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New Ru^{II} Complex for Dual Activity: Photoinduced Ligand Release and ¹O₂ Production

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Abstract

The new complex [Ru(pydpnp)(biq)(py)]²⁺ (**1**) undergoes both py photodissociation in CH₃CN with Φ_{500} =0.0070(4) and ¹O₂ production with Φ =0.75(7) in CH₃OH from a long-lived ³ $\pi\pi^*$ state centered on the pydpnp ligand (pydpnp=3-(pyrid-2-yl)benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine; biq = 2,2'-biquinoline; py= pyridine). This represents an order of magnitude decrease in the Φ_{500} compared to the previously reported model compound [Ru(tpy)(biq)(py)]²⁺ (**3**) (tpy=2,2':6',2''-terpyridine) that undergoes only ligand exchange. The effect on the quantum yields by the addition of a second deactivation pathway through the low-lying ³ $\pi\pi^*$ state necessary for dual reactivity was investigated using ultrafast and nanosecond transient absorption spectroscopy, revealing a significantly shorter ³MLCT lifetime in **1** relative to that of the model complex **3**. Due to the structural similarities between the two compounds, the lower values of Φ_{500} and Φ compared to that of [Ru(pydpnp)(bpy)(py)]²⁺ (**2**) (bpy=2,2'-bipyridine) are attributed to a competitive excited state population between the ³LF states involved in ligand dissociation and the long-lived ³ $\pi\pi^*$ state in **1**. Complex **1** represents a model compound for dual activity that may be applied to photochemotherapy.

Keywords

excited states; ligand exchange; photochemistry; ruthenium; transient absorption

The wide use of Ru^{II} polypyridyl complexes for applications that include photochemotherapy (PCT), solar energy conversion, sensors, and molecular switches stems from their strong absorption throughout the ultraviolet and visible regions that arise from

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ligand-centered $^1\pi\pi^*$ and metal-to-ligand charge transfer ($^1\text{MLCT}$) transitions, together with $^3\text{MLCT}$ excited states that are long-lived, emissive, and redox-active.^[1–16] In addition to regenerating the ground state directly, the deactivation of the $^3\text{MLCT}$ states can occur by population of low-lying excited states, such as non-emissive triplet ligand field (^3LF) or ligand-centered $^3\pi\pi^*$ states.^[17, 18] The ability to control the relative populations of such excited states is useful for the design of metal complexes to undergo specific desired processes, such as ligand dissociation and the generation of $^1\text{O}_2$.^[19, 20]

Distortions of the pseudo-octahedral geometry of Ru^{II} polypyridyl complexes have been shown to lower the energy of the ^3LF state, thereby promoting its more efficient thermal population from the $^3\text{MLCT}$ state.^[21, 22] The introduction of steric bulk on the ligands was demonstrated to decrease the ^3LF state energy in the series $[\text{Ru}(\text{L})_3]^{2+}$, where $\text{L}=2,2'$ -bipyridine (bpy), 6-methyl-2,2'-bipyridine (Me**bpy**), or 4,4',6,6'-tetramethyl-2,2'-bipyridine (Me₄**bpy**), which resulted in the observation of shorter $^3\text{MLCT}$ lifetimes.^[23] Bidentate ligand dissociation occurs in many Ru^{II} complexes with one or more sterically encumbering ligand(s). For example, the irradiation of $[\text{Ru}(\text{biq})(\text{phen})_2]^{2+}$ (**biq**=2,2'-biquinoline; **phen**=1,10-phenanthroline) and $[\text{Ru}(\text{biq})_2(\text{phen})]^{2+}$ with low energy light ($\lambda_{\text{irr}}=600\text{ nm}$) in water promotes exchange of a **biq** ligand for two H_2O molecules;^[24] similar reactivity was observed for $[\text{Ru}(\text{biq})_2(\text{bpy})]^{2+}$.^[25] The addition of bulky methyl-, phenyl-, or chloro-substituents to the bidentate L' ligand in a series of $[\text{Ru}(\text{L})_2(\text{L}')]^{2+}$ complexes, where $\text{L}=\text{bpy}$ or **phen**, promotes the exchange of L' with two solvent H_2O or CH_3CN molecules with Φ of approximately 0.02 ($\lambda_{\text{irr}}=500\text{--}600\text{ nm}$).^[14, 26, 27]

The photoinduced exchange of pyridine coordinated to Ru^{II} is generally less efficient than that of nitrile ligands.^[23, 28] For example, a stark difference is observed in the efficiency of the exchange of the L ligand from $[\text{Ru}(\text{tpy})(\text{bpy})(\text{L})]^{2+}$ (**tpy**=2,2':6',2''-terpyridine; $\text{L}=\text{CH}_3\text{CN}$, **py**) in DMF, with quantum yields, Φ_{436} , of 0.006 and $<10^{-5}$ for $\text{L}=\text{CH}_3\text{CN}$ and **py**, respectively.^[29] In an effort to enhance the pyridine photodissociation process, the **bpy** ligand was replaced by sterically demanding 6,6'-dimethyl-2,2'-bipyridine (Me₂**bpy**) and **biq**, resulting in significantly greater quantum yields of photoinduced **py** exchange in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ with CH_3CN solvent, with Φ_{500} values of 0.16(1) and 0.033(1), respectively.^[30] The lower efficiency measured for $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ is attributed to the lower energy $\text{Ru}\rightarrow\text{biq } ^3\text{MLCT}$ state in this complex relative to the $\text{Ru}\rightarrow\text{tpy } ^3\text{MLCT}$ state in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{bpy})(\text{py})]^{2+}$, such that there is a larger energy gap for the thermal population of the dissociative ^3LF state in the former.^[30] It should be noted, however, that the **biq** ligand imparts a significant red shift in the absorption maximum, a characteristic that is desirable in PCT schemes.^[31]

Dual activity of Ru^{II} complexes can be achieved through the selection of ligands that provide competitive excited state deactivation pathways. For example, the lowest energy excited state in $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$ (**dppn**=benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine) is a $^3\pi\pi^*$ **dppn**-centered excited state. In these complexes, efficient energy transfer takes place to produce $^1\text{O}_2$ with approximately 100% yield.^[32] In $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$, the CH_3CN ligands are capable of photodissociation and the **dppn** ligand is available for $^1\text{O}_2$ generation, such that both processes are possible. The irradiation of $[\text{Ru}(\text{bpy})(\text{dppn})(\text{CH}_3\text{CN})_2]^{2+}$ with visible light results in the exchange of the CH_3CN ligands with

$\Phi_{400}=0.002(3)$ for the first step in H_2O ; however, the lowest excited state is $\text{dppn } ^3\pi\pi^*$ in nature, so the complex also produces $^1\text{O}_2$ with $\Phi = 0.72(2)$ in CH_3OH .^[33] This strategy was also applied in the case of $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$ ($\text{Me}_2\text{dppn}=3,6$ -dimethylbenzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine) to effect py dissociation, $\Phi_{500}=0.053(1)$ in CH_3CN , in conjunction with $^1\text{O}_2$ production, $\Phi = 0.69(9)$ in CH_3OH .^[34]

Herein we report the new photoactive complex $[\text{Ru}(\text{pydppn})(\text{biq})(\text{py})]^{2+}$ (**1**; $\text{pydppn}=3$ -(pyrid-2-yl)benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine) designed to undergo both efficient py exchange and $^1\text{O}_2$ production (Figure 1). The biq ligand was introduced to provide steric bulk and to red-shift the $^1\text{MLCT}$ absorption maximum of **1**,^[20] making this dual-action complex potentially useful for PCT. The pydppn ligand, a tridentate analogue of dppn, is expected to provide a long-lived $^3\pi\pi^*$ state for $^1\text{O}_2$ production with high quantum yield.^[35] The photoactivity of **1** is compared to that of two related complexes, $[\text{Ru}(\text{pydppn})(\text{by})(\text{py})]^{2+}$ (**2**) and $[\text{Ru}(\text{tpy})(\text{biq})(\text{py})]^{2+}$ (**3**), which lack the steric bulk and the extended π system, respectively.

The synthesis and characterization of **1** and **2** are described in detail in the Supporting Information (Figures S1–S3). Both complexes absorb strongly in the visible region, with pydppn-centered $^1\pi\pi^*$ transitions at 391 nm ($\epsilon=12700 \text{ M}^{-1} \text{ cm}^{-1}$ in **1** and $\epsilon=15\,200 \text{ M}^{-1} \text{ cm}^{-1}$ in **2**) and 411 nm ($\epsilon=7570 \text{ M}^{-1} \text{ cm}^{-1}$ in **1** and $\epsilon=11\,900 \text{ M}^{-1} \text{ cm}^{-1}$ in **2**). The lowest energy $^1\text{MLCT}$ maxima of **1–3** are compared in Table 1 and the spectra are displayed in Figure 2a. It is evident from the data in Table 1 that the $\text{Ru} \rightarrow \text{biq } ^1\text{MLCT}$ transitions of **1** and **3**, centered at 529 nm ($8070 \text{ M}^{-1} \text{ cm}^{-1}$) and 530 nm ($9020 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, lie at a lower energy than the $\text{Ru} \rightarrow \text{pydppn } ^1\text{MLCT}$ maximum of **2** at 480 nm ($10\,200 \text{ M}^{-1} \text{ cm}^{-1}$). This finding is consistent with predominately $\text{Ru} \rightarrow \text{tpy}$ based $^1\text{MLCT}$ transitions in **2**, similar to those in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ at 468 nm ($\epsilon=8120 \text{ M}^{-1} \text{ cm}^{-1}$),^[34] as well as the related series $[\text{Ru}(\text{L})_{2-n}(\text{L}')_n]^{2+}$ ($\text{L}=\text{tpy}$, $\text{L}'=\text{pydppn}$; $n=0-2$), which exhibit maxima in the 474–477 nm range.^[35]

The irradiation of **1** with visible light ($\lambda_{\text{irr}} 395 \text{ nm}$) led to both ligand exchange and $^1\text{O}_2$ production. Figure 2b shows the decrease of the absorption of **1** at 529 nm and the concomitant increase in the peak at 507 nm under a N_2 atmosphere. These spectral changes are indicative of the substitution of the py ligand for an CH_3CN solvent molecule to generate $[\text{Ru}(\text{pydppn})(\text{biq})(\text{CH}_3\text{CN})]^{2+}$ with a quantum yield of ligand exchange, Φ_{500} , of 0.0070(4) under $\lambda_{\text{irr}}=500 \text{ nm}$. The exchange of bound py with CH_3CN was also confirmed by mass spectrometry. The compound collected following the photolysis of **1** in CH_3CN ($t_{\text{irr}}=50 \text{ min}$, $\lambda_{\text{irr}} 395 \text{ nm}$) exhibits a new peak at m/z 404.06 that corresponds to the photoproduct $[\text{Ru}(\text{pydppn})(\text{biq})(\text{CH}_3\text{CN})]^{2+}$ and the parent ion peak of the starting material at m/z 423.07 is no longer present. No changes in the electronic absorption spectrum of **1** were observed when the complex was dissolved in CH_3CN and stored in the dark for at least 50 h, establishing the thermal stability of the complex at room temperature (Figure S4 in the Supporting Information). As expected from the lack of steric strain in **2**, the complex does not undergo detectable photoinduced ligand exchange in CH_3CN upon irradiation for up to 18 h under similar experimental conditions. The lower ligand substitution quantum yield of **1** compared to that of **3**, $\Phi_{500}=0.033(1)$, in CH_3CN is consistent with the competitive

population of both the dissociative ^3LF and the low-lying pydppn-centered $^3\pi\pi^*$ from the MLCT states in **1**, whereas in **3**, the ligand-centered tpy $^3\pi\pi^*$ state is expected to lie above the $^3\text{MLCT}$ level and to not be populated. The competitive population predicted for **1** can also be used to explain the lower quantum yield for $^1\text{O}_2$ production, $\Phi = 0.75(7)$, relative to that of **2**, $\Phi = 0.96(8)$, since no ligand exchange is observed in the latter (Table 1). As discussed in detail below, the $^3\text{MLCT}$ lifetime of **3** is too short for that state to be able to produce $^1\text{O}_2$ by bimolecular energy transfer.

The photoinduced ligand exchange observed for **1** is attributed to the presence of steric strain imparted by the bulky biq ligand. Selected bond lengths and angles from the optimized structures of **1–3** are listed in Table 2, along with crystallographic data for **3**, and the calculated structures of **1** and **2** are shown in Figure 3 (additional data can be found in the Supporting Information). The Ru—N bond lengths do not vary significantly among **1–3** (Table S1 in the Supporting Information), but it is evident from Figure 3 that there is significant distortion away from the pseudo-octahedral geometry around the Ru^{II} center in **1**. In particular, the biq ligand in **1** bends away from the N(1) and N(2) atoms of the pydppn ligand, resulting in greater N(1)-Ru-N(4) and N(2)-Ru-N(4) angles in **1** compared to **2** (Table 2 and Table S2 in the Supporting Information). In addition, the pyridine ligand is bent away from the biq ligand in **1** relative to **2**, which leads to smaller N(2)-Ru-N(6) and N(3)-Ru-N(6) bond angles in the former. These distortions result in less directional σ -orbital overlap of the ligand lone pairs and metal orbitals, which lowers the energy of the e_g set and the ^3LF states in **1** relative to those in **2**. The distorted structure calculated for **1** is similar to those reported for **3** and related complexes.^[20, 24, 30]

The excited state dynamics of **1** were investigated using transient absorption spectroscopy and the results were compared to those of **3**. The transient absorption spectrum of **1** in deaerated pyridine features an intense, broad positive signal with a maximum at 550 nm that decays mono-exponentially with $\tau = 13 \mu\text{s}$ ($\lambda_{\text{exc}} = 532 \text{ nm}$, $\text{fwhm} = 8 \text{ ns}$, Figure S5 in the Supporting Information), consistent with the spectral features and lifetime of $\tau = 24 \mu\text{s}$ measured for $[\text{Ru}(\text{pydppn})_2]^{2+}$ in CH_3CN .^[35] Consequently, this feature is assigned to the $^3\pi\pi^*$ excited state of the pydppn ligand, in agreement with the pydppn-centered $^3\pi\pi^*$ of related complexes and free pydppn ligand.^[35] In contrast, the transient absorption spectrum of **3** in deaerated pyridine consists of excited state absorption in the 400–460 nm range and a bleach at approximately 530 nm, both of which decay mono-exponentially with τ of approximately 50 ns ($\lambda_{\text{exc}} = 355 \text{ nm}$, $\text{fwhm} = 8 \text{ ns}$, Figure S6 in the Supporting Information), consistent with the spectral features and lifetime of the Ru→biq $^3\text{MLCT}$ state observed for related complexes.^[36]

Ultrafast transient absorption spectra of **1** were collected following selective low-energy excitation of the Ru→biq $^1\text{MLCT}$ state with 595 nm pulses in acetone ($\text{fwhm} = 300 \text{ fs}$), and the resulting traces are depicted in Figure 4. The Ru→biq $^3\text{MLCT}$ excited state of **1** exhibits a positive transient feature from 380–450 nm at the earliest time delay, 0.3 ps, which decays mono-exponentially with τ of approximately 6 ps. Although the transient feature with a maximum at 550 nm associated with the pydppn $^3\pi\pi^*$ state is partially obscured by the laser line, a strong positive signal grows in from 460–540 nm with τ of approximately 5 ps, concomitant with the decay of the $^3\text{MLCT}$ feature. This approximately 6 ps component is

assigned to internal conversion (IC) from the $^3\text{MLCT}$ state to the $^3\pi\pi^*$ state, reported to occur within 18 ps in $[\text{Ru}(\text{tpy})(\text{Me}_2\text{dppn})(\text{py})]^{2+}$.^[20, 34] Similar spectral features and kinetics are observed for **1** with 515 nm excitation in acetone (fwhm=300 fs, Figure S7 in the Supporting Information). For **3**, which does not possess a low-lying $^3\pi\pi^*$ state, selective excitation of the $\text{Ru}\rightarrow\text{biq}$ $^1\text{MLCT}$ state with 568 nm pulses in CH_3CN results in a broad positive $\text{Ru}\rightarrow\text{biq}$ $^3\text{MLCT}$ transient absorption signal from 380–470 nm, together with ground state bleaching at approximately 530 nm (fwhm=300 fs, Figure S8 in the Supporting Information). Vibrational cooling is observed both in the $^3\text{MLCT}$ signal and the bleach with $\tau=8$ ps, and no further intensity changes are apparent up to 2 ns (Figure S8), consistent with the approximately 50 ns lifetime measured for the $^3\text{MLCT}$ state of the complex (Figure S6 in the Supporting Information).

The Jablonski diagrams of **1** and **3** after excitation into the lowest energy $\text{Ru}\rightarrow\text{biq}$ $^1\text{MLCT}$ state are shown in Figure 5. Due to the structural similarities between these two complexes, the shorter $^3\text{MLCT}$ lifetime of **1** as compared to **3** must be due to the presence of an additional deactivation pathway through the low-lying pydppn $^3\pi\pi^*$ state. Population of the ^3LF state(s) is not directly observed in the transient absorption spectra of either complex, consistent with the ^3LF state lying above the $\text{Ru}\rightarrow\text{biq}$ $^3\text{MLCT}$ state. It remains unclear, however, whether population of the dark ^3LF state occurs through intersystem crossing directly from the $\text{Ru}\rightarrow\text{biq}$ $^1\text{MLCT}$ or $^3\text{MLCT}$ state.

Complex **1** was designed to act as a model dual action photochemotherapy agent that releases py in CH_3CN with $\Phi_{500}=0.0070(4)$ and produces $^1\text{O}_2$ with $\Phi=0.75(7)$. Transient absorption data reveal a shorter-lived $\text{Ru}\rightarrow\text{biq}$ $^3\text{MLCT}$ state in **1** as compared to **3**, explained by the introduction of an additional deactivation pathway in **1**, a low-lying pydppn -centered $\pi\pi^*$ state. The quantum yield for ligand exchange, Φ_{500} , of **1** is an order of magnitude lower than that of **3**; as these two complexes are structurally very similar, this difference can be attributed to competitive population of the ^3LF and $^3\pi\pi^*$ states from the MLCT state in **1**. Ongoing work is being directed at improving the understanding of the ultrafast population of the ^3LF states and controlling excited-state deactivation through multiple pathways in related complexes. The ability of **1** to both release pyridine and produce $^1\text{O}_2$ is promising for use in PCT, as this complex has the potential to induce cell death through both the photoinduced release of a pyridine-containing drug together with imparting oxidative stress by the generation of a reactive oxygen species, $^1\text{O}_2$.

Supplementary Material

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Acknowledgments

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Figure 1.
Schematic representations of the molecular structures of 1–3.

Figure 2.

a) Electronic absorption spectra of **1** (black), **2** (red) and **3** (dashed black) in acetone, and b) spectral changes of **1** as a function of irradiation time in CH_3CN (λ_{irr} 395 nm, t_{irr} =0, 1, 3, 5, 10, 20, and 40 min).

Figure 3. Calculated structures of **1** and **2** highlighting the tilt in the py and biq ligands of **1** relative to **2** (hydrogen atoms are removed for clarity).

Figure 4.

Transient absorption spectra of **1** in acetone collected at 0.3, 0.5, 1, 3, 5, 10, 20, 40, 60, 100, 200, 500, 1000, and 2000 ps following the laser pulse (λ_{exc} =595 nm, fwhm=300 fs, baseline trace collected at -10 ps).

Figure 5.
Jablonski diagrams of: a) **3**, and b) **1**.

Table 1

Lowest energy absorption maxima (λ_{abs}), molar extinction coefficients (ϵ), and quantum yields for ligand exchange (Φ_{500}) and $^1\text{O}_2$ production (Φ) of **1–3** at 298 K.

Complex	λ_{abs} [nm] (ϵ [$\text{m}^{-1}\text{cm}^{-1}$)] ^[a]	Φ_{500} ^[b]	Φ ^[c]
1	529 (8070)	0.0070(4)	0.75(7)
2	480 (10 200)	–	0.96(8)
3 ^[d]	530 (9020)	0.033(1)	–

^[a] In acetone.

^[b] In CH_3CN , $\lambda_{\text{irr}} = 500$ nm.

^[c] In CH_3OH , $\lambda_{\text{irr}} = 460$ nm.

^[d] From ref. [30].

Table 2Selected calculated bond angles [°] for **1–3** and experimental data (in parenthesis) for **3**.^[a]

Angle	1	2	3 ^[b]
N(1)-Ru-N(4)	97.4	89.7	85.1 (83.5)
N(1)-Ru-N(5)	101.6	102.1	100.9 (98.9)
N(1)-Ru-N(6)	94.0	89.4	87.0 (87.5)
N(2)-Ru-N(4)	101.8	97.4	102.2 (98.4)
N(2)-Ru-N(6)	85.7	89.2	85.4 (87.8)
N(3)-Ru-N(4)	85.1	90.7	96.7 (99.5)
N(3)-Ru-N(5)	112.2	100.4	101.5 (102.3)
N(3)-Ru-N(6)	86.6	92.8	94.2 (91.8)
N(5)-Ru-N(6)	95.6	95.7	95.6 (96.1)

^[a]Numbering scheme in Figure 1; additional structural data can be found in the Supporting Information.^[b]From ref. [30].