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# Quenching of a polypyridyl–ruthenium(II) chromophore by covalently attached {ML(NO)Cl} fragments (M = Mo, W; L = tris(3,5-dimethylpyrazolyl)hydroborate)

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## Abstract

The preparation of a series of binuclear complexes is described, in which derivatives of $[Ru(bipy)_3]^{2+}$ bearing a peripheral phenol group attached to the 4-position of one of the bipyridyl ligands are linked to {ML(NO)Cl} fragments (M = Mo, W; L = tris(3,5-dimethylpyrazolyl)hydroborate) via the pendant phenolate. The electrochemical and UV–Vis spectroscopic properties of the binuclear complexes are approximately the sum of those of the component complexes, indicating a small or moderate ground-state interaction between the two fragments. The Mo and W fragments undergo quasi-reversible one-electron reductions at potentials less negative than the first ligand based reduction of the Ru fragment, suggesting that oxidative quenching of the excited Ru chromophore might be feasible. Luminescence studies of the binuclear complexes at 77 and 298 K indicate that quenching of the ruthenium centre does take place and that the mechanism is likely to be energy transfer rather than electron transfer, resulting in a non-luminescent excited state of the Mo or W fragment.

*Keywords:* Electrochemistry; Ruthenium complexes; Polypyridyl complexes; Metal complexes; Nitrosyl complexes

## 1. Introduction

The preparation of supramolecular, multi-component species containing photoactive polypyridyl–Ru(II) groups continues to be of intense interest because of their possible applications as photocatalysts and photochemical devices [1]. The basis of their function is that the Ru(II) chromophore efficiently absorbs light in the visible region to form a long-lived $^3$MLCT (metal-to-ligand charge transfer) excited state; quenching of this excited state by an adjacent group – either by an electron transfer or an energy transfer mechanism – then allows the quencher to enter a reactive excited state which may not be directly accessible photochemically [2]. Electron transfer has been achieved over long distances in assemblies containing polypyridyl–ruthenium(II) 'antennae' covalently attached to electron-accepting groups based on alkylated pyridines, such as diquats and viologens [3]. Such charge-separated excited states are of interest in that one end can act as an electron donor and the other as an electron acceptor with the concomitant possibility of establishing catalytic cycles.

Energy transfer quenching is also common, not least because it does not involve charge separation which suffers from the extra thermodynamic cost of solvent reorganisation [4]. It is of particular interest in complexes where the quenching group itself enters a luminescent excited state, since the nature of the emission from the second metal centre is indicative of the efficiency of the energy transfer process from the Ru(II) chromophore [5,6]. In addition, complexes whose excited states have useful catalytic functions in their own right may be 'driven' by energy transfer from a ruthenium(II) antenna group. Recent examples of this are the complexes in which a Ni(II)–cyclam group (a photocatalyst for $CO_2$ reduction) is covalently attached to a ruthenium(II) photosensitiser [7].

The directed synthesis of such polynuclear species generally relies on a 'complexes as ligands' approach

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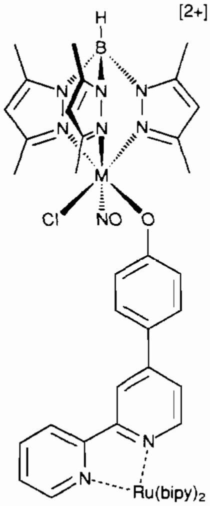
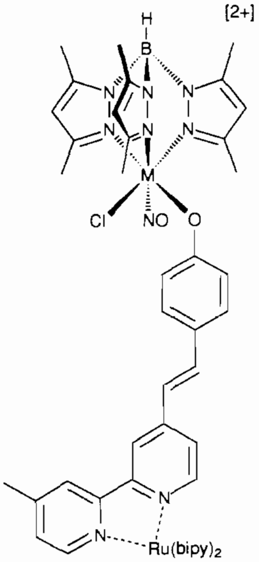
in which a simple complex is prepared containing a vacant, externally directed metal binding site. Subsequent addition of an appropriate metal complex to this secondary binding site permits the controlled, stepwise buildup of polynuclear species [8]. This approach has recently been spectacularly extended to the synthesis of macromolecular cascade molecules (arborols) containing successive 'shells' of photoactive ruthenium(II) groups [9].

We have been interested in using this 'complexes as ligands' approach to prepare heterobinuclear complexes. To that end we recently prepared some simple derivatives of $[Ru(bipy)_3]^{2+}$ containing externally directed, pendant 4-pyridyl or 4-hydroxyphenyl binding sites [10]. In this paper we report the preparation of some heterobinuclear complexes which contain quenching {M(NO)LCl} groups (M = Mo, W; L = tris(3,5-dimethylpyrazolyl)hydroborate) attached to the peripheral phenolic binding sites of some $[Ru(bipy)_3]^{2+}$ derivatives, and their spectroscopic, electrochemical and photophysical properties. A preliminary account of some of this work has been published [11].

**1**: $[Ru(bipy)_2L^1][PF_6]_2$
**2**: $[Ru(bipy)_2L^2][PF_6]_2$
**3**: $[Ru(bipy)_2L^3][PF_6]_2$
**4**: $[Ru(bipy)_2L^4][PF_6]_2$



**5** M = Mo
**6** M = W



**7** M = Mo
**8** M = W

## 2. Experimental

### 2.1. General

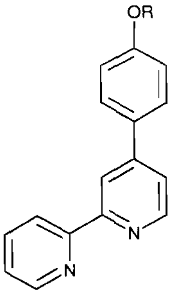
NMR spectra were recorded on Jeol GX270 or GX400 spectrometers. Electron impact (EI) mass spectra were recorded on a Kratos MS9 instrument; fast atom bombardment (FAB) mass spectra were recorded at the SERC Mass Spectrometry Service Centre, Swansea, on a VG Autospec instrument using 3-nitrobenzyl alcohol as matrix. UV–Vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and an SCE reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted versus the ferrocene/ferricenium couple ($Fc/Fc^+$). The solvent was acetonitrile, purified by distillation from $CaH_2$, containing 0.1 mol $dm^{-3}$ $[NBu_4][PF_6]$ as base electrolyte.

### 2.2. Equipment and methods for the luminescence studies

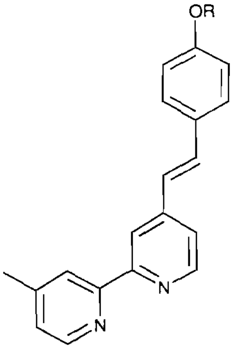
Luminescence experiments were performed in butyronitrile solutions at the indicated temperatures. The butyronitrile was freshly distilled, and the sample solutions deaerated by repeated freeze–pump–thaw cycles. Luminescence spectra were obtained with a Spex Fluorolog II spectrofluorimeter, or with a modified CD9000 Edinburgh instrument using a Spectra Physics 265 Ar laser as an excitation source and equipped with a North Coast EO-8171 germanium-based detector cooled to 77 K for detection of luminescence in the 900–1700 nm range. In the former case, correction of the luminescence profile was performed using the provided software, and luminescence quantum yields were evaluated by comparing areas under luminescence profiles (on an energy scale) with reference to $\phi = 0.028$ for an air-equilibrated aqueous solution of $[Ru(bipy)_3]Cl_2$ [2]. The uncertainty in band maxima positions is ±2 nm; luminescence intensities are ±10%.

Luminescence decay measurements on the Ru-based mononuclear complexes were performed with an IBH single photon counting apparatus. The operating lamp employed deuterium, and excitation and emission wavelengths were selected with monochromators. A laser based system was employed to monitor the luminescence quenching in the binuclear species; the apparatus was based on a mode-locked, cavity-dumped Nd:YAG laser (Continuum PY62-10) and a streak camera (Hamamatsu C1587) equipped with a fast single sweep unit (M1952). Excitation was at 532 or 355 nm and the pulse duration was 35 ps. With this system, the light emitted is collected and fed into the entrance of a spectrograph (HR 250 Jobin-Yvon), then focussed on the slit of the streak camera. Acquisition of the streak images is performed via a cooled CCD camera (Hamamatsu C3140) and the luminescence lifetimes obtained via an iterative non-linear treatment [12]. The time resolutions of the single photon spectrometer and of the laser based system are estimated to be 200 and 30 ps, respectively, and the uncertainty of the evaluated lifetimes is ±10%.

All reaction solvents were dried by standard methods before use. 2,2′-Bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine ($Me_2$bipy) and 4-methoxybenzaldehyde were obtained from Aldrich and used as received. $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ [13] and $[ML(NO)Cl_2]$ (M = Mo, W) [14] were prepared according to literature methods. $L^1$, **1** and **2** were prepared as described previously [10].



$L^1$ : R = Me
$L^2$ : R = H



$L^3$ : R = Me
$L^4$ : R = H

### 2.3. Preparations

#### 2.3.1. 4-Methyl-4′-(4-methoxyphenylethenyl)-2,2′-bipyridine, $L^3$

To a solution of $Me_2$bipy (3.68 g, 20 mmol) in ice-cold thf (20 $cm^3$) under $N_2$, a solution of $LiNPr^i_2$ (20 mmol; freshly prepared by mixing 13.3 $cm^3$ of 1.6 M BuLi in hexanes and 2.65 $cm^3$ of dry diisopropylamine at room temperature under $N_2$) was added dropwise over 15 min. The deep purple solution was stirred at 0 °C for 1 h, after which a solution of 4-methoxybenzaldehyde (2.72 g, 20 mmol) in thf (20 $cm^3$) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After quenching with water and evaporation to dryness in vacuo an oily residue was obtained (the crude intermediate alcohol) which was used without purification for the subsequent dehydration.

The oil was dissolved in dry pyridine (50 $cm^3$), and a solution of $POCl_3$ (3.83 g, 25 mmol) in dry pyridine (50 $cm^3$) was added dropwise under $N_2$ at room temperature with vigorous stirring. After 1 h the pyridine was evaporated in vacuo and crushed ice was added; the mixture was left for 30 min to ensure that all residual $POCl_3$ was destroyed. The pH of the aqueous solution was adjusted to between 3 and 4, and unwanted organic materials were extracted with $CH_2Cl_2$. The solution was then neutralised; the product precipitated, and was collected by filtration. The crude solid was redissolved in acidic solution and reprecipitated, then filtered off, dried, and recrystallised from hot ethanol. Yield 3 g (50%). EI-MS: *m/z* 302 ($M^+$, 100%), 287 ($M^+ - CH_3$, 25%). $^1H$ NMR (270 MHz, $CD_2Cl_2$): $\delta$ 8.57 (1H, d, $J$ = 6.1, $H^{6'}$), 8.51–8.53 (2H, m, $H^6$ and $H^{3'}$), 8.29 (s, 1H, $H^3$), 7.52 (2H, d, $J$ = 8.9, phenyl $H^2$ and $H^6$), 7.41 (1H, d, $J$ = 16.3, ethenyl), 7.36 (1H, dd, $J$ = 5.5, 1.5, $H^{5'}$), 7.16 (1H, d, $J$ = 5.0, $H^5$), 7.01 (1H, d, $J$ = 16.3, ethenyl), 6.93 (2H, d, $J$ = 8.9 Hz, phenyl $H^3$ and $H^5$), 3.82 (3H, s, $OCH_3$), 2.44 (3H, s, $CH_3$). M.p. 172–174 °C. *Anal.* Found: C, 79.1; H, 5.9; N, 9.2. Calc. for $C_{20}H_{18}N_2O$: C, 79.4; H, 6.0; N, 9.3%.

#### 2.3.2. 4-Methyl-4′-(4-hydroxyphenylethenyl)-2,2′-bipyridine, $L^4$

Demethylation of $L^3$ to give $L^4$ was achieved by reaction with molten pyridinium chloride at 190–200 °C for 3 h under $N_2$ according to a published procedure [15]. After addition of water and adjustment of the pH to 6 the product precipitated and was filtered off, washed with water and dried (crude yield 90%). The crude product is sufficiently pure for use in the complexation reactions; it may be recrystallised from ethanol/water. EI-MS: *m/z* 288 ($M^+$, 100%). $^1H$ NMR (270 MHz, $CD_3SOCD_3$): $\delta$ 8.60 (1H, d, $J$ = 5.6, $H^6$ or $H^{6'}$), 8.57 (1H, d, $J$ = 8.6, $H^{6'}$ or $H^6$), 8.48 (1H, s, $H^{3'}$), 8.25 (1H, s, $H^3$), 7.48–7.56 (4H, m, $H^{5'}$, phenyl $H^2$ and $H^6$, and ethenyl), 7.30 (1H, d, $J$ = 5.6, $H^5$), 7.16 (1H, d, $J$ = 16.6, ethenyl), 6.81 (2H, d, $J$ = 8.3 Hz, phenyl $H^3$ and $H^5$), 2.43 (3H, s, $CH_3$). M.p. 226–228 °C. *Anal.* Found: C, 79.5; H, 5.5; N, 9.6. Calc. for $C_{20}H_{18}N_2O$: C, 79.1; H, 5.6; N, 9.7%.

#### 2.3.3. $[Ru(bipy)_2(L^3)][PF_6]_2$ (3) and $[Ru(bipy)_2(L^4)][PF_6]_2$ (4)

A mixture of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.2 g, 0.39 mmol) and the appropriate ligand ($L^3$ or $L^4$, 1 equiv.) was heated to reflux in ethylene glycol (20 $cm^3$) for 1 h. The orange solution was allowed to cool and the complex precipitated by addition of aqueous $KPF_6$. After filtration, washing with water and drying in vacuo the complexes were purified by chromatography on 2 mm thick preparative-scale $SiO_2$ TLC plates (Merck, article 5717) using a mixture of MeCN:$H_2O$:saturated aqueous $KPF_6$ (96:2:2) as eluent. The major orange band was scraped off and the product dissolved out of the silica using the elution solvent. The resulting solution was concentrated in vacuo until the product precipitated; it was then filtered off, washed with water and dried in vacuo. Yields were typically 80–85%.

#### 2.3.4. Binuclear complexes 5, 6, 7 and 8

A mixture of the appropriate Ru(II) complex with a pendant phenol (**2** or **4**; 0.15 mmol) and $[ML(NO)Cl_2]$ (M = Mo or W; 0.18 mmol) and dry $Et_3N$ (1 $cm^3$) was heated to reflux in dry MeCN:toluene (40:60, 30 $cm^3$) under $N_2$ overnight. The mixture was then allowed to cool and evaporated to dryness in vacuo. The solid

Table 1
Analytical, mass spectrometric and IR data for the new complexes **3**–**8**

| Complex | Elemental analysis[a] (%) | | | FAB mass spectrum | | IR |
|---|---|---|---|---|---|---|
| | C | H | N | $M-\mathrm{PF}_6$ | $M-2\mathrm{PF}_6$ | $\nu$(NO) ($\mathrm{cm}^{-1}$) |
| **3** | 47.9 (47.8) | 3.4 (3.4) | 8.1 (8.4) | 861 (100%) | 716 (55%) | |
| **4** | 47.1 (47.2) | 3.2 (3.3) | 8.4 (8.5) | 847 (100%) | 702 (75%) | |
| **5** | 43.8 (43.5) | 3.4 (3.5) | 12.7 (12.9) | 1266 (60%) | 1119 (55%) | 1685 |
| **6** | 41.2 (40.9) | 3.2 (3.3) | 12.1 (12.2) | 1349 (25%) | | 1640 |
| **7** | 45.0 (44.7) | 3.4 (3.7) | 12.2 (12.6) | 1304 (75%) | 1159 (30%) | 1684 |
| **8** | 42.7 (42.2) | 3.3 (3.5) | 11.5 (11.8) | 1392 (70%) | 1246 (55%) | 1642 |

[a] Calculated values are in parentheses.

residue was purified by chromatography on preparative-scale alumina plates (Merck, article 5726) with MeCN:toluene (1:1) as eluent. The major brown fraction was scraped off and the product dissolved off the alumina with MeCN (50 $\mathrm{cm}^3$), to which saturated aqueous $\mathrm{KPF}_6$ (1 $\mathrm{cm}^3$) was added. The resulting solution was concentrated in vacuo until an aqueous suspension resulted from which the product was extracted with $\mathrm{CH}_2\mathrm{Cl}_2$, followed by drying ($\mathrm{MgSO}_4$) and concentration of the organic phase. Finally the product was precipitated from a small volume of $\mathrm{CH}_2\mathrm{Cl}_2$ by addition of n-pentane, filtered off and dried. Yields 23–28%.

Analytical and spectroscopic data for the new complexes **3**–**8** are given in Table 1.

## 3. Results and discussion

### 3.1. Preparation of ligands and complexes

The ruthenium complexes used as 'building blocks' (**2** and **4**) are derivatives of $[\mathrm{Ru(bipy)}_3]^{2+}$ which contain pendant phenol groups as peripheral binding sites. The preparation of **1** and its subsequent demethylation to give **2** have been described earlier [10]. The new ligand $\mathrm{L}^3$ was prepared by reaction of the mono-anion of 4,4′-dimethyl-2,2′-bipyridine with 4-methoxybenzaldehyde, followed by dehydration of the intermediate alcohol with $\mathrm{POCl}_3$/pyridine; this is a strategy that has recently been popular for the synthesis of 4-substituted pyridine and bipy derivatives with unsaturated substituents [16]. Removal of the methyl group to give $\mathrm{L}^4$ was effected with molten pyridinium hydrochloride [15].

Complexes **3** and **4** were then prepared by reaction of $\mathrm{L}^3$ or $\mathrm{L}^4$, respectively, with $[\mathrm{Ru(bipy)}_2\mathrm{Cl}_2]\cdot 2\mathrm{H}_2\mathrm{O}$ in ethylene glycol at reflux. In contrast, **2** has been previously prepared directly from **1** by demethylation of the ligand with $\mathrm{BBr}_3$ after binding of the protected ligand to the ruthenium(II) core [10]. However attempts to demethylate the methoxyphenyl group of **3** in the same way were complicated by the fact that the HBr liberated by hydrolysis of $\mathrm{BBr}_3$ in the workup appeared to react with the double bond to give a mixture of products. Consequently the free ligand was demethylated by a different route before complex formation; fortunately the presence of a free phenol group in $\mathrm{L}^2$ and $\mathrm{L}^4$ does not compete with the bipyridyl binding site for coordination to the ruthenium(II).

Reaction of **2** with $[\mathrm{ML(NO)Cl}_2]$ (M = Mo, W) produced the binuclear complexes **5** (M = Mo) and **6** (M = W) in which the pendant phenol group of **2** is deprotonated and coordinates to the second metal centre by displacement of a chloride ion. Similarly, reaction of **4** with $[\mathrm{ML(NO)Cl}_2]$ afforded the binuclear complexes **7** (M = Mo) and **8** (M = W). The ease with which one of the chloride ligands of $[\mathrm{ML(NO)Cl}_2]$ may be substituted by phenolate ligands has been exploited in the preparation of numerous complexes of the type [ML(NO)Cl(OAr)] [17].

All new complexes (**3**–**8**) were characterised by elemental analysis and FAB mass spectrometry (Table 1). The FAB mass spectra showed a peak corresponding to the expected mass of the cation in each case, and usually an additional peak at 145 mass units higher corresponding to association of one $\mathrm{PF}_6^-$ counter-ion with the complex cation. The complexes were also all examined by $^1$H NMR spectroscopy. The mononuclear ruthenium(II) complexes **3** and **4** showed several, overlapping signals in the aromatic region which were not assigned individually but integrated to the expected number of protons (27 and 28, respectively). The binuclear complexes **5**–**8** all displayed, in addition to these aromatic signals, three signals (intensity 1H each) at around 6 ppm due to the pyrazolyl protons of L, and six signals (intensity 3H each) between 2 and 3 ppm corresponding to the six inequivalent methyl groups of L; these are entirely characteristic of the {ML(NO)Cl} moiety. Finally, the IR spectra of **5**–**8** show the $\nu$(NO) stretch in the expected positions for the phenolate-substituted Mo (~1685 $\mathrm{cm}^{-1}$) and W (~1640 $\mathrm{cm}^{-1}$) centres [17].

Table 2
Electrochemical data for the new complexes

| Complex | Bipy based reductions[a] | | | Mo(16–17)[b] | W(16–17)[c] | $Ru^{II}/Ru^{III}$ |
|---|---|---|---|---|---|---|
| [MoL(NO)Cl(OPh)] | | | | −0.70 (75) | | |
| [WL(NO)Cl(OPh)] | | | | | −1.22 (80) | |
| $[Ru(bipy)_3][PF_6]_2$ | −2.16 (80)[d] | −1.92 (80) | −1.72 (60) | | | +0.89 (70) |
| **1** | | −1.92 (90) | −1.73 (80) | | | +0.85 (80) |
| **2** | | | −1.77 (80) | | | +0.89 (90)[e] |
| **3** | | −1.94 (95) | −1.76 (90) | | | +0.87 (95) |
| **4** | −2.20 | | −1.76 (90) | | | +0.85 (95)[e] |
| **5** | −2.23 (80) | −1.99 (80) | −1.78 (80) | −0.66 (70) | | +0.87 (80) |
| **6** | −2.22 (70) | −1.97 (80) | −1.79 (90) | | −1.18 (70) | +0.86 (80) |
| **7** | −2.21 (110) | −1.94 (90) | −1.77 (80) | −0.68 (80) | | +0.83 (105) |
| **8** | −2.17 (80) | −1.93 (60) | −1.77 (70) | | −1.19 (85) | +0.82 (80) |

[a] All measurements made in acetonitrile containing 0.1 mol $dm^{-3}$ $Bu_4NPF_6$ using a Pt-bead working electrode at a scan rate of 0.2 V $s^{-1}$; potentials are quoted vs. the ferrocene/ferricenium couple.

[b] Potentials of the molybdenum-centred reductions (from 16e configuration to 17e).

[c] Potentials of the tungsten-centred reductions (from 16e configuration to 17e).

[d] Figures in parentheses are peak–peak separations ($E_{p,a}-E_{p,c}$).

[e] Not fully reversible; return wave smaller than outward wave.

### 3.2. Electrochemistry and UV–Vis spectroscopy

The results of cyclic voltammetric studies are summarised in Table 2; results for the reference compounds [ML*(NO)Cl(OPh)] (M = Mo, W) and $[Ru(bipy)_3]^{2+}$, recorded under the same conditions, are included for comparison. The binuclear complexes show all of the expected redox waves (ligand-based reductions on the ruthenium(II) centre [2]; a one-electron reduction of the molybdenum or tungsten centre, from a 16-electron configuration to 17-electron [17]; a ruthenium +2/+3 oxidation [2]) at potentials only slightly different from those of the mononuclear component parts. The ground-state electronic interaction between the components is therefore not strong. A significant point to note is that the molybdenum-centred reductions in **5** and **7** are around 1.1 V more anodic than the first bipy based reductions, and the tungsten-centred reductions in **6** and **8** are around 0.6 V more anodic than the first bipy based reductions. This feature of the complexes could promote oxidative quenching of the $^3$MLCT excited state of the ruthenium(II) centre, since electron transfer from the bipy based excited electron to the peripheral molybdenum or tungsten centre could be thermodynamically favourable, and result in transient charge-separated species containing ruthenium(III) and a reduced (17-electron) molybdenum or tungsten group.

The electronic spectral data are summarised in Table 3. The ruthenium(II) centres show the expected combination of characteristic ligand based $\pi$–$\pi^*$ and MLCT transitions [2]. In the binuclear complexes the additional transitions from the molybdenum and tungsten centres, a phenolate-to-metal LMCT ($\lambda_{max}=534$ nm ($\epsilon=6000$) for [MoL(NO)Cl(OPh)]; $\lambda_{max}=426$ nm ($\epsilon=14000$ $dm^3$ $mol^{-1}$ $cm^{-1}$) for [WL(NO)Cl(OPh)]), are masked by the intense transitions from the ruthenium(II) group and generally only discernible as shoulders. In particular for **5** and **7** the LMCT transition at the molybdenum centre results in the tail of the spectrum extending further out to the red end of the spectrum than for **2** or **4**. The transitions in the binuclear complexes are not very different from their positions in the corresponding mononuclear complexes, which is consistent with the electrochemical results. We note that the absorption spectra of the Mo and W based fragments exhibit tails extending to around 700 nm. Thus, in the binuclear complexes the lowest lying excited states are expected to be centred on the Mo and W moieties and are of a sufficiently low energy that energy transfer quenching could be thermodynamically allowed.

Table 3
Electronic spectra data for the complexes (in MeCN)

| Complex | $\lambda_{max}$ (nm) ($\epsilon$ ($10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$)) |
|---|---|
| **1** | 244 (17), 288 (46), 324 (15), 456 (10) |
| **2** | 244 (22), 288 (58), 325 (18), 456 (13) |
| **3** | 244 (28), 288 (62), 351 (22), 458 (17) |
| **4** | 244 (28), 289 (66), 354 (21), 458 (18) |
| **5** | 242 (36), 288 (71), 330 (22), 462 (20) |
| **6** | 244 (24), 288 (49), 330 (13), 458 (13) |
| **7** | 239 (40), 289 (68), 360 (23), 463 (24) |
| **8** | 244 (32), 289 (55), 370 (20), 462 (21) |

### 3.3. Luminescence behaviour

The luminescence properties of the complexes have been studied both at room temperature and at 77 K (Table 4). The phenol-substituted mononuclear complexes **2** and **4** are both luminescent; **2** is comparable to $[Ru(bipy)_3]^{2+}$ in its emission intensity and lifetime, whereas **4** luminesces much more weakly. Study of the

Table 4
Luminescence data for **2** and **4** at 298 K and 77 K

| Complex | $\lambda_{max}$[a] (nm) 298 K | $\tau$ (ns) 298 K | $\phi_{em}$ 298 K | $\lambda_{max}$ (nm) 77 K | $\phi_{em}$[b] 77 K |
|---|---|---|---|---|---|
| $[Ru(bipy)_3]^{2+}$ | 604 | 1190 | 0.062 | 579 | 0.328 |
| **2** | 608 | 1680 | 0.063 | 585 | 0.273 |
| **4** | 640 | 30 | $1.1\times10^{-3}$ | 638 | $2.4\times10^{-2}$ |

[a] All measurements were made in freshly distilled, deaerated butyronitrile.

[b] No correction made for solvent contraction (≈20%).

binuclear complexes **5**–**8** was slightly complicated by the fact that the molybdenum and tungsten groups are slightly hydrolytically unstable; cleavage of the Mo–O or W–O bonds during their preparation and handling therefore liberated trace amounts of **2** and **4** as luminescent impurities in the samples even though rigorously pre-dried solvents were used and the freshly prepared complexes appeared pure by thin-layer chromatography and NMR. The weak emissions from solutions of **5**–**8** had $\lambda_{max}$ and lifetime values identical to those of the respective mononuclear ruthenium component and can therefore be ascribed to this slight decomposition. It follows that the intact binuclear complexes are completely quenched at both room temperature and at 77 K.

From the electrochemical and luminescence data one sees that formation of the charge-separated species from the excited state precursor [1] at room temperature is (i) an exothermic process for the Ru–Mo complexes **5** and **7** (by 0.59 and 0.43 eV, respectively), and (ii) is practically isoenergetic for the Ru–W complexes **6** and **8**. However, at 77 K the charge-separated state is destabilised by at least 0.6 eV in a rigid solvent [18], which more than cancels out the thermodynamic gradient for electron transfer. In particular, for **6** and **8** the additional 0.6 eV required for charge separation makes oxidative quenching highly endothermic. It is likely therefore that energy transfer quenching is occurring at 77 K and so, by inference, also at room temperature. Energy transfer might be demonstrated if the resulting molybdenum or tungsten excited states were themselves luminescent (as with ruthenium–osmium binuclear species [5]). However no such emission could be detected at wavelengths up to 1700 nm, which is not surprising as we have never observed luminescence from such molybdenum or tungsten complexes.

## 4. Conclusions

We have demonstrated that complexes **2** and **4**, derivatives of $[Ru(bipy)_3]^{2+}$ bearing a pendant phenol group, are useful building blocks for assembling polynuclear complexes via substitution of the phenol group with {M(NO)LCl} (M = Mo, W) fragments, and that attachment of these metal fragments to the $[Ru(bipy)_3]^{2+}$ core results in complete quenching at both room temperature and 77 K. The luminescence measurements indicate that energy transfer is the likely quenching mechanism.

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