

Ruthenium complexes with asymmetric hydroxy- and methoxy-substituted bipyridine ligands

Kaitlyn R. Benson^a, Jaqueline Stash^a, Katherine L. Moffa^a, Russell H. Schmehl^b, Timothy J. Dudley^c, Jared J. Paul^{a,*}

^a Department of Chemistry, Villanova University, 800 E Lancaster Ave., Villanova, PA 19085, United States

^b Department of Chemistry, Tulane University, 6823 St. Charles Ave., New Orleans, LA 70118, United States

^c Math, Science and Technology Department, University of Minnesota, Crookston, 2900 University Ave., Crookston, MN 56716, United States

ARTICLE INFO

Keywords:
Ruthenium
PCET
Bipyridine
Hydroxy
Methoxy

ABSTRACT

The development of metal complexes with ligands capable of proton transfer can result in significant advances in Proton Coupled Electron Transfer (PCET) chemistry, specifically understanding how these reactions occur mechanistically in the excited state. The synthesis of three ruthenium complexes containing asymmetric bipyridine ligands: $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})]^{2+}$, $[\text{Ru}(\text{bpy})_2(4\text{bpyOMe})]^{2+}$, and $[\text{Ru}(\text{bpy})_2(44'\text{bpy}(\text{OH})(\text{OMe}))]^{2+}$ (bpy = 2,2'-bipyridine; 4bpyOH = 4-hydroxy-2,2'-bipyridine; 4bpyOMe = 4-methoxy-2,2'-bipyridine; 44'bpy(OH)(OMe) = 4-hydroxy-4'-methoxy-2,2'-bipyridine) are reported. These complexes were studied using both experimental and computational methods. These studies indicate that the methoxy-substitution gives similar electron-donating properties to the hydroxy-substitution, meaning that the methoxy-substitution is a good control when examining electron transfer in the absence of proton transfer. Potential versus pH diagrams show that $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})]^{2+}$ has a $\text{Ru}^{\text{III/II}}$ reduction potential of 0.97 V vs. Ag/AgCl in aqueous acidic solution that decreases to 0.76 V vs. Ag/AgCl when deprotonated. The $[\text{Ru}(\text{bpy})_2(44'\text{bpy}(\text{OH})(\text{OMe}))]^{2+}$, with an additional methoxy-substituent, has a $\text{Ru}^{\text{III/II}}$ reduction potential that is slightly lower with a potential of 0.92 V vs. Ag/AgCl in acidic aqueous solution that decreases to 0.74 V vs. Ag/AgCl when deprotonated. These complexes are comparable to other hydroxy- and methoxy-substituted polypyridyl ruthenium complexes reported previously, showing the additive effects of hydroxy- and methoxy-substitutions on the reduction potential of the $\text{Ru}^{\text{III/II}}$ wave and spectroscopic shifts that occur as the ligand scaffold is altered.

1. Introduction

Protons and electrons are two of the most fundamental particles involved in many chemical reactions. They are often found coupled to each other to lower activation energy barriers to facilitate chemical reactions [1–3]. This coupling has led to the widely studied field of chemistry dubbed Proton Coupled Electron Transfer (PCET). Coupling electron transfer to proton transfer allows for the avoidance of charge buildup, leading to the possibilities of carrying out multi-electron reactions in a more feasible way [4–6]. Due to the common nature of PCET chemistry, there is a great interest in studying the mechanisms of these reactions [7–10]. From a mechanistic standpoint, PCET reactions can occur sequentially with an electron transfer followed by proton transfer process, ET-PT, or a proton transfer followed by electron transfer process, PT-ET. Another possible mechanism is the concerted process,

whereby an electron and proton are transferred simultaneously, EPT. Detangling the mechanistics of these PCET processes is critical to the development of new catalysts for these reactions of interest [11–15].

Another major and related area of interest is the ability of photons to initiate electron transfer in photoinduced processes [16–18]. Learning how to couple light absorption to PCET reactions in a controlled way can give the energetic driving force needed to make these reactions happen. The ultimate goal of solar energy chemists is using renewable energy from the sun to drive chemical reactions, in a model such as photosynthesis. Photosynthesis is the ultimate model for photoinduced PCET chemistry, where there are many examples of electron and proton transfer processes occurring throughout. This can be observed in the net chemical reactions of photosynthesis: water oxidation to electrons and protons (Eq. 1), and carbon dioxide reduction to carbohydrates (Eq. 2).

* Corresponding author at: Department of Chemistry, Villanova University, 800 E Lancaster Ave., Villanova, PA 19085, United States.

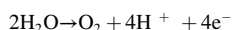
E-mail address: jared.paul@villanova.edu (J.J. Paul).

<https://doi.org/10.1016/j.poly.2021.115300>

Received 24 February 2021; Accepted 26 May 2021

Available online 1 June 2021

0277-5387/© 2021 Elsevier Ltd. All rights reserved.



Another example in the photosynthetic process is the proton-rocking mechanism of the well-studied tyrosine-histidine couple, where tyrosine (TyrZ) oxidation is coupled with proton transfer to a nearby histidine (His190) base [19–22]. As the oxidized tyrosine is reduced, the proton transfers back from the protonated histidine, resulting in the continuous process of electron transfer to and from the tyrosine (Eq. 3).

Furthermore, photosynthesis takes advantage of reversible PCET in mobile plastoquinones (Eq. 4) within the membrane system to participate in the electron-transfer cascade, while also transferring protons across the bilayer membrane, establishing a proton gradient, where the discharge of the gradient leads to ATP Synthase converting ADP to ATP for energy storage in the cell [23,24].

These are just a few of the multitude of PCET events in photosynthesis alone.

With the great interest of electron and proton transfer chemistry, the design of molecules that can help to study light-induced PCET mechanisms is of critical importance [25–29]. Our laboratory has chosen to take advantage of the rich history of ruthenium complexes to learn and gain a more thorough understanding of PCET. We have built complexes mainly consisting of hydroxyl-substituted polypyridyl ligands to learn how protonation state impacts the structure, spectroscopy, and electrochemistry of these complexes [30,31]. For example, the 4,4'-dihydroxy-2,2'-bipyridine ligand (44'bpy(OH)₂) has significant resonance structures that modify the spectroscopy and electrochemistry of these complexes dramatically as the protonation state changes, Fig. 1 [32–35]. This has demonstrated the greater ease of oxidation of the metal center to which the ligand is attached compared to the protonated form. In addition, the molecular orbital structure and corresponding electron transition assignments change significantly in different protonation states and depending upon the quantity and location of the ligands. Most recently, we have used the ruthenium hydroxyl-polypyridyl complexes as a model for studying the mechanism of photoinduced PCET [36]. To this point, most of our complexes have had multiple hydroxyl groups, due to the relative ease of synthesis of symmetric bipyridine ligands. However, this has added great difficulty in studying these photoinduced PCET processes due to the fact that there are multiple potential proton transfers [36]. It would be ideal to develop a system where only a single proton is involved to reduce the complexity in interpreting what species exist in solution. Even in the simplest case to date with a single 44'bpy(OH)₂ ligand, there is the potential for a doubly protonated, singly protonated and doubly deprotonated complex to exist, resulting in more complicated interpretation of the data. As a result, we have recently sought to synthesize asymmetric bipyridine ligands where there are single hydroxyl groups present, which will lead to greater ease of observing spectroscopic data and interpreting what species are present. This work presents the synthesis and fundamental spectroscopic and electrochemical studies of three asymmetric ruthenium-polypyridyl complexes: [Ru(bpy)₂(4bpyOH)]²⁺ (1), [Ru(bpy)₂(4bpyOMe)]²⁺ (2), and [Ru(bpy)₂(44'bpy(OH)(OMe))]²⁺ (3) (bpy = 2,2'-bipyridine; 4bpyOH = 4-hydroxy-2,2'-bipyridine; 4bpyOMe = 4-methoxy-2,2'-bipyridine; 44'bpy(OH)(OMe) = 4-hydroxy-4'-methoxy-2,2'-bipyridine), Fig. 2.

2. Material and methods

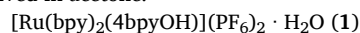
2.1. General

Reagents were obtained from Aldrich Chemical Co. and Oakwood Chemical and used without further purification. RuCl₃·3H₂O was purchased from Pressure Chemical Co. Elemental analyses for ruthenium complexes was carried out by Atlantic Microlab Inc., Norcross, GA. Aqueous solutions were prepared using a Millipore DirectQ UV water purification system.

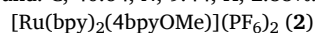
¹H NMR spectra of the metal complexes were collected on a JOEL 500 MHz NMR Spectrophotometer in deuterated acetonitrile (CD₃CN). ¹H NMR spectra of the free ligands were collected on a Varian 300 MHz Fourier Transform spectrometer in deuterated dimethyl sulfoxide (d₆-DMSO) or deuterated chloroform (CD₃Cl). Mass spectrometry data was collected on an AB Sciex TripleTOF 5600⁺ mass spectrometer. Infrared spectroscopy data was collected on a Perkin Elmer Two Fourier Transform infrared spectrometer with an ATR accessory. UV–Visible absorption spectra were collected on a Scinco S-3100 diode-array spectrophotometer at a resolution of 1 nm. All electrochemical studies were carried out on a Bioanalytical Systems (BAS) CW-50 potentiostat. pH measurements were carried out using a VWR SympHony pH meter, utilizing a three-point calibration with pH buffer values at pH = 4, 7, and 10.

2.2. Synthesis

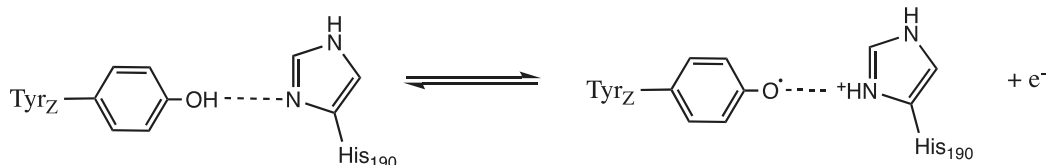
Synthetic procedures for asymmetric bipyridine ligands are reported in the Supporting information. All metal complexes were synthesized using previously reported procedures [34]. For studies done in water, all ruthenium hexafluorophosphate salts were converted to chloride salts by precipitation from acetone using tetrabutylammonium chloride dissolved in acetone.



A round bottom flask containing 30 mL 1:1 EtOH:H₂O was degassed with argon for 30 min. To the flask, 0.31 g (0.65 mmol) [Ru(bpy)₂Cl₂] and 0.17 g (1.0 mmol) 4-hydroxy-2,2'-bipyridine were added to the solution and refluxed overnight under argon. The solution was cooled to room temperature and filtered to remove any insoluble unreacted ligand. Two drops of HCl were added to ensure protonation of the ligand hydroxyl group, followed by the addition of a saturated 10 mL solution of NH₄PF₆ in water, affording a red–orange precipitate. The complex was filtered and washed with water followed by ether. The product was isolated by an alumina column with a gradient mobile phase of 5% water in acetonitrile to remove any [Ru(bpy)₃]²⁺ and 50% water in acetonitrile to elute the desired product. The acetonitrile was removed under reduced pressure and HPF₆ was added to ensure protonation. A saturated solution of NH₄PF₆ dissolved in water was used to precipitate the orange product which was collected by vacuum filtration and rinsed with water followed by ether. Yield: 0.24 g (0.27 mmol), 42%. ¹H NMR (500 MHz, CD₃CN) δ8.48 (s, 4H) δ8.40 (d, 1H) δ8.02 (m, 5H) δ7.89 (s, 1H) δ7.80 (s, 1H) δ7.75 (s, 1H) δ7.71 (s, 3H) δ7.37 (m, 6H) δ6.86 (s, 1H). Anal. Calcd. for RuC₃₀N₆O₂H₂₆P₂F₁₂: C, 40.32; N, 9.41; H, 2.95%. Found: C, 40.64; N, 9.44; H, 2.88%.



A round bottom flask containing 30 mL ethylene glycol was degassed with argon for 30 min. To the flask, 0.48 g (1.0 mmol) [Ru(bpy)₂Cl₂] and



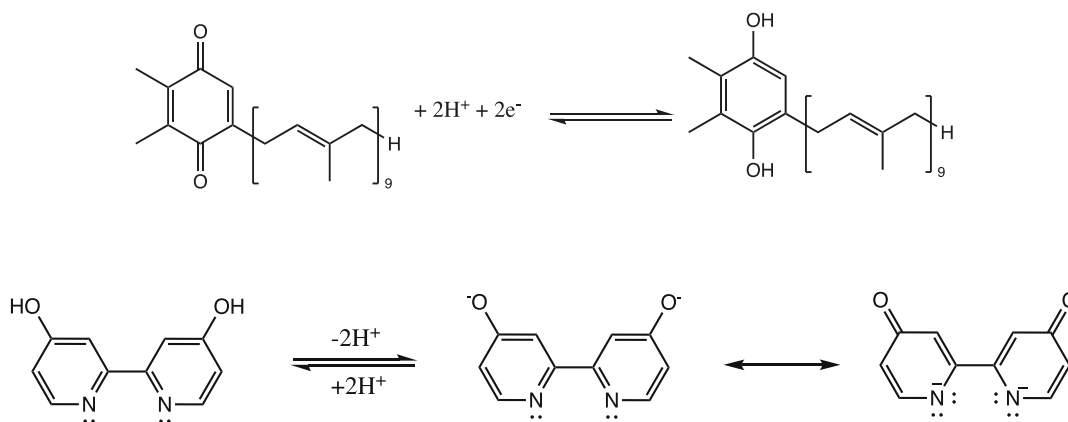


Fig. 1. 4,4'-Dihydroxy-2,2'-bipyridine ligand protonated and deprotonated with resonance structure denotes increased negative charge on the nitrogen portion of the ligand upon deprotonation.

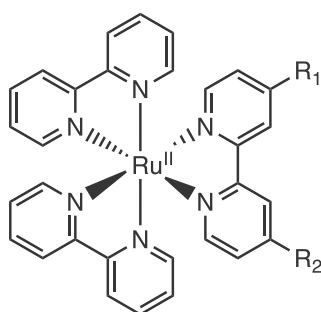
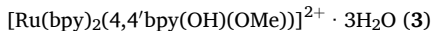


Fig. 2. Ruthenium polypyridyl complex scaffold studied in this work where 1) $R_1 = \text{OH}$, $R_2 = \text{H}$ is $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})]^{2+}$ (1); 2) $R_1 = \text{OCH}_3$, $R_2 = \text{H}$ is $[\text{Ru}(\text{bpy})_2(4\text{bpyOMe})]^{2+}$ (2); and 3) $R_1 = \text{OH}$, $R_2 = \text{OCH}_3$ is $[\text{Ru}(\text{bpy})_2(4,4'\text{bpy}(\text{OH})(\text{OMe}))]^{2+}$ (3).

0.19 g (1.0 mmol) 4-methoxy-2,2'-bipyridine were added and the solution was refluxed for three hours under argon. The solution was cooled to room temperature and filtered to remove any insoluble unreacted ligand. The filtrate was diluted to 180 mL with water. To the solution, an excess of NH_4PF_6 in water was added to precipitate the orange product. The solid was collected by vacuum filtration and rinsed with water followed by ether. Yield: 0.65 g (0.73 mmol), 73%. ^1H NMR (500 MHz, CD_3CN) δ 8.49 (m, 5H) δ 8.04 (m, 6H) δ 7.77 (t, 2H) δ 7.73 (s, 3H) δ 7.41 (m, 6H) δ 6.96 (dd, 1H) δ 3.99 (s, 3H). Anal. Calcd. for $\text{RuC}_{31}\text{N}_6\text{OH}_{26}\text{P}_2\text{F}_{12}$: C, 41.86; N, 9.45; H, 2.95%. Found: C, 42.15%; N, 9.52; H, 3.02%.



A round bottom flask containing 30 mL 1:1 EtOH:H₂O was degassed with argon for 30 min. To the flask, 0.48 g (0.99 mmol) $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and 0.21 g (1.0 mmol) 4-hydroxy-4'-methoxy-2,2'-bipyridine were added and the solution was refluxed for three hours under argon. The solution was cooled to room temperature and a few drops of HCl were added to ensure protonation of the ligand hydroxyl group. A saturated aqueous solution of NH_4PF_6 was added to afford an orange precipitate. The solid was collected and rinsed with water followed by ether. Yield: 0.63 g (0.65 mmol), 66%. ^1H NMR (500 MHz, CD_3CN) δ 8.47 (s, 4H) δ 8.02 (m, 4H) δ 7.93 (d, 2H) δ 7.83 (s, 1H) δ 7.80 (s, 1H) δ 7.70 (s, 2H) δ 7.42 (s, 3H) δ 7.34 (s, 3H) δ 6.92 (s, 1H) δ 6.86 (s, 1H) δ 3.97 (s, 3H). Anal. Calcd. $\text{RuC}_{31}\text{N}_6\text{O}_5\text{H}_{32}\text{P}_2\text{F}_{12}$: C, 38.80; N, 8.76%; H, 3.36%. Found: C, 38.82; N, 8.83; H, 3.22%.

2.3. Electrochemical pH studies in aqueous buffer solutions

For aqueous studies, a standard three electrode setup with Ag/AgCl reference electrode containing 3 M KCl, platinum wire auxiliary

electrode, and glassy carbon working electrode was used for studies. Britton-Robinson buffer solutions ranging from pH values 2–12 were made from a stock solution of 0.04 M acetic acid, 0.04 M boric acid, and 0.04 M phosphoric acid in water. 0.2 M sodium hydroxide was added to correct each buffer and the solution pH was measured after the addition of the metal complex. At pH values below 2, dilute triflic acid was added until the desired pH was reached. Reduction potentials for aqueous studies are reported versus Ag/AgCl.

2.4. Electrochemical studies in nonaqueous solution

For nonaqueous studies, a standard three electrode setup with Ag/Ag⁺ reference electrode containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile supporting electrolyte, platinum wire auxiliary electrode, and glassy carbon working electrode was used for studies. All non-aqueous measurements were taken in acetonitrile with 0.1 M TBAPF₆ supporting electrolyte. The solutions were degassed for approximately 10 min with argon before data collection. Ferrocene was added after data was collected as an internal standard for correction ($E_{1/2} = 0.40$ V vs SCE in acetonitrile with 0.1 M TBAPF₆) [37]. For nonaqueous solutions in acidic and basic conditions, 10 mM hexafluorophosphoric acid (HPF₆) and 10 mM tetrabutylammonium hydroxide (TBAOH), respectively, were prepared with 0.1 M TBAPF₆ supporting electrolyte in acetonitrile to give a 10-fold excess of acid or base.

2.5. Buffer system for UV-visible studies

UV-visible pH studies were carried out with buffers prepared using solutions referenced in the Chemical Technicians' Ready Reference Handbook [38]. Each buffer was checked for pH accuracy and corrected with the use of concentrated HCl or concentrated NaOH to its desired pH, which ranged from 1.0 to 13.0 in half pH unit increments.

2.6. Computational methods

All calculations were performed using Gaussian09 [39]. Geometries were optimized using restricted M06-L functionals with the 6-31G** basis set for the main group elements. The def2-SV [40] basis set was used for Ru, with the default pseudopotential used to represent 28 core electrons. Spherical harmonic d and f orbitals were used in all calculations and a more refined grid size was used for numerical integration in DFT (Int = UltraFine). Default gradient tolerances were used for optimizations and frequencies were calculated using analytic second derivatives. For the structures presented, all vibrational modes were found to be real at the DFT determined stationary points. Vertical excitation energies were calculated at each stationary point using time-dependent

DFT (TDDFT) with the M06-L functionals. The basis set size was increased for both the main group elements (6-311 + G**) and ruthenium (def2-TZVP) [40]. Solvent effects on the optimized geometries, frequencies, and vertical excitation energies were considered using the C-PCM solvation model, with water as the solvent. Default settings were used for all other parameters related to the solvation model (e.g., cavity type).

3. Results and discussion

3.1. Synthesis

Suzuki coupling methods were used to synthesize the asymmetric bipyridine ligands using Hodgson's boronate and methods previously described by Gütz and Lützen [41,42]. The ligands were then complexed to $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ while refluxing in either an ethanol/water mixture or ethylene glycol. In some cases, while preparing mixed-bipyridine complexes, extended reaction times yielded impurities of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. To isolate the desired metal complex and remove $[\text{Ru}(\text{bpy})_3]^{2+}$, an alumina column with a gradient mobile phase of 5% water in acetonitrile to 50% water in acetonitrile was used, resulting in pure complex.

3.2. Computational structure

Optimized structures were calculated using restricted M06-L functionals with the 6-31G** basis set for the main group elements and the def2-SV basis set for ruthenium with water as the PCM solvent. Relevant bond lengths and angles are reported in Table 1. All of the structures adopt a distorted octahedral shape, which is similar to that observed in experimental crystal structures and computational calculations for similar complexes [32–34]. It should be noted that computational data typically give Ru-N bond lengths that are approximately 2% larger than the average bond lengths observed in X-Ray diffraction data [43]. This observation is consistent where the calculated bond lengths are in line with the computational data from similar complexes and slightly longer than the X-Ray data. The Ru-N₁, bond length that contains the hydroxyl substituted-portion of the bipyridine is slightly longer, ~ 0.01 Å, than the other Ru-N bonds, demonstrating little impact on the overall structure. This small lengthening is also observed with the $-\text{OCH}_3$ group substitution. The major structural change occurs with the C—O bond upon deprotonation. When protonated, the CO bond is single bond in character at 1.338 Å for **1**, and 1.339 Å for **3**. This is similar to the C—O bond length with the corresponding methoxy substitution with 1.337 Å for **2** and 1.337 Å for **3**. Upon deprotonation, the C—O bond lengths decrease to 1.255 Å in both **1** and **3**. This decrease in bond length supports the

resonance structure whereby the C—O bond becomes more double bond in character, Fig. 3. This observation is consistent with similar complexes reported previously [32,34,35]. The electronic rearrangement upon deprotonation has a significant impact on the electrochemical and spectroscopic properties of these complexes, *vide infra*.

3.3. Electrochemistry in acetonitrile

Table 2 gives the $\text{Ru}^{\text{III/II}}$ reduction potentials of the varying hydroxy- and methoxy-substituted complexes synthesized in our laboratory. The reduction potentials of the three new complexes prepared in this work fit predictably into the table, demonstrating a decrease in reduction potential as the quantity of hydroxy- and methoxy-substituents are added to the complex. $[\text{Ru}(\text{bpy})_3]^{2+}$, which contains no electron-donating groups has the highest reduction potential at 0.90 V vs. $\text{Fc}^{+/0}$. The reduction potential drops by less than a tenth of a volt with the addition of a single-hydroxy or single-methoxy group in the 4-position of a bipyridine ring in the complex. Having di-substitution in the 4- and 4'-positions of a single bipyridine almost doubles the decrease in reduction potential compared to a single substitution. This systematic decrease in potential with increasing electron-donating groups in the 4- and 4'-positions, while not surprising, gives an idea to how many volts each substitution is "worth". For each hydroxyl group addition in the 4- and 4'-positions, there is an ~ 0.07 V decrease in potential per added substitution. For each methoxy group addition in the 4- and 4'-positions, there is an ~ 0.06 V decrease in potential per added substitution. This indicates that the hydroxyl group is slightly more electron-donating than the methoxy group. This is consistent within the measurements and shows in the extreme case of $[\text{Ru}(\text{bpy}(\text{OH})_2)_3]^{2+}$ (0.48 V vs. $\text{Fc}^{+/0}$) and $[\text{Ru}(\text{bpy}(\text{OMe})_2)_3]^{2+}$ (0.54 V vs. $\text{Fc}^{+/0}$) where six substitutions impact the potential by a total of 0.06 V. The hydroxyl group being slightly more electron-donating than methoxy is most likely due to the ability of the hydroxyl group to hydrogen bond with solvent, making it slightly more electron-donating, which is elucidated by fully deprotonating the ligands, *vide infra*. Also of note, the mixed hydroxy/methoxy complex, **3**, has a $\text{Ru}^{\text{III/II}}$ reduction potential of 0.76 V vs. $\text{Fc}^{+/0}$, in alignment of the other di-substituted complexes.

Upon deprotonation of the hydroxy groups, negative charge builds up on the ligand and complex as a whole. This impacts the complex by making it easier to oxidize the metal center due to significantly increased electron-donation to the metal, which is predicted by the resonance structures, Fig. 3. In acetonitrile, the oxidation of the deprotonated Ru^{II} is masked by the large oxidation of the tetrabutylammonium hydroxide base, which is something we have observed previously in the di-hydroxy-bipyridine complex, $[\text{Ru}(\text{bpy})_2(44'\text{bpy}(\text{OH})_2)]^{2+}$, in the same supporting electrolyte [34]. Fortunately, we were able to observe oxidation of the deprotonated Ru^{II} complexes in aqueous solution, *vide infra*.

Ligand reduction potentials for the three complexes are reported in Table 3. Data for the complexes was collected both in the presence and absence of tetrabutylammonium hydroxide base to determine how increasing the negative charge on the substituted ligands would impact the overall reduction of the unsubstituted bipyridine ligands. The change in reduction potentials for the bipyridine ligands with added base was small, with at most a slight decrease of ~ 0.01 V for complexes **1** and **3**. The single-methoxy-substituted complex, **2**, has three observable reduction features at -1.74 V, -1.95 V, and -2.20 V vs. $\text{Fc}^{+/0}$, with the third reduction occurring at the more electron-rich 4bpyOMe ligand. The two complexes with a hydroxyl group attached to a bipyridine only have observable reductions for the two unsubstituted bipyridine ligands. The reduction of these unsubstituted ligands are virtually identical for the two complexes with $\text{bpy}_1 = -1.85$ V and $\text{bpy}_2 = -2.07$ V vs. $\text{Fc}^{+/0}$ for **1** and $\text{bpy}_1 = -1.86$ V and $\text{bpy}_2 = -2.08$ V vs. $\text{Fc}^{+/0}$ for **3**. These potentials indicate that having a hydroxyl group compared to a methoxy group makes the reduction of the first unsubstituted bipyridine more difficult by slightly over 0.1 V, with the first bipyridine reduction in

Table 1
Relevant bond lengths (Å) and angles (°) of calculated structures.

Bond	R ₁ = OH	R ₁ = O [−]	R ₁ = OCH ₃	R ₁ = OH	R ₁ = O [−]
Lengths	R ₂ = H	R ₂ = H	R ₂ = H	R ₂ = OCH ₃	R ₂ = OCH ₃
Ru-N ₁	2.100	2.098	2.100	2.104	2.098
Ru-N ₂	2.094	2.097	2.093	2.101	2.104
Ru-N ₃	2.091	2.089	2.092	2.088	2.085
Ru-N ₄	2.090	2.095	2.090	2.086	2.093
Ru-N ₅	2.089	2.085	2.089	2.087	2.082
Ru-N ₆	2.091	2.081	2.090	2.090	2.079
C-O ₁	1.338	1.255	1.337	1.339	1.255
C-O ₂	N/A	N/A	N/A	1.337	1.340
O-CH ₃	N/A	N/A	1.428	1.429	1.427
Bond Angles					
N ₁ -Ru-N ₂	77.5	77.5	77.5	77.2	77.2
N ₁ -Ru-N ₃	96.5	95.2	96.5	96.6	95.2
N ₁ -Ru-N ₄	172.3	171.2	172.2	172.2	170.9
N ₁ -Ru-N ₅	96.7	96.2	96.9	96.9	96.7
N ₁ -Ru-N ₆	88.8	89.3	89.1	88.5	89.4

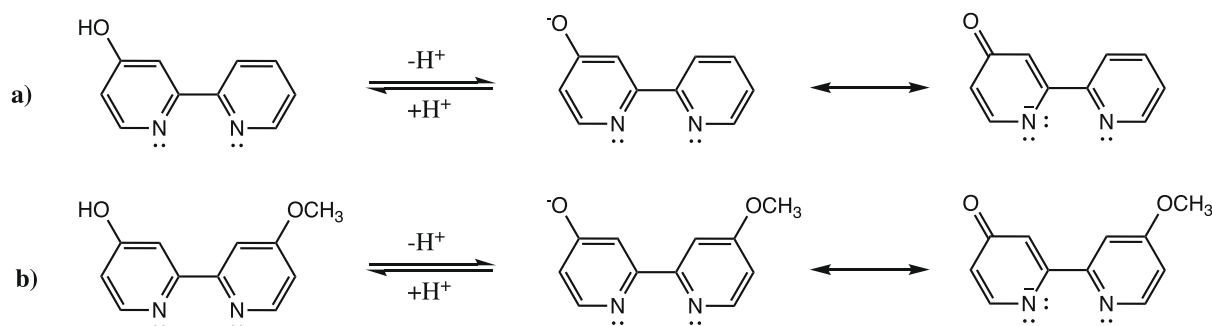


Fig. 3. Structures of asymmetric ligands and resonance structures after deprotonation of the ligands. a = 4-hydroxy-2,2'-bipyridine; b = 4-hydroxy-4'-methoxy-2,2'-bipyridine.

Table 2

$\text{Ru}^{\text{III/II}}$ reduction potentials of ruthenium complexes in acetonitrile with 0.1 M TBAPF₆.

Complex	E° (V) vs. $\text{Fc}^{+/0}$		Reference
	protonated	deprotonated	
$[\text{Ru}(\text{bpy})_3]^n$	0.90	N/A	Fuentes
1 ⁿ	0.82 ^b	–	This work
2 ⁿ	0.83	N/A	This work
$[\text{Ru}(\text{bpy})_2(\text{X})]^n$	0.76 ^a	–	Klein
$[\text{Ru}(\text{bpy})_2(\text{Y})]^n$	0.78	N/A	Klein
3 ⁿ	0.76 ^b	–	This work
$[\text{Ru}(\text{bpy})(\text{X})_2]^n$	0.61 ^b	–0.35 ^c	Charboneau
$[\text{Ru}(\text{bpy})(\text{Y})_2]^n$	0.66	N/A	Charboneau
$[\text{Ru}(\text{X})_3]^n$	0.48 ^b	–0.95 ^c	Fuentes
$[\text{Ru}(\text{Y})_3]^n$	0.54	N/A	Fuentes

X = 4,4'-dihydroxy-2,2'-bipyridine; Y = 4,4'-dimethoxy-2,2'-bipyridine

n = +2, +1, 0, –2, or –4 depending upon number of protons

a = 0.1 M HPF₆; b = 10 mM HPF₆; c = 10 mM TBAOH

Note: methoxy-only-substituted complex potentials are listed in the protonated column due to the fact that they cannot be deprotonated.

Table 3

Ligand reduction potentials (V vs. $\text{Fc}^{+/0}$) of ruthenium complexes in acetonitrile with 0.1 M TBAPF₆.

Complex	bpy ₁	bpy ₂	bpy _{substituted}
1	–1.85	–2.07	–
2	–1.74	–1.95	–2.20
3	–1.86	–2.08	–

complex **2** occurring at –1.74 V vs. $\text{Fc}^{+/0}$. Notably, the reduction of the hydroxy-substituted ligands is not observed, which is consistent with the other previously synthesized hydroxy-substituted bipyridine complexes [32].

3.4. Pourbaix diagrams

To better understand the pH dependence of the $\text{Ru}^{\text{III/II}}$ reduction potential, Pourbaix diagrams were made using the Britton-Robinson buffer system. Complex **2** demonstrated no pH dependence as anticipated (Fig. S22, Supporting information), due to the fact that there are no deprotonatable groups. The reduction potential of $\text{Ru}^{\text{III/II}}$ in this complex is 0.96 V vs. Ag/AgCl. The completely protonated single hydroxy complex (**1**), Fig. 4, gives a similar reduction potential for the $\text{Ru}^{\text{III/II}}$ reduction of 0.97 V vs. Ag/AgCl. This again, supports that the protonated hydroxy and methoxy groups have similar electron-donating properties to each other. However, for complex **1**, the potential begins to decrease at pH ~ 1.6. This value corresponds to the pK_a of the Ru^{III} oxidation state of the complex. The potential then decreases before leveling off at pH ~ 6.0, giving a rough estimate of the pK_a of the Ru^{II}

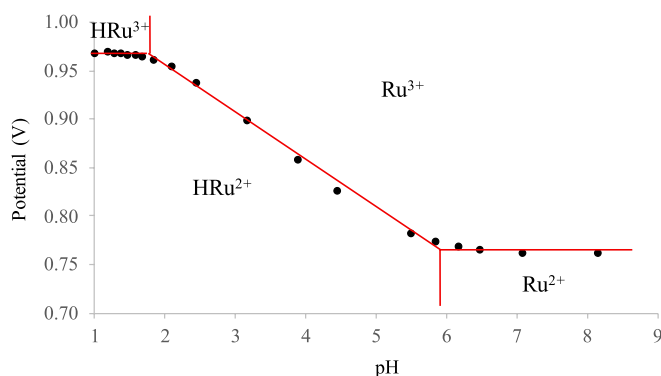


Fig. 4. Pourbaix diagram of $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})][\text{Cl}]_2$ in Britton-Robinson buffer solution. The four forms of the complex are: $[\text{Ru}^{\text{III}}(\text{bpy})_2(4\text{bpyOH})]^{3+} = \text{HRu}^{3+}$, $[\text{Ru}^{\text{II}}(\text{bpy})_2(4\text{bpyOH})]^{2+} = \text{HRu}^{2+}$, $[\text{Ru}^{\text{III}}(\text{bpy})_2(4\text{bpyO})]^{2+} = \text{Ru}^{3+}$, and $[\text{Ru}^{\text{II}}(\text{bpy})_2(4\text{bpyO})]^{+} = \text{Ru}^{2+}$. Potentials are reported versus Ag/AgCl.

oxidation state of the complex. Through pH titrations, the pK_a of the Ru^{II} oxidation state of complex **1** is 5.72 ± 0.05 . The final potential is 0.76 V vs. Ag/AgCl, resulting in a 0.21 V change between the protonated and deprotonated complex. The slope of the pH dependent region is 50 mV/pH unit, close to the predicted slope of 59 mV/pH unit for a $1 \text{ e}^-/1\text{H}^+$ process.

The mixed hydroxy/methoxy complex (**3**), Fig. 5, has a lower reduction potential when fully protonated of 0.92 V vs. Ag/AgCl compared to complexes **1** and **2**, due to the nature of two electron-donating groups. This reduction potential is in line with the 4,4'-dihydroxy-substituted complex, $[\text{Ru}(\text{bpy})_2(4,4'\text{bpy}(\text{OH})_2)]^{2+}$ with a potential

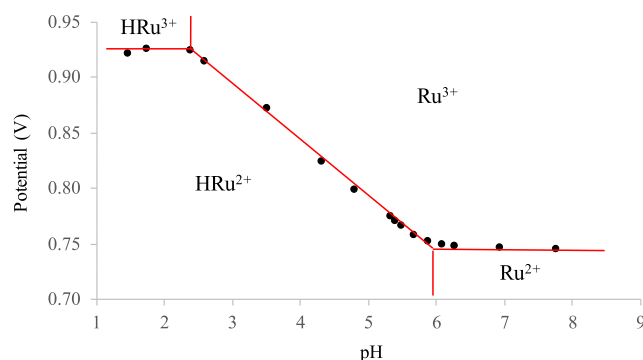


Fig. 5. Pourbaix diagram of $[\text{Ru}(\text{bpy})_2(4,4'\text{bpy}(\text{OH})(\text{OMe}))][\text{Cl}]_2$ in Britton-Robinson buffer solution. The four forms of the complex are: $[\text{Ru}^{\text{III}}(\text{bpy})_2(4,4'\text{bpy}(\text{OH})(\text{OMe}))]^{3+} = \text{HRu}^{3+}$, $[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'\text{bpy}(\text{OH})(\text{OMe}))]^{2+} = \text{HRu}^{2+}$, $[\text{Ru}^{\text{III}}(\text{bpy})_2(4,4'\text{bpy}(\text{O})(\text{OMe}))]^{2+} = \text{Ru}^{3+}$, and $[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'\text{bpy}(\text{O})(\text{OMe}))]^{+} = \text{Ru}^{2+}$. Potentials are reported versus Ag/AgCl.

of 0.91 V vs. Ag/AgCl reported previously [33]. The potential for **3** begins to decrease at pH $\sim$ 2.4 (pK_a of Ru^{III} oxidation state of complex) as the complex starts to deprotonate before leveling off at pH $\sim$ 6.0 (pK_a of Ru^{II} oxidation state of complex). Through pH titrations, the pK_a of the Ru^{II} oxidation state of complex **3** was determined to be 5.69 ± 0.03 . The slope for the pH dependent region is 51 mV/pH unit, indicative of a $1 e^-/1H^+$ transfer process (59 mV/pH unit). The $Ru^{III/II}$ reduction potential for deprotonated **3** is 0.74 V vs. Ag/AgCl, a 0.18 V decrease from the protonated form of the complex. This change in potential is similar to the decrease in potential observed for complex **1** upon deprotonation. In addition, the $[Ru(bpy)_2(44'bpy(O^-)_2)]$ deprotonated complex has a $Ru^{III/II}$ reduction potential of 0.62 V vs. Ag/AgCl, decreasing 0.29 V between the completely protonated and completely deprotonated state of the complex [33]. This equates to approximately 0.15 V per proton, which is comparable to complex **3**.

Comparing the 44'bpy(OH)(OMe) ligand complexed to ruthenium with the 44'bpy(OH)₂ ruthenium complex is an area of great interest to us, because we wanted to develop a system with only one ionizable proton that had similar electronic properties to the protonated $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ complex. In our previous work with $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ having two ionizable protons, we were only able to observe an average pK_a of $\sim$ 5.8 for both protons by titration [34]. This average pK_a phenomenon has been observed in other complexes in the literature [35,44]. The Pourbaix diagram of $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ also did not show two subsequent deprotonation steps, meaning that the second deprotonation of some of the complex in solution is happening before the first deprotonation step of all of the complexes in solution is complete [33]. The Pourbaix diagram did, however, give an estimate of a $pK_{a2} \sim$ 6.8 for the second deprotonation of the di-hydroxy complex. Comparatively the two single hydroxy complexes have distinguishable pK_a values by titration of 5.72 ± 0.05 for **1** and 5.69 ± 0.03 for **3**, with their respective Pourbaix diagrams estimated pK_a values in this range as well. Even more interesting, the $[Ru(44'bpy(OH)_2)_3]^{2+}$ complex with six ionizable protons gives an average $pK_a = 6.5$ even though the complex gains a 4- charge when completely deprotonated [35]. These results demonstrate that although the protonation state affects the overall electronic properties of the ruthenium complexes, each proton dissociation has little effect on subsequent deprotonations. This underscores the importance of these newly synthesized asymmetric hydroxy-substituted ligands for tracking and understanding PCET reaction chemistry in the excited state where we can now track a single proton.

3.5. UV/Visible absorbance spectroscopy

UV/Visible absorbance data was collected in acetonitrile with relevant peaks and extinction coefficients reported in Table 4. All three complexes give typical spectra compared to that of other ruthenium polypyridyl complexes, with a low energy Metal to Ligand Charge Transfer (MLCT) band in the 400–500 nm region and higher energy π to π^* transitions below 300 nm [45,46]. For complexes **1** and **2** with the single-hydroxy or single-methoxy substitution, the lowest energy MLCT

Table 4

UV/Visible absorbance peak wavelengths (λ) and corresponding extinction coefficients (ϵ) of ruthenium complexes in acetonitrile.

1[PF ₆] ₂		2[PF ₆] ₂		3[PF ₆] ₂	
λ (nm)	ϵ (M ⁻¹ ·cm ⁻¹)	λ (nm)	ϵ (M ⁻¹ ·cm ⁻¹)	λ (nm)	ϵ (M ⁻¹ ·cm ⁻¹)
245	26,600	227	25,300	255	30,500
254	24,500	244	25,600	283	67,000
286	76,300	254	23,300	288	70,500
322	10,400	286	74,300	326	11,800
357	6500	324	10,300	358	7850
429	12,600	356	6200	433	12,500
456	14,700	427	11,800	461	14,400
		456	14,400		

occurs at 456 nm in both cases. This shift is very small, approximately 4 nm higher in wavelength (200 cm⁻¹) than the unsubstituted $[Ru(bpy)_3]^{2+}$ ($\lambda_{max} = 452$ nm in acetonitrile) [35]. The mixed methoxy/hydroxy complex, **3**, has a longer wavelength shift to $\lambda_{max} = 461$ nm in acetonitrile. This value is on the order of the di-hydroxy-substituted, $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$, complex ($\lambda_{max} = 462$ nm in acetonitrile) [34]. This trend of longer wavelength shifts with increasing number of hydroxy- and/or methoxy-groups systematically increases for all of the complexes synthesized, where $[Ru(44'bpy(OH)_2)_3]^{2+}$ with six hydroxy groups results in the longest wavelength shift ($\lambda_{max} = 479$ nm in 50:50 acetonitrile/water with 10 mM HPF₆) [35]. It should be noted that in previous work, some of the complexes were prepared in acetonitrile/water mixtures to help with solubility. With higher numbers of hydroxy-substitutions, these complexes lose their solubility in acetonitrile. However, in studies carried out both in this work and the previous work, similar λ_{max} values (within 1 nm) were observed when data was collected in both pure acetonitrile and the 50:50 water/acetonitrile mixture. When all the data is taken into account, it appears that each hydroxy- or methoxy-substitution results in an $\sim$ 200 cm⁻¹ shift to lower energy of the lowest energy MLCT band. These small shifts can be explained by a slight disruption in π -backbonding from the metal d orbitals to the ligand π^* orbitals as electron-donating substituents are added to the polypyridyl scaffold. This results in the metal d orbitals destabilizing in energy, bringing the d orbitals closer in energy to the empty π^* orbitals, lowering the energy gap.

The complexes were deprotonated using NaOH, and UV/Visible absorbance spectra were collected to observe how the lowest energy MLCT band changed in this state, Supporting information. The first observation is that the single-methoxy complex, **2**, has an identical spectrum in the MLCT region in the presence of base, which is unsurprising as the complex has no ionizable protons. There are spectral changes observed for complexes **1** and **3** in the presence of base. For complex **1** (Fig. S26, Supporting information) there is an overall broadening of the spectrum, however, the λ_{max} does not change. The broadening results in absorbance at longer wavelengths, which is supported in the computational studies, *vide infra*. Complex **3** gives a more significant peak shift (Fig. S28, Supporting information), with a new $\lambda_{max} = 475$ nm. However, this spectrum has a higher energy peak with clear shoulder at $\lambda_{max} \sim$ 440 nm. This shifting, with clear peak and shoulder, is also observed for the $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ complex with one molar equivalent of added base, which would be rough indicator of what the singly deprotonated $[Ru(bpy)_2(44'bpy(OH)(O^-))]^+$ looks like spectroscopically [34].

Additional UV/Visible absorbance data was collected in aqueous pH buffers, Fig. 6. This data allows the observation of how the spectra change as the single deprotonation process of **1** and **3** occurs. For complex **1**, it's clear that the λ_{max} does not change as a function of protonation state, however, the spectra broadens as the pH increases. For the mixed hydroxy/methoxy complex, the λ_{max} shifts from 462 nm to 470 nm upon deprotonation. Most notable is that this deprotonated species, $[Ru(bpy)_2(44'bpy(O^-)(OMe))]^+$, has a spectrum that looks virtually the same as the UV/Visible absorbance spectrum at the average pK_a of $[Ru(bpy)_2(44'(bpy(OH)_2))]^{2+}$ where individual deprotonation steps are not readily observable [34]. As a result, this gives a nice spectroscopic handle for observing the properties of the deprotonated complex. As anticipated, the single-methoxy complex **2**, gives a similar UV/Visible absorbance spectrum in aqueous solution to that of acetonitrile. In addition, the UV/Visible absorbance spectrum of **2** does not change in water, the presence of strong acid, the presence of strong base, or in aqueous pH = 7 buffer, due to the lack of ionizable protons, Fig. S29.

3.6. Computational analysis of electronic transitions

Computational studies were carried out to assign the specific charge transfer transitions to the visible spectra of the complexes, Tables 5–7.

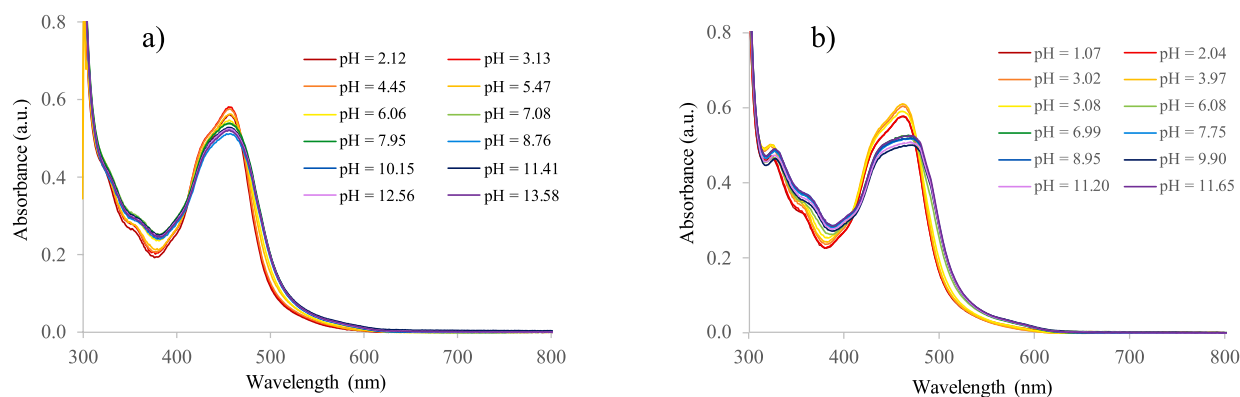


Fig. 6. UV/Visible absorbance spectra in aqueous buffer solutions of a) 0.05 M $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})][\text{Cl}]_2$ and b) 0.05 M $[\text{Ru}(\text{bpy})_2(44'\text{bpy}(\text{OH})(\text{OMe}))][\text{Cl}]_2$.

Table 5

Electronic transition assignments for $[\text{Ru}(\text{bpy})_2(4\text{bpyOH})]^{2+}$ (1) in water.

complex	energy (eV)	λ (nm)	oscillator strength	transition type
protonated	2.494	497	0.098	ML_{12}CT
	2.509	494	0.094	ML_{12}CT
	3.323	373	0.083	ML_{12}CT
	3.338	371	0.064	ML_2CT
	3.409	364	0.048	ML_{12}CT
	3.425	362	0.067	ML_{12}CT
	3.540	350	0.048	ML_2CT
deprotonated	2.274	545	0.042	$\text{ML}_1\text{CT} + \text{L}_2(\text{n})\text{L}_1$
	2.289	542	0.038	$\text{ML}_1\text{CT} + \text{L}_2(\text{n})\text{L}_1$
	2.465	503	0.064	ML_1CT
	2.802	443	0.030	$(\text{ML}_2)\text{L}_{12}\text{CT}$
	2.881	430	0.043	$(\text{ML}_2)\text{L}_{12}\text{CT}$
	3.063	405	0.059	ML_{12}CT
	3.263	380	0.054	ML_{12}CT

L_1 = bpy ligand, L_2 = 4bpyOH ligand, (ML_2) = mixed metal- L_2 orbital, $\text{L}_2(\text{n})$ = lone pair on oxygen

Table 6

Electronic transition assignments for $[\text{Ru}(\text{bpy})_2(4\text{bpyOMe})]^{2+}$ (2) in water.

energy (eV)	λ (nm)	oscillator strength	transition type
2.489	498	0.096	ML_2CT
2.507	495	0.098	ML_{12}CT
3.317	374	0.084	ML_{12}CT
3.410	364	0.046	ML_{12}CT
3.422	362	0.084	ML_1CT
3.572	347	0.053	ML_2CT

L_1 = bpy ligand, L_2 = 4bpyOMe ligand

Table 7

Electronic transition assignments for $[\text{Ru}(\text{bpy})_2(44'\text{bpy}(\text{OH})(\text{OMe}))]^{2+}$ (3) in water.

complex	energy (eV)	λ (nm)	oscillator strength	transition type
protonated	2.354	527	0.069	ML_{12}CT
	2.464	503	0.101	ML_{12}CT
	2.483	499	0.063	ML_2CT
	3.241	383	0.107	ML_1CT
	3.424	362	0.155	ML_1CT
deprotonated	2.250	551	0.083	ML_1CT
	2.432	510	0.053	ML_1CT
	2.842	436	0.040	$(\text{ML}_2)\text{L}_1\text{CT}$
	3.024	410	0.043	$(\text{ML}_2)\text{L}_2\text{CT} + \text{ML}_1\text{CT}$
	3.045	407	0.043	$\text{ML}_1\text{CT} + \text{L}_2(\text{n})\text{L}_1$
	3.339	371	0.084	ML_2CT

L_1 = bpy ligand, L_2 = 44'bpy(OH)(OMe) ligand, (ML_2) = mixed metal- L_2 orbital, $\text{L}_2(\text{n})$ = lone pair on oxygen

All calculations were carried out using the PCM solvent water. For the protonated form of both complexes 1 and 3, as well as the single-methoxy complex 2, all of the major electronic transitions in the visible region are MLCT with charge transfer to molecular orbitals on the unsubstituted bipyridine, substituted bipyridine, or combination of the bipyridines. For complexes 1 and 2, the predicted spectra are very similar in both energy and intensity, which is to be expected with the similarities in experimental electron-donating ability between the hydroxy- and methoxy-substitutions, *vide supra*. For the mixed hydroxy/methoxy ligand complex, 3, there is a predicted longer wavelength shift compared to the singly substituted complexes. Again, these results are confirmed by the experimentally observed lower energy shift in UV/Visible absorbance spectra.

For the deprotonation of the single-substituted hydroxy complex, 1, the absorbance spectrum changes, Table 5. For the protonated complex, there are two predicted intense transitions at 497 and 494 nm with oscillator strengths of 0.098 and 0.094, respectively. Once deprotonated, the complex has six predicted, less intense transitions between 400 and 550 nm, with oscillator strengths ranging from 0.030 to 0.064. These results support the experimental spectra where there is a broadening of the spectrum with increased absorbance at lower energy than the protonated form. In addition, two new types of electronic transitions are observed. The first is a transition from a mixed metal and deprotonated ligand orbital, Fig. 7a, to a delocalized π^* molecular orbital on both the substituted and unsubstituted bipyridine scaffold ($(\text{ML}_2)\text{L}_{12}\text{CT}$). This transition is termed a mixed Metal-Ligand to Ligand Charge Transfer (MLLCT) and have been observed in previous studies upon deprotonation of hydroxy- substituted bipyridine ligands [34]. The second new type of transition occurs from a lone pair electron orbital on the oxygen of the deprotonated ligand, Fig. 7b, to the unsubstituted bipyridine ligand ($\text{L}_2(\text{n})\text{L}_1$). This transition is nearly degenerate with a metal to unsubstituted bipyridine ligand charge transfer, ML_1CT , hence the mixing of transitions in Table 5 at 545 nm and 542 nm.

The deprotonation of the mixed hydroxy/methoxy complex, 3, predicts a more intense transition at 551 nm with an oscillator strength of 0.083 that is assigned as a MLCT to a π^* molecular orbital on the unsubstituted bipyridine ligands, Table 7. Notably, the deprotonated complex 1, gives two predicted peaks at 545 nm and 542 nm with a combined oscillator strength of 0.080, Table 5. These results support the more broadened peak maxima observed in the deprotonated spectra of 1, which appears slightly sharper in complex 3. In addition, complex 3 deprotonated is further red shifted compared to 1 deprotonated, due to the added electron-donating effect of the methoxy group. The deprotonation of complex 3 also has similar new transitions that result from deprotonation. The first is a mixed MLLCT from an orbital of the metal with the deprotonated portion of the bipyridine, Fig. 7c, to the methoxy-substituted portion of the bipyridine, Fig. 7d ($(\text{ML}_2)\text{L}_2\text{CT}$). Similarly to complex 1, there is also a transition from the lone pair electron orbital on the oxygen from the deprotonated ligand to the unsubstituted

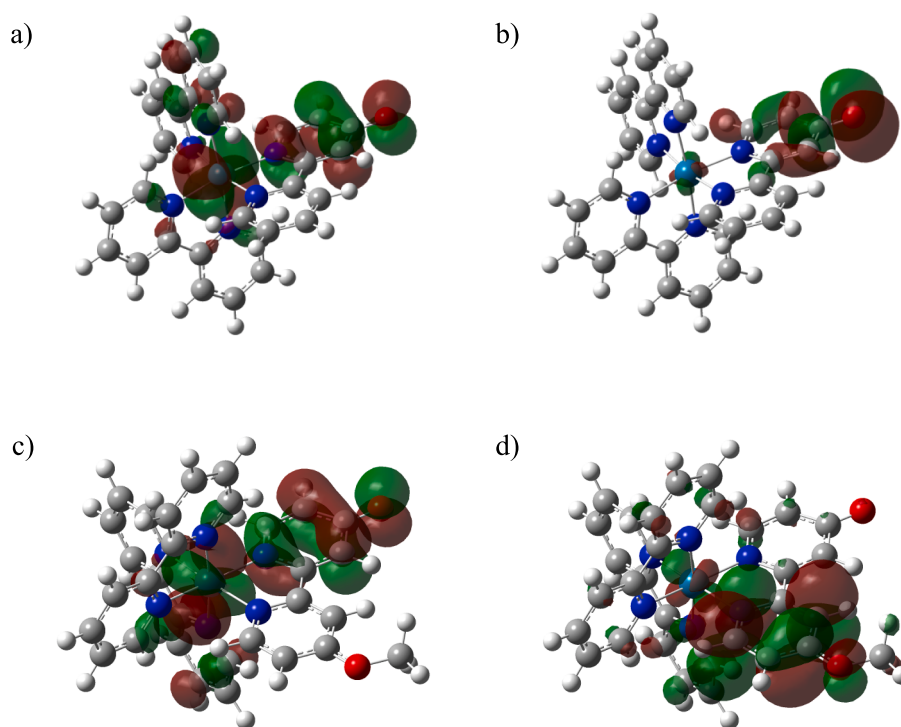


Fig. 7. Molecular orbitals involved in transitions of a) filled mixed metal- L_2 orbital (ML_2) of complex **1**, b) filled lone pair on oxygen $L_2(n)$ on complex **1**, c) filled mixed metal- L_2 orbital (ML_2) on complex **3**, and d) empty π^* orbital (L_2) on methoxy portion of the mixed hydroxy/methoxy ligand of complex **3**.

bipyridines ($L_2(n)L_1$).

4. Conclusions

The work reported herein describes the synthesis, electrochemical, and spectroscopic properties of three ruthenium complexes containing asymmetric ligands. Specifically, two of these complexes, $[Ru(bpy)_2(4bpyOH)]^{2+}$ (**1**) and $[Ru(bpy)_2(44'bpy(OH)(OMe))]^{2+}$ (**3**) have single deprotonatable hydroxy groups, that are more ideal for studying excited-state processes where clear delineation can be made between the protonated and deprotonated states compared to complexes with multiple deprotonatable groups, such as $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$. Both complexes **1** and **3** have a clear $1e^-/1H^+$ PCET that is pH dependent between pH ~ 1.6 and 6.0 for complex **1** and ~ 2.4 and 6.0 for complex **3**. This thermodynamic information is helpful for designing systems to study excited-state PCET processes where PCET does not occur in the ground state, but can be initiated by light sources. Both protonated complexes **1** and **3** have typical MLCT states in the visible region commonly associated with ruthenium polypyridyl complexes, however, upon deprotonation, inter-ligand charge transfer and mixed-metal ligand to ligand charge transfer transitions appear, demonstrating that the deprotonated portion of the ligand has a significant impact on electronic structure. Furthermore, the results reported herein indicate that the methoxy-substitution has similar electron-donating properties to the hydroxy-substitution. This indicates that the $44'bpy(OH)(OMe)$ ligand is a nicely comparable ligand to $44'bpy(OH)_2$ without the complications of multiple deprotonation possibilities.

CRediT authorship contribution statement

Kaitlyn R. Benson: Validation, Formal analysis, Investigation, Visualization. **Jaqueline Stash:** Validation, Investigation. **Katherine L. Moffa:** Investigation. **Russell H. Schmehl:** Conceptualization, Funding acquisition. **Timothy J. Dudley:** Methodology, Formal analysis, Investigation, Visualization. **Jared J. Paul:** Conceptualization, Methodology,

Formal analysis, Investigation, Writing - original draft, Visualization, Supervision, Project administration, Funding acquisition.

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.

Acknowledgments

Funding for this project comes from a grant from the National Science Foundation – Chemical Structure, Dynamics & Mechanisms B (CHE-1900536). This work was also supported by two Major Research Instrumentation grants from the National Science Foundation (CHE-1827930 and CHE-2018399). Support from the College of Liberal Arts and Sciences at Villanova University is gratefully acknowledged. Thank you to Mark Olson for running mass spectrometry samples. This work is dedicated to Robert L. Paul.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2021.115300>.

References

- [1] D.R. Weinberg, C.J. Gagliardi, J.F. Hull, C.F. Murphy, C.A. Kent, B.C. Westlake, A. Paul, D.H. Ess, D.G. McCafferty, T.J. Meyer, Proton-coupled electron transfer, *Chem. Rev.* 112 (7) (2012) 4016–4093, <https://doi.org/10.1021/cr200177j>.
- [2] V.R.I. Kaila, M.I. Verkhovsky, M. Wikström, Proton-coupled electron transfer in cytochrome oxidase, *Chem. Rev.* 110 (12) (2010) 7062–7081, <https://doi.org/10.1021/cr1002003>.
- [3] S. Hammes-Schiffer, Theory of proton-coupled electron transfer in energy conversion processes, *Acc. Chem. Res.* 42 (12) (2009) 1881–1889, <https://doi.org/10.1021/ar9001284>.

- [4] B.D. McCarthy, J.L. Dempsey, Decoding Proton-Coupled Electron Transfer with Potential-pK_a Diagrams, *Inorg. Chem.* 56 (3) (2017) 1225–1231, <https://doi.org/10.1021/acs.inorgchem.6b02325>.
- [5] 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/acsenenergylett.7b00063>.
- [6] A. Dey, N. Ghorai, A. Das, H.N. Ghosh, Proton-coupled electron transfer for photoinduced generation of two-electron reduced species of quinone, *J. Phys. Chem. B.* 124 (49) (2020) 11165–11174, <https://doi.org/10.1021/acs.jpcc.0c07809>.
- [7] J.L. Dempsey, J.R. Winkler, H.B. Gray, Proton-coupled electron flow in protein redox machines, *Chem. Rev.* 110 (12) (2010) 7024–7039, <https://doi.org/10.1021/cr100182b>.
- [8] C. Costentin, Electrochemical approach to the mechanistic study of proton-coupled electron transfer, *Chem. Rev.* 108 (7) (2008) 2145–2179, <https://doi.org/10.1021/cr068065t>.
- [9] G.A. Parada, Z.K. Goldsmith, S. Kolmar, B. Pettersson Rimgard, B.Q. Mercado, L. Hammarström, S. Hammes-Schiffer, J.M. Mayer, Concerted proton-electron transfer reactions in the Marcus inverted region, *Science* 364 (6439) (2019) 471–475.
- [10] R. Tyburski, T. Liu, S.D. Glover, L. Hammarström, Proton-coupled electron transfer guidelines, fair and square, *J. Am. Chem. Soc.* 143 (2) (2021) 560–576, <https://doi.org/10.1021/jacs.0c09106>.
- [11] C. Costentin, Proton-coupled electron transfer catalyst: homogeneous catalysis. Application to the catalysis of electrochemical alcohol oxidation in water, *ACS Catal.* 10 (12) (2020) 6716–6725, <https://doi.org/10.1021/acscatal.0c01195>.
- [12] C. Costentin, Proton-coupled electron transfer catalyst: heterogeneous catalysis. Application to an oxygen evolution catalyst, *ACS Catal.* 10 (14) (2020) 7958–7967, <https://doi.org/10.1021/acscatal.0c02532>.
- [13] B.H. Solis, S. Hammes-Schiffer, Proton-coupled electron transfer in molecular electrocatalysis: theoretical methods and design principles, *Inorg. Chem.* 53 (13) (2014) 6427–6443, <https://doi.org/10.1021/ic5002896>.
- [14] M.W. Kanan, D.G. Nocera, In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co²⁺, *Science* 321 (5892) (2008) 1072–1075, <https://doi.org/10.1126/science.1162018>.
- [15] S.W. Gersten, G.J. Samuels, T.J. Meyer, N. Carolina, Catalytic oxidation of water by an oxo-bridged ruthenium dimer, *J. Am. Chem. Soc.* 104 (1982) 4029–4030.
- [16] J.J. Concepcion, M.K. Brennaman, J.R. Deyton, N.V. Lebedeva, M.D.E. Forbes, J. M. Papanikolas, T.J. Meyer, Excited-state quenching by proton-coupled electron transfer, *J. Am. Chem. Soc.* 129 (22) (2007) 6968–6969, <https://doi.org/10.1021/ja069049g>.
- [17] N.V. Lebedeva, R.D. Schmidt, J.J. Concepcion, M.K. Brennaman, I.N. Stanton, M. J. Therien, T.J. Meyer, M.D.E. Forbes, Structural and pH dependence of excited state PCET reactions involving reductive quenching of the MLCT excited state of [Ru^{II}(bpy)₂(bpz)]²⁺ by hydroquinones, *J. Phys. Chem. A.* 115 (15) (2011) 3346–3356, <https://doi.org/10.1021/jp200381n>.
- [18] A.P. Gamiz-Hernandez, A. Magomedov, G. Hummer, V.R.I. Kaila, Linear energy relationships in ground state proton transfer and excited state proton-coupled electron transfer, *J. Phys. Chem. B.* 119 (6) (2015) 2611–2619, <https://doi.org/10.1021/jp508790n>.
- [19] M. Haumann, O. Bögershausen, D. Cherepanov, R. Ahlbrink, W. Junge, Photosynthetic oxygen evolution: H/D isotope effects and the coupling between electron and proton transfer during the redox reactions at the oxidizing side of photosystem II, *Photosynth. Res.* 51 (1997) 193–208, <https://doi.org/10.1023/A:1005861917596>.
- [20] F. Rappaport, J. Lavergne, Charge recombination and proton transfer in manganese-depleted photosystem II, *Biochemistry* 36 (49) (1997) 15294–15302, <https://doi.org/10.1021/bi971287o>.
- [21] R. Ahlbrink, M. Haumann, D. Cherepanov, O. Bögershausen, A. Mulkidjanian, W. Junge, Function of tyrosine Z in water oxidation by photosystem II: electrostatic promoter instead of hydrogen abstractor, *Biochemistry* 37 (1998) 1131–1142, <https://doi.org/10.1021/bi9719152>.
- [22] H.J. Eckert, G. Renger, Temperature dependence of P680⁺ reduction in O₂-evolving PS II membrane fragments at different redox states Si of the water oxidizing system, *FEBS Lett.* 236 (1988) 425–431, [https://doi.org/10.1016/0014-5793\(88\)80070-X](https://doi.org/10.1016/0014-5793(88)80070-X).
- [23] A. Guskov, J. Kern, A. Gabdulkhakov, M. Broser, A. Zouni, W. Saenger, Cyanobacterial photosystem II at 2.9-Å resolution and the role of quinones, lipids, channels and chloride, *Nat. Struct. Mol. Biol.* 16 (3) (2009) 334–342, <https://doi.org/10.1038/nsmb.1559>.
- [24] L. Qin, J. Liu, D.A. Mills, D.A. Proshlyakov, C. Hiser, S. Ferguson-Miller, Redox-dependent conformational changes in cytochrome c oxidase suggest a gating mechanism for proton uptake, *Biochemistry* 48 (23) (2009) 5121–5130, <https://doi.org/10.1021/bi9001387>.
- [25] M. Kuss-Petermann, O.S. Wenger, Mechanistic diversity in proton-coupled electron transfer between thiophenols and photoexcited [Ru(2,2'-Bipyrazine)₃]²⁺, *J. Phys. Chem. Lett.* 4 (15) (2013) 2535–2539, <https://doi.org/10.1021/jz4012349>.
- [26] C. Bronner, O.S. Wenger, Proton-coupled electron transfer between 4-cyanophenol and photoexcited ruthenium(I) complexes with different protonatable sites, *Inorg. Chem.* 51 (15) (2012) 8275–8283, <https://doi.org/10.1021/ic300834c>.
- [27] J.P. Kirby, J.A. Roberts, D.G. Nocera, Significant effect of salt bridges on electron transfer, *J. Am. Chem. Soc.* 119 (1997) 9230–9236, <https://doi.org/10.1021/ja970176+>.
- [28] J. Rosenthal, J.M. Hodgkiss, E.R. Young, D.G. Nocera, Spectroscopic determination of proton position in the proton-coupled electron transfer pathways of donor-acceptor supramolecule assemblies, *J. Am. Chem. Soc.* 128 (32) (2006) 10474–10483, <https://doi.org/10.1021/ja062430g>.
- [29] E.R. Young, J. Rosenthal, J.M. Hodgkiss, D.G. Nocera, Comparative PCET study of a donor-acceptor pair linked by ionized and nonionized asymmetric hydrogen-bonded interfaces, *J. Am. Chem. Soc.* 131 (22) (2009) 7678–7684, <https://doi.org/10.1021/ja809777j>.
- [30] K.A. Maghacut, A.B. Wood, W.J. Boyko, T.J. Dudley, J.J. Paul, Structural, electronic and acid/base properties of [Ru(tpy)(tpyOH)]²⁺ and [Ru(tpyOH)₂]²⁺ (tpy = 2,2':6',2''-terpyridine, tpyOH = 4'-hydroxy-2,2':6',2''-terpyridine), *Polyhedron* 67 (2014) 329–337, <https://doi.org/10.1016/j.poly.2013.09.029>.
- [31] D.C. Marelus, S. Bhagan, D.J. Chaboneau, K.M. Schroeder, J.M. Kamdar, A. R. McGettigan, B.J. Freeman, C.E. Moore, A.L. Rheingold, A.L. Cooksy, D.K. Smith, J.J. Paul, E.T. Papish, D.B. Grotjahn, How do proximal hydroxy or methoxy groups on the bidentate ligand affect [(2,2':6',2''-terpyridine)Ru(N, N)X] water-oxidation catalysts? Synthesis, characterization, and reactivity at acidic and near-neutral pH, *Eur. J. Inorg. Chem.* (2014), <https://doi.org/10.1002/ejic.201300826>.
- [32] D.J. Chaboneau, N.A. Piro, W.S. Kassel, T.J. Dudley, J.J. Paul, Reprint of: structural, electronic and acid/base properties of [Ru(bpy)(bpy(OH)₂)]²⁺ (bpy = 2,2'-bipyridine, bpy(OH)₂ = 4,4'-dihydroxy-2,2'-bipyridine), *Polyhedron* 114 (2016) 472–481, <https://doi.org/10.1016/j.poly.2016.05.042>.
- [33] E.J. Viere, A.E. Kuhn, M.H. Roeder, N.A. Piro, W.S. Kassel, T.J. Dudley, J.J. Paul, Spectroelectrochemical studies of a ruthenium complex containing the pH sensitive 4,4'-dihydroxy-2,2'-bipyridine ligand, *Dalt. Trans.* 47 (12) (2018) 4149–4161, <https://doi.org/10.1039/C7DT04554A>.
- [34] S. Klein, W.G. Dougherty, W.S. Kassel, T.J. Dudley, 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.* 50 (7) (2011) 2754–2763, <https://doi.org/10.1021/ic1017054>.
- [35] M.J. Fuentes, R.J. Bognanno, W.G. Dougherty, W.J. Boyko, W. Scott Kassel, T. J. Dudley, J.J. Paul, Structural, electronic and acid/base properties of [Ru(bpy(OH)₂)]²⁺ (bpy(OH)₂ = 4,4'-dihydroxy-2,2'-bipyridine), *Dalt. Trans.* 41 (2012) 12514–12523, <https://doi.org/10.1039/c2dt31706k>.
- [36] 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>.
- [37] N.G. Connelly, W.E. Geiger, Chemical redox agents for organometallic chemistry, *Chem. Rev.* 96 (2) (1996) 877–910, <https://doi.org/10.1021/cr940053x>.
- [38] J.T. Ballinger, G.J. Shugar, *Chemical Technicians' Ready Reference Handbook*, 2nd ed., McGraw-Hill Book Company, New York, New York, 1981.
- [39] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Iyaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, T. Nakai, H. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, K. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J. V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, 1st ed., Wallingford, CT, 2009.
- [40] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 7 (2005) 3297–3305.
- [41] Paul B. Hodgson, Fabrice H. Salique, The preparation of a stable 2-pyridylboronate and its reactivity in the Suzuki-Miyaura cross-coupling reaction, *Tetrahedron Lett.* 45 (4) (2004) 685–687, <https://doi.org/10.1016/j.tetlet.2003.11.068>.
- [42] Christoph Gütz, Arne Lützen, Synthesis of 2,2'-Bipyridines via Suzuki-Miyaura Cross-Coupling, *Synthesis (Stuttg)* 2010 (01) (2010) 85–90, <https://doi.org/10.1055/s-0029-1217082>.
- [43] Gregory J. Wilson, Geoffrey D. Will, Density-functional analysis of the electronic structure of tris-bipyridyl Ru(II) sensitizers, *Inorg. Chim. Acta.* 363 (8) (2010) 1627–1638, <https://doi.org/10.1016/j.ica.2010.01.002>.
- [44] S.M. Zakeeruddin, D.M. Fraser, M.-K. Nazeeruddin, M. Gratzel, Towards mediator design: characterization of tris-(4,4'-substituted-2,2'-bipyridine) complexes of iron (II), ruthenium(II) and osmium(II) as mediators for glucose oxidase of *Aspergillus niger* and other redox proteins, *J. Electroanal. Chem.* 337 (1992) 253–283.
- [45] Claude Daul, Evert J. Baerends, Pieter Vernooijs, A Density Functional Study of the MLCT States of [Ru(bpy)₃]²⁺ in D₃ Symmetry, *Inorg. Chem.* 33 (16) (1994) 3538–3543.
- [46] D. Paul Rillema, G. Allen, T.J. Meyer, D. Conrad, Redox properties of ruthenium(II) tris chelate complexes containing the ligands 2,2'-bipyrazine, 2,2'-bipyridine, and 2,2'-bipyrimidine, *Inorg. Chem.* 22 (11) (1983) 1617–1622.