Tuning the Excited State Properties of Ruthenium (II) Complexes with a 4-Substituted Pyridine Ligand

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Abstract. A series of complexes of the type $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})]^{2+}$, where tpy = 2,2';6',2''-terpyridine, bpy = 2,2'-bipyridine, and 4-R-py = pyridine (py, **1**), 4-methoxypyridine (4-CH₃O-py, **2**), 4-aminopyridine (4-NH₂-py, **3**), 4-acetylpypyridine (4-Ac-py, **4**) and 4-trifluoromethylpyridine (4-CF₃-py, **5**), were synthesized and the effect of the pyridine substitution on the ground and excited state properties was examined. Cyclic voltammetry shows that an electron-donating substituent on the pyridine ligand results in complexes that are more easily oxidized, as is the case in **2** and **3**, whereas the electron-withdrawing substituents on the pyridine in **4** and **5** result in more positive oxidation potential. The electronic absorption spectra of **2** and **3** feature a detectable red shift of the metal-to-ligand charge transfer (¹MLCT) as compared to **1**. Additionally, the ¹MLCT maxima of **4** and **5** are blue shifted relative to **1**. Complexes **1** – **3** exhibit phosphorescence with luminescence quantum yields of 2.0×10^{-4} , 4.3×10^{-4} , and 3.1×10^{-4} , respectively. The emission quantum yields of **4** and **5** are approximately an order of magnitude lower, 5×10^{-5} and 4×10^{-5} . Upon irradiation in CH₃CN ($\lambda_{\text{irr}} \geq 395$ nm) all five complexes undergo photoinduced ligand exchange with the solvent to form $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$. This process is completed more rapidly in **4** (30 mins) and **5** (10 mins) as compared to **1** (90 mins), **2** (240 mins) and **3** (>24 hours). Theoretical calculations show that the electron-donating groups increase the energy difference between the ligand field state (LF) and MLCT while the electron-withdrawing groups decrease this value, giving rise to the different excited state properties. These findings demonstrate the synthetic tuning of the series of complexes, which can be useful to vary the photochemistry.

Keywords: Ruthenium (II) complexes, Photochemistry, Photoinduced ligand dissociation

1. Introduction

Ruthenium(II) polypyridyl complexes, such as $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine), have been investigated for application in photocatalysis [1,2], sensing [3], solar energy conversion [4–6], and photochemotherapy [7–9] because of their favorable excited state properties. Upon absorption of a photon by $[\text{Ru}(\text{bpy})_3]^{2+}$, its singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) state is populated, which then undergoes fast (15-40 fs) intersystem crossing to the $^3\text{MLCT}$ state [10,11]. From this state, the molecule can radiatively or non-radiatively decay to the ground state or thermally populate the triplet ligand field (^3LF) state [10,11]. $[\text{Ru}(\text{bpy})_3]^{2+}$ is relatively highly emissive, with a quantum yield of emission (Φ_{em}) of 0.062 in CH_3CN [12], while a similar complex, $[\text{Ru}(\text{tpy})_2]^{2+}$ ($\text{tpy} = 2':6',2''$ -terpyridine), is nonemissive at 298 K [13,14]. This difference is explained by the fact that the deviations from octahedral geometry around the Ru(II) center impaired by tpy makes it a weaker field ligand, thus lowering the energy of the metal-centered state, ^3LF , which serves as a nonradiative decay pathway.

The effect on photophysical properties of the addition of electron-withdrawing and electron-donating substituents to $[\text{Ru}(\text{tpy})_2]^{2+}$ have been previously investigated [15–18]. Homoleptic complexes with electron-withdrawing groups, $[\text{Ru}(\text{tpy-X})_2]^{2+}$ ($\text{X} = \text{Cl}, \text{CH}_3\text{SO}_2$), typically exhibit an increase of Φ_{em} [15], whereas complexes with electron-donating groups are nonemissive ($\text{X} = \text{EtO}, \text{OH}, (\text{CH}_3)_2\text{N}$). Heteroleptic complexes with mixed electron-donating and -withdrawing groups, $[\text{Ru}(\text{tpy-X})(\text{tpy-Y})]$, show a decrease in Φ_{em} compared to the respective homoleptic parent complex with the electron-withdrawing ligand [15]. However, recent studies show that the addition of a strong σ -donating groups on one of the ttpy ligand of $[\text{Ru}(\text{ttpy})_2]^{2+}$ ($\text{ttpy} = 4'-(4\text{-methylphenyl})-2,2':6',2''$ -terpyridine), a weakly emissive complex ($\Phi_{\text{em}} = 0.00003$), to generate $[\text{Ru}(\text{ttpy})(\text{tbtpy})]^{2+}$ ($\text{tbtpy} = 4,4',4''$ -tri-tert-butyl-2,2':6',2''-terpyridine) more than

doubles the Φ_{em} to 0.00007 [18]. This effect is understood to arise from the increased energy barrier from the $^3\text{MLCT}$ to the ^3LF state caused by the sigma donation. The effect of 4-substituted pyridine ligands (4-R-py) on ground and excited state properties has been the subject of investigation in many transition metal systems [19–23]. For example, the irradiation of a series of $[\text{Ru}(\text{tpy})(\text{dppz})(4\text{-R-py})]^{2+}$ complexes where dppz = dipyrido[3,2-a:2',3'-c]phenazine and py = pyridine with $\text{R} = \text{N}(\text{CH}_3)_2$, NH_2 , OCH_3 , H , and NO_2 , show increased $^1\text{O}_2$ production for complexes with more sigma-donating 4-R-py ligands [21]. This results was attributed to the increased $^3\text{MLCT}$ lifetime of these complexes, but could also be due to an increase in the $^3\text{MLCT} - ^3\text{LF}$ energy barrier. The ^3LF state has also been implicated in photoinduced ligand exchange because of the $\text{Ru-L}(\sigma^*)$ character of the state [24–26]. Complexes with an accessible ^3LF state and monodentate ligands, such $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$, undergo ligand dissociation of the monodentate ligand when irradiated with visible light [27]. Moreover, it has been shown that the addition of sterically bulky ligands to the complex can enhance photoinduced ligand exchange efficiency [28–30]. For example, an increase in ligand exchange quantum yield of pyridine of three orders of magnitude was observed in the more sterically bulky complex, $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ (Me_2bpy is 6,6'-methyl-2,2'-bipyridine), as compared with the unsubstituted bpy complex $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ ($\lambda_{\text{irr}} = 500 \text{ nm}$) [28].

In the present work, the photochemistry and photophysics of $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})]^{2+}$, where 4-R-py = pyridine (py , **1**), 4-methoxypyridine (4-MeO-py, **2**), 4-aminopyridine (4-NH₂-py, **3**), 4-acetypyridine (4-Ac-py, **4**), and 4-trifluoromethylpyridine (4-CF₃-py, **5**), are compared. The molecular structures of the complexes are shown in Fig. 1. The R group of the 4-R-py ligand is electron-donating in **2** and **3** and electron-withdrawing in **4** and **5**. Density functional theory (DFT) calculations were employed to aid in the understanding of experimental observations. Cyclic

Fig. 1. Molecular structures of **1** – **5**.

voltammetry and theoretical calculations show the effect of the pyridine substituent on the electronic structure of the complexes. Additionally, luminescence quantum yields and photolysis demonstrate the effect of these groups on excited state properties. These findings may be of interest to investigators aiming to increase ligand exchange quantum yields for applications in drug delivery and caged active molecules, as well as to those who need to eliminate the ligand dissociation pathway, such as for the stable complexes necessary in dye-sensitized solar cells and in sensors.

2. Experimental Section

2.1 Materials

The ligands 2,2'-bipyridine, 2,2':6',2''-terpyridine, pyridine, 4-methoxypyridine, 4-aminopyridine, 4-acetypyridine, and 4-trifluoromethylpyridine, as well as the solvents ethanol, diethyl ether, acetonitrile, deuterated acetonitrile, and deuterated acetone were purchased from

Sigma-Aldrich and used as received. Acetone was purchased from Flinn Scientific. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Strem Chemicals. $\text{Ru}(\text{tpy})\text{Cl}_3$ [31], $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}](\text{PF}_6)$ [32], and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})](\text{PF}_6)_2$ (**1**) [33] were prepared according to literature reports.

2.2 Synthesis of $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})](\text{PF}_6)_2$ complexes

2.2.1 $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-MeO-py})](\text{PF}_6)_2$, **2**

$[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-MeO-py})](\text{PF}_6)_2$ was synthesized by refluxing 255 mg (0.380 mmol) of $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}](\text{PF}_6)$ and 800 μL (7.88 mmol) of 4-methoxypyridine in a 50 mL mixture of 1:1 ethanol and water under nitrogen for 6 h. Excess solid ammonium hexafluorophosphate was added and the mixture was evaporated to dryness. The crude product was then purified using silica chromatography using 100:1 mixture of acetone and saturated aqueous NH_4PF_6 . The dark orange band was collected and solvent was removed under reduced pressure. The product was dissolved in minimal acetone, precipitated with cold water, and stored in a refrigerator overnight. The mixture was filtered and dried under vacuum (0.278 g, 82% yield). Elem. anal. calcd. for $[\text{Ru}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_6\text{H}_7\text{NO})](\text{PF}_6)_2 \cdot 0.5\text{C}_3\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}$: C, 40.13%; H, 3.63%; N, 8.64%, found: C, 40.08%; H, 3.34%; N, 8.34%. ESMS calcd. for $[\text{2}(\text{PF}_6)]^+$: 745, found: 745. ^1H NMR (300 MHz) in acetone- d_6 δ (splitting, integration) 3.84(s, 3H), 6.90 (d, 2H), 7.23 (t, 1H), 7.61 (m, 3H), 7.74 (d, 2H), 7.99 (m, 2H), 8.12 (d, 2H), 8.19 (t, 2H), 8.37(t, 1H), 8.46 (t, 1H), 8.71(d, 1H), 8.76(d, 2H), 8.86(d, 2H), 8.97 (d, 2H).

2.2.2 $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-NH}_2\text{-py})](\text{PF}_6)_2$, **3**

$[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-NH}_2\text{-py})](\text{PF}_6)_2$ was synthesized by refluxing 50 mg (0.075 mmol) of $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}](\text{PF}_6)$ and 701 mg (7.45 mmol) 4-aminopyridine in a 20 mL mixture of 1:1

ethanol and water under nitrogen for 24 h. The reaction solvent mixture was concentrated to approximately half volume and cooled to room temperature. Solid NH_4PF_6 was added to the mixture and the precipitate was collected using vacuum filtration. The crude product was recrystallized using a 1:1 mixture of ethanol and water, collected using vacuum filtration, and washed with 20 mL cold water and 20 mL diethyl ether. A second recrystallization using hot water and ethanol (2:1) was followed by precipitation overnight in the refrigerator. The mixture was filtered and dried under vacuum (0.012 g, 18% yield). Elem. anal. calcd. for $[\text{Ru}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_5\text{H}_6\text{N}_2)](\text{PF}_6)_2 \cdot 1.5\text{H}_2\text{O}$: C, 39.97%; H, 3.13%; N, 10.88%, found: C, 39.89%; H, 2.94%; N, 10.87%. ESMS calcd. for $[\mathbf{3}(\text{PF}_6)]^+$: 730, found: 730. ^1H NMR (300 MHz) in acetone- d_6 δ (splitting, integration) 6.29(s, 2H), 6.49(d, 2H), 7.23(m, 3H), 7.59(m, 3H), 7.95(t, 1H), 8.09(m, 3H), 8.18(t, 2H), 8.36(t, 1H), 8.44(t, 1H), 8.71(d, 1H), 8.76(d, 2H), 8.86(d, 2H), 8.98(d, 1H), 9.03(d, 1H).

2.2.3 $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-Ac-py})](\text{PF}_6)_2$, **4**

$[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-Ac-py})](\text{PF}_6)_2$ was synthesized by refluxing 61 mg (0.091 mmol) of $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}](\text{PF}_6)$ and 201 μL (1.82 mmol) of 4-acetylpyridine in 30 mL of 1:1 ethanol and water under nitrogen for 6 h. Solid NH_4PF_6 was added to the solution and the solvent was completely removed. The crude solid was dissolved in acetone and the solution was filtered. The filtrate was concentrated and product was precipitated with diethyl ether. The product was collected by filtration and dried under vacuum (0.053 g, 65% yield). Elem. anal. calcd. for $[\text{Ru}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_7\text{H}_7\text{NO})](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$: C, 40.99%; H, 3.23%; N, 8.96%, found: C, 40.59%; H, 2.82%; N, 9.13%. ESMS calcd. for $[\mathbf{4}(\text{PF}_6)]^+$: 757, found: 757. ^1H NMR (300 MHz)

in acetone- d_6 δ (splitting, integration) 2.52(s, 3H), 7.26(t, 1H), 7.63(m, 3H), 7.72(d, 2H), 7.99(m, 2H), 8.15(d, 2H), 8.21(t, 2H), 8.29(d, 2H), 8.44(m, 2H), 8.75(m, 3H), 8.88(d, 2H), 8.99(m, 2H).

2.2.4 $[Ru(tpy)(bpy)(4-CF_3-py)](PF_6)_2$, **5**

$[Ru(tpy)(bpy)(4-CF_3-py)](PF_6)_2$ was synthesized by refluxing 153 mg (0.228 mmol) of $[Ru(tpy)(bpy)Cl](PF_6)$ and 528 μ L (4.56 mmol) of 4-trifluoromethylpyridine in 40 mL of ethanol and water (1:1) under nitrogen for 5 h. The reaction mixture was concentrated to approximately 10 mL and NH_4PF_6 was added. The precipitate was collected by vacuum filtration. The crude product was then purified by silica chromatography using a mixture of acetone and saturated aqueous NH_4PF_6 (100:1). The orange fraction was collected, concentrated, and precipitated with cold water. The product was collected using filtration and dried under vacuum (0.025 g, 12% yield). Elem. anal. calcd. for $[Ru(C_{15}H_{11}N_3)(C_{10}H_8N_2)(C_6H_4F_3N)](PF_6)_2 \cdot 1.5C_3H_6O$: C, 42.02%; H, 3.18%; N, 8.28%, found: C, 42.04%; H, 3.10%; N, 8.26%. ESMS calcd. for $[5(PF_6)]^+$: 783, found: 783. 1H NMR (300 MHz) in acetone- d_6 δ (splitting, integration) 7.27(t, 1H), 7.63(m, 5H), 8.00(m, 2H), 8.20(m, 4H), 8.44(m, 4H), 8.76(m, 3H), 8.88(d, 2H), 9.00(d, 1H), 9.09(d, 1H).

2.3. Instrumentation and physical measurements

Electronic absorption measurements were performed on an Agilent Cary 8454 photodiode array spectrophotometer, and emission measurements were collected on a PTI Quantamaster 4. 1H -NMR spectra were obtained on a Bruker Advance III 300 MHz spectrometer, ESMS spectra were recorded on an Advion expression compact mass spectrometer, and IR spectra were recorded on a Thermo Scientific Nicolet iS 5 FT-IR with an iD7 ATR attachment. Electrochemical studies were performed on a Pine Research Instrumentation WaveNow potentiostat using dry solvent from

a VAC solvent purification system. A 75 W Xe arc lamp (USHIO) in an OBB PowerArc lamp housing equipped with a universal power supply was used for photolysis experiments. Wavelengths for irradiation were selected with a long-pass filter (Newport).

Electronic absorption measurements were made in CH₃CN at room temperature in a 1 x 1 cm quartz cuvette. Solutions used in phosphorescence experiments were deoxygenated by bubbling with argon for 15 minutes before use. Emission quantum yields were calculated using [Ru(bpy)₃]²⁺ in deoxygenated CH₃CN ($\Phi_{\text{em}} = 0.062$) as a reference actinometer [12]. Each sample was absorbance matched (~0.1) at the excitation wavelength of 450 nm [18]. Cyclic voltammetry measurements were performed using a three electrode cell with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode, using dry CH₃CN with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Ferrocene (Fc) was added as an internal standard, and $E_{1/2}(\text{Fc}^{+/0}) = 0.389$ V vs SCE was used as a reference for calculating the oxidation and reduction potentials of each complex [34]. An absorbance of approximately 0.5 at the λ_{max} of each sample was used for each photolysis experiment.

2.4. Theoretical calculations

All calculations were performed in the gas phase. Density functional theory (DFT) calculations were performed using the Gaussian 09 program [35]. The B3LYP [36–38] functional along with the 6-31G* basis set for H, C, F, N, O, and S [39], and the SDD energy-consistent pseudopotentials for Ru were used [40]. Geometries were fully optimized using the criteria of the respective programs. Orbital analysis was completed with GaussView [41]. Electronic singlet to singlet transitions were calculated using time-dependent DFT (TDDFT) within the Gaussian 09 program. GaussSum 3.0 was used in data analysis [42].

Table 1. Absorption Maxima and Molar Extinction Coefficients, Emission Maxima, Luminescence Quantum Yields, and Redox Potentials of **1–5**

Complex	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^a	$\lambda_{\text{em}}/\text{nm}$ ^a	Φ_{em} ^a	$E_{1/2}/\text{V}$ ^b
1	288 (33.2), 312 (33.6), 418 sh (6.3) 466 (8.9)	618	0.00020	+1.25, −1.25
2	289 (36.353), 313 (36.7), 418 sh (5.0) 470 (7.7)	635	0.00043	+1.20, −1.26
3	289 (45.8), 314 (42.2), 421 sh (6.2), 476 (9.4)	696	0.00031	+1.10, −1.29
4	286 (39.1), 312 (36.7), 433 (12.7), 470 sh (10.8)	646	0.00005	+1.27, −1.23
5	286 (40.3), 311 (38.4), 422 sh (10.2), 460 (10.5)	658	0.00004	+1.28, −1.21

^aMeasured in acetonitrile at 298 K. ^bvs SCE in CH₃CN with 0.1 M N(*n*-C₄H₉)₄PF

3. Results and Discussion

3.1. Electronic Absorption, Emission, and Electrochemistry

The electronic absorption maxima, molar extinction coefficients, emission properties, and oxidation and reduction potentials of **1 – 5** are listed in Table 1, and their electronic absorption spectra are shown in Fig. 2. All complexes exhibit a characteristic $\pi\pi^*$ transition localized on the tpy and bpy ligands in the UV regions (Table 1). Additionally, the lowest energy band for each

Fig. 2. Electronic absorption spectra of complexes **1** (black solid line), **2** (red dotted line), **3** (blue dash line), **4** (pink dash dot line), and **5** (green dash dot dot line) at 298 K in acetonitrile.

complex is assigned as a metal-to-ligand charge transfer ($^1\text{MLCT}$) attributed to $\text{Ru}(\text{d}\pi) \rightarrow \text{tpy/bpy}(\pi^*)$ transitions for **1** – **3**, and the $\text{Ru}(\text{d}\pi) \rightarrow \text{tpy/bpy/4-R-py}(\pi^*)$ transition for **4** and **5**, with maxima in the visible region, 418 – 476 nm. The $^1\text{MLCT}$ of complex **1** is observed at 466 nm ($\epsilon = 8900 \text{ M}^{-1} \text{ cm}^{-1}$), which is in close agreement with previous reports [28,33]. Complexes **2** and **3** in which the 4-R-py ligand contain an electron donating R group (methoxy or amino) show a red-shift in the $^1\text{MLCT}$ to 470 and 476 nm, respectively. Conversely, complexes **4** and **5** have the electron-withdrawing R groups of acetyl and trifluoromethyl and a blue shift in the $^1\text{MLCT}$ is observed at 433 and 460 nm, respectively. Previous studies have shown that electron-donating groups on pyridine increase the σ -donating capacity of the ligand, destabilizing the $\text{Ru}(\text{d}\pi)$ orbitals and causing a red shift of the $^1\text{MLCT}$ maximum [21]. These studies have also shown that electron-withdrawing groups stabilize the $\text{Ru}(\text{d}\pi)$ orbitals resulting in a blue shift of the $^1\text{MLCT}$ [21]. The present data agrees well with these reports and is consistent with electrochemical data discussed below. It should be noted that the addition of the 4-R-py(π^*) orbitals to $^1\text{MLCT}$ of **4** and **5** may contribute to the increases in molar absorptivity of the bathochromic portion of the transition which in turn may enhance the apparent blue shift. The assignment of the $^1\text{MLCT}$ is discussed further in section 3.3.

Luminescence at 298 K of complex **1** was detected with maximum at 618 nm ($\Phi_{\text{em}} = 0.00020$). Previous reports have demonstrated that this emission arises from the $\text{Ru} \rightarrow \text{tpy/bpy}$ $^3\text{MLCT}$ state [43]. The Φ_{em} is low in comparison to the highly emissive $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\Phi_{\text{em}} = 0.062$), but is comparable to other $\text{Ru}(\text{II})$ complexes with tpy in the coordination sphere, such as $[\text{Ru}(4'-(4\text{-carboxyphenyl})-2,2':6',2''\text{-terpyridine})(\text{tbtpy})]^{2+}$ ($\Phi_{\text{em}} = 0.00027$) [18]. Fig. 3 shows a comparison of the maxima and relative emission intensities all complexes. It is evident in Fig. 3 that the peaks of **2** – **5** exhibit a red shift in comparison to **1**, in agreement with previous work that

Fig. 3. Emission spectra of **1** (black solid line), **2** (red dotted line), **3** (blue dash line), **4** (pink dash dot line), and **5** (green dash dot dot line) at 298 K in acetonitrile. All spectra taken with an absorbance of 0.1 at 450 nm.

show the addition of electron-withdrawing or electron-donating groups leads to a red-shift in the emission maximum, λ_{max} [15]. A larger value of the emission quantum yield, Φ_{em} , is observed for **2** (0.00043) and **3** (0.00031) as compared to **1** (0.00020). This can be attributed to the σ -donor substituents, which raise the energy of ^3LF state in **2** and **3**, making it less accessible as a deactivation pathway from the emissive $^3\text{MLCT}$ state [18]. Complexes **4** and **5** exhibit relatively weak emission under these experimental conditions. It can be concluded that the ^3LF state is more stabilized than the $^3\text{MLCT}$ state by the electron-withdrawing groups, leading to a decrease in the energy barrier and an increased deactivation of the emissive $^3\text{MLCT}$.

The cyclic voltammograms of **1** are in close agreement with previous reports, with $E_{1/2} = +1.25$ and -1.25 V vs SCE in CH_3CN [32]. The reduction potentials of complexes **2** – **5** range between -1.21 V to -1.29 V vs SCE in CH_3CN (see Table 1) and are similar to that of **1** and other tpy containing Ru(II) complexes; this couple is known to correspond to the reduction of the tpy ligand in each complex [15,32]. This assignment is supported by electronic structure calculations

discussed below. Complexes **2** – **5** exhibit an oxidation wave in the range of +1.10 to +1.28 V vs SCE in CH₃CN, which is similar to that of **1** and other Ru(II) polypyridyl compounds, and is typical of the Ru^{III/II} couple [15,18,21]. The change in the oxidation potential can be attributed to the variation of the R group of the 4-R-py ligand. The CF₃ substitution, the most electron-withdrawing group, decreases the σ -donating ability of the CF₃-py ligand, thereby stabilizing the Ru(d π) orbitals and causing an anodic shift of the oxidation potential of **5** to +1.28 V vs SCE, 0.03 V more positive than that of **1**. As expected, similar results are observed for **4** with an oxidation potential of +1.27 V vs SCE. In contrast, **3** contains the most electron donating R group in the series, NH₂, which increases the σ -donating ability of the pyridine ligand causing a destabilization of the Ru(d π) orbitals and a cathodic shift of the oxidation wave to +1.10 V vs SCE in CH₃CN. Complex **2** which contains the less electron-donating group, methoxy, exhibits an oxidation potential of +1.20 V vs SCE in CH₃CN.

3.2. Photochemistry

The photolysis reactions of complexes **1** – **5** were performed in CH₃CN with $\lambda_{\text{irr}} \geq 395$ nm and progress of the reactions were monitored by electronic absorption. Each reaction had a starting absorbance of 0.5 at the corresponding ¹MLCT maximum to allow for a relative comparison. The photolysis of **1** (Fig. 4a) shows a decrease in intensity of the ¹MLCT at 466 nm and a simultaneous increase of a higher energy peak at 454 nm with an isobestic point at 464 nm. The blue shift in the absorbance is consistent with the photosubstitution of py with CH₃CN to produce [Ru(tpy)(bpy)(CH₃CN)]²⁺, which has a reported absorption maximum of 454 nm [33]. The spectra of the photoproduct in Fig. 4a and independently prepared [Ru(tpy)(bpy)(CH₃CN)](PF₆)₂ are shown in Fig. S18. The reaction reached completion in 90 mins, and no change in the electronic

Fig. 4. Changes to the electronic absorption spectrum upon photolysis ($\lambda_{\text{irr}} \geq 395$ nm) in acetonitrile of (a) **1** at $t_{\text{irr}} = 0, 2, 6, 10, 15, 20, 30, 40, 60, 90$ min; (b) **2** at $t_{\text{irr}} = 0, 1, 5, 10, 20, 30, 40, 60, 90, 120, 240$ min; (c) and **5** at $t_{\text{irr}} = 0, 1, 2, 4, 10$ min.

absorption was observed for at least 24 hours in the dark (Fig. S19). It should be noted that previous reports have shown very inefficient photosubstitution of **1** in CH_3CN . However, those experiments used a lower intensity light source or different irradiation wavelengths [28,33].

Similarly, the photolysis of **2**, **3**, and **5** under similar experimental conditions exhibit a decrease in the initial $^1\text{MLCT}$ peak and a concomitant increase in intensity at 454 nm, consistent with the photosubstitution of the 4-R-py ligand for a solvent CH_3CN molecule (Fig. 4 and S20).

Since the $^1\text{MLCT}$ band of **4** completely envelopes and is stronger than the $^1\text{MLCT}$ of its photoproduct, isobestic points are not observed (Fig. S21). However, the peak does decrease and exhibit a new maximum at 454 nm with a shape similar to the photoproducts of the other reactions in the series (**1** – **3** and **5**) and consistent with $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$. The photolysis of **4** in CD_3CN was monitored by ^1H NMR spectroscopy ($\lambda_{\text{irr}} \geq 395$ nm, 0–90 min). A peak at 2.48 ppm corresponding to bound 4-Ac-py decreases in intensity along with the formation of a new peak at 2.59 ppm assigned to free 4-Ac-py (Figs. S22 and S23). Additionally, a comparison of the aromatic region photoproduct and independently made $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ is shown in Fig. 5. The spectrum of the photoproduct exhibits peaks at 7.75 and 8.77 ppm which correspond to free

Fig. 5. ^1H NMR of (a) **4** upon photolysis in CD_3CN at $t_{\text{irr}} = 90$ min ($\lambda_{\text{irr}} \geq 395$ nm) where * mark free 4-Ac-py, and (b) synthetic $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ in CH_3CN .

4-Ac-py and 7.08, 7.27, 7.35, 7.68, 8.00, 8.33, 8.42, 8.56, 8.62, and 9.60 ppm which is consistent with $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})](\text{PF}_6)_2$. Although **1** – **5** form the same photoproducts, the relative efficiency at which each product is produced is vastly different. Completion of photolysis of **2** to product requires 240 min and the ligand substitution of **3** is not complete after 24 h of irradiation. Conversely, **4** and **5** demonstrate significantly more efficient photosubstitution, with the reaction reaching completion after 30 and 10 min, respectively. Plots of $\ln A$ versus t provided rate constants of 3.3×10^{-3} , 2.8×10^{-3} , 1.8×10^{-3} , 2.3×10^{-2} , and $5.1 \times 10^{-2} \text{ min}^{-1}$ for **1** – **5**, respectively. No change to the electronic absorption of complexes **2** – **5** is observed in the dark over 24 hours (Fig. S24 – S27).

The data presented here clearly demonstrates that an electron-withdrawing substituent on the 4-R-py ligand, as in **4** and **5**, facilitates the photosubstitution as compared to those complexes containing either the unsubstituted py ligand (**1**) or a 4-R-py with an electron-donating substituent (**2** and **3**). This can be partly attributed to irradiating the $^1\text{MLCT}$ of **4** and **5** directly populating the antibonding orbitals of the 4-R-py ligand. Additionally, it is generally accepted that ligand photosubstitution in Ru(II) complexes proceeds through population of the ^3LF state, and the data presented here are consistent with the stronger σ -donor ligands in **2** and **3** raising the energy of the ^3LF relative to the $^3\text{MLCT}$ state, while the electron withdrawing groups in **4** and **5** cause the opposite effect. Based on these results, it is reasonable to also attribute the changes in photoinduced ligand exchange efficiency to differences in the activation barriers between the $^3\text{MLCT}$ and ^3LF states among **1** – **5**.

3.3 Electronic Structure Calculations

Fig. 6. (a) Calculated molecular orbital diagrams of **1** – **5** and (b) schematic representation of the state diagrams of $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})]^{2+}$ complexes showing the energy difference between the ³MLCT and ³LF states, ΔE .

Computational studies were undertaken to gain further insights into the differences observed in the photoinduced ligand exchange and luminescent properties of **1** – **5**. The calculated molecular orbital diagram of the complexes is shown in Fig. 6a, for which the highest occupied molecular orbital (HOMO) of **1** was set to 0.0 eV as an arbitrary reference. The electron densities of the HOMO, HOMO-1, and HOMO-2 are mostly centered on the Ru atom in each complex, and represent the $\text{Ru}(\text{d}\pi)$ t_{2g} -type set (Fig. 6a). The set show an increase of energy in **2** and **3**, and a decrease of energy in **4** and **5** as compared to **1**. This trend agrees well with the electrochemical data, where **2** and **3** are more easily oxidized and **4** and **5** are more difficult to oxidize than **1** (Table1).

The electron density of the lowest unoccupied molecular orbital (LUMO) in each complex is centered on the tpy ligand. Each complex exhibits seven additional unoccupied orbitals that are of tpy/bpy character. In **1**, **4**, and **5** these orbitals appear as LUMO+1, LUMO+2, LUMO+4 to

LUMO+7, and LUMO+9. In **2** these orbitals are LUMO+1 to LUMO+6 and LUMO+9, and in **3** they are LUMO+1 to LUMO+6 and LUMO +8. The LUMO+10 and LUMO+11 in each complex can be assigned to Ru–L(σ^*), which is part of the e_g -set. Additionally, the LUMO+3 and LUMO+8 in **1**, **4**, and **5** exhibit electron densities centered on the 4-R-py ligand (Fig. 6). These appear at LUMO+7 and LUMO+8 in **2** and at LUMO+7 and LUMO+9 in **3**.

Gas phase singlet state transition energies were calculated using time dependent density functional theory (TDDFT) and confirm the assignment of the $^1\text{MLCT}$ of **1** as Ru(dp) $\rightarrow$ tpy/bpy(π^*). Calculations show eight transitions with wavelengths greater than 400 nm whose major contributions consist of transitions from the HOMO, HOMO-1, and HOMO-2 to the LUMO, LUMO+1, and LUMO+2 (Table S1). Calculated $^1\text{MLCT}$ transitions of **2** and **3** are summarized in Tables S2 and S3 and are also consistent with the Ru($d\pi$) $\rightarrow$ tpy/bpy(π^*) assignment. In **4** and **5**, 4-R-py(π^*) orbitals also contribute to the $^1\text{MLCT}$ with **5** exhibiting one transition at 400 nm that includes a 19% contribution of the HOMO $\rightarrow$ LUMO+3 (Table S4). Table 2 list all transitions with wavelengths longer than 400 nm for **4**, including six which involve 4-Ac-py (LUMO+3). Therefore the $^1\text{MLCT}$ of **4** and **5** are assigned to Ru($d\pi$) $\rightarrow$ tpy/bpy/4-R-py(π^*).

The thermal population of the ^3LF from the $^3\text{MLCT}$ state has been shown to be a competing pathway with phosphorescence in Ru(II) polypyridyl complexes, where an easily accessible ^3LF state can deactivate an emissive $^3\text{MLCT}$ [13,14]. Moreover, the ^3LF state has been implicated in photoinduced ligand exchange because electron density is placed in an orbital with Ru–L(σ^*) character [24–26]. Therefore, the energy difference between these two states, $\Delta E = E_{\text{LF}} - E_{\text{MLCT}}$ (Fig. 6b), may provide some insight into the ability of a complex to phosphoresce and/or undergo ligand exchange. TDDFT calculations were used to approximate the ΔE . Complexes with a larger ΔE value are expected to exhibit a larger Φ_{em} value and less efficient ligand exchange, whereas

Table 2. Calculated ¹MLCT electronic transitions of **4**.

λ / nm	f	Transition configuration (percent) ^{a,b}	Character ^c
514	0.0094	H→L (28%), H→L+1 (68%)	tpy
479	0.0058	H-1→L+1 (41%), H-1→L (26%), H-2→L+1 (12%), H→L+1 (10%)	tpy
477	0.0126	H→L (61%), H→L+1 (19%), H-1→L+1 (11%)	tpy
454	0.0359	H-2→L (52%), H→L+3 (16%), H-2→L+1 (11%), H-1→L+1 (10%)	tpy, 4-Ac-py
451	0.004	H→L+2 (48%), H→L+3 (45%)	bpy, 4-Ac-py
445	0.0232	H-1→L(47%), H-2→L+1 (16%), H-1→L+1 (15%), H-2→L (13%)	tpy
438	0.0611	H→L+2 (28%), H→L+3 (19%), H-2→L (17%), H-1→L (17%)	tpy, bpy, 4-Ac-py
425	0.0189	H-1→L+3 (40%), H-2→L+2 (19%), H-2→L+1 (13%), H-2→L+3 (13%)	tpy, bpy, 4-Ac-py
420	0.0449	H-1→L+2 (32%), H-2→L+3 (20%), H-2→L+2 (13%), H-2→L+1 (10%), H-1→L+3 (10%)	tpy, bpy, 4-Ac-py
412	0.1088	H-2→L+3 (46%), H-1→L+2 (35%)	bpy, 4-Ac-py
412	0.0812	H-2→L+2 (59%), H-1→L+2 (27%)	bpy

^a Only contributions greater than 10% are listed. ^b H = HOMO; L = LUMO. ^c Ligands involved in the ¹MLCT transition.

complexes with a smaller ΔE should have lower emission intensity and more efficient ligand exchange. The values for Φ_{em} (Table 1) and the photolysis times for complexes **1** – **5** follow this trend. Compared to **1**, with a calculated ΔE value of 8731 cm⁻¹, **2** and **3** have larger values of ΔE , 9062 and 9271 cm⁻¹, respectively, whereas smaller values of ΔE are calculated for **4** and **5**, 7924 and 7874 cm⁻¹, respectively. It is important to note that these calculated ΔE are vertical energy differences within the singlet manifold instead of the activation barrier from the ³MLCT to the ³LF state, however, in this case the calculated singlet ΔE values appear to translate to the triplet

manifold and the trend is consistent with the measured ligand exchange efficiencies.

4. Conclusions

The addition of electron-donating groups in complexes $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-MeO-py})]^{2+}$ (**2**) and $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-NH}_2\text{-py})]^{2+}$ (**3**) increased the Φ_{em} and decreased the efficiency of photoinduced ligand exchange compared to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ (**1**). In contrast, the addition of electron-withdrawing groups in $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-Ac-py})]^{2+}$ (**4**) and $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-CF}_3\text{-py})]^{2+}$ (**5**) decreased the Φ_{em} and increased the efficiency of photoinduced ligand exchange. Because emission and ligand exchange are competing pathways, the differences in excited state properties can be explained by the change in energy difference, ΔE , of the $^3\text{MLCT}$ and ^3LF states. Electron donating groups increase the magnitude of ΔE , thereby increasing Φ_{em} , and electron withdrawing groups decrease ΔE , resulting in an increase in the efficiency of photoinduced ligand exchange. Additionally, the direct population of $4\text{-R-py}(\pi^*)$ orbitals in **4** and **5** also contribute to the increase in the efficiency of photoinduced ligand exchange. Taken together, the data presented here demonstrates that by varying the substituents of a 4-R-py ligand, the excited state properties of $\text{Ru}(\text{II})$ polypyridyl complexes can be predictably altered or tuned with respect to emission potential and ligand exchange efficiency. These results can be potentially useful for research where photochemical ligand dissociation in high yield is required, such as in the photoinduced release of caged molecules, and also to shut down photoinduced ligand exchange for applications where robust complexes or highly emissive complexes are needed, including in dye-sensitized solar cells and luminescent sensors.

Acknowledgements

The authors are grateful for the support from The Welch Foundation (BN-0032), U.S. Department of Education HSI-STEM grant (P031C110145-13), and the UIW Department of Chemistry and Biochemistry. This work also used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation (ACI-1053575).⁴⁴ Additionally, the authors would like to thank Monique Swift, Adrian Gutierrez, and Joshua Marroquin for their contributions to this work.

Supporting Information. Characterization data for **2** – **4**, comparison of photolysis product to synthetic compound, dark controls in CH₃CN for **1** – **5**, UV–vis spectra of photolysis of **3** and **4** in CH₃CN.

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Graphical Abstract

Synopsis:

Investigation of $[\text{Ru}(\text{tpy})(\text{bpy})(4\text{-R-py})]^{2+}$, where tpy = 2,2';6',2''-terpyridine, bpy = 2,2'-bipyridine, and 4-R-py = pyridine (py, **1**), 4-methoxypyridine (4-CH₃O-py, **2**), 4-aminopyridine (4-NH₂-py, **3**), 4-acetylpypyridine (4-Ac-py, **4**) and 4-trifluoromethylpyridine (4-CF₃-py, **5**) shows that complexes containing electron-donating R-groups have larger emission quantum yields, whereas complexes with electron-withdrawing R-groups have more efficient photoinduced ligand exchange.