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New Ru(II) Complexes for Dual Photoreactivity: Ligand Exchange and $^1\text{O}_2$ Generation

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CONSPECTUS

Uncovering the factors that govern the electronic structure of Ru(II)–polypyridyl complexes is critical in designing new compounds for desired photochemical reactions, and strategies to tune excited states for ligand dissociation and $^1\text{O}_2$ production are discussed herein. The generally accepted mechanism for photoinduced ligand dissociation proposes that population of the dissociative triplet ligand field (^3LF) state proceeds through thermal population from the vibrationally cooled triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) state; however, temperature-dependent emission spectroscopy provides varied activation energies using the emission and ligand exchange quantum yields for $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine; $\text{L} = \text{CH}_3\text{CN}$ or py). This suggests that population of the ^3LF state proceeds from the vibrationally excited $^3\text{MLCT}$ state. Because the quantum yield of ligand dissociation for nitriles is much more efficient than that for py , steric bulk was introduced into the ligand set to distort the pseudo-octahedral geometry and lower the energy of the ^3LF state. The py dissociation quantum yield with 500 nm irradiation in a series of $[\text{Ru}(\text{tpy})(\text{NN})(\text{py})]^{2+}$ complexes ($\text{tpy} = 2,2':6',2''$ -terpyridine; $\text{NN} = \text{bpy}$, 6,6'-dimethyl-2,2'-bipyridine (Me_2bpy), 2,2'-biquinoline (biq)) increases by 2–3 orders of magnitude with the sterically bulky Me_2bpy and biq ligands relative to bpy . Ultrafast transient absorption spectroscopy reveals population of the ^3LF state within 3–7 ps when NN is bulky, and density functional theory calculations support stabilized ^3LF states. Dual activity via ligand dissociation and $^1\text{O}_2$ production can be achieved by careful selection of the ligand set to tune the excited-state dynamics. Incorporation of an extended π system in Ru(II) complexes such as $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ ($\text{dppn} = \text{benzo}[i]\text{dipyrido}[3,2-a:2',3'-c]\text{phenazine}$) and $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ ($\text{Me}_2\text{dppn} = 3,6$ -dimethylbenzo[i]dipyrido[3,2- $a:2',3'-c$]phenazine) introduces low-lying, long-lived $\text{dppn}/\text{Me}_2\text{dppn}$ $^3\pi\pi^*$ excited states that generate $^1\text{O}_2$. Similar to $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$, photodissociation of CH_3CN occurs upon irradiation of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$, although with lower efficiency because of the presence of the $^3\pi\pi^*$ state. The steric bulk in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ is critical in facilitating the photoinduced py dissociation, as the analogous complex $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ produces $^1\text{O}_2$ with near-unit efficiency. The ability to tune the relative energies of the excited states provides a means to design potentially more active drugs for photochemotherapy because the photorelease of drugs can be coupled to the therapeutic action of reactive oxygen species, effecting cell death via two different mechanisms. The lessons learned

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Notes

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about tuning of the excited-state properties can be applied to the use of Ru(II)–polypyridyl compounds in a variety of applications, such as solar energy conversion, sensors and switches, and molecular machines.

INTRODUCTION

Excited states of Ru(II) complexes have been used in solar energy conversion,^{1–5} in charge transfer reactions,^{6,7} as sensors and switches,^{8,9} and as potential therapeutic agents in photochemotherapy (PCT) and imaging.^{10–16} Although many complexes are derived from $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) (Figure 1a),¹⁷ these applications often have different demands. For example, the excited-state redox potential is crucial in solar energy schemes and charge transfer reactions, which often require long-lived triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) excited states, whereas strong luminescence and sensitivity to the environment have been important in sensor applications. In contrast, complexes developed for PCT typically require high yields of photo-induced ligand exchange for prodrug delivery or to achieve binding of the metal to biomolecules, which in turn results in short $^3\text{MLCT}$ lifetimes with low luminescence yields. In order to tune the relative energies of the excited states to achieve the desired properties, an understanding of the factors that affect the electronic structure of Ru(II) complexes is necessary.

The electronic structure and excited-state dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ and related complexes have been the subject of numerous reviews.¹⁷ Figure 1b presents a simplified diagram showing the frontier molecular orbitals (MOs) of $[\text{Ru}(\text{bpy})_3]^{2+}$ in a pseudo-octahedral field, for which the lowest-energy $^1\text{MLCT}$ transition has a maximum at 452 nm ($\epsilon = 14\,600\text{ M}^{-1}\text{ cm}^{-1}$) and the bpy $\pi\pi^*$ transitions are observed at 285 nm ($\epsilon = 87\,000\text{ M}^{-1}\text{ cm}^{-1}$) in water.¹⁷ Ultrafast $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ intersystem crossing (ISC) was reported in $[\text{Ru}(\text{bpy})_3]^{2+}$ (15–40 fs),^{18,19} and to our knowledge, significantly lower ISC rates have not been reported for Ru(II) complexes. Therefore, with the exception of charge injection into semiconductors,²⁰ the excited-state chemistry of Ru(II) complexes takes place from the

triplet manifold. The low-lying triplet excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ are schematically shown in Figure 1c, where the metal-centered triplet ligand field (^3LF) state(s) involve transitions from the t_{2g} -type orbitals to the e_g -type orbitals, and the triplet ligand-centered (^3LC) states arise from movement of an electron from the $\text{bpy}(\pi)$ MOs to the $\text{bpy}(\pi^*)$ MOs. In $[\text{Ru}(\text{bpy})_3]^{2+}$, the $^3\text{MLCT}$ state is emissive ($\lambda_{\text{em}} = 607 \text{ nm}$, $\tau = 620 \text{ ns}$, $\Phi = 0.042$ in water at 298 K).¹⁷ The lifetimes of $\text{Ru}(\text{II})$ complexes in which the ^3LC excited state falls below the $^3\text{MLCT}$ state are similar to those of the $^3\pi\pi^*$ state of the free ligand, and these complexes generally are not emissive, exhibit long lifetimes, and feature efficient $^1\text{O}_2$ sensitization.^{21–24} In contrast, stabilization of the ^3LF states results in photoinduced ligand exchange, which may be accomplished by introducing distortions around the metal center. These distortions reduce the orbital overlap and lower the energy of the e_g -type orbitals,¹⁵ thus decreasing the energy of the ^3LF states, sometimes below that of the $^3\text{MLCT}$ state.²⁵

The present Account focuses on the effect of structural changes to ruthenium(II) complexes on the excited-state properties and reactivity. Of particular interest are compounds that undergo photoinduced ligand exchange and those that generate $^1\text{O}_2$, as well as new complexes designed in such a way that both processes are operative in the same complex upon irradiation with low-energy light. This dual reactivity has the potential to be useful in applications related to PCT, where cell death may be achieved via two different mechanisms by the same molecule.

ACTIVATION BARRIER TO PHOTOINDUCED LIGAND EXCHANGE

It is well-established that deactivation of the emissive $^3\text{MLCT}$ state in $\text{Ru}(\text{II})$ complexes proceeds via thermal population of the ^3LF states, which reduces the lifetime of the former. For applications that require charge transfer or high luminescence quantum yields, researchers aim to maximize the gap between the $^3\text{MLCT}$ and ^3LF states, which minimizes deactivation through the latter. In contrast, maximizing photoinduced ligand exchange of ruthenium(II) complexes, such as in the release of active molecules to biological targets and to gain understanding of their function, to inhibit enzymes, and to generate reactive species that can covalently bind to DNA, requires efficient population of the dissociative ^3LF states.^{11,13–15} One limitation is the relatively low quantum yield of ligand exchange in some complexes.

It has been generally accepted that the formation of photosubstituted products in $\text{Ru}(\text{II})$ –polypyridyl complexes proceeds through thermal population of the dissociative ^3LF state(s) from the vibrationally cooled emissive $^3\text{MLCT}$ state ($^3\text{MLCT}_{v=0}$).²⁶ It is also established that deactivation of the emissive $^3\text{MLCT}_{v=0}$ state proceeds via population of the low-lying ^3LF state(s), as depicted in Figure 2a. If it is assumed that the only source of photoinduced ligand exchange is population of the ^3LF state from $^3\text{MLCT}_{v=0}$, then Arrhenius plots of both the photochemical yield and the emission intensity should give rise to the same activation energy, E_a (Figure 2a).

Plots of $\ln(\Phi)$ versus $1/T$ for the photoanation reactions of $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ ($\text{L} = \text{py}$, CH_3CN) to generate the corresponding $[\text{Ru}(\text{bpy})_2(\text{L})\text{Cl}]^+$ product in the presence of excess tetrabutylammonium chloride (TBACl) in CH_2Cl_2 were reported to result in $E_a \approx 700$

cm^{-1} ,²⁷ whereas changes in the emission lifetime of $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ with temperature result in $E_a = 2758 \text{ cm}^{-1}$.²⁸ However, these activation barriers were measured in two different temperature regimes, which can account for the different values. In addition, there have been other reports on the discrepancy between the magnitudes of E_a determined from emission and photochemical yields as well as from emission intensity and lifetime data.^{28,29} The concluding remarks in both reports point to possible direct population of the ^3LF state from the $^1\text{MLCT}$ state together with population of the emissive $^3\text{MLCT}$ state.^{28,29}

To gain further understanding of the photoinduced ligand exchange in $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ ($\text{L} = \text{CH}_3\text{CN}, \text{py}$), the activation energies for photoanation to generate the corresponding complexes $[\text{Ru}(\text{bpy})_2(\text{L})\text{Cl}]^+$, E_a^{P} , were measured over the same temperature range as for the value from the changes in emission intensity, E_a^{Em} , in 4:1 ethanol/methanol above the glass transition temperature.³⁰ The experiments were conducted in a cryostat placed in the sample compartment of the fluorimeter, and the decrease in the emission intensity as the temperature was raised was monitored in the absence of anion immediately after excitation to determine E_a^{Em} . The change in emission intensity as a function of irradiation time in the presence of 20 mM TBACl was used to calculate the value of E_a^{P} , and the results are listed in Table 1.³⁰ It is evident from Table 1 that for both complexes the value of E_a^{P} is significantly lower than that of E_a^{Em} . It may be concluded that the ligand exchange does not proceed from $^3\text{MLCT}_{v=0}$, as shown in Figure 2a. Instead, the population of the dissociative ^3LF state must have a different origin, as previously proposed by us,³¹ and may include direct ISC from the Franck–Condon $^1\text{MLCT}$ state, internal conversion (IC) from a higher-energy $^3\text{MLCT}$ state, or IC from the vibrationally excited lowest-energy $^3\text{MLCT}$ state ($^3\text{MLCT}_{v \gg 1}$). The latter situation is depicted in Figure 2b, where vibrational cooling competes with IC from a vibrational level well above $v = 0$, as previously proposed from ultrafast work.³²

In order for efficient ligand dissociation to be observed, population of the ^3LF state must compete with generation of $^3\text{MLCT}_{v=0}$. In systems such as $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$, there must be strong vibrational coupling between the MLCT (singlet or triplet) and ^3LF states, which is reduced in $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$. For example, strong vibrational coupling is believed to play a role in the ultrafast ISC of <100 fs in $\text{Cr}(\text{acac})_3$ ($\text{acac} = \text{acetylacetonate}$), but interestingly, it decreases by over an order of magnitude when the ligand's peripheral methyl groups are replaced by *tert*-butyl substituents in $\text{Cr}(t\text{-Bu-acac})_3$.³³ In addition to nitriles, thioethers undergo photoinduced ligand dissociation with greater quantum yields than their ammine counterparts, and the $^3\text{MLCT}$ states of the former were calculated to exhibit elongated Ru–S bonds, which may be related to MLCT/LF mixing.³⁴

ENHANCED PHOTOINDUCED LIGAND EXCHANGE WITH STERIC BULK

To increase the quantum yield for pyridine exchange through enhanced population of the ^3LF state, sterically bulky ligands were incorporated to distort the pseudo-octahedral geometry around the metal center. The decrease in the energy of the ^3LF state(s) as a function of increasing steric bulk was demonstrated for a series of complexes $[\text{Ru}(\text{NN})_3]^{2+}$ with $\text{NN} = \text{bpy}$, 6-methyl-2,2'-bipyridine (6-Mebpy), and 4,4',6,6'-tetramethyl-2,2'-

bipyridine (Me_4bpy) using ultrafast transient absorption (TA) spectroscopy.²⁵ On the basis of the difference in the decay of the $^3\text{MLCT}$ state and recovery of the ground state, it was shown that the rate of population of a ^3LF state from the $^3\text{MLCT}$ state increased by an order of magnitude in going from $[\text{Ru}(\text{6-Mebpy})_3]^{2+}$ to the more sterically demanding $[\text{Ru}(\text{Me}_4\text{bpy})_3]^{2+}$, with $^3\text{MLCT}$ lifetimes of 1.6 and 0.16 ps, respectively.²⁵ Distortions around the metal lead to a decrease in the calculated energy of the ^3LF state by $\sim 4000\text{ cm}^{-1}$ in $[\text{Ru}(\text{6-Mebpy})_3]^{2+}$ and $\sim 7000\text{ cm}^{-1}$ in $[\text{Ru}(\text{Me}_4\text{bpy})_3]^{2+}$ relative to that in $[\text{Ru}(\text{bpy})_3]^{2+}$. Therefore, while the ^3LF state lies above the $^3\text{MLCT}$ state in the latter, it falls below the $^3\text{MLCT}$ state in the former, resulting in fast $^3\text{MLCT}$ decay to populate the ^3LF state.

The enhanced population of the ^3LF state(s) in ruthenium(II) complexes with bulky ligands leads to greater photo-induced ligand exchange. For example, photodissociation of 2,2'-biquinoline (biq) from $[\text{Ru}(\text{biq})(\text{phen})_2]^{2+}$ (phen = 1,10-phenanthroline) and $[\text{Ru}(\text{biq})_2(\text{phen})]^{2+}$ in H_2O occurs with $\lambda_{\text{irr}} = 600\text{ nm}$, while this photoactivity is not observed in $[\text{Ru}(\text{phen})_3]^{2+}$.³⁵ The crystal structures of the biq complexes reveal lengthened Ru–N bonds compared with those in $[\text{Ru}(\text{phen})_3]^{2+}$ as well as significant twisting of biq along the C–C bond connecting the two quinoline moieties and bending of biq by $\sim 20^\circ$ out of the normal plane. Similar photoreactivity was reported for $[\text{Ru}(\text{biq})_2(\text{bpy})]^{2+}$ in CH_3CN .³⁶ The presence of methyl, phenyl, or chloro substituents positioned toward the Ru(II) center also induces geometric distortions and facilitates photosubstitution of the bulky bidentate ligands with solvent molecules.^{15,37,38}

To increase the photodissociation quantum yield of pyridine from pseudo-octahedral ruthenium(II) complexes, steric bulk was introduced in the series $[\text{Ru}(\text{tpy})(\text{NN})(\text{py})]^{2+}$ (tpy = 2,2':6',2''-terpyridine; NN = bpy, 6,6'-dimethyl-2,2'-bipyridine (Me_2bpy), biq) (Figure 3).³⁹ The lowest-energy electronic transition observed in $[\text{Ru}(\text{tpy})(\text{NN})(\text{py})]^{2+}$ (NN = bpy, Me_2bpy) is the $\text{Ru}(\text{d}\pi) \rightarrow \text{tpy}(\pi^*)$ $^1\text{MLCT}$ transition with maxima at 468 nm ($8120\text{ M}^{-1}\text{ cm}^{-1}$) and 471 nm ($8020\text{ M}^{-1}\text{ cm}^{-1}$), respectively, whereas that in $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ is assigned as the $\text{Ru}(\text{d}\pi) \rightarrow \text{biq}(\pi^*)$ $^1\text{MLCT}$ transition at 530 nm ($9020\text{ M}^{-1}\text{ cm}^{-1}$). Photoinduced exchange of py is not observed in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ ($\Phi_{500} < 0.0001$), but irradiation of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ in CH_3CN generates the corresponding products $[\text{Ru}(\text{tpy})(\text{NN})(\text{CH}_3\text{CN})]^{2+}$ (NN = Me_2bpy , biq) with $\Phi_{500} = 0.16(1)$ and $0.033(1)$, respectively (Table 2). All three complexes are stable in CH_3CN and H_2O solutions in the dark for at least 24 h at room temperature.

The crystal structures reveal key structural distortions in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ afforded by steric bulk from the bidentate ligands compared with $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$. In particular, the angle between the plane defined by the bidentate ligand and that of the tpy ligand, determined to be 83.34° in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$, is reduced to 67.87° and 61.89° in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$, respectively, similar to distortions reported for related complexes.^{35,40,41} More importantly, the pyridine ligand in the Me_2bpy and biq complexes is distorted relative to that in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$. The enhanced photoinduced ligand exchange efficiency is correlated to structural distortions, which are believed to stabilize ^3LF states and weaken the Ru–py σ bond.

Ultrafast TA spectroscopy reveals the consequences of added steric bulk on the excited-state dynamics of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ compared with $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ (Figure 4). For both complexes, the spectra feature a ground-state bleach centered at ~ 470 nm as well as positive transient absorption signals at ~ 375 and >500 nm associated with the $\text{Ru}(\text{d}\pi) \rightarrow \text{tpy}(\pi^*)$ $^3\text{MLCT}$ state.⁴² While the spectral features are similar for the two complexes, stark differences are observed in the kinetics. The absorption changes of the bleach signal at 470 nm for $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ in CH_3CN (Figure 4a) can be fitted to a biexponential decay with $\tau_1 = 28$ ps (8%) and $\tau_2 = 544$ ps (92%). The absorption changes associated with the reduced ligands in the $^3\text{MLCT}$ states in the 350–420 nm range display a broad maximum at ~ 370 nm at 1–10 ps delay but sharpen and red-shift to ~ 375 nm with a shoulder at ~ 390 nm at later times. These changes are accompanied by biexponential decays at 375 and 575 nm with $\tau_1 \approx 3$ ps and a long component with $\tau_2 \approx 500$ ps. The $\text{Ru} \rightarrow \text{bpy}$ $^1\text{MLCT}$ state is preferentially excited at 350 nm, resulting in fast ISC to the corresponding $\text{Ru} \rightarrow \text{bpy}$ $^3\text{MLCT}$ state with maximum at ~ 370 nm associated with reduced bpy. This state decays to populate the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state within ~ 23 ps, with a maximum at ~ 375 nm and a shoulder at ~ 410 nm, similar to the spectral features for $[\text{Ru}(\text{tpy})_2]^{2+}$.^{43,44} Since the 28 ps component represents a minor fraction (8%) of the bleach recovery, it corresponds to changes in absorption during $^3\text{MLCT}(\text{bpy}) \rightarrow ^3\text{MLCT}(\text{tpy})$ IC. The 23 ps component for the $^3\text{MLCT}(\text{bpy}) \rightarrow ^3\text{MLCT}(\text{tpy})$ IC is consistent with the value of 26 ps previously reported for a related complex with two low-lying $^3\text{MLCT}$ states.⁴⁵

Excitation of the red edge of the $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ absorption band of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ with $\lambda_{\text{exc}} = 568$ nm produces a bleach signal that can be fitted to $\tau_1 = 6$ ps (12%) and $\tau_2 = 437$ ps (88%); similar kinetics are observed at 375 nm. The 6 ps component is attributed to vibrational relaxation in the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state, which then decays to regenerate the ground state with $\tau = 470$ ps (Figure 5a). As expected, the 23–28 ps component is not present with 568 nm excitation. The 470 ps lifetime of the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state compares well to those of $[\text{Ru}(\text{tpy})_2]^{2+}$ (120 ps in CH_3CN and 250 ps in H_2O).^{42–44}

The TA spectra that result from 568 nm excitation of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ are shown in Figure 4b, where selective population of the $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ state results in observation of the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ absorption signals at ~ 375 and ~ 400 nm with monoexponential decay of $\tau = 6$ ps and a biexponential bleach recovery at 470 nm with $\tau_1 = 7$ ps (16%) and $\tau_2 = 38$ ps (84%). The 6–7 ps component can be ascribed to IC from the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state to populate the ^3LF state, which competes with vibrational cooling in the former, and the ^3LF state regenerates the ground state with time constant of 38 ps (Figure 5b). Excitation of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ at 350 nm provides similar kinetics but with an additional ~ 3 ps component associated with decay of the $\text{Ru} \rightarrow \text{Me}_2\text{bpy}$ $^3\text{MLCT}$ state (Figure 5b). These experiments are consistent with generation of the ^3LF state within 3–7 ps, which then deactivates via ligand dissociation and thermal decay to the ground state. It is evident in the ultrafast TA data for $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ in Figure 4b that the ground state does not fully recover in the final trace (2 ns), consistent with formation of the monosubstituted CH_3CN photoproduct, $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{CH}_3\text{CN})]^{2+}$. However, the kinetics of the photoproduct formation cannot be determined because of its spectral overlap with the

ground and excited states of the starting compound and the relatively small quantity of photoproduct formed.

Distortions around the metal center in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ compared with $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ can explain the differences in excited-state dynamics, resulting in a lower-energy ^3LF state in the former that falls below the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state (Figure 5). The lower-energy ^3LF state leads to enhanced ligand exchange for the Me_2bpy complex; the ^3LF lifetime of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ is similar to those of $\text{Ru}(\text{II})$ complexes with sterically bulky ligands, 45 ps for $[\text{Ru}(\text{6-Mebpy})_3]^{2+}$ and 7.5 ps for $[\text{Ru}(\text{Me}_4\text{bpy})_3]^{2+}$.²⁵ The formation of a pentacoordinate intermediate (PCI) from the ^3LF state is possible, such that the dynamics of the ground-state regeneration are due to geminate recombination of the PCI and pyridine. However, the cage escape and geminate recombination kinetics for the related complex $[\text{Ru}(\text{bpy})_2(\text{NA})_2]^{2+}$ (NA = nicotinamide) in water were reported as 377 and 263 ps, respectively.³² This order of magnitude difference between the bleach recovery of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{NA})_2]^{2+}$ is inconsistent with the 38 ps component assigned as geminate recombination. Ultrafast population of the ^3LF state from the $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ or vibrationally excited $^3\text{MLCT}$ state, $^3\text{MLCT}_v$, to afford py dissociation is supported by efficient ligand exchange for $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ with low-energy light ($\lambda_{\text{irr}} = 600$ nm) and the excited-state dynamics measured with 568 nm excitation. This finding is also consistent with the differences in E_a^{Em} and E_a^{P} measured for $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ (Table 1).

Density functional theory (DFT) calculations on $[\text{Ru}(\text{tpy})(\text{NN})(\text{py})]^{2+}$ (NN = bpy, Me_2bpy) show that the unoccupied $d_{x^2-y^2}$ orbital, directed along the Ru–py bond, is at a lower energy than the d_{z^2} orbital in each complex. Therefore, population of the lowest-energy LF state results in additional electron density in the $d_{x^2-y^2}$ orbital, weakening the Ru–py bond. The distortions in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ lower the calculated $d_{x^2-y^2}$ orbital energy by 0.82 eV relative to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$, consistent with stabilization of the LF states with Ru–py(σ^*) character.

DUAL ACTIVITY: PHOTOINDUCED LIGAND EXCHANGE AND $^1\text{O}_2$ GENERATION

$[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ (dppn = benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine) (Figure 6) combines the ligand exchange photochemistry of $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$ and the $^1\text{O}_2$ production of $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$ to enhance cellular photo-toxicity.⁴⁶ The electronic absorption spectrum of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ features a $^1\text{MLCT}$ maximum at 430 nm ($11\,000\text{ M}^{-1}\text{ cm}^{-1}$) and dppn-centered $^1\pi\pi^*$ transitions at 382 nm ($11\,100\text{ M}^{-1}\text{ cm}^{-1}$) and 405 nm ($13\,500\text{ M}^{-1}\text{ cm}^{-1}$). The lowest-energy excited state of the complex is the dppn-centered $^3\pi\pi^*$ state with $\tau = 20\text{ }\mu\text{s}$ in CH_3CN , similar to those of $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$ ($\tau = 33\text{ }\mu\text{s}$ in CH_3CN) and free dppn ($\tau = 18\text{ }\mu\text{s}$ in CHCl_3).²¹ In $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$, both the lowest-energy $^3\text{MLCT}$ excited state ($\tau = 51\text{ ps}$) and the low-lying ^3LF state are populated upon ultrafast excitation, and the complex undergoes efficient photoinduced ligand exchange.³¹

Irradiation of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ in water promotes sequential substitution of the two CH_3CN ligands ($\lambda_{\text{irr}} = 400 \text{ nm}$); the first step forms $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})(\text{OH}_2)]^{2+}$ with $\Phi_{400} = 0.002(3)$, which is 2 orders of magnitude lower than that in $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$ ($\Phi_{400} = 0.21$).³¹ The quantum yield for production of $^1\text{O}_2$ (Φ) from the $^3\pi\pi^*$ state of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ is 0.72(2), which is slightly lower than that of $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$ (0.88(2)). The lower yields of ligand exchange and $^1\text{O}_2$ generation in $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ relative to the parent complexes are explained by competitive population of the ^3LF and $^3\pi\pi^*$ states. A phthalocyanine Ru(II) complex with bound NO ligands was previously shown to produce $^1\text{O}_2$ with $\Phi = 0.29$ and photorelease NO.⁴⁷

Ultrafast TA spectroscopy reveals the excited-state dynamics of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$. Because of spectral overlap of the $^1\text{MLCT}$ and $^1\pi\pi^*$ bands, one cannot be accessed selectively. Excitation in the 300 to 400 nm range results in the observation of both the $^3\text{MLCT}$ and $^3\pi\pi^*$ states within the laser pulse, with absorption at ~ 360 and ~ 540 nm, respectively (Figure 7). Additionally, the lower-lying $^3\pi\pi^*$ state is also populated from the $^3\text{MLCT}$ state through IC with $\tau = 22 \text{ ps}$ (Figure 7). Although the observed ligand exchange is expected to occur through the ^3LF state, the latter was not detected, likely because of its low quantum yield and weak oscillator strength.

$[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ ($\text{Me}_2\text{dppn} = 3,6\text{-dimethylbenzo-}[i]\text{dipyrido}[3,2\text{-}a':2',3'\text{-}c]\text{phenazine}$) (Figure 8) undergoes both pyridine dissociation and $^1\text{O}_2$ production with visible light. The Me_2dppn ligand causes geometric strain similar to that caused by Me_2bpy , but the complex maintains the Me_2dppn $^3\pi\pi^*$ lowest-energy excited state.⁴⁸ $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ absorbs strongly in the visible region with dppn-centered $^1\pi\pi^*$ transitions at 382 nm ($11\,400 \text{ M}^{-1} \text{ cm}^{-1}$) and 404 nm ($12\,400 \text{ M}^{-1} \text{ cm}^{-1}$) and a $^1\text{MLCT}$ peak at 486 nm ($12\,900 \text{ M}^{-1} \text{ cm}^{-1}$). When photolyzed in CH_3CN ($\lambda_{\text{irr}} = 500 \text{ nm}$), $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{CH}_3\text{CN})]^{2+}$ is formed with $\Phi_{500} = 0.053(1)$ in the absence of O_2 , but ligand exchange is not observed in $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ ($\Phi_{500} < 10^{-4}$), which lacks steric strain (Table 2). Photosensitization of $^1\text{O}_2$ by $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ occurs with $\Phi = 0.69(9)$, which is lower than the value of 0.98(6) measured for $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ ($\lambda_{\text{irr}} = 460 \text{ nm}$), as listed in Table 2. The reduced quantum yield for $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ can be attributed to competitive deactivation through the ^3LF state afforded by distortions around the metal. Competitive population of excited states also explains the lower ligand exchange quantum yield of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ relative to $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$.

Following selective $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ excitation of $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ at 568 nm, the $\text{Ru} \rightarrow \text{tpy}$ $^3\text{MLCT}$ state of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ is observed at ~ 390 and $\sim 415 \text{ nm}$ within the laser pulse, along with a strong ground-state bleach centered at $\sim 480 \text{ nm}$ (Figure 9a). Although the signal at 535 nm corresponding to the Me_2dppn $^3\pi\pi^*$ state is not observed at early times, it evolves with $\tau_1 = 2 \text{ ps}$ (28%) and $\tau_2 = 17 \text{ ps}$ (72%), concomitant with the decay of the $^3\text{MLCT}$ signals fitted to $\tau_1 = 3 \text{ ps}$ (13%) and $\tau_2 = 18 \text{ ps}$ (87%) at 415 nm and changes in the bleach signal with $\tau_1 = 1 \text{ ps}$ (16%) and $\tau_2 = 18 \text{ ps}$ (84%). The $\sim 2 \text{ ps}$ decay is believed to have contributions from ISC, IC, and vibrational cooling, while the 18 ps component is assigned to population of the $^3\pi\pi^*$ state from the $^3\text{MLCT}$ state. Similar spectral features and kinetics were measured for $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ in CH_3CN under 568 nm excitation, for which the growth of the 540 nm peak

and bleach recovery at 470 nm can be fitted to $\tau_1 = 1$ ps (21%) and $\tau_2 = 22$ ps (79%). The long component is ascribed to IC from the $^3\text{MLCT}$ state to the $\text{dppn } ^3\pi\pi^*$ state, while the short component is related to ISC, IC, and vibrational cooling processes.

The Jablonski diagram of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$, depicted in Figure 9b, shows that IC from the $\text{Ru} \rightarrow \text{tpy } ^3\text{MLCT}$ state to the $\text{dppn } ^3\pi\pi^*$ state occurs with $\tau = 18$ ps in the Me_2dppn complex, as opposed to 22 ps in $[\text{Ru}(\text{tpy})-(\text{dppn})(\text{py})]^{2+}$. Since photoinduced ligand exchange is observed in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ with $\lambda_{\text{irr}} = 550$ nm, low-energy light must populate the dissociative ^3LF state. The similarity in the $^3\pi\pi^*$ lifetimes of $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ ($\tau = 50$ and $47 \mu\text{s}$, respectively; $\lambda_{\text{exc}} = 355$ nm, fwhm ≈ 8 ns) is consistent with the ^3LF state being located at a higher energy, as shown in Figure 9b.

CONCLUSIONS

The ability of Ru(II) complexes to undergo both photoinduced ligand exchange and $^1\text{O}_2$ generation efficiently provides a means to design potentially more active PCT therapeutics. In particular, photorelease of drugs can be coupled to the activity of reactive oxygen species, enabling these compounds to effect cell death via two different mechanisms upon visible-light irradiation. Steric strain can be used to lower the energy of the metal-centered state(s), resulting in greater yields of ligand photodissociation, even when these states(s) are not the lowest in energy. Mixing between the ^3LF state(s) and MLCT and/or LC states is believed to play an important role in efficient photoinduced ligand exchange, which is greater when these states are closer in energy. Work is underway to gain further understanding of the coupling between states with the goal of increasing the ligand exchange yields in these dual-action complexes while retaining relatively high sensitization of $^1\text{O}_2$ upon irradiation in the photodynamic window (600–900 nm).

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Figure 1.

(a) Molecular structure and simplified (b) MO and (c) state diagrams of $[\text{Ru}(\text{bpy})_3]^{2+}$.

Figure 2. Schematic representation of the potential energy surfaces showing (a) the activation energy, E_a , for going from $^3\text{MLCT}_{v=0}$ to the ^3LF state and (b) the proposed sources of E_a^{Em} and E_a^P .

Figure 3.

Structural representations of $[\text{Ru}(\text{tpy})(\text{L})(\text{py})]^{2+}$ (NN = bpy, Me₂bpy, biq).

Figure 4. Transient absorption spectra of (a) $[Ru(tpy)(bpy)(py)]^{2+}$ ($\lambda_{exc} = 350$ nm) and (b) $[Ru(tpy)(Me_2bpy)(py)]^{2+}$ ($\lambda_{exc} = 568$ nm) in CH_3CN collected 1, 5, 10, 20, 40, 60, 100, 200, 500, 1000, and 2000 ps following the laser pulse (fwhm = 300 fs, baseline collected at -10 ps).

Figure 5. Jablonski diagrams for (a) $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ and (b) $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$.

Figure 6.

Structural representations of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$, and $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$.

Figure 7. Transient absorption spectra of $[\text{Ru}(\text{bpy})(\text{dppn})-(\text{CH}_3\text{CN})_2]^{2+}$ in CH_3CN ($\lambda_{\text{exc}} = 300$ nm, fwhm = 300 fs).

Figure 8.
Structural representations of [Ru(tpy)(Me₂dppn)(py)]²⁺ and [Ru(tpy)(dppn)(py)]²⁺.

Figure 9.

(a) Ultrafast transient absorption of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ in CH_3CN ($\lambda_{\text{exc}} = 568$ nm, fwhm = 300 fs) and (b) the corresponding Jablonski diagram.

Table 1

Quantum Yields of Photoinduced Ligand Exchange for $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ Complexes, Absorption Maxima, and Activation Barriers with the Corresponding Temperature Ranges

L	Φ_{L}^a	$\lambda_{\text{abs}}/\text{nm}^b$	$E_{\text{a}}^{\text{Em}}/\text{cm}^{-1}\text{c}$	$E_{\text{a}}^{\text{P}}/\text{cm}^{-1}\text{c}$	T/K
CH_3CN	0.31	420	1310 ± 65	515 ± 100	130–170
py	0.17	460	2040 ± 100	940 ± 85	180–230

^a At 25 °C in CH_2Cl_2 with 20 mM TBACl ($\lambda_{\text{irr}} = 400 \text{ nm}$).

^b In H_2O .

^c Irradiated at the absorption maximum.

Table 2Quantum Yields of Ligand Exchange, Φ_{LE} , and $^1\text{O}_2$ production, Φ , for Selected Complexes

complex	Φ_{LE}^a	Φ^b
$[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$	$<10^{-4}$	
$[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$	0.16(1)	
$[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$	0.033(1)	
$[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$	$<10^{-4}$	0.98(6)
$[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$	0.053(1)	0.69(9)

^a CH_3CN , $\lambda_{\text{irr}} = 500 \text{ nm}$.^b MeOH , $\lambda_{\text{irr}} = 460 \text{ nm}$.