ChemComm

Iridium(III) bis-terpyridine complexes displaying long-lived pH sensitive luminescence

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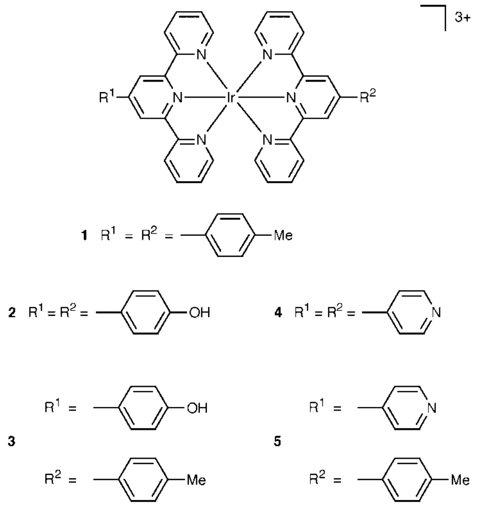
Received (in Cambridge, UK) 30th July 1999, Accepted 27th August 1999

A bis-terpyridine complex of iridium(III) incorporating a pendent pyridyl group displays long-lived emission at pH 7 in air-equilibrated aqueous solution, but both the lifetime and intensity are reduced by a factor of > 8 upon protonation of the pyridyl nitrogen; structurally similar complexes with pendent phenolic groups are only weakly emissive and their ground-state absorption spectra show a new, low-energy band (λ = 468 nm) upon deprotonation.

Molecular luminescent sensors that are able to signal the presence of molecules or ions in aqueous solution are of current interest because of their application to the analysis of biological or environmental samples.[1] Luminescent metal complexes are under investigation for such applications owing in part to the long-lived emission which some of them display, allowing discrimination from the shorter-lived background fluorescence often present in such samples.[2] Although systems based on certain lanthanide(III) ions show promise,[2,3] there are few complexes of transition metal ions with suitably long luminescence lifetimes under ambient conditions. The photophysical properties of polypyridyl ruthenium(II) complexes continue to attract a great deal of attention; sensors for pH incorporating a $Ru(bpy)_3^{2+}$ reporter have been described[4] and a study of a range of derivatives of $Ru(bpy)_3^{2+}$ bearing pyridyl and phenolic substituents has revealed pH-sensitive MLCT emission.[5] Similarly, a bis-terpyridine ruthenium(II) complex incorporating a pendent terpyridyl group displayed enhanced luminescence upon protonation, the lifetime increasing from 4 to 80 ns.[6] Short lifetimes of this magnitude are typical and seriously limit the utility of such ruthenium complexes in applications where longer lifetimes are desirable.

Recent work on bis-terpyridine complexes of iridium(III), such as **1**, has highlighted the very different photophysical properties compared to the Ru(II) analogues.[7,8] Intense ligand-centred emission has been observed in solution (τ > 1 μs under ambient conditions). We have now prepared complexes **2**–**5** in which the terpyridine ligands bear pendent protonatable (pyridyl) or deprotonatable (phenolic) groups. The ligands used here, 4′-tolyl-2,2′:6′,2″-terpyridine (ttpy), 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (qtpy) and 4′-(4-hydroxyphenyl)-2,2′:6′,2″-terpyridine (tpy-OH), were prepared using established methods.[9a–c] Complexes **3** and **5** were prepared *via* the intermediacy of $(ttpy)IrCl_3$, itself obtained by reaction of $IrCl_3\cdot 3H_2O$ with 1 equiv. of ttpy in refluxing ethanol. Subsequent reaction with 1 equiv. of tpy-OH or qtpy in ethylene glycol at 200 °C for 1 h led to **3** and **5** respectively after chromatographic separation on silica. The symmetric complex **4** was prepared by a related route involving reaction of $(qtpy)IrCl_3$ with qtpy, whilst complex **2** could be obtained by the direct reaction of $IrCl_3\cdot 3H_2O$ with 2 equiv. of tpy-OH in refluxing ethylene glycol.†



The ground-state absorption spectra of all four complexes in aqueous solution at pH 6 (NO_3^- salts) showed strong absorption bands (ε 10^4–10^5 $dm^3\ mol^{-1}\ cm^{-1}$) in the region 250–400 nm. In the case of the pyridyl-appended complexes **4** and **5**, which are pale yellow, no significant change in the absorption spectrum was observed upon protonation. This is consistent with predominantly ligand-centred transitions (as proposed tentatively for the parent complex **1**[8]), rather than MLCT transitions: the latter would be expected to show a significant red-shift upon protonation, as the π-acceptor ability of the ligand is enhanced [*e.g.* for the Ru(II) and Fe(II) analogues of **4**, a red-shift of the MLCT absorption of 14 and 25 nm, respectively, has been reported upon protonation[10]]. On the other hand, the phenolic-substituted complexes **2** and **3**, also pale yellow at pH 6, became deep orange upon increasing the pH to 10 and a new, well defined band appeared in the absorption spectrum centred at 468 nm (Fig. 1). A somewhat similar colour change was seen for the free ligand itself but, in this case, arises from the tailing of a band centred below 400 nm into the visible region. The appearance of the long-wavelength band in the present instance must reflect the efficacy of the tripositive iridium centre in promoting delocalisation of the negative charge of the phenolate over the entire ligand framework, imparting some quinone character to the ligand and an associated ligand-centred transition of low energy.[11] From the change in absorbance as a function of pH, the ground-state

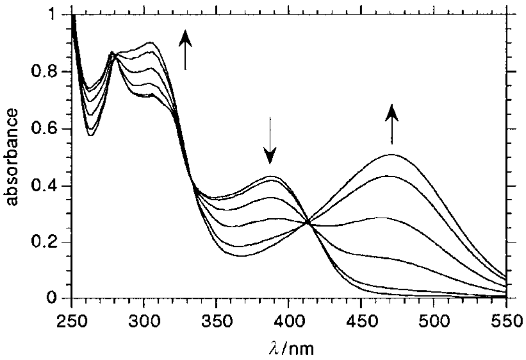


Fig. 1 Room temperature absorption spectra of complex **2** in aqueous solution at pH 5.3, 6.7, 7.6, 8.3, 9.0, 10.1. The arrows indicate the changes in the spectrum which occur as the pH is increased (addition of KOH).

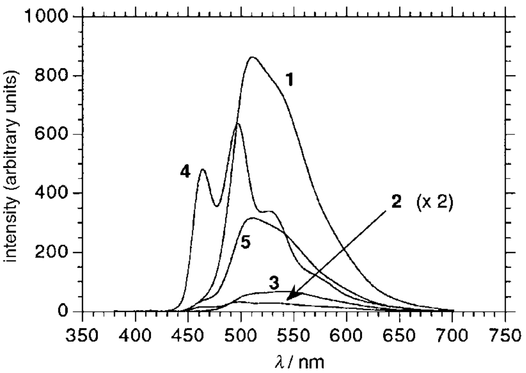


Fig. 2 Room temperature luminescence spectra of air-equilibrated, isoabsorbant aqueous solutions of **1**–**5** at pH 6.0, λ_{ex} = 364 nm.

pK_a of the complex was found to be 8.1. This is considerably more acidic than phenol itself (pK_a 10.0), which is a further indication of the stabilisation of the negative charge which may occur in the complex.

Room temperature luminescence spectra of air-equilibrated aqueous solutions of the complexes are shown in Fig. 2. Whereas the well resolved bands and emission maxima of complex **4** (and, to a somewhat lesser extent, **2**) resemble those of the unsubstituted bis-terpyridine complex, Ir(terpy)$_2{}^{3+}$,[7,8] the spectra of complexes **3** and **5** are more similar to the tolyl-substituted complex **1**. The sensitive dependence of the emission profile on the presence of 4′-substituents has been noted previously and discussed in terms of a greater delocalisation of the LC excited state over the 4′-aryl substituents.[8] Thus, it appears that the tolyl group must be more effective in this role than either the phenol or pyridyl substituents, or that the dihedral angle between the tolyl and terpy fragments in the excited state is more favourable for such delocalisation than for the other ligands. The phenol-appended complex **2** was only weakly emissive and found to be completely quenched upon deprotonation of the phenol. For the mixed ligand complex **3**, the emission was considerably more intense and only modestly reduced (by a factor of 1.6) over the pH range 6–10; the residual emission at high pH in this complex is thus likely to be due to the tolyl-terpyridine ligand only.

The effect of protonation on the luminescence of complex **5** is striking. Although no significant change in the spectral profile of **5** was observed (again supporting the assignment of the transitions as predominantly ligand-centred), the intensity of the emission was reduced by *ca.* 8-fold on lowering the pH from 7 to 2 (Fig. 3). Significantly, the lifetime was also reduced by a comparable factor, from 4.7 μs at pH 7 to 0.48 μs at pH 2 (caption to Fig. 3). It is well established that the mixing of d–π* charge transfer excited states into emissive π–π* ligand-centred states can promote deactivation and thereby shorten the observed lifetimes.[7] Protonation of complex **5** will lower the energy of the MLCT excited states, as noted above, leading to increased mixing with the emissive LC state and hence to the shorter lifetimes and reduced intensities which are observed. The pK_a of the excited state was found to be 4.1, significantly lower than the value of 5.25 for pyridine itself. This may be ascribed in part to electrostatic effects: protonation of the pendent pyridine increases the overall charge from +3 to +4, and also to the presence of the electron-withdrawing metal–terpyridyl unit on the 4-position of the pendent pyridine, which will serve to reduce the basicity of the uncoordinated nitrogen. Complex **4** also showed a reduction in lifetime and intensity over the same pH range, but by a smaller factor (τ = 1.1 μs at pH 7, τ = 0.34 μs at pH 2, in air-equilibrated aqueous solution).

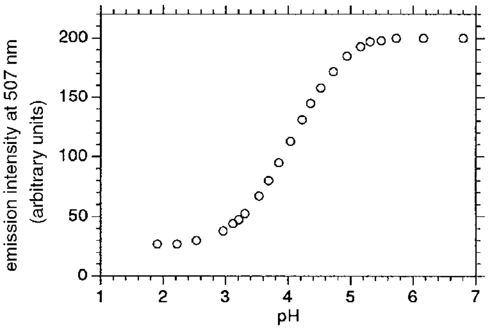


Fig. 3 Effect of pH on the emission intensity of complex **5** (monitored at 507 nm) in air-equilibrated aqueous solution, λ_{ex} = 360 nm. At the pH extremes, monoexponential decay of emission was observed and the following lifetimes were obtained: pH 6.2, τ = 4.7 μs; pH 2.0, τ = 0.48 μs. The corresponding values in degassed solution were 11.1 and 0.60 μs, respectively.

In summary, the iridium complexes described, especially complex **5**, constitute potential new sensory systems for pH, where changes in lifetime as well as intensity may be used to characterise the pH dependence, and which may be amenable to time-resolved detection methods.

We thank Dr A. Beeby for assistance with time-resolved spectroscopy and Drs L. Flamigni, F. Barigelletti, J.-P. Collin and J.-P. Sauvage, with whom the foundatory work for these studies was carried out.[8] Financial support from the University of Durham is gratefully acknowledged.

Notes and references

† The identity and purity of the complexes were confirmed by high-resolution NMR spectroscopy and electrospray ionisation mass spectrometry. *Selected spectroscopic data*: complex **4**: ^{1}H NMR (300 MHz, D$_2$O, NO$_3{}^-$ salt): δ 9.50 (4H, s, H$^{3'}$), 9.21 (4H, d, ^3J 6.3 Hz, H^m), 8.97 (4H, d, ^3J 8.4 Hz, H^3), 8.64 (4H, d, ^3J 6.3 Hz, H^o), 8.42 (4H, dd, ^3J 8.4, 7.8 Hz, H^4), 8.02 (4H, d, ^3J 5.4 Hz, H^6), 7.71 (4H, dd, ^3J 7.8, 5.4 Hz, H^5); (H^o and H^m denote protons *ortho* and *meta* to the nitrogen of the pendent pyridine). ESMS (+) (PF$_6{}^-$ salt): *m/z* 479 [M^{3+} + PF$_6{}^-$]$^{2+}$, 407 [M^{3+} + e$^-$]$^{2+}$, 271 [M]$^{3+}$, where M denotes cation **4**, mass 813. Interpretation of the NMR data of the mixed ligand complexes **3** and **5** was facilitated by the spectra of **1**, **2** and **4**, and was fully consistent with the structures shown.

1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. R. Rice, *Chem. Rev.*, 1997, **97**, 1515; *Fluorescent Chemosensors of Ion and Molecule Recognition*, ed. A. W. Czarnik, American Chemical Society, Washington DC, 1993.
2 E. F. G. Dickson, A. Pollak and E. P. Diamandis, *J. Photochem. Photobiol. B*, 1995, **27**, 3; D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613.
3 A. P. de Silva, H. Q. N. Gunaratne and T. E. Rice, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2116; D. Parker, P. K. Senanayake and J. A. G. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2129.
4 R. Grigg, J. M. Holmes, S. K. Jones and W. D. J. A. Norbert, *J. Chem. Soc., Chem. Commun.*, 1994, 185.
5 A. M. W. Cargill Thompson, M. C. C. Smailes, J. C. Jeffery and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1997, 737.
6 F. Barigelletti, L. Flamigni, M. Guardigli, J.-P. Sauvage, J.-P. Collin and A. Sour, *Chem. Commun.*, 1996, 1329.
7 N. P. Ayala, C. M. Flynn, Jr., L. Sacksteder, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, 1990, **112**, 3837.
8 J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009.
9 (*a*) J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. de Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230; (*b*) L. Persaud and G. Barbiero, *Can. J. Chem.*, 1991, **69**, 315; (*c*) W. Spahni and G. Calzaferri, *Helv. Chim. Acta*, 1984, **67**, 450.
10 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 1409.
11 Ward and coworkers have reported on the appearance of a similar band (albeit at higher energy) accompanying the deprotonation of a phenol-appended ruthenium trisbipyridine complex,[5] which only appeared when the substitution pattern was such as to provide a direct pathway of conjugation from the phenol-OH to a metal-coordinated nitrogen, as is also possible in the terpyridyl ligand described here. The lower energy of the band in the present instance probably reflects the higher positive charge on Ir(III) compared to Ru(II).

Communication 9/06203C