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Tuning iridium(III) phenylpyridine complexes in the "almost blue" region†

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Received (in Cambridge, UK) 7th May 2004, Accepted 1st June 2004
First published as an Advance Article on the web 30th June 2004

We report on the synthesis and photophysical properties of blue emitting iridium(III) complexes. The use of a negatively charged ligand, such as a triazolyl pyridine, allows a facile preparation, maintaining the high energy emission (blue region) of heteroleptic complexes. We discuss the role played by electron withdrawing substituents of a different nature and also how the substitution position of the same group influences the spectroscopical behaviour.

Iridium(III) phenylpyridine based complexes are becoming increasingly important in applications such as light emitting devices[1] and luminescent biological labels,[2] due to their high quantum yields of luminescence and electroluminescence, stability, colour tunability and their versatility to form homo- and hetero-leptic complexes.[3] Similarly to the widely investigated ruthenium(II) complexes, their emission is often arising from a triplet metal to ligand charge transfer (^{3}MLCT) excited state, even though the mixing of the charge transfer state with the ligand centered (LC) states is under debate in the literature.[4] Unlike the ruthenium analogues, iridium(III) complexes are highly tunable in the colour of the emission. Appropriate substituents on the phenylpyridine ligands cause shifting of the light emission from the red to the "almost blue" region of the visible spectrum.[5]

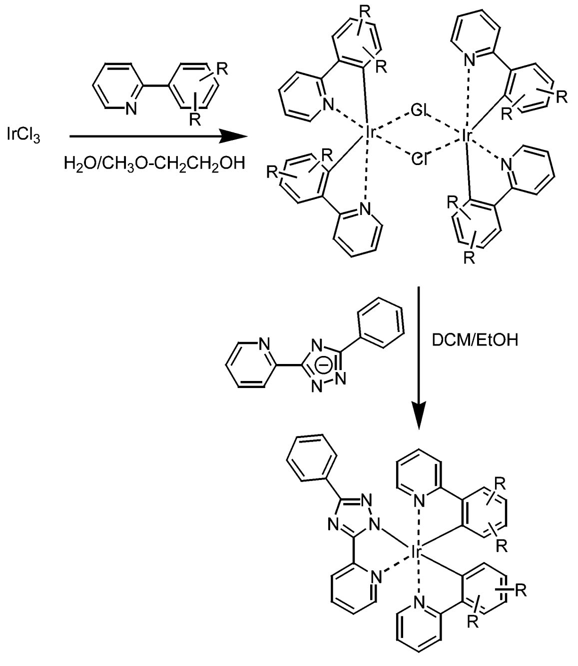
Recently, iridium(III) complexes carrying fluorinated phenylpyridines as ligands were reported, showing emission in the blue region.[6] In addition, a major effect on the emission energy in phenylpyridine based iridium(III) complexes was reported, when a strong electron withdrawing group was inserted in the *ortho* rather than *meta* position, with respect to the iridium ion.[7]

Despite considerable attention to the potential application of such organometallic systems, the difficult preparation and tedious purification has limited their production, especially for the heteroleptic neutral complexes. In fact, in most cases, their preparation proceeds *via* addition of the third ligand, to the iridium dichloro-precursor, at very high temperature.[1a,8]

In this communication, we report a room temperature procedure to prepare blue emitting complexes based on new phenylpyridines, carrying fluorides and trifluoromethyl groups and a triazolyl pyridine as the third ligand (see Scheme 1). The different effects of fluorine and trifluoromethyl groups in different positions on the phenylpyridine ligands lead to different emission properties. These electronic effects are proposed as a way to finely tune the colour of emission of the complexes.

Complexes **1–5** were prepared according to the synthetic procedures shown in Scheme 1. The novel strategy based on the use of the negatively charged third ligand, 2-(5-phenyl-4H-[1,2,4]triazol-3-yl)-pyridine,[9] allows the preparation to proceed under mild conditions, avoiding scrambling of the ligands and the formation of undesired iridium(III) tris-phenylpyridine derivatives. A similar procedure was reported for bipyridine ligands leading in that case to charged complexes.[10] Purification was performed *via* chromatography, as described in the supplementary material†.

The complexes show very similar absorption spectra with a weak ^{1}MLCT band in the 350–450 nm region and a strong π–π* transition in the UV. Complexes **1** and **2** emit at room temperature in dichloromethane solutions, with maxima ranging from 461 nm to 484 nm (see Fig. 1 and Table 1). The emission is attributed to a transition from the lowest excited state, ^{3}MLCT, that has some triplet ligand centered (^{3}LC) character, to the ground state. The different energies of the luminescence for the different complexes indicate that the position of the fluorides on the phenyl ring is essential in determining the properties of the iridium(III) complexes. Complex **2**, where the fluorides are in positions 2 and 4 with



Scheme 1 Synthetic protocol to prepare complexes **1–5**. R (the position of the substituents on the phenyl ring is given with respect to the coordinating carbon): **1** = 3,5 F; **2** = 2,4 F; **3** = 3,5 CF$_3$; **4** = 2,4 CF$_3$; **5** = H.

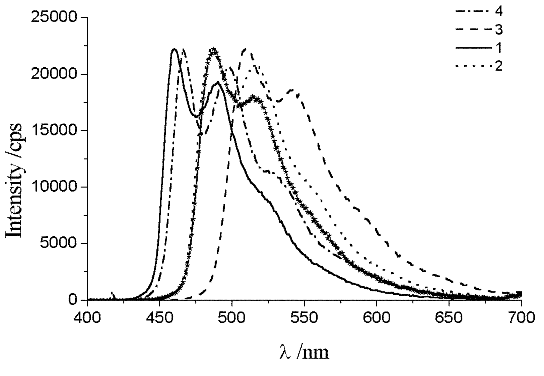


Fig. 1 Emission spectra of complexes **1–5** in degassed dichloromethane, at 293 K.

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† Electronic Supplementary Information (ESI) available: experimental procedures, characterisation of the complexes and UV–visible absorption spectra. See http://www.rsc.org/suppdata/cc/b4/b406851c/

DOI: 10.1039/b406851c

Table 1 Absorption and emission spectra, quantum yield, lifetime and redox potentials of complexes **1–5**[a]

Complex	λ_{max}Abs/nm	λ_{max}Em/nm	Φ	t/μs	$E_{\frac{1}{2}\,Ox}$/V	$E_{\frac{1}{2}\,Red}$/V
1	339(0.22); 280(0.82); 257(1)	461(1); 491(0.86)	0.27	1.4	0.99	−2.47
2	389(0.12); 347(0.23); 282(0.87); 262(1)	484(1); 518(0.95)	0.38	2.4	0.84	−2.52
3	447(0.05); 375(0.17); 346(0.22); 268(0.99); 259(1)	511(1); 544(0.83)	0.39	3.0	1.10	−2.44
4	325(0.27); 272(1)	466(1); 499(0.92)	0.30	3.7	1.16	−2.35
5	422(0.06); 377(0.14); 340(0.22); 263(1)	489(1); 517(0.81)	0.45	1.9	0.64	−2.53

[a] Absorption and emission spectra were recorded in spectroscopic grade dichloromethane at 293 K. Quantum yields of emission were measured in degassed dichloromethane solutions, using quinine bisulfate in 0.5 M H_2SO_4 (Φ = 0.546) as reference standard. The potentials were measured in anhydrous, freshly distilled butyronitrile, and are reported against the redox couple Cp_2Fe/Cp_2Fe^+ used as internal standard.

respect to the iridium ion, shows negligible blue shift in the emission, when compared to the unfluorinated analogue **5** (see Table 1 and Fig. 1).[7] Conversely, complex **1** shows an almost blue emission, with a hypsochromic shift in the maximum emission of 28 nm. This different behaviour is consistent with the double nature of the fluorine atom, inductive and mesomeric. The *meta* position on the phenyl ring, with respect to the fluoride, is the most electron deficient, causing a lowering of the σ donation from the cyclometallated ligand. This results in an energy increase of the ^{3}MLCT emitting level in complex **1**. In the case of complex **2**, the coordinating carbon is less electron deficient than for complex **1**, causing only a negligible effect on the spectroscopic properties, when compared to unfluorinated complex **5**.

The trifluoromethyl substituted complexes (**3–4**) show opposite behaviour. In the case of complex **4**, where the CF_3 groups are in position 2 and 4 with respect to the metal centre, there is a strong hypsochromic effect (λ_{max} = 466), compared to the unsubstituted complex **5**, indicating those positions to be the most effective in tuning the emission towards the blue region. Conversely, complex **3**, where the CF_3 groups are in *meta* position with respect to the coordinating carbon, shows a bathochromic shift in the emission maximum of 22 nm, when compared to complex **5**. This different behaviour is consistent with the inductive-only nature of the CF_3 group, which renders the *meta* positions the less electron deficient on the aromatic ring.

The excited state lifetimes of the emitting species, measured at 293 K with a streak camera interfaced to an infinity laser, tuned at 430 nm, are, in deaerated solutions, in the microsecond region (see Table 1), consistent with previous reports on the *fac* isomers of iridium(III) tris-phenylpyridine complexes.[3] Such long lived excited states and their sensitivity towards dioxygen, suggest, as already mentioned, that the emitting state has a triplet character.

Furthermore, the emission spectra are very structured and the low temperature spectra are barely shifted when compared with the room temperature measurements, confirming the low CT character. The quantum yields of emission are significantly lower for the most blue complexes **1** and **4**, when compared to the green complexes **2, 3** and **5**. All the complexes show emission quantum yields comparable to those obtained for the *fac* isomers of iridium(III) tris-phenylpyridines.[6]

Cyclic voltammograms are not fully reversible and show the expected increase in the oxidation potential for complexes **1–4** with respect to the unfluorinated complex **5**. The trifluoromethyl substituted complexes **3–4**, in particular, show oxidation potentials at about 1.1 V *vs.* Cp_2Fe/Cp_2Fe^+. If the first reduction occurs on the triazolyl pyridine, we would not expect significant differences when changing the substitution on the cyclometallated ligands. Indeed the reduction potentials are all very similar, indicating little effect of the electron withdrawing substituents. Furthermore, we believe that in such a case the electrochemical orbital involved is also the spectroscopic one. Indeed, the nature of the groups and their position, as already discussed before, influence the electron density on the iridium ion. It is expected that the “stronger” electron withdrawing effect of the fluorine for complex **1** and of the CF_3 for complex **4** cause a blue shift of the ^{3}MLCT, since the electron density on the metal centre is lower than for the analogous complex **2** and **3**.

In conclusion, we have shown that blue emitting hetero-leptic iridium complexes can be easily prepared by using a triazolyl pyridine derivative as the third ligand. We have shown how the choice of a purely inductive substituent or a mixed mesomeric–inductive one on a phenylpyiridine ligand and the position of the substituent on the phenyl ring have major effect on the emitting properties of iridium(III) complexes. The careful derivatisation of the coordinated ligands can produce a fine tuning of the emission colour in the green–blue region of the visible spectrum. The use of these materials for electroluminescent devices and for diagnostic applications is under investigation.

We wish to acknowledge Roche Diagnostics and Philips Research for funding the project, Prof. P. Belser and the Fribourg mass spectrometry department for characterisation of the complexes. P. C. wishes to acknowledge EU, project HPMT-CT-2001–00311.

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