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Excited State Investigation of a New Ru(II) Complex for Dual Reactivity with Low Energy Light

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Abstract

The new complex $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ efficiently photodissociates py in CH_3CN with $\Phi_{500} = 0.053(1)$ induced by steric bulk from methyl substituents and produces $^1\text{O}_2$ with $\Phi = 0.69(9)$ from its long-lived $^3\pi\pi^*$ excited state. The unique excited state processes that result in dual reactivity were investigated using ultrafast transient absorption spectroscopy.

Ruthenium(II) complexes are widely investigated for applications in photochemotherapy (PCT), solar energy conversion, and molecular switches and devices, among others.^{1–3} The design of complexes with unusual excited state dynamics, such that they undergo more than one useful process upon visible light irradiation, was recently demonstrated with the dual action compound, $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ (bpy = 2,2'-bipyridine; dppn = benzo[*l*]dipyrido[3,2-*a*:2',3'-*c*]phenazine).⁴ This compound exchanges CH_3CN with a H_2O solvent molecule with a quantum yield of ligand exchange, Φ_{400} , of 0.002(3) with $\lambda_{\text{irr}} = 400$ nm. Additionally, the compound produces $^1\text{O}_2$ with a quantum yield, Φ , of 0.72(2) with $\lambda_{\text{irr}} = 460$ nm. The dual activity is a result of competitive population of a dissociative ^3LF state and a long-lived, dppn-centred $^3\pi\pi^*$ excited state with a 20 μs lifetime in CH_3CN .

Introduction of steric bulk to distort the pseudo-octahedral geometry around the Ru(II) center has been pursued to lower the energy of dissociative ^3LF state, thereby enhancing its population and subsequent ligand dissociation. Ultrafast transient absorption spectroscopy of a series of $[\text{Ru}(\text{L})_3]^{2+}$ complexes, where L = bpy, 6-methyl-2,2'-bipyridine (6-Mebpy), and 4,4',6,6'-tetramethyl-2,2'-bipyridine (4,4',6,6'-Me₄bpy) demonstrates a decrease in ^3LF state energy as a function of increased steric strain.⁵ The calculated ^3LF state energies decrease by $\sim 4,000\text{ cm}^{-1}$ for $[\text{Ru}(6\text{-Mebpy})_3]^{2+}$ and $\sim 7000\text{ cm}^{-1}$ for $[\text{Ru}(4,4',6,6'\text{-Me}_4\text{bpy})_3]^{2+}$ relative to that of $[\text{Ru}(\text{bpy})_3]^{2+}$. The increased bulk of $[\text{Ru}(4,4',6,6'\text{-Me}_4\text{bpy})_3]^{2+}$ results in faster ^3LF state population from the $^3\text{MLCT}$ state, 0.16 ps, as compared to the 1.6 ps in $[\text{Ru}(6\text{-Mebpy})_3]^{2+}$. While the ^3LF state is higher in energy than the $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$, it is stabilized below the $^3\text{MLCT}$ state in the methyl-substituted analogues, resulting in fast ^3LF state population.

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[†]Electronic Supplementary Information (ESI) available: Experimental details, ^1H NMR data, nanosecond TA of **2**, ultrafast TA of **2** and **4**. See DOI: 10.1039/c000000x/

The introduction of steric bulk to induce more efficient population of the ^3LF state with $\text{Ru}-\text{L}(\sigma^*)$ character has been used to enhance ligand dissociation in $\text{Ru}(\text{II})$ complexes with sterically demanding ligands. The photoactivated exchange of 2,2'-biquinoline (biq) for two solvent H_2O molecules in $[\text{Ru}(\text{biq})(\text{phen})_2]^{2+}$ and $[\text{Ru}(\text{biq})_2(\text{phen})]^{2+}$ ($\text{phen} = 1,10$ -phenanthroline) proceeds with $\lambda_{\text{irr}} = 600$ nm; conversely, no ligand exchange occurs in $[\text{Ru}(\text{phen})_3]^{2+}$ with visible light.⁶ The photoreactivity of the strained biq complexes are attributed to lengthened $\text{Ru}-\text{N}$ bonds compared to those in $[\text{Ru}(\text{phen})_3]^{2+}$, twisting of the biq ligands along the $\text{C}-\text{C}$ bond between the two quinoline units, and a $\sim 20^\circ$ tilt of biq out of the normal plane. Visible light irradiation of the related complex $[\text{Ru}(\text{biq})_2(\text{bpy})]^{2+}$ in CH_3CN provides similar reactivity.⁷ Geometric distortion via addition of methyl-, phenyl-, or chloro-groups oriented toward the $\text{Ru}(\text{II})$ center facilitates the exchange of bulky bidentate L' ligands with coordinating solvent CH_3CN or H_2O in a series of $[\text{Ru}(\text{L})_2(\text{L}')]^{2+}$ ($\text{L} = \text{bpy}$ or phen) complexes, albeit with relatively low quantum yields ($\Phi \sim 0.02$, $\lambda_{\text{irr}} = 500$ -600 nm in water).⁸⁻¹⁰

While the photodissociation of nitriles from $\text{Ru}(\text{II})$ -polypyridyl compounds typically occurs with relatively high quantum yield, the photodissociation of pyridine is less efficient. The irradiation of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ ($\text{tpy} = 2,2':6',2''$ -terpyridine) in DMF with $\lambda_{\text{irr}} = 436$ nm forms the photoproduct $[\text{Ru}(\text{tpy})(\text{bpy})(\text{DMF})]^{2+}$ with $\Phi = 0.006$, and the same process occurs for $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ with $\Phi < 10^{-5}$.¹¹ The exhaustive photolysis required to release py has made applications requiring py photodissociation from $\text{Ru}(\text{II})$ complexes impractical. The series of $[\text{Ru}(\text{tpy})(\text{L})(\text{py})]^{2+}$ complexes, where $\text{L} = \text{bpy}$, 6,6'-dimethyl-2,2'-bipyridine (Me_2bpy), and biq, was designed to probe the impact of steric bulk on the excited state dynamics and on the efficiency of photoinduced py exchange.¹² Significant geometric distortion imparted by the bulky methyl or quinoline moieties greatly enhances py photodissociation in CH_3CN compared to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ ($\Phi_{500} < 10^{-4}$), with Φ_{500} values of 0.16(1) and 0.033(1) when $\text{L} = \text{Me}_2\text{bpy}$ and biq, respectively.

The new complex $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ (**1**; $\text{Me}_2\text{dppn} = 3,6$ -dimethylbenzo[*d*]dipyrido[3,2-*a*:2',3'-*c*]phenazine) shown in Figure 1 was designed to achieve both efficient py dissociation and $^1\text{O}_2$ production with visible light irradiation. The related complex $[\text{Ru}(\text{tpy})(\text{dppn})(\text{py})]^{2+}$ (**2**) is a model which undergoes only $^1\text{O}_2$ production in detectable yield. The previously reported analogues $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ (**3**) which only undergoes ligand dissociation and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ (**4**) which exhibits neither py dissociation nor $^1\text{O}_2$ production, were also analysed to aid in interpretation of the excited state dynamics.

Complexes **1** – **4** were prepared and characterized as described in the Supporting Information (Figures S1-S2). Complex **1** absorbs visible light strongly, 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 predominantly $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ (metal-to-ligand charge transfer) transitions centered at 486 nm ($12,900 \text{ M}^{-1} \text{ cm}^{-1}$). Table 1 highlights the similar energies of the $\text{Ru} \rightarrow \text{tpy}$ $^1\text{MLCT}$ transition of **2**, **3**, and **4**, with maxima at 474 nm ($12,900 \text{ M}^{-1} \text{ cm}^{-1}$), 471 nm ($8,020 \text{ M}^{-1} \text{ cm}^{-1}$) and 468 nm ($8,120 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, indicating that the energy of metal t_{2g} orbitals are not significantly impacted by varying the bidentate ligand in this series.

Irradiation of **1** with visible light promotes both ligand exchange and $^1\text{O}_2$ production. The py ligand is substituted for a CH_3CN solvent molecule to form the photoproduct $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{CH}_3\text{CN})]^{2+}$ with $\lambda_{\text{irr}} = 395$ nm, observed by the decreased absorption of **1** at 486 nm and a concomitant increase in absorption of the photoproduct at 464 nm (Figure 2). The isosbestic points at 411 and 470 nm indicate the formation of a single photoproduct. This process occurs with $\Phi_{500} = 0.053(1)$, which is several orders of magnitude larger than that of **2** and **4**, owing to the presence of steric bulk in **1** that lowers the energy of the dissociative ^3LF state and weakens the Ru–N(py) bond. The complex is stable in CH_3CN in the dark for at least 24 hours (Figure S3). The lower value of Φ_{500} of **1** as compared to 0.16(1) for **3** is attributed to competitive population of the ^3LF and $^3\pi\pi^*$ states in the former and the absence of a $^3\pi\pi^*$ state in the latter. The $^1\text{O}_2$ quantum yield of **1**, $\Phi = 0.69(9)$, is slightly lower than that of **2**, $\Phi = 0.98(6)$ (Table 1); this trend is also attributed to the competitive population of the ^3LF and $^3\pi\pi^*$ states of **1** and very inefficient population of ^3LF states in **2**. For comparison, $[\text{Ru}(\text{bpy})_2(\text{Me}_2\text{dppn})]^{2+}$ produces $^1\text{O}_2$, but does not undergo ligand exchange.¹³ Furthermore, **3** and **4** do not produce $^1\text{O}_2$, owing to their short $^3\text{MLCT}$ excited state lifetimes, 38 and 470 ps, respectively, in CH_3CN , compared to the $^3\pi\pi^*$ lifetimes of 47 and 50 μs for **1** and **2**, respectively, in pyridine (discussed below).

The excited state dynamics of **1** were investigated by nanosecond (ns) and ultrafast transient absorption (TA) spectroscopy and the results were compared to those for **2** – **4**. The ns TA spectrum of **1** in deaerated pyridine features a strong positive signal with a maximum at ~ 540 nm that decays monoexponentially with $\tau = 50$ μs , similar to the spectrum and lifetime, 47 μs , measured for **2** ($\lambda_{\text{exc}} = 355$ nm, fwhm = 8 ns, Figure S4). The broad peak at ~ 540 nm is assigned to the $^3\pi\pi^*$ excited state of the Me_2dppn or dppn ligand in each complex, consistent with the reported TA spectra of the dppn -centered $^3\pi\pi^*$ excited states of related compounds in CH_3CN , such as $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ ($\tau = 20$ μs), $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$ ($\tau = 33$ μs), and among others.^{4, 14–16} It should be noted that while **1** undergoes efficient py dissociation similar to **3**, the $^3\text{MLCT}$ excited state of **3** is not observed on the ns timescale owing to its short lifetime, as it lacks low-lying $^3\pi\pi^*$ excited states.

The ultrafast TA spectra of **1** and **2** were recorded following selective excitation of the Ru→tpy $^1\text{MLCT}$ state with 568 nm pulses (fwhm = 300 fs), and the resulting traces for the former are shown in Figure 3a. The Ru→tpy $^3\text{MLCT}$ state of **1** exhibits positive signals at ~ 390 nm and ~ 415 nm at the earliest time monitored, 0.3 ps, along with a strong ground state bleach centred at ~ 480 nm. Although the signal at 535 nm that corresponds to the Me_2dppn $^3\pi\pi^*$ state is not observed at early times, it evolves with $\tau_1 = 2$ ps (28%) and $\tau_2 = 17$ ps (72%), concomitant with the decay of the $^3\text{MLCT}$ signals fitted to $\tau_1 = 3$ ps (13%) and $\tau_2 = 18$ ps (87%) at 415 nm. The intensity changes in the bleach signal at 480 nm can be attributed to the superimposed growth of the broad peak at 535 nm, not ground state recovery, since it can be fitted to nearly identical lifetime components, $\tau_1 = 1$ ps (16%) and $\tau_2 = 18$ ps (84%). The ~ 2 ps component is assigned as arising from intersystem crossing (ISC), internal conversion (IC), and vibrational cooling. The 18 ps component corresponds to the population of the $^3\pi\pi^*$ state from the $^3\text{MLCT}$ state. Similar spectral features and kinetics were measured for **2** in CH_3CN under 568 nm excitation, for which ISC takes place

within the laser pulse and the growth of the 540 nm peak and bleach recovery at 470 nm can be fitted to $\tau_1 = 1.1$ ps (21%) and $\tau_2 = 22$ ps (79%) (Figure S5).

The Jablonski diagram for the excited state dynamics of **1** following 568 nm excitation is depicted in Figure 4a. The major difference in the kinetics of the corresponding dppn complex is the IC from the Ru→tpy $^3\text{MLCT}$ to the dppn $^3\pi\pi^*$ state in **2** takes place with a time constant of 22 ps, instead of 18 ps in **1**. Since photoinduced ligand exchange in **1** is observed with $\lambda_{\text{irr}} = 550$ nm, the dissociative ^3LF state(s) must be populated with low energy light, however, it is unclear at this time whether this process takes place through ISC directly from the singlet manifold to the dissociative ^3LF state or from the Ru→tpy $^3\text{MLCT}$ state. Because the experiment is performed in CH_3CN , a portion of the sample is expected to proceed to form the $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{CH}_3\text{CN})]^{2+}$ photoproduct upon excitation. However, owing to the relatively small amount of photoproduct formed and its spectral overlap with features of the ground state and excited state of the starting material, kinetics of its formation cannot be discerned in the present experiments using TA spectroscopy.

To further investigate the consequences of the presence of steric bulk and geometric distortion around the metal on the excited state dynamics involved in pyridine ligand dissociation, the ultrafast TA spectra of **3** (Figure 3b) and **4** (Figure S6) were collected in CH_3CN ($\lambda_{\text{exc}} = 568$ nm, fwhm = 300 fs). While the spectral features are similar for both **3** and **4**, stark differences are observed in the excited state kinetics. Selective population of the Ru→tpy $^1\text{MLCT}$ state with 568 nm excitation results in the observation of the absorption signals at ~375 and ~390 nm associated with reduced tpy ligand in the Ru→tpy $^3\text{MLCT}$ state. The bleach recovery signal for **3** at 470 nm can be fitted to a biexponential function with $\tau_1 = 7$ ps (16%) and $\tau_2 = 38$ ps (84%). The decay of the signal at 375 nm proceeds with $\tau = 6$ ps, which can be ascribed to IC from the Ru→tpy $^3\text{MLCT}$ to the ^3LF state; this process is also evident in the 7 ps component of the bleach recovery with low amplitude changes, reflecting the difference in extinction coefficient of the $^3\text{MLCT}$ and ^3LF states at 470 nm. The ^3LF state repopulates the ground state with time constant of 38 ps, as depicted in Figure 4b. This experiment is consistent with the population of the ^3LF state within 7 ps, which then deactivates via ligand dissociation and thermal decay to the ground state.

In complex **4**, the bleach signal can be fitted to $\tau_1 = 6$ ps (12%) and $\tau_2 = 437$ ps (88%) and similar biexponential kinetics are observed for the decay of the $^3\text{MLCT}$ signal at 375 nm with $\tau = 470$ ps. Unlike the case for **3**, the $^3\text{MLCT}$ signal at 375 nm decays in **4** to regenerate the ground state. This result is consistent with the ^3LF state lying above the $^3\text{MLCT}$ in **4**, such that the 6 ps component can be assigned to vibrational relaxation in the Ru→tpy $^3\text{MLCT}$ state. The 470 ps lifetime of the Ru→tpy $^3\text{MLCT}$ state compares well with those reported for $[\text{Ru}(\text{tpy})_2]^{2+}$, 120 ps in CH_3CN and 250 ps in H_2O .¹⁷⁻¹⁹

It is clear in the ultrafast TA data of **3** in Figure 3b that the ground state does not fully recover, as the negative bleach signal is still observable in the final trace (2 ns after the laser pulse), while the ground state is fully recovered for the bpy analog, **4**, because a portion of the sample undergoes photoinduced ligand exchange in CH_3CN generating $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{CH}_3\text{CN})]^{2+}$. Overlaying the difference spectrum between **3** and that of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ with the final trace in the ultrafast TA experiment from Figure 3b

supports the formation of the mono-substituted CH₃CN photoproduct in the ultrafast experiment (Figure S7). However, owing to the relatively small amount of product formed and its spectral overlap with features of the ground state and excited state of the starting material, kinetics of its formation cannot be discerned.

The difference in the excited state dynamics observed between **3** and **4** can be explained by the additional distortions around the metal centre in the former imposed by the Me₂bpy ligand, resulting in lowering the energy of the ³LF state, such that it falls below the Ru→tpy ³MLCT state. These results are also consistent with the enhanced ligand exchange quantum yield measured for **3**. It should be noted that these lifetimes are similar to those reported by Hauser for Ru(II) complexes with sterically bulky ligands, where the decay of the ³LF state to regenerate the ground state was reported to be 45 ps for [Ru(6-Mebpy)₃]²⁺ and 7.5 ps for [Ru(4,4',6,6'-Me₄bpy)₃]²⁺.⁵ 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 PCI and pyridine. However, the cage escape and geminate recombination kinetics for the related complex [Ru(bpy)₂(NA)₂]²⁺ (NA = nicotinamide) in H₂O were reported to be 377 ps and 263 ps, respectively.²⁰ The difference by approximately an order of magnitude in the bleach recovery observed for **3** as compared to [Ru(bpy)₂(NA)₂]²⁺ is inconsistent with the assignment of the 38 ps component as geminate recombination of PCI and pyridine within the solvent cage. It is proposed that population of the vibrationally excited ³LF state results in efficient ligand dissociation, a process that kinetically competes with vibrational cooling. This model remains to be investigated, but can account for lower than unit quantum yield for ligand exchange, along with recombination within the solvent cage. The efficient photochemistry observed for **3** with low energy light (λ_{irr} 590 nm), as well as the excited state dynamics observed with 568 nm excitation, support ultrafast population of the ³LF state from the Ru→tpy ¹MLCT or ³MLCT state leading to py dissociation, and not from direct excitation of the ¹LF state.

Conclusions

Complex **1** was designed as a dual action molecular device that releases py in CH₃CN with $\Phi_{500} = 0.053(1)$ in addition to producing ¹O₂ with $\Phi = 0.69(9)$. The design of this complex was inspired by the efficient py dissociation from **3** with the sterically bulky Me₂bpy ligand, as well as the ¹O₂ sensitizing dppn-containing compounds previously reported. The TA data reveals spectral and kinetic information regarding the excited state dynamics involved in ³LF and ³ $\pi\pi^*$ state population. In order for the observed photochemical properties, competitive population of both states must be operative with selective excitation into the red-edge of the Ru→tpy ¹MLCT state with 568 nm light. The ³ $\pi\pi^*$ state is formed from the ³MLCT state, however, it is not yet fully understood whether the ³LF state is populated directly through ISC from the singlet manifold or from vibrationally excited ³MLCT state, as previously proposed for [Ru(bpy)₂(NA)₂]²⁺.²⁰ Analysis of **3** and **4** provide simplified models to compare the kinetics involved in ³LF state population, as they lack the low-lying dppn/Me₂dppn ³ $\pi\pi^*$ excited state. Work is ongoing to better understand the ultrafast evolution of the ³LF state in related complexes. The ability of **1** to both release pyridine and produce ¹O₂ in relatively high yields can serve as a platform for related complexes to exhibit enhanced

photochemotherapeutic action through the ability of these molecules to induce cell death via two different, independent mechanisms, drug release and oxidative stress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Structural representations of **1-4**.

Figure 2. Electronic absorption spectra of **1** in CH_3CN irradiated with $\lambda_{\text{irr}} = 395 \text{ nm}$ for 0, 0.5, 1, 2, and 4 min.

Figure 3.

Transient absorption spectra of (a) **1** and (b) **3** in CH_3CN with $\lambda_{exc} = 568$ nm collected 1, 5, 10, 20, 40, 60, 100, 200, 500, 1000, and 2000 ps following the laser pulse (fwhm = 300 fs, baseline trace collected at -10 ps).

Table 1

Lowest Energy Absorption Maximum, Quantum Yields for Ligand Exchange (Φ_{500}) and $^1\text{O}_2$ Production (Φ), and Excited State Lifetimes (τ) of **1** – **4** at 298 K.

Complex	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) ^a	Φ_{500} ^b	Φ ^c	τ
1	486 (12,900)	0.053(1) ^e	0.69(9)	47 μs ^d
2	474 (12,900)	< 0.0001 ^e	0.98(6)	50 μs ^d
3	471 (8,020)	0.16(1)	-	38 ps ^e
4	468 (8,120)	< 0.0001	-	470 ps ^e

^aIn acetone.

^bIn CH_3CN , $\lambda_{\text{irr}} = 500 \text{ nm}$.

^cIn MeOH , $\lambda_{\text{irr}} = 460 \text{ nm}$.

^dIn deaerated pyridine, $\lambda_{\text{exc}} = 355 \text{ nm}$, fwhm = 8 ns.

^eIn deaerated CH_3CN , $\lambda_{\text{exc}} = 568 \text{ nm}$, fwhm = 300 fs.