Synthesis, crystal structure, electrochemical properties, and photophysical characterization of ruthenium(II) 4,4'-dimethoxy-2,2'-bipyridine polypyridine complexes

David A. Santos, An T. Vu, William W. Brennessel, Carly R. Reed and Robert N. Garner

ABSTRACT
A series of ruthenium(II) polypyridine complexes of the type [Ru(tpy)((CH$_3$O)$_2$bpy)(4-R-py)]$^{2+}$, where tpy = 2,2';6',2''-terpyridine, (CH$_3$O)$_2$bpy = 4,4'-dimethoxy-2,2'-bipyridine, and 4-R-py = pyridine (py, 2), 4-methoxypyridine (4-CH$_3$O-py, 3), 4-aminopyridine (4-NH$_2$-py, 4), were synthesized and their crystal structures, electronic absorption, luminescence, and electrochemical properties were investigated. The effect of adding electron-donating groups to the bidentate and monodentate ligand was investigated and compared with [Ru(tpy)(bpy)(py)]$^{2+}$ (1) where bpy = 2,2'-bipyridine. While anticipated trends were not observed for the Ru-N(6) bond length as 4-R-py was varied, noticeable modifications of the measured photophysical properties were observed. A red-shift of the metal-to-ligand charge transfer (MLCT) is observed from 466 nm in 1 to 474 nm, 478 nm, and 485 nm for 2–4, respectively. Additionally, a red-shift in the luminescence maxima is observed in 2–4 as compared to 1, with 4 exhibiting the greatest shift of more than 100 nm. Complexes 2–4 exhibited luminescence quantum yields of $2.7 \times 10^{-4}$, $7.2 \times 10^{-4}$, and $7.4 \times 10^{-4}$, respectively, which are increased compared to the quantum yield of $2.0 \times 10^{-4}$ in 1. These findings demonstrate systematic tuning of absorbance and luminescence properties of ruthenium polypyridine complexes by addition of π-donating substituents to the monodentate and bidentate ligand.

CONTACT Robert N. Garner, rgarner@uiwtx.edu, Department of Chemistry and Biochemistry, University of the Incarnate Word, San Antonio, TX 78209, USA; Carly R. Reed, creed@brockport.edu, Department of Chemistry and Biochemistry, SUNY Brockport, Brockport, NY, USA.

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1. Introduction

[Ru(tpy)(LL₁)(L₂)]²⁺ (tpy = 2,2';6',2''-terpyridine, LL₁ = bidentate ligand, and L₂ = monodentate ligand) complexes have received considerable attention due to their favorable photochemical and photophysical properties [1–6]. Complexes of this type have been investigated for potential application in information storage [5], photocatalysis [7], light-activated drug delivery [6, 8], and dye-sensitized solar cells [9, 10] due to the tunability of their excited-state properties [11].

The systematic optimization of complexes for increased stability in the dark and maximum ligand dissociation upon irradiation holds considerable promise for light-activated drug delivery [6, 8]. For example, the ligand dissociation quantum yield of the py (py = pyridine) ligand in [Ru(tpy)(bpy)(py)]²⁺ (1), where bpy = 2,2'-bipyridine, in CH₃CN when irradiated with λᵣᵣᵣ = 500 nm, is <10⁻⁴. When 6,6'-dimethyl-2,2'-bipyridine (Me₂bpy) is substituted for bpy to form [Ru(tpy)(Me₂bpy)(py)]²⁺, the ligand dissociation quantum yield increases by >1000 fold to 0.16. Here, the increased efficiency is attributed to increased steric strain caused by the methyl groups rather than the electronic effect of donating electron density [12]. Additionally, substituting electron-withdrawing groups, such as acetyl or trifluoromethyl, in the para position of the py ligand also increases the efficiency of photoinduced ligand dissociation in those complexes as compared to [Ru(tpy)(bpy)(py)]²⁺ [11]. The rate of photoinduced ligand dissociation of [Ru(tpy)(bpy)(4-trifluoromethylpyridine)]²⁺ in CH₃CN at λᵣᵣᵣ = 450 nm increases 15-fold relative to [Ru(tpy)(bpy)(py)]²⁺ under similar conditions [11].

Complexes with greater photostability and reduced susceptibility to photo-induced ligand dissociation are imperative for applications in sensing and dye-sensitized solar cells [9, 10]. Complexes of the type [Ru(tpy)(bpy)(4-R-py)]²⁺, where R = electron donating groups, such as methoxy and amino, have been shown to shut down the excited state ligand dissociation pathway thereby increasing luminescence [11]. [Ru(tpy)(bpy)(4-amino-pyridine)]²⁺ has an approximate 1.8-fold decrease in the rate of photoinduced ligand dissociation as compared to [Ru(tpy)(bpy)(py)]²⁺ in CH₃CN with λᵣᵣᵣ = 450 nm [11]. Additionally, the π-donating amino group induces a 10 nm red-shift in the lowest energy electronic band, which corresponds to a metal-to-ligand charge transfer (1MLCT). The phosphorescence maximum (λₑₑₑ) of [Ru(tpy)(bpy)(4-aminoypyridine)]²⁺ is red-shifted by 78 nm from 618 to 696 nm as compared to [Ru(tpy)(bpy)(py)]²⁺, and the quantum yield of
emission increases by fifty percent. The example of [Ru(tpy)(bpy)(4-aminopyridine)]^{2+}, with amino as a π-donating group on the py ligand, demonstrates that π-donating substituents in the 4 position of the py ligand induce a red-shift in absorption and emission, a decreased photoinduced ligand dissociation, and an increased emission quantum yield.

In this work, a series of complexes of the type [Ru(tpy)((CH$_3$O)$_2$bpy)(4-R-py)]^{2+}, where (CH$_3$O)$_2$bpy = 4,4′-methoxy-2,2′-bipyridine and 4-R-py = py (2), 4-methoxypyridine (3), and 4-aminopyridine (4), were synthesized and their structures and photophysical properties were investigated (Figure 1). In light of the previous work described above, the (CH$_3$O)$_2$bpy ligand was chosen to examine the effect of more strongly π-donating methoxy groups on the bpy ligand, in addition to the π-donating groups of methoxy and amino on the pyridine ligand, in hopes of discovering complexes that will provide excellent low energy absorption and emission qualities while being stable against unwanted ligand loss.

2. Experimental

2.1. Materials and methods

All reagents were purchased from commercial sources and used as received. Ligands tpy, (CH$_3$O)$_2$bpy, pyridine, 4-methoxypyridine, and 4-aminopyridine as well as NMR solvents and acetonitrile were purchased from Sigma Aldrich. Methanol was purchased from Pharmco. Ethanol, acetone, chloroform and diethyl ether were purchased from Fisher.
Scientific. RuCl₃ was purchased from Strem Chemicals. Ru(tpy)Cl₃ [13] and [Ru(tpy)((CH₃O)₂bpy)Cl]⁺ [14] were prepared according to previously reported methods.

¹H NMR and ¹³C NMR spectra were obtained on a Bruker Avance III 300 MHz spectrometer, and ESMS spectra were recorded on an Advion expression compact mass spectrometer. Electronic absorption, phosphorescence and emission quantum yield, and cyclic voltammetry measurements were all collected in CH₃CN at room temperature. Electronic absorption experiments were performed on an Agilent Cary 8454 photodiode array spectrophotometer using a 1 x 1 cm quartz cuvette. Emission experiments were conducted using a PTI Quantamaster 4 with an excitation wavelength (λ_exc) of 450 nm. Emission quantum yields were calculated using [Ru(bpy)₃]²⁺ in deoxygenated CH₃CN (Φ_em = 0.062) as a reference actinometer. For each sample, absorbance was matched (~0.1) at 450 nm [15, 16]. Electrochemical studies were performed on a Pine Research Instrumentation WaveNow potentiostat using a three-electrode cell with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. Dry acetonitrile from a VAC solvent purification system with 0.1 M tetra-n-butylammonium hexafluorophosphate as a supporting electrolyte was used for cyclic voltammetry measurements. Ferrocene (Fc) was added as an internal standard, and E₁/₂(Fc⁺/₀) = 0.389 V versus SCE was used as a reference for calculating the oxidation and reduction potentials of each complex [17].

2.2. Synthesis

(4,4'-Dimethoxy-2,2'-bipyridine-κ²N,N')(pyridine)(2,2':6',2'''-terpyridine-κ³N,N',N'')ruthenium(II) bis(hexafluoridophosphate): [Ru(tpy)(4-4'-((CH₃O)₂-bpy)(py))][PF₆]₂, 2, was synthesized by refluxing 100 mg (0.137 mmol) of [Ru(tpy)(4-4'-((CH₃O)₂-bpy)Cl][PF₆] and 220 mL of pyridine (2.75 mmol) in a 40 mL mixture of 1:1 ethanol and water for 5 h. The ethanol was evaporated, reducing the mixture’s volume by 50%. Approximately 5 mL of saturated ammonium hexafluorophosphate aqueous solution was then added to the solution. The resulting solid was collected by filtration, washed with 3 x 10 mL of cold water and diethyl ether, and dried under vacuum. The sample was dissolved in a minimal amount of acetone and precipitated with diethyl ether (106 mg, 84.26% yield). Elem. anal. calcd. for [Ru(C₁₅H₁₁N₃)(C₁₂H₁₂N₂O₂)(C₅H₅N)][PF₆]₂·0.5H₂O: C, 41.39%; H, 3.15%; N, 9.05%, found: C, 41.42%; H, 3.18%; N, 8.94%. ESMS calcd. for [2][PF₆]⁺: 774.65, found: 774.92. ¹H NMR (300 MHz) in acetone-d₆ (splitting, integration): 3.92 (s, 3H), 4.23 (s, 3H), 6.79 (dd, 1H), 7.33 (m, 3H), 7.61 (m, 3H), 7.89 (t, 1H), 8.01 (d, 2H), 8.18 (m, 4H), 8.29 (m, 4H), 8.55 (d, 1H), 8.73 (t, 3H), 8.83 (d, 2H) ppm. ¹³C NMR (75 MHz) in acetone-d₆: 57.15, 57.45, 111.71, 112.22, 114.10, 115.05, 124.80, 125.77, 127.45, 129.84, 136.63, 139.11, 139.44, 152.72, 153.25, 153.41, 154.02, 158.48, 159.30, 159.32, 159.50, 167.94, 168.42 ppm.

(4,4'-Dimethoxy-2,2'-bipyridine-κ²N,N')(4-methoxyppyridine-κN)(2,2':6',2'''-terpyridine-κ³N,N',N'')ruthenium(II) bis(hexafluoridophosphate): [Ru(tpy)(4-4'-((CH₃O)₂-bpy)(4-MeO-py)][PF₆]₂, 3, was synthesized in a similar manner as 2 using 100 mg (0.137 mmol) of [Ru(tpy)(4-4'-(CH₃O)₂-bpy)Cl][PF₆] and 280 mL of 4-methoxyppyridine (2.76 mmol). (75 mg, 57.73% yield). Elem. anal. calcd. for [Ru(C₁₅H₁₁N₃)(C₁₂H₁₂N₂O₂)(C₆H₇NO)][PF₆]·0.5H₂O: C, 41.35%; H, 3.26%; N, 8.77%, found: C, 41.36%; H, 3.12%; N, 8.63%. ESMS calcd. for [3][PF₆]⁺: 805.11, found: 804.96. ¹H NMR (300 MHz) in acetone-d₆ (splitting, integration): 3.77 (s, 3H),
3.93 (s, 3H), 4.24 (s, 3H), 6.79 (dd, 1H), 6.88 (dd, 2H), 7.32 (d, 1H), 7.63 (m, 3H), 7.72 (dd, 2H), 8.20 (m, 4H), 8.33 (m, 2H), 8.56 (d, 1H), 8.75 (m, 3H), 8.84 (d, 2H) ppm. \(^{13}\text{C}\) NMR (75 MHz) in acetone-\(d_6\): 56.68, 57.12, 57.41, 111.64, 112.13, 113.75, 114.06, 115.05, 124.65, 125.68, 129.80, 136.29, 139.32, 152.78, 153.36, 153.73, 153.90, 158.43, 159.32, 159.40, 159.53, 167.83, 167.94, 168.36 ppm.

\((4,4',4''\text{-Dimethoxy-2,2''-bipyridine-κ-N,N'})\)(4-aminopyridine-κ-N\(^2\))\((2,2':6',2''\text{-terpyridine-κ-N,N',N'}\)) ruthenium(II) bis(hexafluoridophosphate): \([\text{Ru(tpy})(4-4'-(CH}_3\text{O})_2\text{-bpy})(4-\text{NH}_2\text{-py})\text{(PF}_6\text{)}_2\text{, 4, was synthesized in a similar manner as 2, using 100 mg (0.137 mmol) of } [\text{Ru(tpy)}(4-4'-(CH}_3\text{O})_2\text{-bipyridine})\text{Cl}(\text{PF}_6)\text{] and 257.5 mg of 4-aminopyridine (2.74 mmol). (103 mg, 80.56% yield).\)

Elem. anal. calcd. for \([\text{Ru(C}_15\text{H}_{11}\text{N}_3\text{)(C}_12\text{H}_12\text{N}_2\text{O}_2\text{(C}_5\text{H}_6\text{N}_2)}\text{(PF}_6\text{)}_2\text{]}\): C, 41.12%; H, 3.13%; N, 10.49%. Found: C, 40.92%; H, 2.88%; N, 10.49%. ESMS calcd. for \([\text{4(PF}_6\text{)}]^+: 790.11, found: 789.93. \(^1\text{H}\) NMR (300 MHz) in acetone-\(d_6\): 3.89 (s, 3H), 4.22 (s, 3H), 6.23 (s, 2H), 6.44 (d, 2H), 6.74 (dd, 1H), 7.18 (d, 2H), 7.25 (d, 1H), 7.60 (m, 3H), 8.15 (m, 4H), 8.28 (m, 2H), 8.53 (d, 1H), 8.72 (m, 3H), 8.80 (d, 2H) ppm. \(^{13}\text{C}\) NMR (75 MHz) in acetone-\(d_6\): 57.10, 57.41, 111.59, 111.95, 112.02, 113.99, 115.05, 124.44, 125.50, 129.65, 135.71, 139.05, 151.54, 152.78, 153.34, 153.70, 156.41, 158.40, 159.35, 159.42, 159.55, 167.72, 168.29 ppm.

### 2.3. X-Ray crystallography

Single crystals of 2–4 were obtained through similar procedures. Each compound was dissolved in a mixture of acetonitrile, methanol, and chloroform and then layered with diethyl ether. The solutions were then stored in a \(-25^\circ\)C freezer and allowed to slowly evaporate until small dark red crystals formed.

Crystals were placed onto the tips of glass optical fibers and mounted on a Bruker SMART platform diffractometer equipped with an APEX II CCD area detector for data collection [18]. For each crystal a preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. Full data collections were carried out using MoK\(\alpha\) radiation (0.71073 Å, graphite monochromator) with frame times ranging from 45 to 60 seconds and at detector distances of approximately four cm. Randomly oriented regions of reciprocal space were surveyed: four or five major sections of frames were collected with 0.50° steps in \(\omega\) at four or five different \(\varphi\) settings and a detector position of \(-38^\circ\) in 2\(\theta\). The intensity data were corrected for absorption [19]. Final cell constants were calculated from the \(x\), \(y\), \(z\) centroids of approximately 4000 strong reflections from the actual data collections after integration [20].

Structures were solved using SHELXT [21] and refined using SHELXL [22]. Space groups were determined based on systematic absences or just intensity statistics. Direct-methods solutions were calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. In 4, the amino group’s hydrogen atoms were found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Full matrix least squares refinements on \(F^2\) were run to convergence.
In 4, highly disordered solvent was found in channels along [001]. Reflection contributions from this solvent were fixed and added to the calculated structure factors using the SQUEEZE routine of the program Platon [23], which determined there to be 52 electrons in 221 Å³ treated this way. Because the exact amount and identity of the solvent was not known, no solvent was included in the atom list or molecular formula. Thus all calculated quantities that derive from the molecular formula (e.g. F(000), density, molecular weight, etc.) are known to be inaccurate.

Crystallographic data for 2–4 are listed in Table 1.

### Table 1. Crystal data summary for structures 2, 3, and 4.

|   | 2               | 3               | 4               |
|---|-----------------|-----------------|-----------------|
| Formula | C₃₆H₃₄F₁₂N₈O₂P₂Ru | C₃₆H₃₄F₁₂N₈O₂P₂Ru | C₃₂H₂₉F₁₂N₇O₂P₂Ru |
| Formula weight | 1001.72         | 1022.73         | 934.63          |
| T (K) | 100.0(5)       | 100.0(5)       | 100.0(5)        |
| Wavelength (Å) | 0.71073        | 0.71073        | 0.71073         |
| Crystal system | Triclinic       | Triclinic       | Monoclinic      |
| Space group | P-1            | P-1            | P2₁/c           |
| a (Å) | 10.522(10)      | 11.070(15)      | 10.954(16)      |
| b (Å) | 13.184(12)      | 13.480(19)      | 25.242(4)       |
| c (Å) | 15.666(15)      | 14.654(2)       | 14.539(2)       |
| α (deg) | 105.2588(19)   | 103.875(3)     | 90              |
| β (deg) | 99.306(2)      | 95.071(3)      | 109.040(3)     |
| γ (deg) | 104.566(2)     | 105.904(3)     | 90              |
| V (Å³) | 1968.1(3)       | 2013.7(5)      | 3800.2(10)     |
| Z | 2               | 2               | 4               |
| μ (g cm⁻³) | 1.690          | 1.687          | 1.634          |
| Color, shape | Red, needle    | Red-orange, needle | Dark red, needle |
| Refl. collected | 43690          | 30452          | 41575          |
| Refl. independent | 15601         | 13265          | 4681           |
| Rint | 0.0835            | 0.0736          | 0.1386          |
| Refl. observed | 9861           | 8418           | 4611           |
| No. of parameters | 554            | 565            | 515            |
| GOF² on F² | 0.989          | 1.001          | 0.984          |
| R1 [I > 2σ(I)] | 0.0525         | 0.0566         | 0.0539         |
| wR² | 0.1019          | 0.1191         | 0.1359         |

In 4, highly disordered solvent was found in channels along [001]. Reflection contributions from this solvent were fixed and added to the calculated structure factors using the SQUEEZE routine of the program Platon [23], which determined there to be 52 electrons in 221 Å³ treated this way. Because the exact amount and identity of the solvent was not known, no solvent was included in the atom list or molecular formula. Thus all calculated quantities that derive from the molecular formula (e.g. F(000), density, molecular weight, etc.) are known to be inaccurate.

Crystallographic data for 2–4 are listed in Table 1.

### 3. Results and discussion

#### 3.1. Structure

The structure of 1 was previously reported [24], and the structures of 2–4 are shown in Figure 2. The three new complexes exhibit distorted octahedral geometry about the metal center. The Ru-N bond lengths from 2–4 show no significant difference compared to the structure of 1 (Table 2). Due to the large deviation in bond lengths for 1, 2–4 were analyzed separately for structural trends.

The shortest Ru-N bond in all three complexes occurs to the central tpy nitrogen, with the two terminal tpy Ru-N bond lengths being 0.11–0.12 Å longer. The Ru-N(2) bond of 2 is only slightly longer than 3, with no significant difference observed between 3 and 4. The Ru-N(3) bond of 4 is only slightly longer than 2, with no
significant differences observed between 3 and either 2 or 4. The Ru-N(1) bond shows no difference between 2, 3, and 4. The asymmetric coordination of the bipyridine results in a typical bpy Ru-N bond length cis to the tpy ligand and a longer Ru-N bond cis to the pyridine ligand. This elongation of the Ru-N(4) bond has been ascribed to steric crowding between the pyridine ligand and the bpy ligand [24]. However, on investigating the bond length in comparison to torsion between pyridine and bipyridine, no clear trend is observed (Figure 3 and Table 2).

However, we do notice slight trends with respect to Hammett parameters (Table S2) of the pyridine substituents and Ru-N(5) and Ru-N(4) bond lengths (Figure 3). There is a decrease in bond length of Ru-N(5) as the Hammett parameter increases and there is an increase in the Ru-N(4) bond length as the Hammett parameter increases. The Ru-N bond to the pyridine ligand is the longest in all four complexes. We had expected to see a trend in the Ru-N(6) bond lengths of 2–4 when compared to the Hammett parameters; however, while 3 is longer than 4, neither are significantly different from unsubstituted 2 and there is no trend observed (Figure 3).

Differences due to substitution at the 4,4′-positions of the bipyridine were also analyzed by comparing 2 to previously reported [Ru(tpy)(4,4′-dimethylbpy)(pyridine)][PF₆]₂, 5, and [Ru(tpy)(4,4′-bis(trifluoromethyl)bpy)(pyridine)][PF₆]₂, 6 (Table 2) [25]. As the Hammett parameter of the substituent (Table S2) on the bipyridine ligand becomes more positive, the Ru-N(4) bond decreases in length. The unusual length of the Ru-N(4) bond has previously been attributed to steric effects [24]; however, in this series we see that bond length increases with increasing dihedral angle between the bipyridine and pyridine (Figure S10). This may indicate that the Ru-N(4) bond length is

Table 2. Ru-N Bond distances (Å).

| Bond   | Bond 1° | Bond 2 | Bond 3 | Bond 4 | Bond 5° | Bond 6° |
|--------|---------|--------|--------|--------|---------|---------|
| Ru-N(1) | 2.078(6) | 2.072(2) | 2.075(3) | 2.069(4) | 2.085(2) | 2.072(3) |
| Ru-N(2) | 1.963(6) | 1.962(19) | 1.958(2) | 1.954(4) | 1.961(2) | 1.974(3) |
| Ru-N(3) | 2.079(7) | 2.071(2) | 2.075(3) | 2.078(4) | 2.055(2) | 2.081(3) |
| Ru-N(4) | 2.097(7) | 2.103(2) | 2.099(2) | 2.090(4) | 2.089(2) | 2.077(3) |
| Ru-N(5) | 2.060(6) | 2.052(2) | 2.061(3) | 2.066(4) | 2.056(2) | 2.057(3) |
| Ru-N(6) | 2.114(6) | 2.106(2) | 2.110(3) | 2.100(4) | 2.100(2) | 2.103(3) |

aFrom ref. [24]. bFrom ref. [25].

Figure 2. Thermal ellipsoid plot of (a) 2, (b) 3, and (c) 4 drawn with 50% probability level. Solvent, most hydrogen atoms, and counter ions omitted for clarity.

Table 2. Ru-N Bond distances (Å).
impacted by both electronics and steric effects. As is typical for these types of complexes, the Ru-N(2) bond is the shortest in all these complexes, where 6 has the longest Ru-N(2) bond of the three complexes, possibly due to the trans influence, though 2 and 5 do not differ significantly from each other (Figure S10).

The Ru-N(5) and Ru-N(6) bond lengths, respectively, show no significant differences across 2, 5, and 6. Finally, when analyzing the Ru-N(1) and Ru-N(3) bonds, 5 stands out the most for its differences in lengths. There is no obvious explanation for this, however, in viewing the distortion of the tpy ligand by analysis of the C15-N3-Ru1-N4 and C1-N1-Ru1-N4 dihedrals (Table S3), it may be possible that distortions accrue because of crystal packing.

### 3.2. Electronic absorption, emission, and electrochemistry

The absorption maxima, molar extinction coefficients, emission maxima and quantum yields, and redox potentials are summarized in Table 3. The cyclic voltammogram of 1 has been previously reported [11]. The oxidation potential of $+1.25\text{V}$ versus SCE in CH$_3$CN was attributed to Ru$^{III/II}$ couple, and the reduction potential of $-1.25\text{V}$ versus SCE in CH$_3$CN was attributed to the reduction of the tpy ligand. The reduction waves of 2–4 are in the range of $-1.29$ to $-1.33\text{V}$ versus SCE in CH$_3$CN, which is similar to 1 and other tpy containing Ru(II) polypyridine complexes and are attributed to the reduction of the tpy ligand. Complex 2 exhibits an oxidation wave at $+1.11\text{V}$ versus...
SCE in CH₃CN, which is similar to 1 and other Ru(II) polypyridyl complexes and are also assigned to the RuII/III couple. Complexes 3 and 4 exhibit an oxidation wave at +1.07 and +1.00 V versus SCE, respectively, which are also attributed to the RuII/III couple. The observed cathodic shift of 2–4 from +1.11 to +1.00 V versus SCE has a linear correlation with Hammett constants of the R-groups in 2–4 (Figure S14). This shift is due to the increasing strength of the π-donating groups, which destabilize the Ru(dπ) orbitals.

The electronic absorption spectra of 1–4 are shown in Figure 4. The electronic absorption of 1 has been previously reported and exhibits characteristic π-π* transitions at 288 and 312 nm localized in the tpy and bpy ligands [11]. Electronic absorptions of 2–4 exhibit transitions at 272 and 315 nm that can be attributed to π-π* transitions localized on the tpy and (CH₃O)₂bpy ligands. Complex 1 exhibits a metal-to-ligand charge transfer (1MLCT) at 466 nm, which has been reported as Ru(dπ)→tpy/bpy(π*). Similarly, the 1MLCT of 2 is observed at 474 nm and is attributed to the Ru(dπ)→tpy/(CH₃O)₂bpy(π*). This represents an 8 nm red-shift due to methoxy substituents on the (CH₃O)₂bpy. The 1MLCT is observed at 478 and 485 nm for 3 and 4, respectively. A linear correlation is observed with the 1MLCT absorption maxima (λabs) and Hammett parameters of the 4-R-py ligand in 2–4 (Figure S14). This red-shift of 4 nm in 3 and 11 nm in 4 as compared to 2 is similar to the red-shift observed of 4 nm in [Ru(tpy)(bpy)(4-methoxypyridine)]²⁺ and 10 nm in [Ru(tpy)(bpy)(4-aminopyridine)]²⁺ as compared to 1. The red-shift in the latter complexes and in 3 and 4 is caused by the increased electron-donation of the 4-MeO-py and 4-NH₂-py ligand. A plot of ΔE_{redox} (E_{ox}}

### Table 3. Absorption maxima and molar extinction coefficients, emissions maxima, luminescence quantum yields, and redox potentials of 1–4.

| Complex | λ_{abs}/nm (ε/× 10³ M⁻¹ cm⁻¹)ᵃ | λ_{em}/nmᵇ,c | Φₘₑₜᵃ | E_{1/2}/Vᶜ |
|---------|----------------------------------|---------------|--------|-------------|
| 1       | 288 (33.2), 312 (33.6), 418 sh (6.3) 466 (8.9) 618 0.00020 +1.25, −1.25 |
| 2       | 272 (40.3), 315 (39.0), 420 sh (6.5), 474 (9.0) 697 0.00027 +1.11, −1.29 |
| 3       | 272 (37.9), 315 (36.4), 420 sh (5.2), 478 (7.9) 695 0.00072 +1.07, −1.29 |
| 4       | 272 (52.9), 315 (45.3) 425 sh (6.0), 485 (9.1) 720 0.00074 +1.00, −1.33 |

ᵃMeasured in acetonitrile at 298 K.ᵇλ_{exc} = 450 nm.ᶜvs. SCE in CH₂CN with 0.1 M N(n-C₄H₉)₄PF.ᵈFrom ref. [11].

Figure 4. Electronic absorption spectra of 1 (black solid line), 2 (blue dashed line), 3 (red dotted line), and 4 (green dash dot line) at 298 K in acetonitrile.
– $E_{\text{red}}$ versus $\lambda_{\text{abs}}$ of 1–4 (Figure S15) shows the decrease in $\Delta E_{\text{redox}}$ corresponds to a red-shift in the $^1$MLCT of 1–4, respectively. Methoxy groups on the bpy in 2–4 and the methoxy and amino groups on the py in 3 and 4, respectively, increase the $\pi$-donating ability of the ligands, which causes a destabilization of the Ru(d$\pi$) HOMO orbitals. Conversely, the reduction potential of the tpy($\pi^*$) LUMO is relatively stable. Taken together, this will decrease the energy gap between the ground state and the $^1$MLCT, which explains the observed red-shift of the $^1$MLCT in 1–4. This is in agreement with previous studies [11]. The overall 19 nm red-shift of the $^1$MLCT from 466 nm in 1 to 485 nm in 4 demonstrates the combined effect of electron-donating groups added to the bpy and py ligands.

The luminescence spectra of 1–4 in CH$_3$CN at 298 K are shown in Figure 5. The luminescence of 1 has been previously reported and exhibits an emission maximum ($\lambda_{\text{em}}$) at 618 nm ($\Phi_{\text{em}} = 0.00020$) [11], which has been assigned to the Ru $\rightarrow$ tpy/bpy $^3$MLCT state. Emission maxima of 2–4 are observed at 697, 695, and 720 nm, respectively, and are assigned to the Ru $\rightarrow$ tpy/(CH$_3$O)$_2$bpy $^3$MLCT state. The 79 nm red-shift from 1 to 2 demonstrates the effect of increased electron-donation of the (CH$_3$O)$_2$bpy ligand compared to unsubstituted bpy. The shift caused by the addition of two methoxy groups to the bpy ligand is over four times greater than the shift of 17 nm observed from only the addition of one methoxy group to the py ligand in [Ru(tpy)(bpy)(4-CH$_3$O-py)]$^{2+}$ [11]. This suggests that the addition of $\pi$-donating groups on the bpy ligand is more effective at destabilizing Ru(d$\pi$) orbitals, causing a large red-shift in $\lambda_{\text{em}}$. Conversely, the $\Phi_{\text{em}}$ increased 35% from 0.00020 in 1 to 0.00027 in 2, but increased 115% from 1 to [Ru(tpy)(bpy)(4-CH$_3$O-py)]$^{2+}$ (0.00043) [11]. Previous reports suggest that more $\pi$-donating ligands cause an increase in $\Phi_{\text{em}}$ by destabilizing the Ru($\sigma^*$) orbitals thereby increasing the energy of the triplet ligand field ($^3$LF) state, widening the $\Delta E$ between the $^3$MLCT and the $^3$LF, which makes a competing pathway to the phosphorescence less likely [11]. Taken together, these data suggest that the addition of CH$_3$O groups on the bpy ligand has a greater effect on the Ru(d$\pi$) orbitals and the red shift of the $\lambda_{\text{em}}$, whereas, the addition of CH$_3$O on the py ligand

![Figure 5. Normalized emission spectra of 1 (black solid line), 2 (blue dashed line), 3 (red dotted line), and 4 (dash dot line) at 298 K in acetonitrile.](image-url)
has a greater effect on the Ru(σ*) orbitals and $\Phi_{em}$. This is further confirmed by emission data from 3, which exhibits a similar red-shift of its emission maximum as 2 compared to 1, however the $\Phi_{em}$ increases 160% to 0.00072 in 3 as compared to 2. Complex 4 has the strongest σ-donating ligand in 4-NH$_2$-py and further red-shifts the $\lambda_{em}$ to 720 nm and has the highest $\Phi_{em}$ at 0.0074. This seems to indicate that the stronger π-donating groups will continue to increase the red-shift of the $\lambda_{em}$, however, the effect on $\Phi_{em}$ may plateau. This plateau could be a result of non-radiative decay from the triplet state coming into play due to the decrease in ΔE between the ground state and triplet excited state. Given the relationship of the σ-donating ligands and $\lambda_{em}$ discussed above, we were surprised to observe that a linear correlation is not observed in the plot of $\lambda_{em}$ versus the Hammett parameters in 2–4 (Figure S14). The results presented here show that the $\lambda_{em}$ and $\Phi_{em}$ can be independently tuned by placement of the π-donating groups on either the bidentate or monodentate ligand.

4. Conclusion

The synthesis and structure of three new complexes, [Ru(tpy)((CH$_3$O)$_2$bpy)(py)]$^{2+}$ (2), [Ru(tpy)((CH$_3$O)$_2$bpy)(4-MeO-py)]$^{2+}$ (3), and [Ru(tpy)((CH$_3$O)$_2$bpy)(4-MeO-py)]$^{2+}$ (4), are reported, and their properties were investigated and compared to [Ru(tpy)(bpy)(py)]$^{2+}$ (1). The addition of electron-donating methoxy groups to the bpy as well as methoxy and amino groups to the py generally showed a red-shift of the absorbance and emission maxima and an increase in quantum yield of emission. However, the π-donating groups on the bpy ligand have a greater effect on the emission maxima, and the π-donating groups on the py ligand have a greater effect on the quantum yield of emission. These results demonstrate the ability to tune the photophysical properties of Ru(II) polypyridine complexes, which may be useful in studying and developing dye-sensitized solar cells and luminescent sensors.

Supplemental material

Supporting information includes $^1$H NMR and $^{13}$C NMR spectra, ESI mass spectra, cyclic voltammograms, and Hammett graphs of 2–6. CCDC 2111562, 2111563, and 2111564 contain the supplementary crystallographic data for 2–4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223–336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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ORCID

David A. Santos http://orcid.org/0000-0003-0712-9125
William W. Brennessel http://orcid.org/0000-0001-5461-1825
Carly R. Reed http://orcid.org/0000-0003-0268-1017
Robert N. Garner http://orcid.org/0000-0003-0888-3322

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