

Cite this: DOI: 10.1039/c0xx00000x

PAPER

www.rsc.org/xxxxxx

# Photochemistry between a ruthenium(II) pyridylimidazole complex and benzoquinone: Simple electron transfer versus proton-coupled electron transfer

Roland Hönes, Martin Kuss-Petermann and Oliver S. Wenger\*

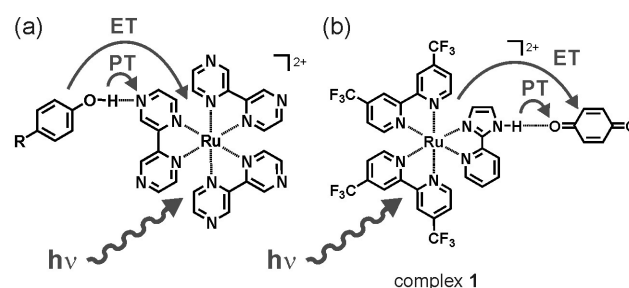
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A ruthenium(II) complex with two 4,4'-bis(trifluoromethyl)-2,2'-bipyridine chelates and a 2-(2'-pyridyl)imidazole ligand was synthesized and characterized by electrochemical and optical spectroscopic means. The respective complex has the potential to act as a combined electron / proton donor when promoted to its long-lived  $^3\text{MLCT}$  excited state with visible light. The possibility of proton-coupled electron transfer (PCET) between the ruthenium(II) complex and 1,4-benzoquinone as an electron / proton acceptor was explored by steady-state and time-resolved luminescence spectroscopy, as well as by transient absorption spectroscopy in the nanosecond time regime. Excited-state deactivation is found to occur predominantly via simple oxidative quenching involving no proton motion, but a minor fraction of the photoexcited complex appears to react via PCET since there is spectral evidence for semiquinone as a photoproduct. Presumably, PCET is not kinetically competitive with simple electron transfer because the latter process is sufficiently exergonic and because there is little thermodynamic benefit from coupling proton transfer to the photoinduced electron transfer.

## Introduction

The photophysical properties of ruthenium(II) complexes with 2,2'-biimidazole, 2,2'-bibenzimidazole, 2-(2'-pyridyl)imidazole and 2-(2'-pyridyl)benzimidazole ligands have first been explored more than 30 years ago by Haga.<sup>1-6</sup> An important finding from this work was that the redox chemistry and the acid-base chemistry of these complexes are intimately coupled to each other, a fact which was further explored in related iron(II) complexes by the Williams group and in other ruthenium(II) complexes by Thomas and coworkers.<sup>7-9</sup> To name just one particularly spectacular result, it was found that four-fold deprotonation of a homoleptic iron(II) complex with two terdentate 2,6-(benzimidazol-2'-yl)pyridine ligands shifted the electrochemical potential for oxidation of Fe(II) to Fe(III) by nearly 1.5 Volts.<sup>7</sup> From a photochemistry point of view there is special interest in ruthenium(II) complexes with long-lived excited states which can undergo coupled redox and acid-base chemistry. Indeed, as is evident from the review by Vos there exist a great many of  $d^6$  metal complexes which fall into this category.<sup>10</sup> This family of photoactive complexes is by far not restricted to the abovementioned ligands derived from imidazole, but it further encompasses carboxyl-, hydroxyl-, and amidinium-substituted 2,2'-bipyridine or 1,10-phenanthroline ligands, just to name a few.<sup>11-16</sup>



**Scheme 1.** Photoinduced electron transfer (ET) and proton transfer (PT) in two reaction couples used for mechanistic investigations of phototriggered proton-coupled electron transfer (PCET). (a) Previously investigated systems; R = OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, Br, CN;<sup>17</sup> (b) reaction couple investigated in the present study.

The increasing interest in proton-coupled electron transfer (PCET) in recent years stimulated further research on metal complexes which can potentially act as combined electron/proton donors or combined electron/proton acceptors when irradiated with visible light.<sup>18</sup> Ultimately, such photochemistry may be of interest in the context of artificial photosynthesis,<sup>19</sup> but the primary goal of many current studies is quite simply to elucidate the reaction mechanisms of excited-state PCET. An important question is for example whether electron and proton are transferred from one substrate to the other in individual (consecutive) reaction steps or whether they are transferred in a

concerted manner.<sup>20-21</sup> In this context, ruthenium(II) complexes with 2,2'-bipyrazine (Scheme 1a) ligands and related rhenium(I) complexes have provided valuable insight recently: We and others were able to show that concerted proton-electron transfer (CPET) from phenol molecules to photoexcited complexes of these types are indeed possible under favorable circumstances,<sup>15, 17, 22-24</sup> manifesting in hydrogen/deuterium kinetic isotope effects of up to 10.<sup>17</sup> In these earlier studies, ruthenium(II) 2,2'-bipyrazine complexes acted as combined electron/proton acceptors upon photoexcitation. Here, we report our findings from a study in which we explored the potential of the ruthenium(II) complex from Scheme 1b to act as a combined electron-proton donor in its long-lived excited state. Benzoquinone was chosen as a reaction partner because it is well known as combined electron/proton acceptor.

We have previously explored the excited-state PCET chemistry of an iridium(III) complex with a 2,2'-biimidazole ligand but the results were less clear than anticipated, inter alia because of the fact that two deprotonatable sites were present and because transient absorption spectroscopy was not particularly helpful for following the redox chemistry of the iridium(III) center.<sup>25-26</sup> In this sense ruthenium(II) complex **1** from Scheme 1b with only one deprotonatable site represents a significant advance. Haga and Tsunemitsu considered the possibility of PCET between a related ruthenium(II) complex and pyridine molecules already in 1989,<sup>3, 18</sup> while Kramer and coworkers used a deprotonated ruthenium(II) pyridylbenzimidazole complex as a combined electron/proton acceptor for PCET investigations.<sup>18, 27</sup> We are unaware of prior experimental studies of excited-state PCET using complexes with imidazole-derived ligands as combined electron/proton donors.

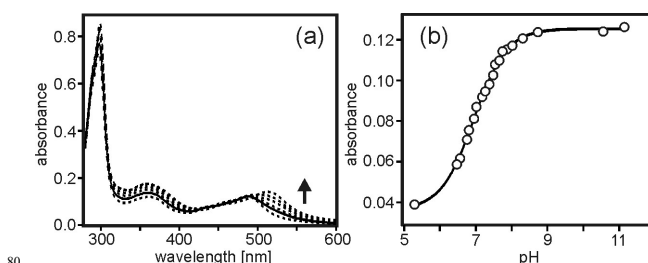
## Experimental section

Synthesis of the ligands and of the [Ru(4,4'-bis(trifluoromethyl)-2,2'-bipyridine)<sub>2</sub>Cl<sub>2</sub>] precursor complex occurred following previously published protocols as described in the results and discussion section.<sup>28-30</sup> A solution of [Ru(4,4'-bis(trifluoromethyl)-2,2'-bipyridine)<sub>2</sub>Cl<sub>2</sub>] (71 mg, 9.4·10<sup>-5</sup> mol) in a 1:1 (v:v) mixture of ethanol and water (10 mL) was refluxed for 30 minutes until the precursor complex was completely dissolved. Subsequently, 2-(2'-pyridyl)imidazole was added (17 mg, 1.1·10<sup>-4</sup> mol), and the mixture was refluxed for 3 hours. Then, a few drops (~5) of concentrated aqueous HCl were added, and the ethanol was removed on a rotary evaporator. The aqueous solution was filtered and a saturated aqueous solution of KPF<sub>6</sub> was added. The precipitate was collected by filtration and washed with water and Et<sub>2</sub>O yielding 80 mg (76%) of the title compound as a dark-reddish black solid. Product which remained in the filtrate was recovered by rinsing with acetone. <sup>1</sup>H-NMR (300 MHz, acetone-d<sub>6</sub>): δ (ppm) = 13.53 (s<sub>br</sub>, 1 H), 9.45-9.39 (m, 4 H), 8.64 (d, *J* = 5.9 Hz, 1 H), 8.56 (d, *J* = 5.9 Hz, 2 H), 8.51 (d, *J* = 5.9 Hz, 1 H), 8.43 (d, *J* = 7.9 Hz, 1 H), 8.21 (td, *J* = 7.9 Hz, 1.4 Hz, 1 H), 8.03 (d, *J* = 5.6 Hz, 1 H), 8.00-7.94 (m, 2 H), 7.85 (dd, *J* = 6.0 Hz, 1.5 Hz, 1 H), 7.80 (dd, *J* = 6.0 Hz, 1.5 Hz, 1 H), 7.76 (d, *J* = 1.5 Hz, 1 H), 7.54 (ddd, *J* = 7.8 Hz, 5.6 Hz, 1.3 Hz, 1 H), 6.98 (d, *J* = 1.5 Hz, 1 H). MS (ESI) *m/z*: 415.5271, calc.: 415.5276. Anal. Calcd for C<sub>32</sub>H<sub>19</sub>F<sub>24</sub>N<sub>7</sub>P<sub>2</sub>Ru·0.5(CH<sub>3</sub>)<sub>2</sub>CO: C, 35.00; H, 1.94; N,

8.53. Found: C, 35.14, H, 2.04; N, 8.20.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker B-ACS-120 instrument. Electron-impact mass spectrometry was made with a Finnigan MAT 95 spectrometer. Elemental analyses were performed with a Vario EL3 instrument.

Cyclic voltammetry was performed using a Versastat3-200 potentiostat from Princeton Applied Research and with a glassy carbon disk working electrode. Two separate silver wires served as counter- and reference electrodes, respectively. Prior to voltage sweeps at rates of 0.1 V/s the dried solvent was flushed with nitrogen; 0.1 M TBAPF<sub>6</sub> served as a supporting electrolyte. UV-Vis spectra were measured on a Cary 300 instrument from Varian. Steady-state luminescence experiments were performed on a Fluorolog-3 apparatus from Horiba Jobin-Yvon. Luminescence lifetime and transient absorption experiments occurred on a LP920-KS spectrometer from Edinburgh Instruments equipped with an iCCD from Andor. The excitation source was the frequency-doubled output from a Quantel Brilliant b laser. For all optical spectroscopic experiments the samples were de-oxygenated via three subsequent freeze-pump-thaw cycles in home-built quartz cuvettes that were specifically designed for this purpose.



**Figure 1.** (a) UV-Vis absorption spectra of complex **1** in 1:1 (v:v) CH<sub>3</sub>CN/H<sub>2</sub>O solution at ambient temperature. The solid line was obtained from a solution giving a pH meter reading of 6.7. The arrow shows the changes as the pH rises. (b) Titration curve monitoring the absorbance of complex **1** in 1:1 (v:v) CH<sub>3</sub>CN/H<sub>2</sub>O at 525 nm as a function of pH meter reading in this solvent mixture.

## Results and discussion

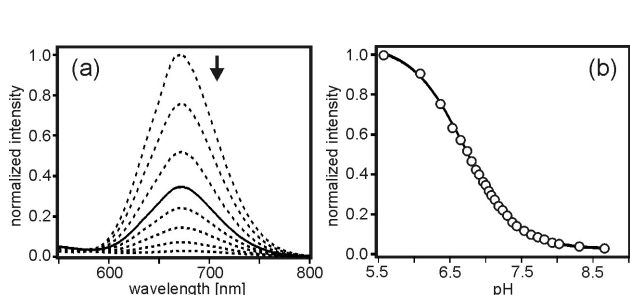
### Synthesis

The 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ligand of complex **1** was synthesized from commercially available 2-chloro-4-(trifluoromethyl)pyridine in a homocoupling reaction using NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as a catalyst as described previously.<sup>28</sup> The 2-(2'-pyridyl)imidazole ligand was synthesized from 2-cyanopyridine as reported recently.<sup>30</sup> Complexation followed the standard synthetic route,<sup>28-29</sup> involving the synthesis of a Ru(4,4'-bis(trifluoromethyl)-2,2'-bipyridine)<sub>2</sub>Cl<sub>2</sub> precursor complex prior to ligation of the 2-(2'-pyridyl)imidazole ligand.

### Absorption and luminescence spectroscopy

The solid line in Figure 1a is the UV-Vis spectrum of complex **1** in 1:1 (v:v) CH<sub>3</sub>CN/H<sub>2</sub>O solution at ambient temperature and pH 7 (concentration: 3·10<sup>-5</sup> M). The lowest-energetic absorption band with a maximum near 490 nm is due to spin-allowed metal-to-ligand charge transfer (MLCT) transitions between the

ruthenium(II)  $t_{2g}$  orbitals (in the limiting case of octahedral symmetry) and  $\pi^*$  orbitals of the bipyridine and pyridylimidazole ligands. The intense band at 300 nm is attributed to  $\pi$ - $\pi^*$  transitions localized on 4,4'-bis(trifluoromethyl)-2,2'-bipyridine, in analogy to the bipyridine-localized bands in  $\text{Ru}(2,2'$ -bipyridine) $_3^{2+}$ .<sup>31</sup> The additional band at 360 nm has been observed previously in  $[\text{Ru}(2,2'$ -bipyridine) $_2(2'$ -pyridyl)imidazole] $^{2+}$  and was interpreted in terms of a ligand-to-ligand charge transfer (LLCT) transition.<sup>32</sup>



**Figure 2.** (a) Luminescence of a  $\sim 10^{-5}$  M solution of complex **1** in 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  after excitation at 470 nm showing the fall of the intensity as the pH rises; the solid trace was measured from a solution giving a pH meter reading of 7.0. (b) Titration curve monitoring the emission intensity of complex **1** at 670 nm at different pH meter readings in the 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent mixture.

When increasing the pH of the solution from 7 to 11.5 one observes spectral changes mainly in the MLCT region, and this is illustrated by a few exemplary spectra represented by the dashed lines in Figure 1a. In alkaline solution the MLCT band shifts to longer wavelengths, in line with prior reports by Haga and others,<sup>1-6, 32</sup> and this is a direct consequence of pyridylimidazole deprotonation. Figure 1b shows a titration curve in which the absorbance at 525 nm is plotted versus the pH meter reading in the 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution. From this curve one obtains a  $\text{pK}_a$  value of  $6.7 \pm 0.2$  for complex **1** in its electronic ground state.

The solid trace in Figure 2a is the luminescence spectrum of complex **1** in pH-neutral 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  obtained after photoexcitation at 470 nm at ambient temperature (concentration:  $6 \cdot 10^{-5}$  M). By analogy to related ruthenium(II) complexes with pyridylimidazole or biimidazole ligands this emission is assigned to  $^3\text{MLCT}$  luminescence.<sup>2</sup> Compared to  $\text{Ru}(2,2'$ -bipyridine) $_3^{2+}$  the emission is red-shifted because the pyridylimidazole ligand is acting as a  $\pi$ -donor and thus increases the electron density at the metal center.<sup>2</sup> The deprotonated form of pyridylimidazole is an even stronger  $\pi$ -donor, which explains the observed red-shift of the MLCT absorption (Figure 1a) and, in consequence, the emission quenching (Figure 2a). The result of a titration monitoring the emission maximum at 670 nm as a function of pH in 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  is shown in Figure 2b. The inflection point of the titration curve is at  $\text{pH}_i = 6.8 \pm 0.2$ . The true excited-state acid ionization constant ( $\text{pK}_a^*$ ) is obtained from  $\text{pH}_i$  when taking into account the different excited-state lifetimes of the protonated ( $\tau_{\text{HB}}$ ) and deprotonated forms ( $\tau_{\text{B}}$ ) of the complex.<sup>2, 33</sup> Using equation 1 with  $\tau_{\text{HB}} = 160$  ns and  $\tau_{\text{B}} = 17 \pm 5$  ns (Table 1) one obtains  $\text{pK}_a^* = 7.8 \pm 2$ .

$$\text{pK}_a^* = \text{pH}_i + \log(\tau_{\text{HB}}/\tau_{\text{B}})$$

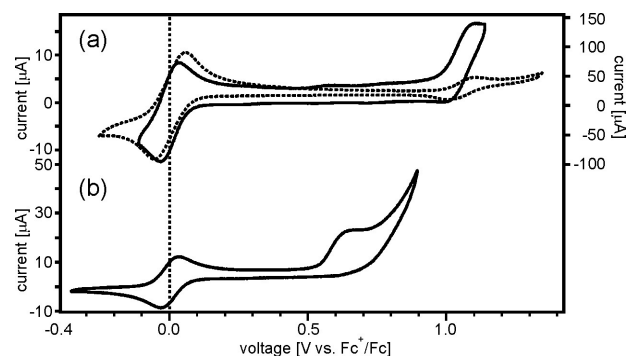
eq. 1

This analysis suggests that complex **1** is a somewhat weaker acid in its emissive  $^3\text{MLCT}$  excited state than in its electronic ground state (Table 1). This contrasts the prior findings of Haga and Gray who had used unsubstituted bipyridines as ancillary ligands in ruthenium(II) pyridylimidazole complexes.<sup>2, 32</sup> Our result is particularly intriguing because our 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ligand has energetically lower-lying  $\pi^*$  orbitals than unsubstituted 2,2'-bipyridine,<sup>34</sup> and therefore one could expect complex **1** to be an even stronger photoacid than the complexes of Haga and Gray. However, the short excited-state lifetime of the deprotonated complex ( $\tau_{\text{B}} = 17 \pm 5$  ns) introduces serious uncertainty to the  $\text{pK}_a^*$  value calculated with eq. 1 since it is possible that proton equilibrium is not reached in such a short-lived excited state. Using the Förster equation,<sup>43</sup> one obtains  $\text{pK}_a^* = 5.0 \pm 1.0$  (Table 1).

Table 1. Ground and excited-state properties of complex **1** in de-aerated 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution.

	protonated	deprotonated
$\text{pK}_a$	$6.7 \pm 0.2$	
$\text{pK}_a^*$	$5.0 \pm 1.0$	
$\text{pK}_a$ (oxidized form)	$4 \pm 1$	
$\tau$ [ns]	$160 \pm 16$	$17 \pm 5$
$E_{\text{ox}}$ [V vs. $\text{Fc}^+/\text{Fc}$ ]	1.0	0.65
$E_{\text{ox}}^*$ [V vs. $\text{Fc}^+/\text{Fc}$ ]	-0.85	
$E_{\text{red}}$ [V vs. $\text{Fc}^+/\text{Fc}$ ]	-1.38/-1.68	

The  $\text{pK}_a$  value of the one-electron oxidized form of complex **1** is more difficult to determine. An acid-base titration is technically not feasible in our spectroelectrochemical cell, hence we rely here on the following estimation: Prior investigations of related Fe(II) and Ru(II) complexes have lead to the collective conclusion that one-electron oxidation of the metal center increases the acidity of the peripheral N-H groups by 3 – 4  $\text{pK}_a$  units relative to the parent complex in its electronic ground state.<sup>1-2, 6-7, 9</sup> Thus, it appears plausible to expect a  $\text{pK}_a$  value of  $4 \pm 1$  for the one-electron oxidized form of complex **1** (Table 1).



**Figure 3.** Cyclic voltammograms of complex **1** in dry and de-oxygenated  $\text{CH}_3\text{CN}$  solution: (a) Solid line: For complex **1** as shown in Scheme 1b; dotted line: for complex **1** in presence of a small amount of aqueous HCl (b) for the deprotonated form of complex **1**. The prominent reversible wave at 0.0 V vs.  $\text{Fc}^+/\text{Fc}$  (dashed vertical line) is due to ferrocene which was added in small quantities for internal voltage calibration. The potential sweep rate was 100 mV/s. 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) was used as an electrolyte.

## Electrochemistry

Figure 3a shows the cyclic voltammogram of complex **1** in dry and deoxygenated CH<sub>3</sub>CN measured in presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) electrolyte with a potential sweep rate of 100 mV/s. The reversible wave at 0.0 V vs. Fc<sup>+</sup>/Fc is due to ferrocene which was added in small quantities for internal voltage calibration. The irreversible wave with an estimated half-wave potential of 1.0 V vs. Fc<sup>+</sup>/Fc is assigned to the metal-based one-electron oxidation of complex **1**. This compares to a Ru(II)/Ru(III) potential of 0.76 V vs. Fc<sup>+</sup>/Fc for [Ru(2,2'-bipyridine)<sub>2</sub>(2-(2'-pyridyl)imidazole)]<sup>2+</sup> in CH<sub>3</sub>CN.<sup>32</sup> The shift to more positive potentials (+0.24 V) presumably reflects the stabilization of the metal-based HOMO by the electron-withdrawing 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ligand.<sup>34</sup> When adding excess sodium methoxide to the solution used for the voltammogram in Figure 3a one subsequently obtains the voltammogram shown in Figure 3b. Oxidation of Ru(II) to Ru(III) now occurs at 0.65 V vs. Fc<sup>+</sup>/Fc. Thus, there is a potential shift of nearly 350 mV upon deprotonation, and this is in line with prior investigations that had reported potential shifts on the order of 300 mV – 400 mV for redox processes in comparable systems.<sup>2, 6-8, 35</sup>

In ordinary CH<sub>3</sub>CN solution the ruthenium oxidation is irreversible (solid line in Figure 3a), but when adding a small amount of aqueous HCl it becomes reversible (dotted line in Figure 3a). This shows that in absence of acid the ruthenium oxidation process is coupled to deprotonation.

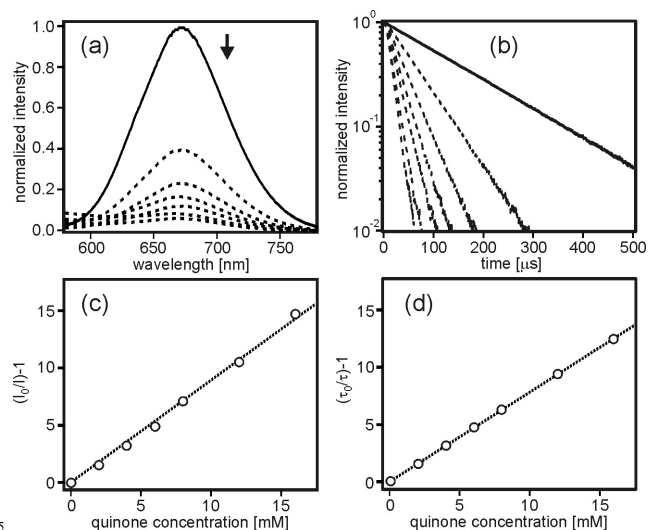
A voltammogram showing the result of a reductive potential sweep performed on a solution of complex **1** in CH<sub>3</sub>CN is given in the supporting information. One extracts reduction potentials of -1.38 V vs. Fc<sup>+</sup>/Fc and -1.63 V vs. Fc<sup>+</sup>/Fc for the two 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ligands (Table 1), in line with prior investigations.<sup>28</sup>

From the emission data in Figure 2a one extracts a value of 1.85 eV for the energy of the <sup>3</sup>MLCT excited state. Using the ground-state oxidation potential of 1.0 V vs. Fc<sup>+</sup>/Fc from above and the standard approximations,<sup>31</sup> one obtains an electrochemical potential of -0.85 V vs. Fc<sup>+</sup>/Fc as an approximative value for oxidation of complex **1** in its emissive excited state. Thus, complex **1** is a significantly less potent photoreductant than Ru(2,2'-bipyridine)<sub>3</sub><sup>2+</sup>.<sup>31, 36</sup> Nevertheless, given an electrochemical potential of -0.53 V vs. Fc<sup>+</sup>/Fc for benzoquinone in water,<sup>21, 37</sup> one estimates a reaction free energy for electron transfer ( $\Delta G_{ET}$ ) between photoexcited complex **1** and benzoquinone of -0.32 eV. Even though this estimate is accurate to  $\pm 0.1$  eV at best, it appears safe to state that oxidative excited-state quenching by benzoquinone is thermodynamically possible.

## Luminescence quenching by benzoquinone

The solid trace in Figure 4a is the emission spectrum obtained after exciting a de-oxygenated 10<sup>-5</sup> M CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) solution of complex **1** at 470 nm. The pH value of this solution was adjusted to 4 using aqueous HCl in order to ensure protonation of the complex (see Figure 2b). The solid trace in Figure 4b is the decay of the luminescence emitted at 670 nm by the same solution after excitation at 532 nm with laser pulses of ~8 ns width. When adding increasing amounts of 1,4-benzoquinone to

this solution, one obtains the luminescence spectra represented by the dashed lines in Figure 4a and the luminescence decays shown as dashed traces in Figure 4b. Without benzoquinone the luminescence lifetime ( $\tau$ ) is 160 ns, while in presence of 16 mM benzoquinone  $\tau$  has dropped to ~15 ns (Figure 4b). The luminescence intensity decreases simultaneously by a factor of ~15 (Figure 4a).



**Figure 4.** (a) Luminescence spectra of a ~10<sup>-5</sup> M solution of complex **1** in 1:1 (v:v) CH<sub>3</sub>CN/H<sub>2</sub>O acidified with aqueous HCl to a pH meter reading of 4; excitation occurred at 470 nm; solid trace: solution containing complex **1** only; dashed traces: solutions containing 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, 16 mM benzoquinone; the data is normalized arbitrarily to a value of 1.0 for the highest intensity. (b) Decays of the luminescence intensities at 670 nm of the solutions from (a) after excitation at 532 nm with laser pulses of ~8 ns width. (c) Stern-Volmer plot based on the luminescence intensity data from (a); the dashed line is the result of a linear regression fit (forced to an ordinate of 0) yielding the K<sub>SV</sub> value of 852±21 M<sup>-1</sup> in Table 2. (d) Stern-Volmer plot based on the luminescence lifetime data from (b); the dashed line is the result of a linear regression fit (forced to an ordinate of 0) yielding the K<sub>SV</sub> value of 788±2 M<sup>-1</sup> in Table 2.

The emission quenching by benzoquinone is analyzed quantitatively by the Stern Volmer plots in Figure 4c/d. Both sets of data, the luminescence intensity data in Figure 4c and the luminescence lifetime data in Figure 4d, yield nearly identical results from which we conclude that the emission quenching is dynamic. From linear regression fits to the experimental data we obtain Stern-Volmer constants of K<sub>SV</sub> = 852±21 M<sup>-1</sup> (from intensities) and K<sub>SV</sub> = 788±2 M<sup>-1</sup> (from lifetimes) (Table 2). Given the <sup>3</sup>MLCT lifetime of 160±16 ns for complex **1**, we calculate rate constants for bimolecular excited-state quenching of k<sub>Q</sub> = (5.6±0.6)·10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (from intensities; k<sub>Q</sub> = K<sub>SV</sub> /  $\tau$ ) and k<sub>Q</sub> = (5.0±0.5)·10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (from lifetimes) (Table 2). These values are near the diffusion-controlled limit and are close to that reported for <sup>3</sup>MLCT excited-state quenching of Ru(2,2'-bipyridine)<sub>3</sub><sup>2+</sup> by benzoquinone (6.32·10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> in DMF).<sup>38</sup>

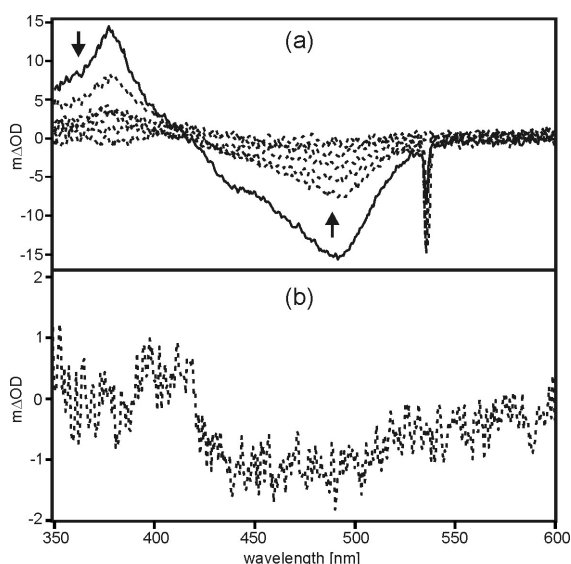
A strictly analogous series of experiments was performed using the same solvent mixture with heavy water (and DCl in D<sub>2</sub>O to acidify). Under these experimental conditions the peripheral N-atom of the pyridylimidazole ligand of complex **1** (present at 10<sup>-5</sup> M concentration) is deuterated and  $\tau$  = 242 ns in absence of benzoquinone (Table 1). The respective experimental

data and Stern-Volmer plots analogous to those in Figure 4 are given in the Supporting Information (Figure S2), the Stern-Volmer constants ( $K_{SV}$  values) and the rate constants for bimolecular excited-state quenching ( $k_Q$  values) from these experiments are reported in Table 2. We note that there is no significant H/D kinetic isotope effect (KIE); the ratio between  $k_Q$  values in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  and  $k_Q$  values in  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  (= KIE values in Table 2) is  $1.2 \pm 0.3$  (from intensities) and  $1.1 \pm 0.3$  (from lifetimes). This finding will be important for the discussion of reaction mechanisms below.

Table 2. Stern-Volmer constants ( $K_{SV}$ ), rate constants for bimolecular excited-state quenching ( $k_Q$ ), and H/D kinetic isotope effects (KIE) for the complex **1** / benzoquinone reaction couple as determined from the experimental data in Figures 4 / S1 and Table 1.

	hydrogenated		deuterated	
	intensity	lifetime	intensity	lifetime
$K_{SV} [\text{M}^{-1}]$	$852 \pm 21$	$788 \pm 2$	$1129 \pm 27$	$1124 \pm 28$
$k_Q [\text{M}^{-1}\text{s}^{-1}]^a$	$(5.6 \pm 0.6) \cdot 10^9$	$(5.0 \pm 0.5) \cdot 10^9$	$(4.7 \pm 0.5) \cdot 10^9$	$(4.7 \pm 0.5) \cdot 10^9$
KIE	$1.2 \pm 0.3$	$1.1 \pm 0.3$		

<sup>a</sup> The  $^3\text{MLCT}$  lifetime of complex **1** is 160 ns (Table 1) in the undeuterated form and 242 ns in the deuterated form. These lifetimes are accurate to  $\pm 10\%$ , and this determines to a large extent the error bars associated with the  $k_Q$  and KIE values.

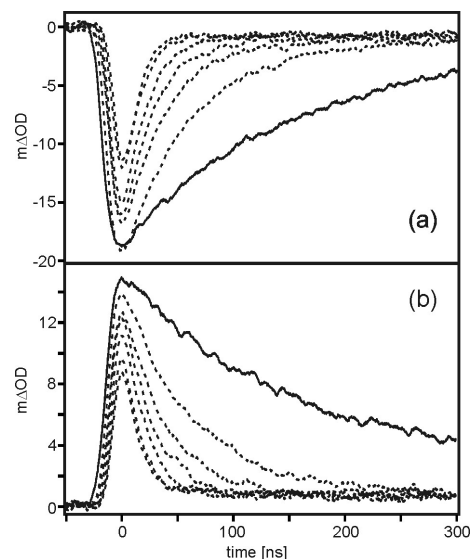


**Figure 5.** (a) Transient absorption spectra detected from a deoxygenated  $\sim 10^{-5}$  M solution of complex **1** in 1:1 (v:v)  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  acidified with aqueous DCl to a pH meter reading of 4. Excitation was at 532 nm with laser pulses of  $\sim 8$  ns width. Detection occurred in a time-averaged fashion over the first 200 ns after the excitation pulses. Solid trace: spectrum obtained in absence of benzoquinone; dashed traces: spectra obtained in presence of 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, 16 mM benzoquinone. (b) Spectrum measured from the solution containing 16 mM benzoquinone with a time delay of 10  $\mu\text{s}$  after excitation.

### Transient absorption spectroscopy

The solid line in Figure 5a is the transient absorption spectrum detected from a 1:1  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  solution of complex **1** after excitation at 532 nm; the excitation pulse width was  $\sim 8$  ns and the spectrum is time-averaged over a period of 200 ns starting immediately after the laser pulse. One observes the typical features of  $^3\text{MLCT}$ -excited ruthenium(II)  $\alpha$ -diimine complexes,<sup>39</sup>

namely an MLCT bleach between 420 nm and 535 nm, as well as an absorption peaking at 378 nm caused by the reduced  $\alpha$ -diimine ligands. As a consequence of  $^3\text{MLCT}$  excited-state quenching, the intensity of these two signals decreases rapidly with increasing benzoquinone concentration (dashed traces in Figure 5a). When monitoring the temporal evolution of the bleach at 490 nm and the absorbance at 380 nm in presence of different benzoquinone concentrations one obtains the transients shown in Figure 6a/b. Within experimental accuracy, the bleach recoveries at 490 nm (Figure 6a) and the transient absorption decays at 380 nm (Figure 6b) occur with time constants which are identical to the luminescence lifetimes extracted from Figure 4b. This observation confirms that one is principally monitoring  $^3\text{MLCT}$ -excited complex **1** in Figure 5a.



**Figure 6.** (a) Temporal evolution of the MLCT bleach at 490 nm in the transient absorption spectra from Figure 5a. (b) Temporal evolution of the transient absorption signal at 380 nm in the spectra from Figure 5a. Solid traces: Transients obtained in absence of benzoquinone; dashed traces: transients obtained from solutions containing 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, 16 mM of benzoquinone.

Turning our attention back to the transient absorption spectra in Figure 5a we note that at a benzoquinone concentration of 16 mM a weak positive signal near 410 nm is discernible, in addition to a nearly equally weak MLCT bleach at longer wavelengths. The same two spectral features can be detected 10  $\mu\text{s}$  later (Figure 5b); i. e., in an experiment in which complex **1** is photoexcited at  $t = 0$  but detection of the photoproducts only starts at  $t = 10 \mu\text{s}$ . The absorption band at 410 nm is reminiscent of the spectrum of neutral semiquinone radical, i. e., one-electron reduced and singly protonated benzoquinone,<sup>40</sup> while the remaining bleach is in line with oxidized ruthenium complex.<sup>41</sup> Whether or not the complex is oxidized and deprotonated (or only oxidized) is unclear from the spectrum in Figure 5b, mostly because of the weakness of the signal that we interpret as the MLCT bleach of a Ru(III) species. At any rate, the data in Figure 5 seems compatible with excited-state deactivation of complex **1** by benzoquinone through proton-coupled electron transfer (PCET), because there is spectral evidence for the semiquinone radical. However, the extinction coefficient of the bleach at 490 nm for the  $^3\text{MLCT}$ -excited form of the complex and for its one-

electron oxidized form is expected to be of similar magnitude.<sup>41</sup> The relative weakness of the remaining MLCT bleach in presence of 16 mM benzoquinone (Figure 5a/b) therefore suggests that the majority of the photochemistry occurs through a different reaction pathway. One obvious possibility is simple photoinduced electron transfer (without proton transfer) which is then followed by rapid thermal electron transfer in the reverse sense, thereby re-establishing the initial Ru(II) species and precluding the observation of an intense MLCT bleach

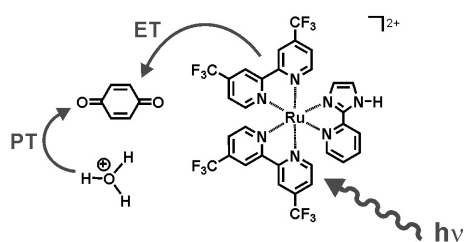
## Summary and conclusions

Even though photoexcited complex **1** has nearly 0.39 V less reducing power than photoexcited Ru(2,2'-bipyridine)<sub>3</sub><sup>2+</sup>, the principal photochemical reaction pathway for <sup>3</sup>MLCT-excited complex **1** seems to be simple electron transfer rather than PCET.

We had specifically chosen complex **1** with its 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ligand with the aim to increase the probability for observing PCET by making simple electron transfer thermodynamically more difficult; the abovementioned electron-withdrawing chelate ensures a relatively high oxidation potential. Despite this strategy, we principally observe simple ET as evidenced by the absence of a significant H/D kinetic isotope effect in excited-state deactivation and by our results from transient absorption spectroscopy. However, the latter technique also provides evidence for the photoproduction of semiquinone radical as a minor side product.

It appears plausible that the most important reason for observing chiefly simple photoinduced electron transfer in lieu of PCET is the fact that the former process is already exergonic by approximately 0.3 eV while proton-coupling only adds another ~0.2 eV of driving force. The semiquinone radical has a pK<sub>a</sub> value of 4.1 in aqueous solution,<sup>21</sup> while the pK<sub>a</sub> of oxidized complex is also around 4±1. Consequently, coupling proton transfer to the photoinduced electron transfer reaction does not provide significant additional driving-force to an overall PCET reaction. This problem could potentially be overcome by using more electron-rich benzoquinones, but so far our efforts in this direction have been plagued by solubility issues and by difficulties to observe meaningful transient absorption spectra.

On a final note we point out that complex **1** and benzoquinone need not necessarily be oriented in the hydrogen-bonded fashion depicted in Scheme 1b. Other non-hydrogen bonded encounter complexes are conceivable as well, especially in a protic solvent. Experiments in CH<sub>2</sub>Cl<sub>2</sub> have been performed in an attempt to address this issue, but the results have been inconclusive as far as the possibility of static excited-state quenching in pre-formed hydrogen-bonded ruthenium(II)-benzoquinone adducts is concerned.



**Scheme 2.** A possible alternative reaction pathway for PCET between complex **1** and benzoquinone.

An important issue in our experiments is that CH<sub>3</sub>CN/H<sub>2</sub>O solutions at pH 4 must be used in order to ensure that the pyridylimidazole ligand of complex **1** is protonated. However, at an H<sub>3</sub>O<sup>+</sup> concentration of 10<sup>-4</sup> M protonation of benzoquinone may occur directly from hydronium ions instead of from complex **1** (Scheme 2). Direct protonation of the benzoquinone unit by H<sub>2</sub>O (pK<sub>a</sub> = 15.7) appears unlikely for thermodynamic reasons.<sup>43-45</sup>

Much is yet to be learned about multi-site PCET reactions which involve photoexcited molecules, i. e., in terms of understanding PCET at a fundamental level the proposed mechanism in Scheme 2 is no less interesting and no less important than that from Scheme 1b.<sup>46,47</sup>

## Acknowledgments

Funding from the Deutsche Forschungsgemeinschaft (DFG) through IRTG-1422 and through grant number INST186/872-1 is gratefully acknowledged. The MWK Niedersachsen is acknowledged for co-funding the transient absorption spectrometer.

## References

- Georg-August-Universität Göttingen, Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany. Fax: +49 (0)551 33 73; Tel: +49 (0)551 39 19424; E-mail: oliver.wenger@chemie.uni-goettingen.de
- † Electronic Supplementary Information (ESI) available: Additional cyclic voltammogram, additional luminescence quenching data and transient absorption data, additional Stern-Volmer plots. See DOI: 10.1039/b000000x/
- M.-A. Haga, Synthesis and electrochemical properties of mononuclear and binuclear ruthenium complexes containing 2,2'-bibenzimidazole *Inorg. Chim. Acta*, 1980, **45**, L183.
- M.-A. Haga, Synthesis and protonation-deprotonation reactions of ruthenium(II) complexes containing 2,2'-bibenzimidazole and related ligands, *Inorg. Chim. Acta*, 1983, **75**, 29.
- M.-A. Haga and A. Tsunemitsu, The outer-sphere interactions in ruthenium and osmium complexes. 1. Spectrophotometric and voltammetric studies on the hydrogen-bonding interactions of bis(2,2'-bipyridine)(2-(2'-pyridyl)-benzimidazole)ruthenium(II) cation and its derivatives with aromatic nitrogen-heterocycles, *Inorg. Chim. Acta*, 1989, **164**, 137.
- A. M. Bond and M.-A. Haga, Spectrophotometric and voltammetric characterization of complexes of bis(2,2'-bipyridine)(2,2'-bibenzimidazole)ruthenium and bis(2,2'-bipyridine)(2,2'-bibenzimidazole)osmium in oxidation state II, state III, and state IV in acetonitrile-water mixtures, *Inorg. Chem.*, 1986, **25**, 4507.
- X. M. Xiao, M.-A. Haga, T. Matsumurainoue, Y. Ru, A. W. Addison and K. Kano, Synthesis and proton transfer-linked redox tuning of ruthenium(II) complexes with tridentate 2,6-bis(benzimidazol-2-yl)pyridine ligands, *J. Chem. Soc., Dalton Trans.*, 1993, 2477.
- M.-A. Haga, T. Ano, T. Ishizaki, K. Kano, K. Nozaki and T. Ohno, Synthesis and proton-coupled redox properties of mononuclear or asymmetric dinuclear complexes of ruthenium, rhodium, and/or osmium containing 2,2'-bis(2-pyridyl)-6,6'-bibenzimidazole, *J. Chem. Soc., Dalton Trans.*, 1994, 263.
- R. F. Carina, L. Verzeqnessi, G. Bernardinelli and A. F. Williams, Modulation of iron reduction potential by deprotonation at a remote site, *Chem. Commun.*, 1998, 2681.
- H. Jones, M. Newell, C. Metcalfe, S. E. Spey, H. Adams and J. A. Thomas, Deprotonation of a ruthenium (II) complex incorporating a bipyrazole ligand leading to optical and electrochemical switching, *Inorg. Chem. Commun.*, 2001, **4**, 475.

- 9 G. Stupka, L. Gremaud and A. F. Williams, Control of redox potential by deprotonation of coordinated 1H-imidazole in complexes of 2-(1H-imidazol-2-yl)pyridine, *Helv. Chim. Acta*, 2005, **88**, 487.
- 10 J. G. Vos, Excited-state acid-base properties of inorganic compounds, *Polyhedron*, 1992, **11**, 2285.
- 11 P. J. Giordano, C. R. Bock and M. S. Wrighton, Excited-state proton-transfer of ruthenium(II) complexes of 4,7-dihydroxy-1,10-phenanthroline - increased acidity in excited-state, *J. Am. Chem. Soc.*, 1978, **100**, 6960.
- 10 12 Y. Q. Deng, J. A. Roberts, S. M. Peng, C. K. Chang and D. G. Nocera, The amidinium-carboxylate salt bridge as a proton-coupled interface to electron transfer pathways, *Angew. Chem. Int. Ed.*, 1997, **36**, 2124.
- 13 W. D. Bare, N. H. Mack, J. N. Demas and B. A. DeGraff, pH-dependent photophysical behavior of rhenium complexes containing hydroxypyridine ligands, *Appl. Spectr.*, 2004, **58**, 1093.
- 15 14 S. Y. Reece and D. G. Nocera, Direct tyrosine oxidation using the MLCT excited states of rhenium polypyridyl complexes, *J. Am. Chem. Soc.*, 2005, **127**, 9448.
- 20 15 C. J. Gagliardi, B. C. Westlake, C. A. Kent, J. J. Paul, J. M. Papanikolas and T. J. Meyer, Integrating proton coupled electron transfer (PCET) and excited states, *Coord. Chem. Rev.*, 2010, **254**, 2459.
- 25 16 S. Klein, W. G. Dougherty, W. S. Kassel, T. J. Dudley and J. J. Paul, Structural, electronic, and acid/base properties of Ru(bpy) 2(bpy(OH)(2)) (2+) (bpy=2,2 '-Bipyridine, bpy(OH)(2)=4,4 '-Dihydroxy-2,2 '-bipyridine), *Inorg. Chem.*, 2011, **50**, 2754.
- 17 C. Bronner and O. S. Wenger, Kinetic isotope effects in reductive excited-state quenching of Ru(2,2'-bipyrazine)<sub>3</sub><sup>2+</sup> by phenols, *J. Phys. Chem. Lett.*, 2012, **3**, 70.
- 30 18 O. S. Wenger, Proton-Coupled Electron Transfer Originating from Excited States of Luminescent Transition-Metal Complexes, *Chem.-Eur. J.*, 2011, **17**, 11692.
- 19 A. Magnuson, M. Anderlund, O. Johansson, P. Lindblad, R. Lomoth, T. Polivka, S. Ott, K. Stensjö, S. Styring, V. Sundström and L. Hammarström, Biomimetic and Microbial Approaches to Solar Fuel Generation, *Acc. Chem. Res.*, 2009, **42**, 1899.
- 35 20 M. H. V. Huynh and T. J. Meyer, Proton-coupled electron transfer, *Chem. Rev.*, 2007, **107**, 5004.
- 40 21 J. J. Warren, T. A. Tronic and J. M. Mayer, Thermochemistry of Proton-Coupled Electron Transfer Reagents and its Implications, *Chem. Rev.*, 2010, **110**, 6961.
- 22 J. J. Concepcion, M. K. Brennaman, J. R. Deyton, N. V. Lebedeva, M. D. E. Forbes, J. M. Papanikolas and T. J. Meyer, Excited-state quenching by proton-coupled electron transfer, *J. Am. Chem. Soc.*, 2007, **129**, 6968.
- 45 23 N. V. Lebedeva, R. D. Schmidt, J. J. Concepcion, M. K. Brennaman, I. N. Stanton, M. J. Therien, T. J. Meyer and M. D. E. Forbes, Structural and pH dependence of excited state PCET reactions involving reductive quenching of the MLCT excited state of RuII(bpy)<sub>2</sub>(bpz)<sup>2+</sup> by hydroquinones, *J. Phys. Chem. A*, 2011, **115**, 3346.
- 50 24 D. J. Stewart, M. K. Brennaman, S. E. Bettis, L. Wang, R. A. Binstead, J. M. Papanikolas and T. J. Meyer, Competing pathways in the photo-proton-coupled electron transfer reduction of fac-Re(bpy)(CO)<sub>3</sub>(4,4'-bpy)<sup>+</sup> by hydroquinone, *J. Phys. Chem. Lett.*, 2011, **2**, 1844.
- 55 25 J. C. Freys, G. Bernardinelli and O. S. Wenger, Proton-coupled electron transfer from a luminescent excited state, *Chem. Commun.*, 2008, 4267.
- 60 26 J. C. Freys, D. Hanss, M. E. Walther and O. S. Wenger, Chemistry with photons, protons, and electrons, *Chimia*, 2009, **63**, 49.
- 27 J. L. Cape, M. K. Bowman and D. M. Kramer, Reaction intermediates of quinol oxidation in a photoactivatable system that mimics electron transfer in the cytochrome bc(1) complex, *J. Am. Chem. Soc.*, 2005, **127**, 4208.
- 65 28 M. Furue, K. Maruyama, T. Oguni, M. Naiki and M. Kamachi, Trifluoromethyl-substituted 2,2'-bipyridine ligands - synthetic control of excited-state properties of ruthenium(II) tris-chelate complexes, *Inorg. Chem.*, 1992, **31**, 3792.
- 29 P. A. Anderson, R. F. Anderson, M. Furue, P. C. Junk, F. R. Keene, B. T. Patterson and B. D. Yeomans, Protonation studies of reduced ruthenium(II) complexes with polypyridyl ligands, *Inorg. Chem.*, 2000, **39**, 2721.
- 75 30 M. E. Voss, C. M. Beer, S. A. Mitchell, P. A. Blomgren and P. E. Zhichkin, A simple and convenient one-pot method for the preparation of heteroaryl-2-imidazoles from nitriles, *Tetrahedron*, 2008, **64**, 645.
- 31 D. M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1994.
- 80 32 K. M. Lancaster, J. B. Gerken, A. C. Durrell, J. H. Palmer and H. B. Gray, Electronic structures, photophysical properties, and electrochemistry of ruthenium(II)(bpy)<sub>2</sub> pyridylimidazole complexes, *Coord. Chem. Rev.*, 2010, **254**, 1803.
- 85 33 J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, 1976, **12**, 131.
- 34 M. S. Lowry and S. Bernhard, Synthetically tailored excited states: Phosphorescent, cyclometalated iridium(III) complexes and their applications, *Chem. Eur. J.*, 2006, **12**, 7970.
- 90 35 G. Stupka, L. Gremaud, G. Bernardinelli and A. F. Williams, Redox state switching of transition metals by deprotonation of the tridentate ligand 2,6-bis(imidazol-2-yl)pyridine, *Dalton Trans.*, 2004, 407.
- 36 J. Hankache and O. S. Wenger, Photoinduced electron transfer in covalent ruthenium-anthraquinone dyads: relative importance of driving-force, solvent polarity, and donor-bridge energy gap, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2685.
- 95 37 V. V. Pavlishchuk and A. W. Addison, Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25 degrees C, *Inorg. Chim. Acta*, 2000, **298**, 97.
- 100 38 A. Vlcek and F. Bolletta, Oxidative quenching of \*Ru(bpy)<sub>3</sub><sup>2+</sup> by ortho-quinones and para-quinones in aprotic media, *Inorg. Chim. Acta*, 1983, **76**, L227.
- 39 A. Yoshimura, M. Z. Hoffman and H. Sun, An evaluation of the excited-state absorption-spectrum of Ru(bpy)<sub>3</sub><sup>2+</sup> in aqueous and acetonitrile solutions, *J. Photochem. Photobiol. A*, 1993, **70**, 29.
- 105 40 G. E. Adams and B. D. Michael, Pulse radiolysis of benzoquinone and hydroquinone, *Trans. Faraday Soc.*, 1971, **67**, 1171.
- 41 R. Lomoth, T. Haupl, O. Johansson and L. Hammarström, Redox-switchable direction of photoinduced electron transfer in an Ru(bpy)<sub>3</sub><sup>2+</sup> - Viologen dyad, *Chem.-Eur. J.*, 2002, **8**, 102.
- 110 42 L. M. Tolbert and K. M. Solntsev, Excited-state proton transfer: From constrained systems to "super" photoacids to superfast proton transfer, *Acc. Chem. Res.*, 2002, **35**, 19.
- 115 43 J. Hankache, O. S. Wenger, Large increase of the lifetime of a charge-separated state in a molecular triad induced by hydrogen-bonding solvent, *Chem. Eur. J.*, 2012, **18**, 6443.
- 44 J. Hankache, M. Niemi, H. Lemmetyinen and O. S. Wenger, Hydrogen-bonding effects on the formation and lifetimes of charge-separated states in molecular triads, *J. Phys. Chem. A*, 2012, **116**, 8159.
- 120 45 J. Hankache, D. Hanss and O. S. Wenger, Hydrogen-bond strengthening upon photoinduced electron transfer in ruthenium-anthraquinone dyads interacting with hexafluoroisopropanol or water, *J. Phys. Chem. A*, 2012, **116**, 3347.
- 125 46 M. Kuss-Petermann, H. Wolf, D. Stalke and O. S. Wenger, Influence of donor-acceptor distance variation on photoinduced electron and proton transfer in ruthenium(I)-phenol dyads, *J. Am. Chem. Soc.*, 2012, **134**, 12844.
- 130 47 C. Bronner and O. S. Wenger, Proton-coupled electron transfer between 4-cyanophenol and photoexcited rhenium(I) complexes with different protonatable sites, *Inorg. Chem.*, 2012, **51**, 8275.