089–3096.
- 18 P. Sun, X. Lu, Q. Fan, Z. Zhang, W. Song, B. Li, L. Huang, J. Peng and W. Huang, *Macromolecules*, 2011, **44**, 8763–8770.
- 19 H.-F. Shi, H.-B. Sun, H.-R. Yang, S.-J. Liu, G. Jenkins, W. Feng, F.-Y. Li, Q. Zhao, B. Liu and W. Huang, *Adv. Funct. Mater.*, 2013, **23**, 3268–3276.
- 20 S.-J. Liu, H. Liang, K. Y. Zhang, Q. Zhao, X.-B. Zhou, W.-J. Xu and W. Huang, *Chem. Commun.*, 2015, **51**, 7943–7946.
- 21 S. Stimpson, D. R. Jenkinson, A. Sadler, M. Latham, A. Wragg, A. J. H. M. Meijer and J. A. Thomas, *Angew. Chem., Int. Ed.*, 2015, **54**, 3000–3003.
- 22 B. J. Coe, *Coord. Chem. Rev.*, 2013, **257**, 1438–1458 and references therein.
- 23 C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang and C.-C. Wu, *Angew. Chem., Int. Ed.*, 2008, **47**, 4542–4545.
- 24 H. Sasabe, J.-i. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido, *Adv. Mater.*, 2010, **22**, 5003–5007.
- 25 S. B. Meier, W. Sarfert, J. M. Junquera-Hernández, M. Delgado, D. Tordera, E. Ortí, H. J. Bolink, F. Kessler, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin and E. Baranoff, *J. Mater. Chem. C*, 2013, **1**, 58–68.
- 26 F. Monti, M. G. I. La Placa, N. Armaroli, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin and F. Kessler, *Inorg. Chem.*, 2015, **54**, 3031–3042.
- 27 M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal Jr., G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712–5719.
- 28 J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J.-J. Wang, S. Parker, R. Rohl, S. Bernhard and G. G. Malliaras, *J. Am. Chem. Soc.*, 2004, **126**, 2763–2767.
- 29 Y. You and S. Y. Park, *J. Am. Chem. Soc.*, 2005, **127**, 12438–12439.

