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Iridium(III) bis-terpyridine complexes incorporating pendent *N*-methylpyridinium groups: luminescent sensors for chloride ions†

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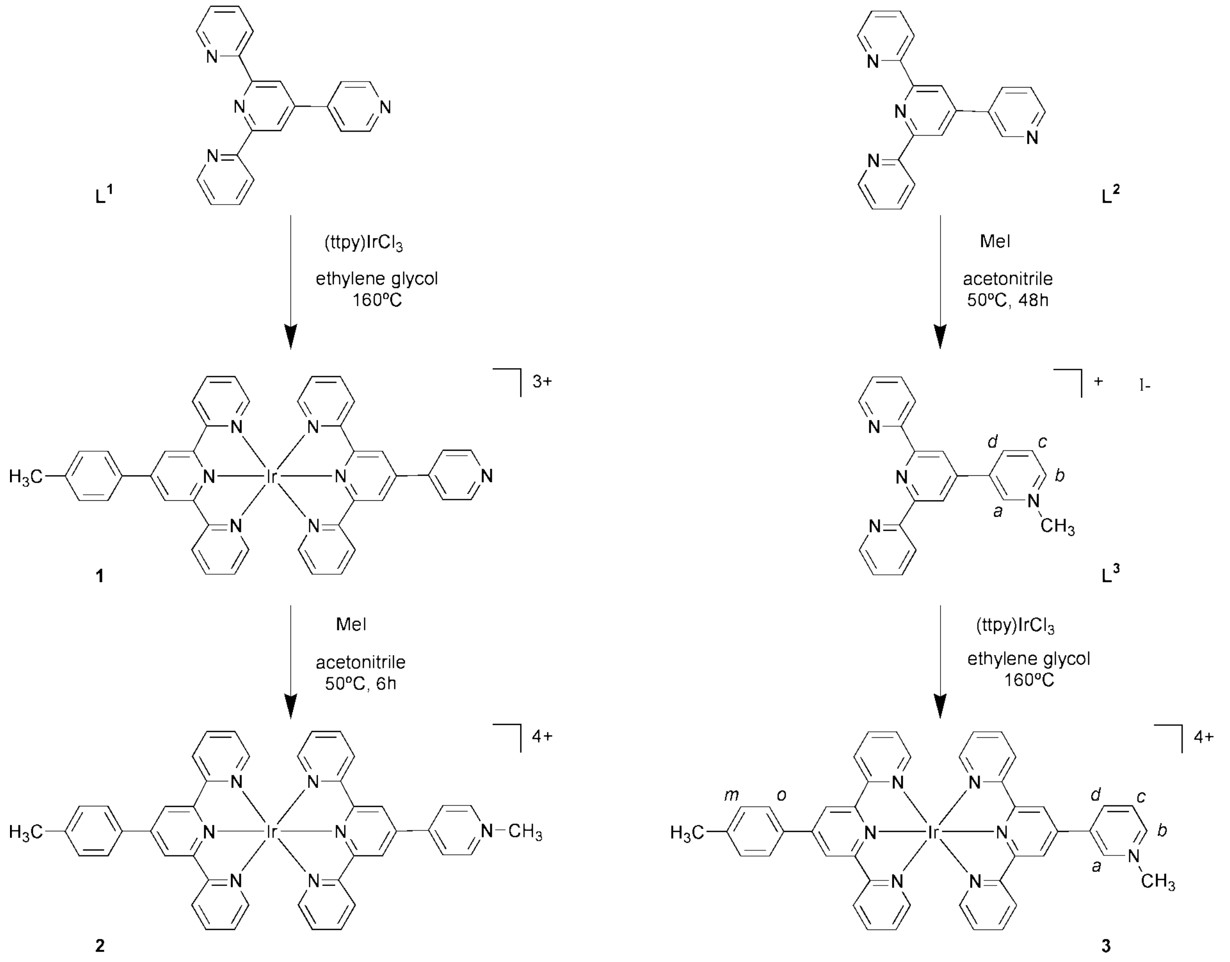
Received 23rd June 2000, Accepted 24th July 2000

Isomeric bis-terpyridine complexes of iridium(III) incorporating *meta*- or *para*-*N*-methylpyridyl substituents at the terpyridine 4′-position display long-lived luminescence in solution which is quenched by chloride ions to very different extents.

Molecular luminescent sensors which display long-lived emission are of interest in the analysis of bioactive ions or molecules in solution, since their emission may be discriminated readily from scattered light and shorter-lived background fluorescence normally present in biological and clinical samples.[1] Lifetimes in excess of about 1 μs are desirable for this purpose. Amongst the ions of importance *in vivo* is chloride, which occurs at relatively high concentrations (100 mM extracellular and 5–75 mM intracellular) and has crucial functions, for example in the control of osmotic pressure. Recently, we have reported iridium(III) bis-terpyridine complexes which emit in the visible following near-UV excitation, with lifetimes in the range 1–10 μs in air-equilibrated aqueous solutions at room temperature.[2,3] In particular, the incorporation of a pendent pyridyl group on the 4′-position of the terpyridine (**1**) led to pH sensitive emission: both the lifetime and intensity were reduced by a factor of >8 upon protonation of the pyridyl nitrogen, owing to mixing of the shorter-lived, higher-lying d–π* state with the emissive π–π* state.[3]

The preparation of the structurally related complexes **2** and **3**, which incorporate pendent *N*-methylpyridinium groups, is reported here, together with preliminary results on the quenching of their luminescence by chloride ions. Two synthetic routes were investigated, as shown in Scheme 1. Complex



Scheme 1

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† Electronic supplementary information (ESI) available: selected synthetic details and analytical data. See http://www.rsc.org/suppdata/dt/b0/b005046f/

DOI: 10.1039/b005046f

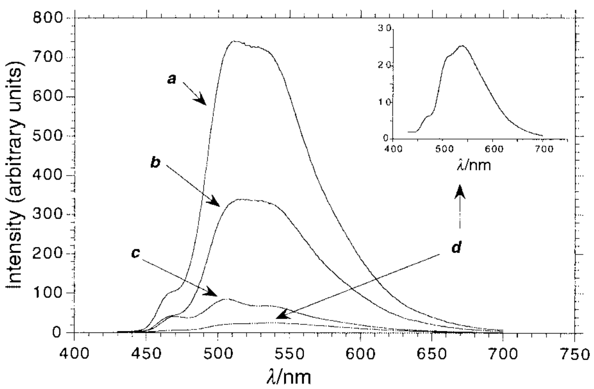

Fig. 1 Room temperature luminescence spectra of isoabsorbant, air-equilibrated, aqueous solutions of (a) complex **3**; (b) **3** in the presence of Cl^- (0.045 M); (c) complex **2**; (d) **2** in the presence of Cl^- (0.045 M), expanded in the inset. In each case, $I = 0.1$ M KNO_3, $\lambda_{ex} = 366$ nm.

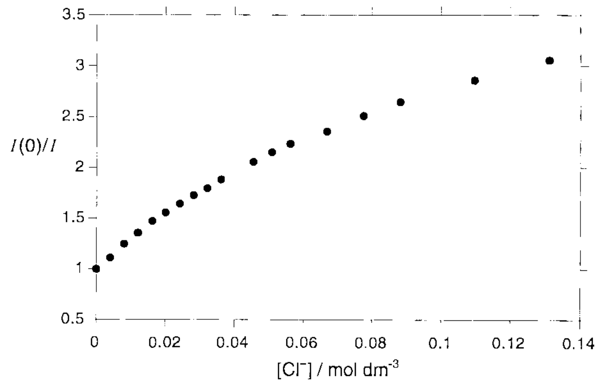

Fig. 2 Stern–Volmer plot of the dependence of the emission intensity of complex **3** (λ_{em} 510 nm, $\lambda_{ex} = 366$ nm) on chloride ion concentration ($I = 0.1$ M KNO_3).

1 was prepared as described previously[3] and methylation of the pendent pyridyl nitrogen was accomplished by reaction with excess methyl iodide, leading to the desired complex **2** after purification by chromatography on a short column of silica.[4a] An alternative method was investigated for complex **3**: ligand $\mathbf{L}^2$ was first prepared by a procedure analogous to that described in the literature[4b] for $\mathbf{L}^1$, involving base-catalysed condensation of 3-pyridinecarboxaldehyde with two equivalents of 2-acetylpyridine, followed by ring closure with ammonium acetate. Subsequently, selective *N*-methylation of the pendent pyridine was achieved by reaction with excess methyl iodide in acetonitrile solution to generate the iodide salt of $\mathbf{L}^3$, which precipitated as a pale yellow solid. No evidence of competitive alkylation of the other three, more sterically-hindered nitrogen atoms was observed. Ion exchange with aqueous KPF_6 led to the more organic-soluble hexafluorophosphate salt of $\mathbf{L}^3$, and reaction with (ttpy)$IrCl_3$ {ttpy = 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine} gave the required complex **3** after purification by column chromatography.†

Luminescence spectra of air-equilibrated aqueous solutions of the complexes are shown in Fig. 1, together with the spectra in the presence of chloride ions. The emission maximum and spectral profile of complex **3** resembles that of the parent $Ir(ttpy)_2^{3+}$ complex. The temporal decay of the emission, monitored at 510 nm, revealed biexponential kinetics, the major component having a lifetime of 5.8 (±0.2) µs and that of the minor component 1.4 (±0.2) µs.‡ From the magnitudes of the pre-exponential factors, the proportions of the two components were reversed when the emission was monitored at 470 nm. We attribute the long- and short-lived components to ligand-centred emission from the tolyl-terpyridine and *N*-methylpyridyl-terpyridine ligands respectively, based on the behaviour of related homoleptic complexes. Thus, the parent $Ir(ttpy)_2^{3+}$ complex displays an emission maximum of 505 nm and a lifetime of 6.2 (±0.2) µs under the same conditions. In contrast, the complexes containing pyridyl substituents on *each* of the terpyridines emit at rather higher energy, with an additional band centred at 470 nm not present in $Ir(ttpy)_2^{3+}$ (and closely resembling the unsubstituted $Ir(terpy)_2^{3+}$ complex), probably due to less extensive conjugation compared to the tolyl system.[2,3] The lifetime is also consistently shorter for these complexes (1.1 ± 0.2 µs for the bis-3-pyridyl complex) and similar to that of the shorter-lived component here. Dual emission, whilst unusual, is not unprecedented for complexes of iridium(III) with diimine ligands.[5]

The emission intensity of complex **2** was lower than that of an isoabsorbant solution of **3**, by a factor of about 8 (Fig. 1); the lifetimes of the two components were also substantially shorter (1.7 and 0.3 ± 0.1 µs). The lower intensity and shorter lifetimes for complex **2** may be attributed to the direct conjugation of the alkylated pyridine nitrogen with the terpyridine, which will serve to make the ligand more electron-deficient, lowering the energy of the higher-lying d–π* state and thus favouring mixing with the emissive π–π* state. Such mixing of charge-transfer excited states can promote deactivation, as reported previously for complex **1**, where protonation led to an 8-fold decrease in intensity and lifetime for this reason.[3] In complex **3**, the charge-transfer state is expected to lie at higher energy, since the pyridine nitrogen is not in conjugation with the terpyridine in this system.

N-Alkylquinolinium ions are well known to possess fluorescence which is quenched selectively by addition of halide ions, an effect believed to occur by charge transfer from the halide to the singlet excited state of the electron-poor cation.[6] Since the emission in the iridium complexes is primarily ligand-centred, sensitivity to halide might then be expected for complexes incorporating *N*-alkylpyridinium units. Addition of aqueous potassium chloride solution led to partial quenching of the emission for both complexes. For complex **3**, no change in the spectral profile was observed. The Stern–Volmer plot (Fig. 2) was approximately linear at low chloride concentrations (0–20 mM, $K_{sv}^{-1} = 34$ mM), but displayed marked negative curvature at higher concentrations (*vide infra*). The addition of chloride also led to a reduction in the lifetimes of both components of the emission, but to differing extents. The site of interaction of the chloride ion with the complex is expected to be the *N*-methylpyridyl substituent; the emission from the pyridyl-substituted ligand does indeed display the greater sensitivity to chloride, decreasing by a factor of 6 over the chloride concentration range 0–0.1 M, compared to a more modest 2.5-fold reduction in the emission lifetime of the tolyl-terpyridine ligand.§ That the latter is affected by added chloride, even though the homoleptic complex $Ir(ttpy)_2^{3+}$ is insensitive to halide ions, is indicative of a thermally-activated equilibration of energy between the excited states of the two ligands at room temperature. The lower sensitivity of the tolyl-terpyridine ligand to chloride then reflects the thermal activation necessary for energy transfer from the excited state of this ligand to that of the pyridyl-substituted ligand at higher energy, upon which the chloride acts. Under such conditions where a quencher is acting on two species both emitting at the observed wavelength, the Stern–Volmer plot is expected to curve downward (as observed here) due to the increasing fractional contribution of the more weakly quenched species at higher concentrations.¶

The effect of other common anions at similar concentrations was also investigated. Bromide and iodide quenched the luminescence efficiently as expected, but nitrate, sulfate, dihydrogen phosphate, hexafluorophosphate and tetrafluoroborate were found to have no effect. A modest quenching effect was observed for acetate (about 20% of that of chloride) whilst tartrate gave rise to only a very small reduction in the intensity of emission.

Complex **2** displayed a much steeper dependence on chloride concentration: 20 mmol dm^{-3} was sufficient to reduce the intensity of emission at 505 nm by a factor of 3. In this case, quenching was accompanied by a marked change in the form of the spectrum, with a red-shift in the emission maximum, apparently associated with the onset of a new emission band centred at 540 nm (inset to Fig. 1). A more complex temporal decay of the emission was observed in the presence of chloride, which could not be fitted satisfactorily to a double exponential equation and the Stern–Volmer plot displayed marked negative curvature even at very low chloride concentrations. Clearly, this complex exhibits a more profound interaction with chloride; exciplex formation is a possibility, the dissociative ground state of which would lead to a red shift, as observed.[7] The more complicated behaviour of this complex, its substantially weaker emission even in the absence of quencher (Fig. 1), together with its maximum sensitivity to chloride lying at concentrations lower than those typically of relevance in practical applications, makes it a less attractive system than its *meta* isomer **3**.

In summary, complex **3** exhibits luminescence which is sensitive to chloride at physiologically relevant concentrations ($K_{\mathrm{sv}}{}^{-1} = 34$ mmol dm^{-3}). In contrast to typical fluorescent sensors, the emission occurs on the microsecond timescale. Both the intensity and the lifetime are perturbed by chloride with good selectivity over many other anions, rendering this complex a potential sensory system for chloride.

Acknowledgements

We thank Dr Andrew Beeby for access to instrumentation for time-resolved measurements and assistance therewith. Financial support from the Nuffield Foundation, the Royal Society, EPSRC and the University of Durham is gratefully acknowledged.

Notes and references

‡ Samples for time-resolved measurements were excited at 355 nm using a Nd:YAG laser and the luminescence detected with a photomultiplier tube (Hamamatsu R928) and recorded using a digital storage oscilloscope. Decays were fitted to an equation of the form $I_{(t)} = A_1\exp(-k_1t) + A_2\exp(-k_2t)$, where k_1 and k_2 are the first order decay constants from which the lifetimes were obtained together with an estimate of the relative contributions of the two components from the pre-exponential factors A_i.

§ Stern–Volmer plots of the dependence of the lifetimes of the two components on chloride ion concentration are provided in the ESI.†

¶ The use of a modified Stern–Volmer equation to estimate two quenching constants is discussed in the ESI.†

1 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.

2 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.

3 M. Licini and J. A. G. Williams, *Chem. Commun.*, 1999, 1943.

4 (*a*) *N*-Methylation of a related ruthenium(II) complex has been reported: E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 2947; (*b*) L. Persaud and G. Barbiero, *Can. J. Chem.*, 1991, **69**, 315.

5 Previous reports have centred on $[\mathrm{Ir(phen)_2Cl_2}]^+$, $[\mathrm{Ir(bpy)_2Cl_2}]^+$ and analogues, wherein the observed dual emission was attributed to LC and CT transitions. See, for example, K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992, ch. 7. In the present instance, the possibility that the higher energy component is a CT state is considered unlikely, for the same reasons as those discussed in reference 2 for the parent $\mathrm{Ir(terpy)_2}^{3+}$ complex.

6 For example, the fluorescent chloride sensor SPQ, 6-methoxy-*N*-(3-sulfopropyl)quinolinium: R. Krapf, N. P. Illsley, H. C. Tseng and A. S. Verkman, *Anal. Biochem.*, 1988, **169**, 142; M. Vasseur, R. Frange and F. Alvarado, *Am. J. Physiol.*, 1993, **264**, C27.

7 The possible formation of an exciplex between $\mathrm{Ir(terpy)_2}^{3+}$ and $\mathrm{HgCl_2}$ has been discussed, although the absence of a red-shift suggests that this is not a true exciplex: N. P. Ayala, C. M. Flynn, Jr., L. Sacksteder, J. N. Demas and B. A. DeGraff, *J. Am. Chem. Soc.*, 1990, **112**, 3837.