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Ruthenium tris-(bipyridyl) complexes with pendant protonatable and deprotonatable moieties: pH sensitivity of electronic spectral and luminescence properties

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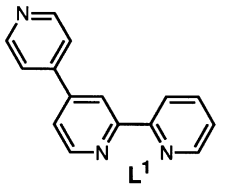
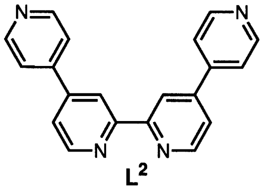
The effect of pH on the electronic absorption spectra and luminescence behaviour of four complexes consisting of $\{Ru(bipy)_3\}^{2+}$ chromophores (bipy = 2,2′-bipyridine) bearing pendant pH-sensitive functional groups has been investigated by pH titrations. For $[Ru(bipy)_2L^1]^{2+}$ **1** (L^1 = 2,2′ : 4′,4″-terpyridine) protonation of the pendant pyridyl group ($pK_a = 3.2$) results in a red-shift of the lowest-energy metal-to-ligand charge-transfer (m.l.c.t.) band by 870 cm^{-1} due to the lowering of the π^* level of L^1 which occurs on protonation. For $[Ru(bipy)_2L^2]^{2+}$ **2** [L^2 = 4(4-pyridyl)-2,2′ : 4′,4″-terpyridine] both pendant pyridyl sites protonate simultaneously ($pK_a = 3.6$); the red-shift of the lowest-energy m.l.c.t. band is 1570 cm^{-1}, approximately double that which occurred for **1**. The pK_a^* values of **1** and **2** were estimated to be 5.0 and 5.2 respectively, indicating that their excited states are more basic than the ground state due to the presence of an additional electron on L^1 or L^2 as a reslt of the m.l.c.t. process. The luminescence of $[Ru(bipy)_2(HL^3)]^{2+}$ **3** [HL^3 = 4-(4-hydroxyphenyl)-2,2′-bipridine] is completely quenched on deprotonation of the pendant phenol group, while that of isomeric $[Ru(bipy)_2(HL^4)]^{2+}$ **4** [HL^4 = 4-(3-hydroxyphenyl)-2,2′-bipyridine] is only partially quenched, owing to the inability of the ligand π system of $[L^4]^-$ to allow internal charge transfer of the phenolate negative charge to the metal centre across a *meta*-substituted linkage. The pK_a values for **3** and **4** are 8.6 and 8.9 respectively, and their pK_a^* values are essentially the same as the pK_a values because the m.l.c.t. excited states involve the ancillary bipy ligands rather than HL^3 or HL^4. The new compound HL^4 was crystallographically characterised revealing that molecules of HL^4 associate *via* OH · · · N hydrogen-bonding interactions to give a one-dimensional ribbon.

Derivatives of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) have been used extensively as molecular subunits from which to assemble metallosupramolecules due to their desirable photophysical and photochemical properties, in particular their long-lived metal-to-ligand charge-transfer excited states and strong luminescence in fluid solution at ambient temperature.[1] The ability to modify reversibly the luminescence properties of this chromophore by modifying the periphery of such complexes (*e.g.* by protonation/deprotonation, or co-ordination of a metal ion) is of particlar interest for the possible development of switching mechanisms in future photochemical molecular devices:[2–8] if photoinduced electron or energy transfer between a chromophore and a quencher across a conjugated bridge is thought of as constituting a simple molecular wire, then the ability to quench the chromophore, or otherwise modify its behaviour reversibly, constitutes a switching mechanism for the long-distance electron or energy transfer.

The simplest such switching mechanism is protonation or deprotonation of a peripheral acidic or basic functional group; the properties of $\{Ru(bipy)_3\}^{2+}$ derivatives bearing pH-sensitive functional groups have recently been reviewed.[2] Sauvage's group have developed the use of $[Ru(bipy)_2(dppz)]^{2+}$ (dppz = dipyrido[3,2-*a* : 2′,3′-*c*]phenazine) as a luminescent probe for DNA in which intercalation of the dppz fragment modifies the luminescence of the metal core.[3] Moore and co-workers[4] have prepared a $\{Ru(bipy)_3\}^{2+}$ derivative bearing a pendant tetraaza macrocycle, with the luminescence of the ruthenium fragment being quenched on co-ordination of Ni^{2+} or Cu^{2+} by the macrocycle, but not on co-ordination of Zn^{2+}. Beer *et al.*[5] have similarly prepared $\{Ru(bipy)_3\}^{2+}$ derivatives with pendant crown ethers which recognize Group IA and IIA metal ions. Grigg and co-workers[6] have described various luminescent pH-sensitive $\{Ru(bipy)_3\}^{2+}$ derivatives, including one bearing a pendant calix[4]arene. Wrighton and co-workers[7] have performed in-depth studies on the acid–base equilibria of $[Ru(bipy)_2(dhphen)]^{2+}$ (dhphen = 4,7-dihydroxy-1,10-phenanthroline) and related complexes. A recent innovation in this area is the use of protonation of a pendant pyridine moiety to switch on luminescence from $\{Ru(terpy)_2\}^{2+}$ derivatives (terpy = 2,2′ : 6′,2″-terpyridine) which are normally non-emissive at ambient temperature.[8]

As part of a program to prepare high-nuclearity co-ordination complexes containing luminescent fragments, we have prepared a range of derivatives of $[Ru(bipy)_3]^{2+}$ which bear pendant ligating groups such as pyridyl or phenol for attachment to a second metal centre.[9] These groups are also pH sensitive, which offers the additional possibility of reversibly modifying the luminescence of the metal centre by varying the pH. Herein we present a study of the pH sensitivity of the four complex cations $[Ru(bipy)_2L^n]^{2+}$ (n = 1 **1** or 2 **2**), $[Ru(bipy)_2(HL^n)]^{2+}$ (n = 3 **3** or 4 **4**) (see below for details of the ligands L^1–HL^4). Complexes **1** and **2** incorporate one and two pendant 4-pyridyl substituents which may be protonated under mildly


L^1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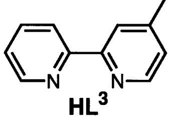
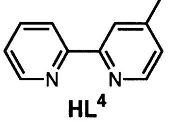

HL^3


HL^4

acidic conditions to afford positively charge ‘viologen-like’ groups attached to the metal core. Complexes **3** and **4** each contain one phenol substituent which may be deprotonated under basic conditions, and we discuss the positional effect of the resultant negative charge on the quenching of the luminescence.

Experimental

General details

The following instruments were used for routine spectroscopic studies: ^{1}H NMR spectroscopy, a JEOL λ-300 spectrometer; electron impact (EI) and positive-ion fast-atom bombardment (FAB) mass spectra, a VG-Autospec; UV/VIS spectra, Perkin-Elmer Lambda-2 or Lambda-19 instruments; luminescence spectra, a Perkin-Elmer LS-50B instrument. The pH measurements were made using a Unicam 9450 pH meter with a BDH Gelplas combination pH electrode. Electrochemical measurements were made with an EG&G PAR 273A potentiostat, using platinum-bead working and auxiliary electrodes and a saturated calomel reference electrode (SCE). Acetonitrile (distilled over calcium hydride) with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ was used as supporting electrolyte. Ferrocene was added at the end of each experiment as an internal reference, and all redox potentials are quoted *vs.* the ferrocene–ferrocenium couple.

3-Methoxycinnamaldehyde,[10] *N*-[2-oxo-2-(2-pyridyl)ethyl]-pyridinium iodide[11] and $[Ru(bipy)_2Cl_2]$[12] were prepared according to published procedures. The complexes $[Ru(bipy)_2L^1][PF_6]_2$ **1**, $[Ru(bipy)_2L^2][PF_6]_2$ **2** and $[Ru(bipy)_2(HL^3)][PF_6]_2$ **3** were prepared as previously described.[9]

Syntheses

4-(3-Methoxyphenyl)-2,2′-bipyridine. 3-Methoxycinnamaldehyde (4.05 g, 25 mmol), *N*-[2-oxo-2-(2-pyridyl)ethyl]-pyridinium iodide (9.78 g, 30 mmol) and ammonium acetate (30 g, large excess) were heated at reflux under nitrogen in dry methanol (80 cm^3) for 20 h. On cooling, the reaction mixture was added to water (300 cm^3) and extracted with CH_2Cl_2 (4 × 100 cm^3). The organic extracts were dried over $MgSO_4$, concentrated *in vacuo* to an oil and chromatographed on neutral alumina (Brockmann activity 3), eluting with CH_2Cl_2. All fractions which gave a red colouration on addition of methanolic iron(II) chloride were combined and the solvent removed to give a yellow oil (2.87 g, 44%). The crude product (EI mass spectrum: *m*/*z* 262, M^+) was used in the next step without further purification.

4-(3-Hydroxyphenyl)-2,2′-bipyridine (HL^4). Pyridium hydrochloride was prepared by careful addition of concentrated hydrochloric acid (17.6 cm^3) to pyridine (16 cm^3), followed by heating at 190 °C for 1.5 h under a flow of nitrogen to drive off water from the mixture. The resulting molten salt was cooled to ≈140 °C and the above compound (2.87 g, 11 mmol) added under N_2. The temperature was increased again to 190 °C for 2 h. On cooling, the solid obtained was dissolved in water (200 cm^3) and the solution adjusted to pH 7 by careful addition of aqueous NaOH. The oily suspension was extracted with CH_2Cl_2 (3 × 100 cm^3) and the organic phases were combined, dried over $MgSO_4$, and evaporated to give a brown oil. This was chromatographed on neutral alumina (Brockmann activity 3), using 1.5% (v/v) EtOH in CH_2Cl_2 as eluent. Two minor impurities were eluted rapidly, followed by the main product band, which was collected as fractions. Clean fractions (TLC) were combined, evaporated to dryness and recrystallised from methanol, affording HL^4 as white microcrystals (0.68 g, 25%). EI mass spectrum: *m*/*z* 248 (M^+) (Found: C, 77.2; H, 5.0; N, 11.2. Calc. for $C_{16}H_{12}N_2O$: C, 77.4; H, 4.9; N, 11.3%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (ddd, 1 H, $H^{6'}$), 8.69 (dd, 1 H, H^6), 8.62 (dd, 1 H, H^3), 8.47 (ddd, 1 H, $H^{3'}$), 7.89 (ddd, 1 H, $H^{4'}$), 7.62 (br s, 1 H, H^{OH}), 7.48 (dd, 1 H, H^5), 7.39 (ddd, 1 H, $H^{5'}$), 7.26 (m, 3 H, 3 × H^{Ph}) and 6.88 (ddd, 1 H, Ph H^4 or H^6).

$[Ru(bipy)_2(HL^4)][PF_6]_2$ 4. The compound HL^4 (0.038 g, 0.15 mmol) and $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.078 g, 0.15 mmol) were heated to reflux for 5 min in ethane-1,2-diol (10 cm^3). The mixture rapidly changed from purple to red-orange. Crude $[Ru(bipy)_2(HL^4)][PF_6]_2$ was precipitated by addition of an excess of aqueous KPF_6 and was collected on Celite and washed with water. The complex was redissolved in the minimum volume of MeCN, and chromatographed on flash-grade silica, eluting with acetonitrile–saturated aqueous KNO_3–water (30 : 2 : 1 v/v). The main red-orange band was collected, an excess of aqueous KPF_6 added, and the acetonitrile removed *in vacuo*. The oily red aqueous mixture was extracted with CH_2Cl_2 (4 × 30 cm^3), and the organic extracts were dried over $MgSO_4$ and evaporated to give $[Ru(bipy)_2(HL^4)][PF_6]_2$ as a red powder (0.087 g, 61%). FAB mass spectrum: *m*/*z* 992 (991), $[M - PF_6]^+$; 846 (846), $[M - 2(PF_6)]^+$ (Found: C, 45.6; H, 3.1; N, 8.8. Calc. for $C_{36}H_{28}F_{12}N_6OP_2Ru$: C, 45.4; H, 3.0; N, 8.8%). ^{1}H NMR (300 MHz, CD_3CN): δ 8.68 (m, 2 H), 8.51 (m, 4 H), 8.07 (m, 5 H), 7.75 (m, 6 H), 7.60 (dd, 1 H), 7.41 (m, 7 H), 7.28 (dd, 1 H) and 7.01 (ddd, 1 H).

Conversion of acetonitrile-soluble $[PF_6]^-$ salts onto water-soluble $[NO_3]^-$ salts. All complexes were obtained as nitrate salts in aqueous solution by passing the hexafluorophosphate salt (10–20 mg) down a short silica column eluted with acetonitrile–saturated aqueous KNO_3–water (100 : 10 : 1 v/v), followed by removal of the acetonitrile *in vacuo*.

Crystallography

Suitable crystals of compound HL^4 were grown by slow evaporation of a methanol solution. One (dimensions 0.5 × 0.5 × 0.5 mm) was mounted in a stream of cold N_2 at −100 °C on a Siemens SMART three-circle diffractometer fitted with a CCD area detector. Graphite-monochromatised Mo-Kα radiation ($\bar{\lambda} = 0.710\,73$ Å) was used.

Crystal data. $C_{16}H_{12}N_2O$, *M* 248.28, monoclinic, space group *C*2/*c*, $a = 17.142(4)$, $b = 7.9310(13)$, $c = 19.923(3)$ Å, $\beta = 113.712(12)°$, $Z = 8$, $F(000) = 1040$, $D_c = 1.330$ g cm^{-3}, $\mu = 0.085$ mm^{-1}.

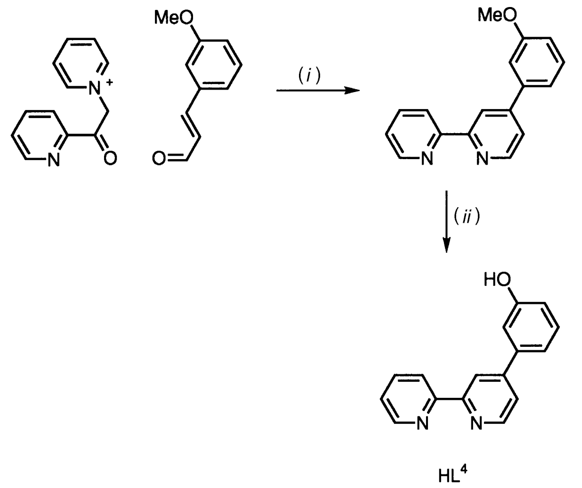
7399 Data were collected ($5 < 2\theta < 55°$) at −100 °C, which after merging afforded 2820 unique data ($R_{int} = 0.020$). Data were corrected for Lorentz-polarisation and absorption effects, the latter using an empirical method based on multiple measurements of equivalent data.

The structure was solved by conventional direct methods using SHELXTL and was refined by the full-matrix least-squares method on all F^2 data with the SHELXTL 5.03 package using a Silicon Graphics Indy computer.[13] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. Refinement of 173 parameters converged at $wR2$ (for all data) = 0.111, $R1$ [for selected data with $F > 4\sigma(F)$] = 0.039. The largest residual peak and hole were +0.361 and −0.226 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/379.

Luminescence and UV/VIS spectrophotometric titrations

For each complex, an aqueous solution of the nitrate salt was prepared for which the optical density (*A*) of the metal-to-ligand charge-transfer (m.l.c.t.) transition at *ca.* 450 nm was



Scheme 1 Synthesis of HL^4. (*i*) NH_4O_2CMe, MeOH, reflux; (*ii*) pyridine, HCl, 190 °C

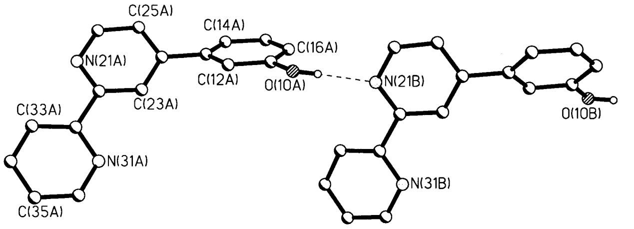


Fig. 1 Crystal structure of HL^4, showing the numbering scheme and the intermolecular hydrogen-bonding interaction

about 0.1. The pH was varied over the necessary range by addition of very small portions of solid K_2CO_3 or KOH, or HCl vapour. The excess of KNO_3 present from the column chromatography step ensured that the ionic strength of the solution remained approximately constant except at the extremes of the pH scale. The UV/VIS spectra of the samples were recorded in the range 200–600 nm. The emission spectra were then recorded in the range 500–850 nm, with excitation being performed at the absorption maximum for the ^{1}m.l.c.t. transition at neutral pH. In all cases, this transition was sufficiently broad that slight changes to the exact position of the maximum with pH were not deemed to necessitate a change in the excitation wavelength. The excitation slit was set to 5.0 nm and the emission slit to 8.0 nm for all luminescence measurements. The pH of each sample was measured directly after both the UV/VIS and emission spectra had been recorded. Quantum yields were calculated from corrected emission spectra by comparison with $[Ru(bipy)_3][PF_6]$ ($\varphi = 0.028$) in aerated aqueous solution at 25 °C.

Results and Discussion

Syntheses

Complexes **1**–**3** were available from a previous study.[9] The synthesis of HL^4 follows the standard Kröhnke-type methodology, as presented in Scheme 1.[14] The yield was somewhat disappointing owing to the formation of a variety of by-products. The aromatic region of the ^1H NMR specrum ($CDCl_3$ solution) integrated to 12 protons, and included a broad singlet at δ 7.62 assigned to the OH proton. The pyridine-ring resonances were ascribed unambiguously with the aid of a two-dimensional correlation spectroscopy (COSY) experiment; the phenyl protons appeared at the high-field end as a multiplet (δ 7.26, 3 H) and an additional resonance at δ 6.88 (ddd, 1 H).

The crystal structure of HL^4 is shown in Fig. 1. The most interesting feature is the formation of a one-dimensional hydrogen-bonded ribbon, *via* interaction of the hydroxyl group of one molecule with one of the pyridyl rings [N(21)] of an adjacent molecule. The O · · · N separation is 2.776 Å. The bipyridyl fragment is approximately transoid, with a torsion angle of 165° between the pyridyl rings; there is also a torsion angle of 42° between the pyridyl and phenol rings. Other bond lengths and angles are unremarkable.

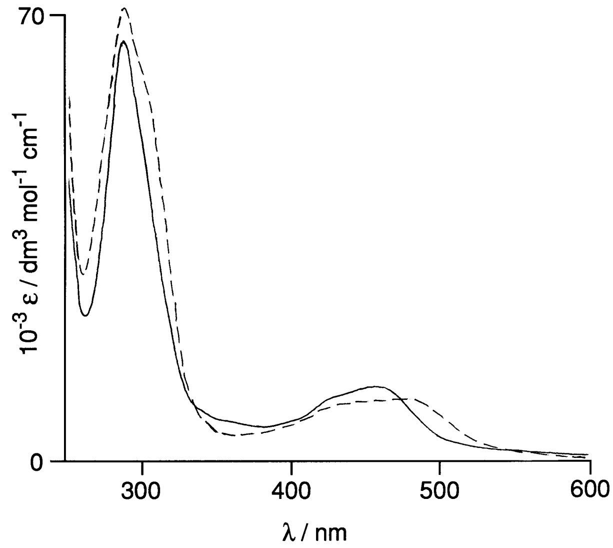


Fig. 2 The UV/VIS spectrum of complex **1** (——) and upon protonation (– – – –) in water

The compound HL^4 reacts cleanly and quickly with $[Ru(bipy)_2Cl_2]$ in ethane-1,2-diol, affording orange $[Ru(bipy)_2(HL^4)][PF_6]_2$ **4** following column chromatography and anion metathesis; the complex was satisfactorily characterised on the basis of its FAB mass spectrum, elemental analysis and ^1H NMR spectrum which, although not fully assigned, contained the correct number of aromatic resonances. The cyclic voltammogram in MeCN shows a chemically reversible Ru^{II}–Ru^{III} couple at +0.89 V *vs.* the ferrocene–ferrocenium couple, identical to the potentials of both **3** and $[Ru(bipy)_3][PF_6]_2$,[9] which suggests that the pendant phenol moieties in **3** and **4** have little effect on the ground-state properties of the $\{Ru(bipy)_3\}^{2+}$ core. In addition, **4** exhibits a number of ligand-centred reductive processes, though these are partially obscured by an intense desorption spike at −1.68 V and hence are unresolved. The UV/VIS spectrum of **4** in MeCN solution consisted of transitions which were assigned[9] by comparison with the spectra of related complexes as follows: λ_{max} 454 (ε 16 100) and ≈425 (shoulder), ^{1}m.l.c.t.; 288 (77 500), ligand-centred π–π^*; and 243 nm (35 300 dm^3 mol^{-1} cm^{-1}), another m.l.c.t. process.

All complexes were subsequently converted into water-soluble nitrate salts for the titration studies.

UV/VIS and luminescence titrations

Complexes 1 and 2. Ligands L^1 and L^2 incorporate one and two pendant pyridyl moieties, respectively, attached to bidentate 2,2′-bipyridine groups. In the complexes **1** and **2** these non-co-ordinated pyridines may be protonated, and hence we investigated what effect the resultant positive charge on the periphery of the ligand would have on the luminescence of the $\{Ru(bipy)_3\}^{2+}$ chromophore; UV/VIS and fluorescence titrations were performed on the nitrate salts of **1** and **2** over the range pH 1–13.

The m.l.c.t. region of the UV/VIS spectra of both complexes is quite sensitive to pH. At pH 5 and above the low-energy m.l.c.t. band of **1** contains a maximum at 458 nm with a shoulder at *ca.* 425 nm. At lower pH the maximum red-shifts to 476 nm, while the shoulder remains unchanged, resulting in an overall broadening and flattening of the band (Fig. 2). The result is

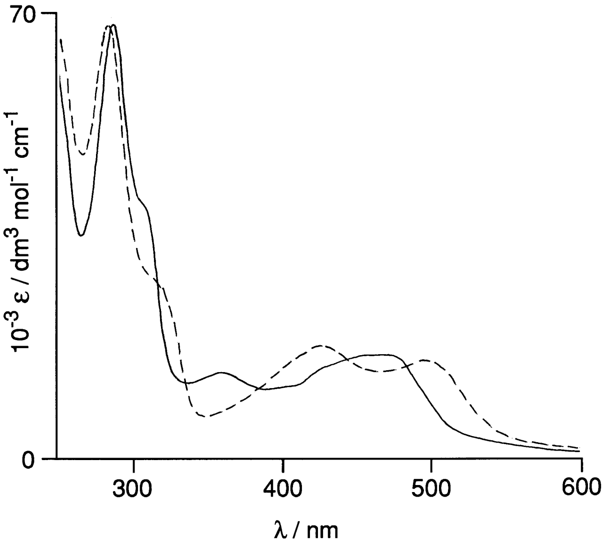


Fig. 3 The UV/VIS spectrum of complex **2** (——) and upon diprotonation (– – – –) in water

a deepening in colour from a yellow-orange to brown-orange at low pH. Under neutral or basic conditions the m.l.c.t. transition of **2** comprises a maximum at 460 nm with a shoulder on the high-energy side: under acidic conditions two distinct maxima at 430 and 500 nm become apparent (Fig. 3). The UV/VIS spectra of these fully protonated complexes are very similar to those of the related complexes in which the pendant pyridyl sites were methylated rather than protonated,[9] indicating that protonation and methylation are electronically comparable, and we have noted elsewhere the similarity of the effects of protonation and methylation on the behaviour of other {Ru(bipy)$_3$}$^{2+}$ derivatives bearing pendant pyridyl groups.[15] The protonation-induced red-shifts of the lowest-energy m.l.c.t. maxima indicate that the ^{1}m.l.c.t. transition involves electron transfer to the protonated ligand rather than the ancillary bipy ligands, which is consistent with our earlier electrochemical studies on the analogous methylated complexes.[9] The magnitudes of these red-shifts on protonation are approximately 1570 cm^{-1} for **2** and 870 cm^{-1} for **1**, suggesting that the double protonation of **2** lowers the energy of the co-ordinated L^2 by approximately double the amount that occurs on single protonation of L^1 in **1**. This allows us to estimate that monoprotonation of **2** would result in a red-shift of *ca.* 785 cm^{-1} for the m.l.c.t. band, a figure which is of significance for determining the excited-state pK_a* value (see later).

The magnitude of the perturbation of the m.l.c.t. band on protonation will depend on the extent to which the protonated moiety communicates electronically with the co-ordinated bipyridyl fragment to which it is attached. In complexes with ligands such as bipyrimidine and bipyrazine the protonatable sites are part of the co-ordinated heterocyclic rings, so protonation has a very strong effect. In contrast, we recently examined the properties of the complex [Ru(bipy)$_2$(AB)]$^{2+}$, in which AB is a quaterpyridine ligand containing two independent bipy-type binding sites (site A, which is co-ordinated and site B, which is pendant) with a substantial dihedral twist between them.[15] Protonation of the B site therefore has a relatively small effect on the properties of the metal centre, as the pendant positive charge cannot delocalise effectively between near-orthogonal fragments. Complexes **1** and **2** fall between these two extremes. The protonatable pyridyl rings of L^1 and L^2 can adopt a conformation which is not far from coplanar with the co-ordinated bipy fragment, but this is offset by the distance between the protonated site and the metal complex core.

Plots of λ_{max}(m.l.c.t.) *vs.* pH for complexes **1** and **2** are in Fig. 4. Both have the expected sigmoidal shape, with the pH at the

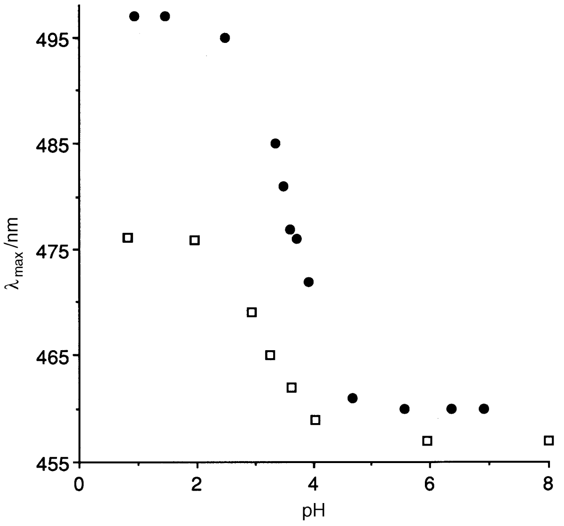


Fig. 4 Plots of λ_{max} *vs.* pH for the lowest-energy m.l.c.t. bands of complexes **1** (□) and **2** (●) in water

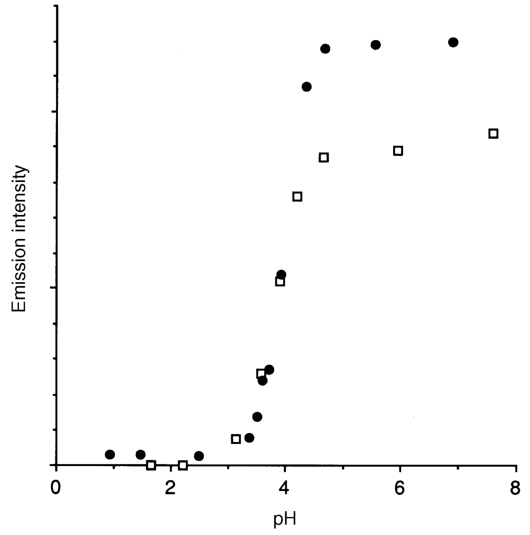


Fig. 5 Plots of emission intensity (arbitrary units) *vs.* pH for complexes (□) and **2** (●) in water

point of inflection giving the ground-state pK_a values of 3.2 for **1** and 3.6 for **2** (both ±0.2 units). Both complexes are therefore weaker bases than is free pyridine (pK_a 5.25), as their dipositive charges will electrostatically inhibit further protonation. The single point of inflection for protonation of **2** suggests simultaneous or near-simultaneous protonation of both pyridyl rings. Further support from this comes from the earlier observation that this protonation step results in a shift of the m.l.c.t. band of **2** approximately twice as great as that which occurs on monoprotonation of **1**. In addition, simultaneous protonation of both pendant pyridyl moieties was observed to occur at pH 2.9 in [Fe(pyterpy)$_2$]$^{2+}$ [pyterpy = 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine].[16]

At pH values above *ca.* 5 both complexes **1** and **2** are luminescent (**1**, φ = 0.013; **2**, φ = 0.010; both in aerated water). The plots of emission intensity *vs.* pH for **1** and **2** both have the expected sigmoidal shape (Fig. 5), with the emission being entirely quenched below pH 2 in each case. Given that protonation of the pendant sites will result in them becoming effective electron acceptors, it is likely that quenching in the protonated species occurs by rapid electron transfer from the ^{3}m.l.c.t. excited state to the protonated pyridine rings: methylated pendant pyridyl groups are known to act as electron-transfer quenchers in this manner.[17] Since protonation of **1** results in complete luminescence quenching we might also expect monoprotonation of **2** to have the same effect, with addition of the second proton having no further effect on the luminescence. The points of inflection of the emission *vs.* pH curves (pH_i) are 3.7 for **1** and 4.0 for **2** (both ±0.2 units).

The pK_a of the excited state (pK_a*) for luminescent ruthenium–polypyridyl complexes may be derived in two ways.[2] The more satisfactory method is based on luminescence data, and requires knowledge of the lifetimes of both basic (B, unprotonated) and acidic (HB, fully protonated) states (τ_B and τ_{BH}). Together with the inflection point pH_i from the plot of emission intensity *vs.* pH, equation (1) gives pK_a*. However,

$$pK_a^* = pH_i + \log(\tau_B/\tau_{BH}) \qquad (1)$$

this requires that *both* B and HB are luminescent with lifetimes that are substantially longer than protonation/deprotonation equilibration rates. If one state (here, the protonated one) is non-luminescent then equation (1) does not apply and a more approximate method has to be used. Equation (2) only requires

$$pK_a^* = pK_a + (0.625/T)(\nu_B - \nu_{HB}) \qquad (2)$$

ground-state electronic spectral data: the pK_a value from the λ_{max} *vs.* pH titration and the energies in cm^{-1} of the lowest-energy m.l.c.t. band maxima in non-protonated and protonated states. The problem in applying this equation of ruthenium–polypyridyl complexes is that the absorption energies (ν_B and ν_{HB}) relate to formation of the singlet m.l.c.t. excited state, whereas the chemically relevant protonatable excited state is the much longer-lived triplet state which is lower in energy. However, when equation (1) is inapplicable, (2) may be used to give approximate pK_a* values.[2] For complex **1** we have $pK_a = 3.2$ and $(\nu_B - \nu_{HB}) = 870\ cm^{-1}$, which gives $pK_a^* \approx 5.0$. For complex **2** we do not know the spectroscopic properties of the mono-protonated species since simultaneous double protonation occurs, but as mentioned earlier it is reasonable to approximate $(\nu_B - \nu_{HB})$ as 785 cm^{-1} (half the value that arises from double protonation); together with the pK_a value of 3.6 this gives $pK_a^* \approx 5.2$. The excited states of **1** and **2** are therefore between 1 and 2 pK_a units more basic than the ground states.

The increased basicity of the excited state compared to the ground state is typical for complexes with pendant basic sites. In **1** and **2** the m.l.c.t. process will render ligands L^1 and L^2 more electron-rich than in the ground state, if (as is reasonable to assume) the lowest-energy m.l.c.t. state involves L^1 and L^2 respectively rather than the ancillary bipy ligands. The pendant pyridyl sites of L^1 and L^2 will therefore have an increased affinity for protons. The magnitude of the difference between pK_a and pK_a* values is again a measure of the electronic communication between the metal complex core and the pendant functional group. In complexes where the protonatable sites are part of the co-ordinated heterocyclic rings on which the excited-state electron is localised, excitation can result in a greatly increased basicity, of several pK_a units:[2] for example for $[Ru(bipy)_2(bpz)]^{2+}$ (bpz = bipyrazine), the pK_a and pK_a* values are −0.15 and +8.2 respectively, a difference of 8.35 units.[18] In $[Ru(bipy)_2(AB)]^{2+}$, where the pendant bipy site B is approximately orthogonal to the co-ordinated bipy site A, the pK_a and pK_a* values differ by just 0.4 units, as the excited electron cannot delocalise effectively to the pendant bipy site.[15] The pK_a shifts of **1** and **2** (1–2 units) are intermediate between these two extremes.

Complexes 3 and 4. In contrast to the complexes just discussed, **3** and **4** contain acidic phenol groups pendant from the $\{Ru(bipy)_3\}^{2+}$ core, which may be deprotonated under basic conditions. The UV/VIS and fluorescence titrations were performed on these complexes in the range pH 3–12.

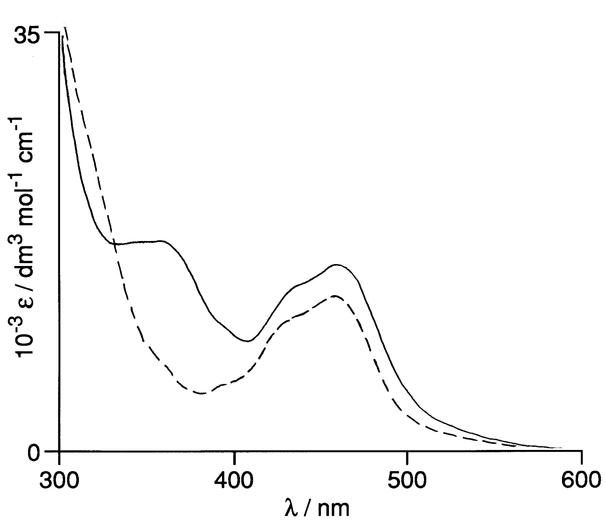


Fig. 6 The UV/VIS spectrum of complex **3** (– – – –) and upon deprotonation (——) in water

For complex **3**, λ_{max} for the lowest-energy m.l.c.t. absorption band remained virtually constant throughout the titration at 459 ± 1 nm. This band is a $Ru^{II}\rightarrow$bipy m.l.c.t. involving the ancillary bipy ligands; the $Ru^{II}\rightarrow HL^3$ m.l.c.t. band will be at higher energy due to the electron-donating hydroxyphenyl substituent attached to the bipy fragment. In contrast to **1** and **2**, therefore, the pH-sensitive site is not attached to the ligand involved in formation of the lowest-energy excited state. However a marked change in the UV/VIS spectrum occurs on deprotonation with the appearance of a broad peak at *ca.* 360 nm, of similar intensity to the m.l.c.t. transition (Fig. 6). We assign this to a ligand-centred process involving the deprotonated ligand, with the relatively low energy of the transition consistent with the presence of a highly extended conjugated system. By monitoring the change in absorbance at this wavelength as a function of pH [Fig. 7(*a*)] we find that the ground-state pK_a of **3** is 8.6. For complex **4** in contrast no such new transition appears at high pH values. The UV/VIS spectra of **4** over the range pH 3–12 are virtually superimposable, with the single exception of a slight increase in intensity (about 10%) of the ligand-centred $\pi \longrightarrow \pi^*$ transition at 240 nm. From this change in absorbance as a function of pH [Fig. 7(*b*)] we find that the ground-state pK_a of **4** is 8.9.

Both complexes are slightly more acidic than phenol (pK_a 10), which may be ascribed to electrostatic effects: deprotonation of the pendant phenol group will reduce the overall charge from +2 to +1. The slightly greater acidity of **3** compared to **4**, and the fact that deprotonation of **3** results in much greater changes to the UV/VIS spectrum than does deprotonation of **4**, are both due to the different position of the hydroxyl substituent. In **3** deprotonation of the pendant phenolate will afford a negative charge which can be delocalised onto one of the nitrogen atoms of the co-ordinated bipy fragment *via* an internal charge transfer (Scheme 2); the negative charge is therefore stabilised by being brought into proximity to the positively charged metal. The anion $[L^3]^-$ will therefore be planar (or near-planar) due to the quinonoidal character which arises from the delocalisation and the co-ordinated bipy fragment will become much more electron-rich. In contrast, the *meta*-substitution pattern of the hydroxyphenyl substituent of **4** means that the negative charge of the phenolate must remain localised in the phenyl ring and cannot be stabilised by delocalisation towards the positively charged metal (which accounts for the slightly higher pK_a value). Deprotonation will therefore have a much weaker effect on the metal centre and the co-ordinated bipy fragment of $HL^4/[L^4]^-$ will be more like an unsubstituted bipy ligand. We have noted in related mixed pyridine–phenol ligands how the extent of communication between metal fragments co-ordinated to the pyridyl and phe-

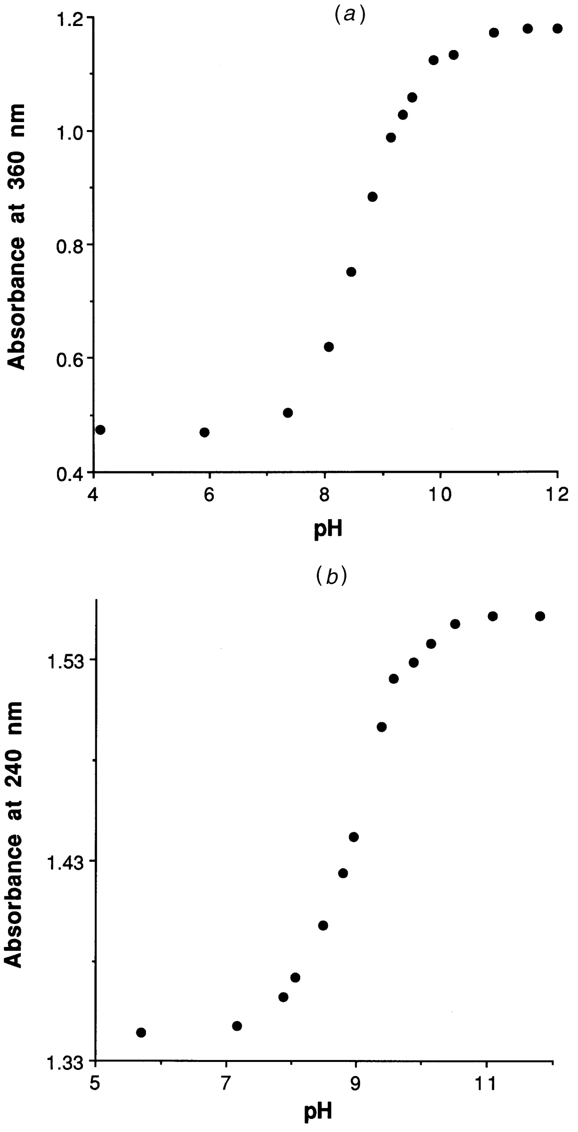
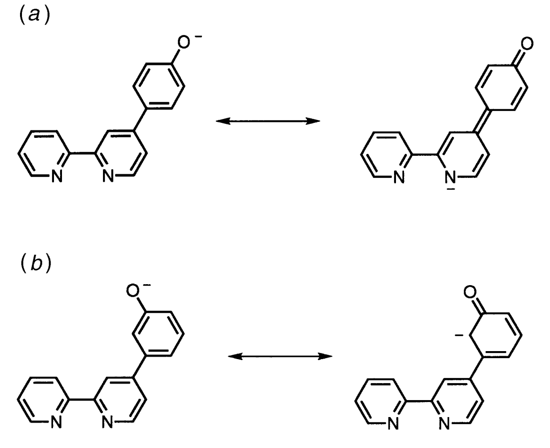


Fig. 7 Plots of (*a*) absorbance at 360 nm *vs.* pH for complex **3** and (*b*) absorbance at 240 nm *vs.* pH for **4**



Scheme 2 Effect of substituent position on negative-charge delocalisation in (*a*) $[L^3]^-$ and (*b*) $[L^4]$

nol termini is strongly dependent on the substitution pattern of the ligand.[19]

Since deprotonation of HL^3 renders the co-ordinated bipy fragment more electron-rich than the other two ancillary bipy ligands, we would expect that the m.l.c.t. transition involving $[L^3]^-$ shifts to higher energy. However since the lowest-energy m.l.c.t. band (involving an unsubstituted bipy ligand) at 459 nm has not shifted significantly, it follows from equation (2) that $pK_a^* \approx pK_a = 8.6$. The protonation/deprotonation equilibrium of HL^3 is clearly not much affected by m.l.c.t. processes involving the other ligands. In complex **4** the lowest-energy m.l.c.t. transition (also involving an ancillary bipy ligand) is likewise unaffected by deprotonation of the pendant phenol, so $pK_a^* \approx pK_a = 8.9$ from equation (2).

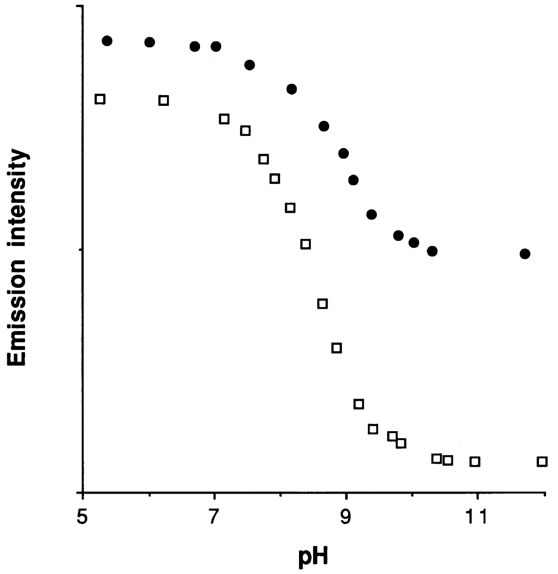


Fig. 8 Plots of emission intensity (arbitrary units) *vs.* pH for complexes **3** (□) and **4** (●) in water

The effect of the position of the hydroxyl substituents in complexes **3** and **4** on the luminescence behaviour of the complexes is quite dramatic. Complex **3** is luminescent under neutral and acidic conditions ($\lambda_{em} = 616$ nm, $\varphi = 0.036$), but deprotonation of the phenol at higher pH values resulted in nearly complete quenching of the emission (Fig. 8), with less than 10% of the original emission intensity remaining (λ_{em} does not change). The pH_i value is 8.5, which is very close to the expected pK_a^* value of *ca.* 8.6. We have seen how the negative charge on the deprotonated 4-hydroxyphenyl substituent may be delocalised onto one of the pyridyl N atoms, giving the deprotonated ligand partial quinonoidal character. In this form the ligand $[L^3]^-$ becomes a strong π donor, which will weaken the ligand-field strength around the metal centre and lower the metal d_{σ^*} orbitals so that they are nearer the ligand-based π* levels. This is known to have the effect of reducing the emission intensity, because the m.l.c.t. excited state can thermally equilibrate with the d–d excited state which undergoes rapid radiationless decay.[20]

Complex **4** is also luminescent when the phenol is protonated, at pH 7 and below ($\varphi = 0.032$). In contrast to **3**, however, the emission was only *partially* quenched under basic conditions, with the quantum yield roughly being halved ($\varphi = 0.015$) above pH 10 (Fig. 8). The pH_i value is 8.9, again very close to the expected pK_a^* value. Since deprotonation of the pendant phenol of **4** cannot result in delocalisation of the negative charge on to the co-ordinating bipyridyl fragment, the ligand-field strength will not be decreased to the extent that occurs when **3** is deprotonated, and access to the d–d state will be less easy resulting in less-efficient non-radiative quenching. The effect of the pH-sensitive functional group on the luminescence of the complex is therefore strongly influenced by the position at which the substituent is attached.

Conclusion

Pendant protonatable or deprotonatable functionalities may be appended to a ruthenium(II) tris(bipyridyl) moiety and used to switch on or off the $\{Ru(bipy)_3\}^{2+}$ luminescence. For complexes **1** and **2**, in which the lowest-energy m.l.c.t. state involves ligands L^1 or L^2 respectively, protonation of the pendant sites of these ligands results in luminescence quenching and a red-shift of the lowest-energy m.l.c.t. maximum, and the difference between the values of pK_a and pK_a^* is 1–2 units. For **3** and **4** the lowest-energy m.l.c.t. state involves the ancillary bipy ligands, so deprotonation of HL^3 or HL^4 has no effect on the energy of this transition. However deprotonation of the pendant phenol group does result in a degree of luminescence quenching which depends on the position of the hydroxyl substituent.

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