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# Polyhedron



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# Photophysics of Ru(II) complexes with hydroxylated diimine ligands: Photoinduced electron/proton transfer to anthraquinone

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A R T I C L E I N F O	A B S T R A C T			
A R T I C L E I N F O Keywords: Excited state proton coupled electron transfer Ru(II) Diimine Complex Photophysics Photoinduced electron transfer	This manuscript reports the reaction of the <sup>3</sup> MLCT excited states of two luminescent chromophores, $[(bpy)_2Ru$ (OHbyy)] <sup>2+</sup> and $[(bpy)_2Ru(OMebpy)]^{2+}$ (bpy = 2,2'-bipyridine, OHbyy = 4-hydroxy-2,2'-bipyridine, OMebpy = 4-methoxy-2,2'-bipyridine), with anthraquinone (AQ). A series of luminescence, electrochemical, spectrophotometric and transient absorption studies were done in order to determine free energies for the potential reaction paths between the photoexcited complexes and AQ. For the OMebpy complex, only excited state electron transfer (ET*) from the <sup>3</sup> MLCT state of the complex to AQ was possible. However, for the OHbpy complex, the excited state could react with AQ via a variety of pathways including excited state electron transfer, ET*, excited state proton transfer (PT*) and excited state proton coupled electron transfer (PCET*). The thermodynamic analysis revealed that, for the OHbpy complex PT* was very endergonic and not a viable reaction pathway, however both ET* and PCET* could occur. Luminescence quenching studies revealed that both the OHbpy and the OMebpy excited complexes reacted with AQ (k <sub>q</sub> ~ 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup> for both). Transient absorption analysis showed that, for the OMebpy complex, no photoproducts escaped the encounter complex associated with the quenching reaction. The result is consistent with strong electrostatic association of PCET* products from the encounter complex. For the OHbpy complex, for the OHbpy complex, for the OHbpy complex the strate case association of PCET* products from the encounter complex.			

coupled electron transfer within an encounter complex.

# 1. Introduction:

It is a well-established idea that the redox behavior of species capable of coupled electron and proton transfer is unique relative to that of systems that only exchange electrons. For instance, oxidation of a system capable of subsequently losing a proton will result in a radical species that can more easily undergo a second oxidation relative to the protonated species. This is commonly observed in the Pourbaix diagrams (E<sup>0</sup> vs pH) of transition metal complexes with acidic functionalities [1,2]. The proton transfer coupled to the electron transfer occurs on time scales that are rapid relative to the electrochemical experiment and the processes cannot be disentangled experimentally. Detailed analysis of the activation parameters of electron transfer, proton transfer and the coupled electron/proton transfer are generally necessary to establish that the proton and electron transfer are indeed coupled in reactions between electron/proton donors and acceptors [3].

In considering the similar behavior of excited states of molecules, the

https://doi.org/10.1016/j.poly.2021.115376 Received 4 March 2021; Accepted 15 July 2021 Available online 21 July 2021 0277-5387/© 2021 Elsevier Ltd. All rights reserved. electron and proton transfer reactions must compete kinetically with the relaxation of the excited state to the ground state [4-7]. In fact, a variety of complex situations arise as illustrated in Fig. 1. The figure shows the ground-state (green) redox and acid-base reactions of a generic Ru(II) complex chromophore with an attached hydroxyl group along with the accompanying reactions of the photoexcited complex (orange). In the ground state, formation of the deprotonated and oxidized species can occur via sequential reactions or via the direct proton coupled electron transfer (diagonal in the ground-state square scheme). For Ru(II) diimine complex chromophores, the excited state is of triplet spin multiplicity and the ground state is a singlet; this influences the observed excited-state processes.. For instance, deprotonation of \*Ru(II)-OH likely only yields \*Ru(II)-O, also a triplet. Direct formation of the ground state species, Ru(II)-O, requires deprotonation and an accompanying spin change. It is likely that the required spin change will increase the activation barrier relative to proton transfer to the excited state. However, \*Ru(II)-OH can react with electron acceptors to yield

The result represents one of a small number of examples of excited states of chromophores reacting via proton

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**Fig. 1.** Diagram illustrating processes associated with ground and excited-state electron and proton transfer processes of a Ru(II)–OH chromophore.

both Ru(III)–OH, the excited-state electron transfer product (ET\*), or the deprotonated excited state electron transfer product (PCET\*), Ru(III)-O directly, where the triplet excited state evolves to a doublet product. If the electron/proton acceptor species is a singlet, the PCET\* will be spin allowed and does not involve spin pairing considerations as a part of the reaction.

Given the array of possibilities for reaction of a photoexcited electron/proton donor with a proton/electron acceptor (A), is it possible to experimentally distinguish the various pathways? An interesting advantage of investigating systems of this sort is that the use of pulsed-laser excitation to create the reactive species allows the direct observation of the photoproducts that emerge from the interaction of the excited species with the electron/proton acceptor (eq. (1)). Time resolved UV/vis or IR measurements, under particular conditions, can selectively detect the species that escape the encounter complex, {[Ru (II)OH]<sup>2+\*</sup>, A}. As long as the emerging products are spectrophotometrically distinct, determination of the outcome of the reaction in the short-lived (~ns) encounter complex becomes straightforward.

transfer within the encounter complex followed by intermolecular proton transfer in solution. In this particular system the free energies for ET\* and PT\*\* were endergonic, while the overall PCET\* reaction was exergonic. However, activated electron transfer was still observed to be kinetically favored over PCET\*. We have recently observed that the PCET\* reaction can be observed in related systems in which the chromophore has been modified to make the ET\* process more endergonic and the PT\*\* reaction slightly less endergonic [13].

Evaluation of systems that can exhibit ET\*, PT\*\* and PCET\* requires the determination of redox and acid/base constants for each of the potentially reactive species in both the ground state and, where necessary, excited state. In addition, any potential system must be unreactive when the chromophore and acceptor are mixed in the ground state.

In this work we present evidence for direct PCET\* between a Ru(II) hydroxy bipyridine complex and anthraquinone. Photoreaction of the chromophores  $[(bpy)_2Ru(OHbpy)]^{2+}$  (OHbpy = 4-hydroxy-2,2'-bipyridine) and the corresponding 4-methoxy-2,2'-bipyridine complex,  $[(bpy)_2Ru(OMebpy)]^{2+}$ , with anthraquinone (AQ) illustrates the uniqueness of the ET\* and PCET\* photoproducts and the benefit of coupled electron/proton transfer to the formation of photoproducts that escape the encounter complex in this particular system.

# 2. Materials and methods

#### 2.1. Materials

9,10-anthraquinone was purchased from TCI Chemicals and purified as previously reported [14]. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was obtained from Alfa Aesar and was recrystallized from ethanol and dried *in vacuo*. Tetrabutylammonium hydroxide (TBAOH) was purchased from Alfa Aesar as a 40% solution in CH<sub>3</sub>OH and was used without further purification. 1,8-Diazabicyclo [5.4.0]-7-undecene (DBU) was purchased from TCI and used without further purification.

# 2.2. Synthesis 4-methoxy-2,2'-bipyridine (OMebpy)

15 mL of THF was added to a 100 mL round bottom flask containing 715 mg 2-pyridineboronic acid *N*-phenyl-diethanolamine ester (1.7 mmol), 76 mg copper(I) iodide (0.4 mmol), 275 mg anhydrous potas-

$$[Ru(II)OH]^{2+*} + A \longleftrightarrow \{[Ru(II)OH]^{2+*}, A\} \qquad \qquad PT^* \qquad [Ru(II)O^{-}]^{+*} + HA^{+} \\ PT^{**} \qquad [Ru(II)O^{-}]^{+*} + HA^{+} \\ PCET^* \qquad [Ru(III)O^{-}]^{2+} + HA \\ Encounter complex \qquad \qquad ET^* \qquad [Ru(III)OH]^{3+} + A^{-} \end{cases}$$
(1)

Of course, finding systems that actually exhibit clearly distinguishable differences in spectra between the reactants and each of the different reaction outcomes— proton transfer (PT\* or PT\*\*), protoncoupled electron transfer (PCET\*), and electron transfer (ET\*)—is a matter of a mix of experience and luck. Indeed, there are a group of systems that have been examined that serve as examples [8-11]. We also have contributed to this area, investigating the photophysical behavior of  $[(bpy)_2Ru(4,4'-dhbpy)]^{2+}$  (4,4'-dhbpy = 4,4'-dihydroxy-2,2'-bipyridine) in the presence of the *N*-methyl-4,4'-bipyridinium ion in nonaqueous solution [12]. The work illustrated the versatility of transient absorption spectroscopy in the direct observation of electron sium carbonate (2.0 mmol), and 115 mg tetrakis(triphenylphosphine) palladium(0) (10 mol%). To the flask, 190 mg 2-bromo-4-methoxypyridine (1.01 mmol) and 0.04 mL of deionized water was added to the solution and refluxed overnight under argon. The solution was cooled to room temperature and quenched by 40 mL of a saturated aqueous EDTA solution. The THF was removed under reduced pressure. The product was extracted with 50 mL x 3 DCM and dried over sodium sulfate. The DCM was removed under reduced pressure. The crude product was isolated by a silica column with a gradient mobile phase of 100 mL 10% ethyl acetate/ 5% triethylamine in hexanes which was then switched to 400 mL 30% ethyl acetate/ 5% triethylamine in hexanes. The collected fractions were monitored by TLC with a mobile phase 30% ethyl acetate/ 5% triethylamine in hexanes. The solvent system was removed

under vacuum, affording a light pink solid. Yield: 0.0911 g (0.49 mmol), 49%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 8.67 (d, 1H, J = 3.9)  $\delta$ 8.49 (q, 1H, J = 6.0)  $\delta$ 8.40 (d, 1H, J = 7.5)  $\delta$ 7.98 (d, 1H, J = 2.7)  $\delta$ 7.81 (td, 1H, J = 7.8, 1.8)  $\delta$ 7.31 (dd, 1H, J = 7.8, 6.6)  $\delta$ 6.85 (dd, 1H, J = 5.1, 2.4)  $\delta$ 3.96 (t, 3H, J = 5.4).

#### 2.3. Synthesis 4-hydroxy-2,2'-bipyridine (OHbpy)

1.0 mL of 48% aqueous HBr solution was added to a 100 mL round bottom flask containing 176 mg 4-methoxy-2,2'-bipyridine (0.95 mmol) in 25 mL glacial acetic acid. The solution was refluxed overnight open to the atmosphere. The solution was cooled to room temperature and the product was collected by vacuum filtration to afford a white solid. Yield: 0.317 g (0.95 mmol), 100%.

# 2.4. Synthesis of [(bpy)2Ru(4-hydroxy-2,2'-bipyridine)](PF\_6)\_2 , $[(bpy)_2Ru(OHbpy)]^{2+}$

Ru(bpy)<sub>2</sub>Cl<sub>2</sub> was synthesized as previously reported [15]. A round bottom flask containing 30 mL 1:1 EtOH:H<sub>2</sub>O was degassed for 30 min by bubbling argon through it. To the flask, 0.3142 g Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (0.649 mmol) and 0.174 g OHbpy·2Br<sup>-</sup> (0.6451 mmol) were added to the solution and refluxed overnight under argon. The solution was cooled to room temperature, followed by filtration to remove any insoluble, unreacted ligand. Two drops of HCl were added to ensure protonation of the complex, followed by the addition of a saturated 10 mL solution of NH<sub>4</sub>PF<sub>6</sub> in water, affording a red–orange precipitate. The solid was collected and rinsed with water. Yield: 0.245 g (0.279 mmol), 43.2%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ 8.50 (d, 5H, J = 7.8)  $\delta$ 8.42 (d, 1H, J = 8.1)  $\delta$ 8.06 (dd, 5H, J = 14.1, 8.4)  $\delta$ 7.92 (d, 1H, J = 3.0)  $\delta$ 7.80 (dd, 2H, J = 13.5, 5.4)  $\delta$ 7.74 (t, 3H, J = 5.1)  $\delta$ 7.453–7.36 (m, 5H)  $\delta$ 6.89 (dd, 1H, J = 6.3, 2.4). Anal. Calc. for RuC<sub>30</sub>N<sub>6</sub>OH<sub>24</sub>P<sub>2</sub>F<sub>12</sub>: C, 41.15; N, 9.60; H, 2.76%. Found: C, 40.64; N, 9.44; H, 2.88%.

# 2.5. Synthesis of $[(bpy)_2Ru(4-methoxy-2,2'-bipyridine)](PF_6)_2$ $[(bpy)_2Ru(OMebpy)]^{2+}$

A round bottom flask containing 30 mL ethylene glycol was degassed for 30 min by bubbling argon through it. To the flask, 0.485 g (1.00 mmol) Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, and 0.192 g (1.03 mmol) OMebpy were added and the solution was refluxed for 3 h under argon. The solution was cooled to room temperature, followed by filtration to remove insoluble, unreacted ligand. The solution was diluted to 180 mL with water and the product was precipitated with the addition of a saturated 10 mL solution of NH<sub>4</sub>PF<sub>6</sub> in water, affording the product as a bright orange precipitate. The solid was collected and rinsed with water. Yield: 0.647 g (0.727 mmol), 72%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN)  $\delta$ 8.54–8.49 (m, 5H)  $\delta$ 8.10–8.02 (m, 6H)  $\delta$ 7.78 (t, 2H, J = 3.9)  $\delta$ 7.74 (d, 3H, J = 5.7).  $\delta$ 7.47 (d, 1H, J = 6.3)  $\delta$ 7.44 (q, 2H, J = 1.2)  $\delta$ 7.39 (t, 3H, J = 6.6)  $\delta$ 6.98 (dd, 1H, J = 6.3, 2.4)  $\delta$ 4.01 (s, 3H). Anal. Calc. for RuC<sub>31</sub>N<sub>6</sub>OH<sub>26</sub>P<sub>2</sub>F<sub>12</sub>: C, 41.86; N, 9.45; H, 2.95%. Found: C, 42.15; N, 9.52; H, 3.02%.

# 2.6. Electrochemical measurements

Cyclic voltammetry, differential pulse voltammetry and spectroelectrochemical measurements were carried out using a CH Instruments 630 E Electrochemical Analyzer. Acetonitrile was dried over CaH<sub>2</sub> and distilled before use and TBAPF<sub>6</sub> was used as supporting electrolyte. Cyclic voltammetric measurements were done using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl psuedoreference electrode with an internal ferrocene standard. Spectroelectrochemical measurements were carried out using an Ocean Optics HR2000 spectrophotometer along with a Pine Research Instruments platinum honey-comb working electrode and a platinum wire counter electrode.

## 2.7. Nanosecond transient absorption spectroscopy

Nanosecond transient absorption measurements were done on an Applied Photophysics LKS 60 Laser Flash Photolysis system with laser excitation from a Quantel Brilliant B Q-switched laser with second and third harmonic attachments and an OPO (OPOTEK) for visible light generation, and data recorded using an Agilent Infinium digitizer. Laser excitation of the sample was typically done at 450 nm, unless otherwise stated.

#### 2.8. Steady-State emission spectroscopy

Steady-state emission measurements were done on a PTI Quantamaster spectrophotometer fit with a Hammamatsu R928 PMT detector system. Sample excitation was done at 450 nm and the emission spectra were observed from 500 to 800 nm.

# 2.9. UV-Visible absorption spectroscopy

UV–Visible absorption spectra were recorded on either a Hewlett-Packard 8452A diode array system or Ocean Optics HR2000 + spectrophotometer.

# 3. Results:

#### 3.1. Synthesis of ligands and complexes.

The ligands OHbpy and OMebpy were prepared by previously published literature methods [12]. The complexes  $[(bpy)_2Ru(OHbpy)]^{2+}$ and  $[(bpy)_2Ru(OMebpy)]^{2+}$  were prepared from  $[(bpy)_2RuCl_2]$  and the monosubstituted bipyridine ligands were prepared as stated in the Materials and Methods section. The complexes were purified by column chromatography, paying particular attention to removal of traces of  $[(bpy)_3Ru]^{2+}$ . The complexes were characterized by a variety of methods including <sup>1</sup>H NMR spectroscopy, ESI mass spectroscopy, as well as electroanalytical, UV–vis and luminescence methods.

#### 3.2. Absorption spectra and titration of the OHbpy complex.

The UV–vis absorption spectra of  $[(bpy)_2Ru(OHbpy)]^{2+}$  and  $[(bpy)_2Ru(OMebpy)]^{2+}$  in acetonitrile resemble $[(bpy)_3Ru]^{2+}$ . Thus, the spectra have a bpy localized  $\pi \to \pi^*$  transition around 290 nm and two close lying  $d\pi \to \pi^*$  metal-to-ligand charge transfer transitions near 450 nm (Table 1). Fig. 2a shows absorption spectra of  $[(bpy)_2Ru(OHbpy)]^{2+}$  in CH<sub>3</sub>CN as well as the complex in the presence of an 10x molar excess of TBAOH, yielding the spectrum of the deprotonated complex  $[(bpy)_2Ru(Obpy)]^{+}$ . Fig. 2b shows the spectrum of  $[(bpy)_2Ru(Obpy)]^{2+}$  in CH<sub>3</sub>CN. Maxima for the complexes are given in Table I; the maxima illustrate that the hydroxy and methoxy complexes have very similar spectra.

Table 1

Redox and photophysical properties of  $[(bpy)_2RuL]^{2+}$  (L = OHbpy, O<sup>-</sup>bpy and OMebpy) in CH<sub>3</sub>CN.

Complex [(bpy) <sub>2</sub> RuL] <sup>2+</sup>	$\begin{array}{l} \text{MLCT} \\ \lambda_{max} \ , \\ \text{CH}_3\text{CN}, \\ \text{nm} \end{array}$	λ <sub>max</sub> <sup>em</sup> , RT CH <sub>3</sub> CN, nm	λ <sub>max</sub> <sup>em</sup> , 77 K 1:1 MeOH: EtOH, nm	E <sub>em</sub> , RT CH <sub>3</sub> CN, eV	E <sup>0</sup> (Ru (III/ II)) V vs. Fc <sup>+</sup> / Fc	E <sup>0</sup> (Ru (III/ II*)) V vs. Fc <sup>+</sup> /Fc
OH-bpy O⁻-bpy OMebpy	458 472 460	624 - 620	590 617 -	$1.99 \\ \sim 1.92^{*} \\ 2.0$	0.82 0.55 0.83	$-1.17 \\ \sim -1.4 \\ -1.17$

\*estimated from correlation of 77 K and 298 K emission maxima for a series of complexes.



**Fig. 2.** (a) UV–vis absorption spectrum of  $[(bpy)_2Ru(OHbpy)]^{2+}$  in CH<sub>3</sub>CN (black) and in the presence of an excess of tetra-*n*-butylammonium hydroxide. (red) (b) the UV–vis absorption spectrum of  $[(bpy)_2Ru(OMebpy)]^{2+}$  in CH<sub>3</sub>CN.

Titration of  $[(bpy)_2Ru(OHbpy)]^{2+}$  with the base triethylamine (TEA) in CH<sub>3</sub>CN allowed for the determination of the  $pK_a$  of the hydroxy bipyridine; spectra are shown in the supplementary material. Given the  $pK_a$  of TEA in CH<sub>3</sub>CN and the spectral data, the  $pK_a$  of the hydroxy bipyridine coordinated to Ru was found to be 19.1, indicating that the ground state of the complex is a very weak acid relative to most protonated pyridines in acetonitrile.

# 3.3. Electrochemistry and spectroelectrochemistry.

Redox potentials for the one-electron oxidation of  $[(bpy)_2Ru$   $(OHbpy)]^{2+}$ , its deprotonated form and the OMebpy complex in CH<sub>3</sub>CN solution were determined by cyclic voltammetry. The potential for the deprotonated complex was obtained by DPV following addition of DBU to solutions of the complex in CH<sub>3</sub>CN. DBU was used because it is basic enough to react with the hydroxy complex (K<sub>eq</sub> > 10<sup>4</sup>)[16], but also has a positive enough DBU<sup>+</sup>/DBU potential that it will not undergo oxidation competitively with the hydroxy complex. Fig. 3 shows the anodic voltammetry of the OHbpy complex in CH<sub>3</sub>CN, illustrating the fully reversible oxidation of the complex with no indication that the complex undergoes deprotonation following oxidation. The DPV analysis in the presence of DBU (Fig. 3b) shows that the Ru(III/II) potential maximum

goes from 0.82 V vs. Fc<sup>+</sup>/Fc to 0.55 V following addition of over 100 equivalents of DBU to the solution. Rather than observing a steady shift in the Ru(III/II) potential, the results illustrate two separate oxidation waves when sub-stoichiometric quantities of DBU are added. A cyclic voltammogram of  $[(bpy)_2Ru(OMebpy)]^{2+}$  in CH<sub>3</sub>CN is presented in the supplementary material. Addition of DBU results in no change to the Ru (III/II) potential.

In order to spectroscopically evaluate the products of photoreactions between the photoexcited complexes and AQ, the absorption spectra of  $[(bpy)_2Ru(OHbpy)]^{3+}$  and  $[(bpy)_2Ru(Obpy)]^{2+}$  are required. For  $[(bpy)_2Ru(OHbpy)]^{3+}$  this was accomplished through spectroelectrochemistry (Fig. S5). The oxidized species had a prominent absorption maximum at 340 nm and a much weaker, broad absorption with a maximum near 500 nm. Generation of the oxidized and deprotonated complex,  $[(bpy)_2Ru(Obpy)]^{2+}$ , required a different approach. The complex can be photochemically oxidized by one electron by irradiation with visible light in the presence of the oxidative quencher, 4-bromobenzenediazonium BF<sub>4</sub>, in the presence of a tenfold excess of pyridine (Fig. S6). The spectral changes observed included a new maximum at 340 nm and broad, featureless absorption throughout the visible out to 650 nm.

Although the voltammetry of AQ in CH<sub>3</sub>CN has been reported earlier,



Fig. 3. (a) Cyclic voltammetry of  $[(bpy)_2Ru(OHbpy)]^{2+}$  in CH<sub>3</sub>CN / 0.1 M TBAPF<sub>6</sub> obtained at 0.1 V/s and (b) DPV of  $[(bpy)_2Ru(OHbpy)]^{2+}$  in the presence of 0 – 11 mM DBU. Potentials vs. Fc<sup>+</sup>/Fc.



Fig. 4. Cyclic voltammetry of 3 mM AQ in CH<sub>3</sub>CN / 0.1 M TBAPF<sub>6</sub> obtained at 0.1 V/s in the presence of (a) 0 M and (b) 15 mM triflic acid). Potentials vs. Fc<sup>+</sup>/Fc.

the measurements were repeated for internal consistency [17]. Fig. 4 shows CV data for reduction of AQ in CH<sub>3</sub>CN and reduction in CH<sub>3</sub>CN containing triflic acid (HOTf). Two reversible reductions are observed in the absence of added HOTf, resulting in formation of the 9,10-dihydroxvanthracene dianion  $(E^{0}_{AO}(0/-) = -1.32 \text{ V vs. Fc}^{+}/\text{Fc})$ . In the presence HOTf, a strong acid in CH<sub>3</sub>CN, the voltammetry is considerably more complex. The first reduction is observed at much more positive potentials  $(E^{0}_{HAO+}(+/0) = -0.22 \text{ V vs Fc}^{+}/\text{Fc})$  and appears to be followed by a second reduction. An oxidation wave is observed as well, but with a large  $\Delta E_{p}$ ; this type of behavior is observed for quinone reduction in protic solvents and is the result of sequential reduction and protonation (or reduction, protonation and disproportionation) to yield the dihydroxyanthracene. According to literature reports, the reduction is likely a proton-coupled electron transfer at the electrode as there is no direct evidence to suggest protonation precedes reduction [17]. This is important, as it makes determination of the one-electron reduction potential of the protonated quinone nontrivial.

The absorption spectra of AQ<sup>-</sup> and HAQ<sup> $\bullet$ </sup> in CH<sub>3</sub>CN are also needed to generate the anticipated spectra for the ET<sup>\*</sup> and the PCET<sup>\*</sup> reactions, respectively (eq. (1)). The AQ<sup>-</sup> spectrum was obtained by spectroelectrochemistry of AQ in CH<sub>3</sub>CN (Fig. S7). The HAQ species readily disproportionates and the spectrum must be obtained by generating the transient species via pulsed laser excitation. The AQ triplet excited state reacts with 2-propanol via a H atom transfer process to yield the semiquinone radical (*vide infra*) [18]. 3.4. Luminescence, excited state energies and AQ Quenching of the Ru complexes

Room temperature emission spectra of of  $[(bpy)_2Ru(OHbpy)]^{2+}$  and of  $[(bpy)_2Ru(OMebpy)]^{2+}$  in CH<sub>3</sub>CN solutions are shown in Fig. 5. For  $[(bpy)_2Ru(OHbpy)]^{2+}$  no luminescence is observed upon the addition of a small molar excess of tetrabutylammonium hydroxide. The spectrum of  $[(bpy)_2Ru(O'bpy)]^+$  was obtained at 77 K in 1:1 methanol: ethanol. Correlation of the 77 K emission maxima with room temperature maxima for a series of hydroxy bipyridine Ru(II) complexes allowed estimation of the room temperature excited-state energy of the nonluminescent deprotonated complex (supplementary material). The spectra were used to determine energies for the reactive MLCT (\*Ru(II)– OH and \*Ru(II)-O') species. The emission maxima were used for the approximate excited-state energies; thus, these energies are slightly lower than the  $E_{00}$  energies that might be obtained from a Franck-Condon fit of 77 K luminescence spectra.

The excited-state singlet and triplet energies of AQ are well established and were obtained from literature sources [19]. Most important to the discussion below is the triplet energy of AQ ( ${}^{3}$ AQ), which, at 2.7 eV, is well above the energies of the triplet states of the two complexes used here as electron and/or proton donors.

Luminescence lifetime quenching of  $[(bpy)_2Ru(Xbpy)]^{2+}$  (X = OH or OCH<sub>3</sub>) by AQ in N<sub>2</sub> degassed room temperature CH<sub>3</sub>CN solution was examined and the Stern-Volmer quenching kinetic plots are shown in Figures S9 and S10. While the solubility limit of AQ in CH<sub>3</sub>CN is less than 5 mM, at least 70% of the luminescence of each complex was quenched



Fig. 5. (a) Luminescence spectra of  $[(bpy)_2Ru(4-OHbpy)]^{2+}$  in CH<sub>3</sub>CN at room temperature. (b) Room temperature luminescence of  $[(bpy)_2Ru(4-OHbpy)]^{2+}$  in CH<sub>3</sub>CN. Excitation wavelength : 450 nm.



Fig. 6. TA of AQ in presence of i-prOH : spectrum of the HAQ radical.

and quenching rate constants obtained were near  $10^9$  M<sup>-1</sup>s<sup>-1</sup>. Rate constants obtained were for either ET\*, PT\*\* or PCET\* reaction of the excited state with AQ.

#### 3.5. Transient Absorption Spectroscopy

Nanosecond time-resolved absorption spectroscopy was used for the determination of excited-state lifetimes and also in the evaluation of radical ion products produced in bimolecular reactions of the excited states of complexes.

HAQ<sup>•</sup> was generated by 355 nm excitation of AQ in CH<sub>3</sub>CN/2propanol (0.1 M). The photoreaction involves H atom transfer from 2propanol to the <sup>3</sup>AQ to yield HAQ and the acetone ketyl radical (Fig. 6). The spectral features observed for the semiquinone radical are consistent with what has been reported in previously published work [18].

Both  $[(bpy)_2Ru(OHbpy)]^{2+}$  and  $[(bpy)_2Ru(OMebpy)]^{2+}$  have excited-state absorption features that are closely related to that of  $[(bpy)_3Ru]^{2+}$ . Along with bleaching of the MLCT absorption in the 400 to 500 nm region, a strong excited state absorption is observed between 350 and 400 nm. This absorption has been attributed to a  $\pi_1^* \rightarrow \pi_2^*$  transition of the bpy<sup>-</sup> like component of the <sup>3</sup>MLCT excited state. The spectra for the two complexes reported here are shown in Fig. 7a and 8a. Both complexes exhibit relatively strong luminescence in the absence of quenching species, but subtraction of luminescence from TA spectra is assumed to yield viable spectra in the red.

The spectra resulting from AQ bimolecular quenching of the <sup>3</sup>MLCT state of each Ru complex in pure CH<sub>3</sub>CN are shown in Figures S11 and S12. In each case very low yields of charge separated ions were observed for both complexes. Earlier reports of photoinduced electron transfer involving electron donors and anthraquinones in nonaqueous solvents were observed to have higher charge separation yields in the presence of added electrolytes [20]. When transient spectra were obtained for each of the Ru(II) complexes with AQ in N2 degassed CH3CN in the presence of TBAPF<sub>6</sub>, the resulting spectra are shown in Fig. 7b and 8b. In each case the AQ concentration, 2.6 mM, was close to the saturation concentration and resulted in quenching of between 65 and 75% of the excited chromophores. The magnitude of the transient signals at longer times were small for both complexes, indicating that only a small fraction of the radical ion species created escape the encounter complex. If the excited-state reaction is ET\*, the encounter complex would consist of a 3+/1- radical ion pair, while PCET\* would yield a 2+/0 pair. Despite the low yield of radical ions, the spectral features are clearly defined for the species escaping the encounter complex. The recombination of the ions to return to starting materials, typically on the scale of hundreds of microseconds, is not shown and was not evaluated. However, no net products were formed upon prolonged photolysis of the reactants.

#### 4. Discussion:

Before discussing the results of the excited-state reaction between the Ru(II) chromophores and AQ, it is important to clearly define the thermodynamics of electron transfer and proton transfer reactions in the ground state. Starting with [(bpy)<sub>2</sub>Ru(OHbpy)]<sup>2+</sup> (Ru(II)OH) species and AQ, formation of the oxidized and deprotonated complex and the reduced and protonated AQ (the semiquinone radical) can occur via electron transfer followed by proton transfer or the converse, as shown in Scheme 1. The redox potentials for the Ru complex oxidation and the AQ reduction in CH<sub>3</sub>CN are well established and have small margins of error, thus  $\Delta G_{ET}$  is accurate. However, the associated  $\Delta G_{PT}$ , are much more difficult to determine. Alternatively, the  $pK_a$  of the Ru(II)OH can be determined accurately (see Fig. S4), but the  $pK_a$  of HAQ<sup>+</sup> is not known in CH<sub>3</sub>CN, but can be estimated to be lower than 2 (more likely



Fig. 7. TA spectra of [(bpy)<sub>2</sub>Ru(OHbpy)]<sup>2+</sup> in CH<sub>3</sub>CN solution at room temperature in the presence of (a) 0 M and (b) 2.6 mM AQ and 20 mM TBAPF<sub>6</sub>.



Fig. 8. TA spectra of [(bpy)<sub>2</sub>Ru(OMebpy)]<sup>2+</sup> in CH<sub>3</sub>CN at room temperature in the presence of (a) 0 and (b) 2.6 mM AQ and 20 mM TBAPF<sub>6</sub>.

Scheme 1. Ground state reactions of Ru(II)-OH and AQ.

less than 0); this estimate was made using a reported bond dissociation energy for the semiquinone radical obtained computationally [21]. Using this value and the measured redox potential for the semiquinone, the  $pK_a$  of  $HAQ^+$  can be calculated from a thermodynamic cycle. The bond dissociation energy was converted to a bond dissociation free energy by incorporating a free energy term specific to acetonitrile solvent for H-atom transfer processes [17]. Thus, an estimate of the proton transfer equilibrium between Ru(II)OH and AQ can be made, yielding  $\Delta \dot{G}_{PT}$ . It is also possible to obtain an estimate of the potential for oxidation of  $Ru(II)O^{-}$ ,  $E^{0}_{RuO-}(III/II)$ , and the reduction potential for  $AQH^+$ ,  $E^0_{AOH}(+/0)$ , as shown by the DPV of Ru(II)OH in various concentrations of the base DBU (Fig. 3) and the CV of AQ in the presence of triflic acid (Fig. 4). With this information  $\Delta \dot{G_{ET}}$  (-nF( $E^0_{AQH}(+/0)$  - $E^0_{RuO}(III/II)))$  and  $\Delta \dot{G_{PT}}$  (2.3RT(pK\_{Ru(II)OH} – pK\_{HAQ+}) can be determined and the overall free energy for the ground-state ET/PT process  $(\Delta G_{PT} + \Delta G_{ET})$  can be estimated to be + 27 kcal/mol, and is therefore very endergonic. Thus, there is no concern about ground state proton transfer or electron transfer occurring to any extent upon mixing Ru(II)-OH and AQ in any ratio.

The free energies for excited-state electron transfer and proton transfer differ markedly since the excited-state energy is approximately 2 eV above the ground state. Scheme 2 shows the reactions associated



Scheme 2. Reactions of Ru(II)-OH\* (photoexcited) and AQ in CH<sub>3</sub>CN.

with excited-state electron and proton transfer. Of particular note is the fact that excited-state proton transfer can result in either the ground state (eq (1), PT\*) or the excited state (eq.1, PT\*\*) of the deprotonated complex. Determination of the free energy of the PT\*/ET reaction can be approached by determining  $\Delta G^*_{PT}$  and  $\Delta G^*_{ET}$ . An good estimate of  $\Delta G^*_{PT}$  can be obtained using the approximate pK<sub>a</sub> for HAQ<sup>+</sup> discussed above and the pK<sub>a</sub> for \*Ru(II)–OH. The excited-state acid dissociation constant is a function of the ground-state pK<sub>a</sub> for Ru(II)–OH and the maximum emission energies for the protonated and deprotonated complexes (eq. (2)). Since the deprotonated

$$pK_{a}^{*} = pK_{a} - \frac{(E_{em}(Ru(II) - OH) - E_{em}(Ru(II) - O^{-})))}{2.303RT}$$
(2)

complex is nonluminescent at room temperature, an estimate of the room temperature emission energy was obtained from extrapolation from 77 K emission data (supplementary material). The pK<sub>a</sub>\* was found to be 18.4, using a Förster thermodynamic cycle for excited-state  $pK_a$ determination (eq. (2)), indicating that the MLCT state of  $[(bpy)_2Ru$ (OHbpy)<sup>2+</sup> is slightly more acidic than the ground state; this suggests the MLCT state is largely  $Ru(d\pi) \rightarrow bpy(\pi^*)$  in character. Combining this with the pK<sub>a</sub> of HAQ<sup>+</sup> (above), the  $\Delta G^{*'}_{PT}$  value is + 24.7 kcal/mol. Thus, excited-state proton transfer to form HAQ<sup>+</sup> and the excited state of the deprotonated complex,  $[(bpy)_2Ru(O^{*}bpy)]^{2+*}$  is very endergonic. The excited state of [(bpy)<sub>2</sub>Ru(Obpy)]<sup>2+</sup> is 44 kcal/mol above the ground state and thus proton transfer to yield the ground state of the deprotonated complex (eq. (1), PT\*) is exergonic by over 19 kcal/mol. However, the transient absorption spectra obtained for the complex in the presence of AQ clearly indicate that PT\* to yield the ground state of the complex does not occur, since the spectrum expected for PT\* to the ground state should resemble Fig. S4b. A possible explanation for the absence of evidence for this highly exergonic process is that the required spin change from the <sup>3</sup>MLCT state to the singlet ground state of the complex may introduce a kinetic barrier to the PT\* reaction that allows other reaction pathways to dominate.

Given that PT\* to form either  $[(bpy)_2Ru(O bpy)]^{2+}$  or its excited state is not observed, the efficient excited-state reaction with AQ that is observed must either be associated with ET\* or PCET\*. The free energy for excited-state electron transfer from  $[(bpy)_2Ru(OHbpy)]^{2+*}$  to AQ is determined from  $E^0_{RuOH}(III/II)$  (0.82 V vs Fc<sup>+</sup>/Fc),  $E^0_{AQ}(0/-)$  (-1.32 V vs Fc<sup>+</sup>/Fc) and the excited-state energy of  $[(bpy)_2Ru(OHbpy)]^{2+}$  (1.98 eV). This results in a  $\Delta G^*_{ET}$  of + 3.7 kcal/mol, much smaller than that for excited-state proton transfer, but still endergonic.

The free energy of the PCET\* reaction can most easily be obtained from the sum of  $\Delta G^*_{PT}$  (24.7 kcal/mol, above) and  $\Delta G^*_{ET}$ . The latter is the sum of  $E^0_{HAQ+}(+/0)$  (-0.22 V vs. Fc<sup>+</sup>/Fc),  $E^0_{RuO-}(III/II)$  (-0.55 V vs. Fc<sup>+</sup>/Fc) and the excited-state energy of [(bpy)<sub>2</sub>Ru(II)(O<sup>-</sup>bpy)]<sup>+</sup> (1.92 eV). This results in a  $\Delta G^*_{ET}$  of -26.5 kcal/mol and an overall  $\Delta G^*_{PCET}$ 



Fig. 9. Energies of different states resulting from ground and excited-state electron and proton transfer reactions.

of approximately -2 kcal/mol or very nearly zero. The free energies of all of the processes discussed above are shown in Fig. 9. From the diagram it is clear that, thermodynamically, the excited state of  $[(bpy)_2Ru (HObpy)]^{2+}$  should react by PCET\*, however, the free energy for electron transfer (ET<sub>1</sub>\*) is only slightly endergonic and, in comparison to related systems involving reaction of similar Ru(II) hydroxybipyridine chromophores and 4-(4'-pyridyl)-*N*-alkylpyridinium ions, electron transfer would be expected to be the kinetically favored process.

At this point it is necessary to comment on the observed behavior of  $[(bpy)_2Ru(OMebpy)]^{2+}$  (the methoxy complex). The excited state of this complex does react with AQ and the only thermodynamically accessible path is ET\* to yield  $[(bpy)_2Ru(OMebpy)]^{3+}$  and AQ<sup>--</sup>. From the supplementary information it is clear that AQ<sup>--</sup> has a strong absorption at 550 nm and this would be expected to appear in the spectrum of the radical ions generated following charge separation of the electron transfer products. What is observed (Fig. 8) in the presence of added electrolyte is relaxation of the excited state in the span of a few microseconds with *a small signal for radical ions*. As a result, it appears that, while excited state electron transfer is certainly the reaction between the photoexcited methoxy complex and AQ, the yield of radical ions from the encounter complex (a 3+/1- complex) is very small, but suggests the formation of AQ<sup>--</sup>. In the absence of added electrolyte there is no measurable signal for radical ion products, only the excited state decay.

For [(bpy)<sub>2</sub>Ru(HObpy)]<sup>2+</sup>, the transient absorption spectrum of Fig. 7, obtained in the presence of added electrolyte, clearly illustrates the appearance of long lived radical ions. The spectrum exhibits features expected for ET<sub>1</sub>\* and for PCET\*. For PCET\* the spectrum would be expected to include absorption characteristics of [(bpy)2Ru(III)  $(O^{-}bpy)]^{2+}$  and HAQ<sup>0</sup>. The spectrum of HAQ<sup>0</sup>, shown in Fig. 6, has spectral features similar to that of Fig. 7, which also has a bleach in the 450-500 nm region that would be characteristic of the Ru(III) species. However, between a few hundred nanoseconds and 3 µs there is absorption between 500 and 550 nm that is not characteristic of the excited state or  $HAQ^0$ , but would be expected for  $AQ^{-}$ , the ET\* product. However, spectroelectrochemical data for [(bpy)<sub>2</sub>Ru(III)(O<sup>-</sup>bpy)]<sup>2+</sup> and AQ<sup>-</sup> indicate that (a) the [(bpy)<sub>2</sub>Ru(III)(O<sup>-</sup>bpy)]<sup>2+</sup> does absorb in the 500–550 nm region and (b) that the absorbance of the AQ<sup>-•</sup> species in the 500-550 nm region should be greater than that between 350 and 400 nm, which is not the case in Fig. 7. Also, the ET\* product observed for [(bpy)<sub>2</sub>Ru(OMebpy)]<sup>2+</sup> (Fig. 8) differs significantly from the spectrum obtained for the hydroxy complex in the presence of AQ. The combined transient absorption and spectroelectrochemistry data lead to the conclusion that the photoreaction occurring between  $[(bpy)_2Ru (HObpy)]^{2+}$  and AO is PCET\*.

#### 5. Conclusions

In summary, reaction of a Ru(II) 4-hydroxy-2,2'-bipyridine complex excited state with anthraquinone resulted in products emerging from the reaction cage that were consistent with a coupled electron transfer from the Ru(II) center and proton transfer from the hydroxy substituent to the anthraquinone acceptor. Related reaction of the <sup>3</sup>MLCT state of a Ru(II) 4-methoxy-2,2'-bipyridine complex with AQ resulted in only electron transfer products out of the reaction cage. This system thus serves as an example of an excited-state PCET reaction. In this case the excited-state electron transfer is endergonic and the net PCET is exergonic. This result adds to the very limited number of bimolecular systems that definitively exhibit excited-state proton-coupled electron transfer within an encounter complex [4].

# CRediT authorship contribution statement

Kristina Martinez: Writing – original draft, Formal analysis, Data curation, Investigation, Methodology. Kaitlyn Benson: Formal analysis, Data curation, Investigation, Methodology. Jared Paul: Supervision, Writing. Russell H. Schmehl: Supervision, Writing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

This material is based upon work supported by the National Science Foundation under grants number CHE-1900570 (RHS) and CHE-1900536 (JP).

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115376.

# References

- E.S. Rountree, B.D. McCarthy, J.L. Dempsey, Decoding Proton-Coupled Electron Transfer with Potential-pK(a) Diagrams: Applications to Catalysis, Inorg. Chem. 58 (10) (2019) 6647–6658, https://doi.org/10.1021/acs.inorgchem.8b03368.
- [2] M.H.V. Huynh, T.J. Meyer, Proton-Coupled Electron Transfer, Chem. Rev. 107 (11) (2007) 5004–5064, https://doi.org/10.1021/cr0500030.
- [3] J.M. Mayer, Proton-coupled electron transfer: a reaction chemist's view, Annu. Rev. Phys. Chem. 55 (1) (2004) 363–390, https://doi.org/10.1146/annurev. physchem.55.091602.094446.
- [4] J.C. Lennox, D.A. Kurtz, T. Huang, J.L. Dempsey, Excited-State Proton-Coupled Electron Transfer: Different Avenues for Promoting Proton/Electron Movement with Solar Photons, ACS Energy Lett. 2 (5) (2017) 1246–1256, https://doi.org/ 10.1021/acsenergylett.7b00063.
- [5] O.S. Wenger, Proton-Coupled Electron Transfer with Photoexcited Metal Complexes, Acc. Chem. Res. 46 (7) (2013) 1517–1526, https://doi.org/10.1021/ ar300289x.
- [6] C.J. Gagliardi, B.C. Westlake, C.A. Kent, J.J. Paul, J.M. Papanikolas, T.J. Meyer, Integrating proton coupled electron transfer (PCET) and excited states, Coord. Chem. Rev. 254 (21-22) (2010) 2459–2471, https://doi.org/10.1016/j. ccr.2010.03.001.
- [7] C.-C. Hsieh, C.-M. Jiang, P.-T. Chou, Recent experimental advances on excited-state intramolecular proton coupled electron transfer reaction, Acc. Chem. Res. 43 (10) (2010) 1364–1374.
- [8] A. Pannwitz, O.S. Wenger, Proton coupled electron transfer from the excited state of a ruthenium(II) pyridylimidazole complex, Phys. Chem. Chem. Phys. 18 (2016) 11374–11382, https://doi.org/10.1039/c6cp00437g.
- [9] T.T. Eisenhart, J.L. Dempsey, Photo-induced Proton-Coupled Electron Transfer Reactions of Acridine Orange: Comprehensive Spectral and Kinetics Analysis,

#### K. Martinez et al.

J. Am. Chem. Soc. 136 (35) (2014) 12221–12224, https://doi.org/10.1021/ja505755k.

- [10] Y.S. Zhuravleva, O.B. Morozova, Y.P. Tsentalovich, P.S. Sherin, Proton-coupled electron transfer as the mechanism of reaction between triplet state of kynurenic acid and tryptophan, J. Photochem. Photobiol., A. 396 (2020) 112522, https://doi. org/10.1016/j.jphotochem.2020.112522.
- [11] W.B. Swords, G.J. Meyer, L. Hammarström, Excited-state proton-coupled electron transfer within ion pairs, Chem. Sci. 11 (13) (2020) 3460–3473, https://doi.org/ 10.1039/C9SC04941J.
- [12] K. Martinez, J. Stash, K.R. Benson, J.J. Paul, R.H. Schmehl, Direct Observation of Sequential Electron and Proton Transfer in Excited-State ET/PT Reactions, J. Phys. Chem. C 123 (5) (2019) 2728–2735, https://doi.org/10.1021/acs.jpcc.8b09268. s001.
- [13] K.P. Martinez, R.H. Schmehl, Preparation (2021).
- [14] Purification of Organic Chemicals, Butterworth-Heinemann, 2009. https://doi.org/ 10.1016/B978-1-85617-567-8.50012-3.
- [15] M.E. Marmion, K.J. Takeuchi, Ruthenium(IV)-oxo complexes: the novel utilization of tertiary pnicogen ligands, J. Am. Chem. Soc. 110 (5) (1988) 1472–1480, https:// doi.org/10.1021/ja00213a019.
- [16] I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito, I.A. Koppel, Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile

to a Full Span of 28 pKa Units: Unification of Different Basicity Scales, J. Org. Chem. 70 (2005) 1019–1028, https://doi.org/10.1021/jo048252w.

- [17] J.J. Warren, T.A. Tronic, J.M. Mayer, Thermochemistry of Proton-Coupled Electron Transfer Reagents and its Implications, Chem. Rev. 110 (12) (2010) 6961–7001, https://doi.org/10.1021/cr100085k.
- [18] H. Görner, Photoreduction of 9,10-Anthraquinone Derivatives: Transient Spectroscopy and Effects of Alcohols and Amines on Reactivity in Solution¶, Phot. 77 (2003) 171–179, https://doi.org/10.1562/0031-8655(2003)077<0171: POADTS>2.0.CO:2.
- [19] Handbook of Photochemistry, 3rd ed., 2006. https://www.crcpress.com/ Handbook-of-Photochemistry-Third-Edition/Montalti-Credi-Prodi-Gandolfi/p/ book/9780824723774 (accessed August 14, 2018).
- [20] R. Frank, G. Greiner, H. Rau, Photoinduced electron transfer from excited [tris (2,2'-bipyridine)ruthenium(II)] 2+ to a series of anthraquinones with small positive or negative Gibbs energy of reaction, Marcus behavior and negative activation enthalpies, Phys. Chem. Chem. Phys. 1 (1999) 3481–3490, https://doi. org/10.1039/A902486G.
- [21] X.-Q. Zhu, C.-H. Wang, H. Liang, Scales of Oxidation Potentials, pKa, and BDE of Various Hydroquinones and Catechols in DMSO, J. Org. Chem. 75 (21) (2010) 7240–7257, https://doi.org/10.1021/jo101455m.