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Two Emissive Long-Lived Excited States of an Imidazole-Functionalized Ruthenium Dipyridophenazine Complex

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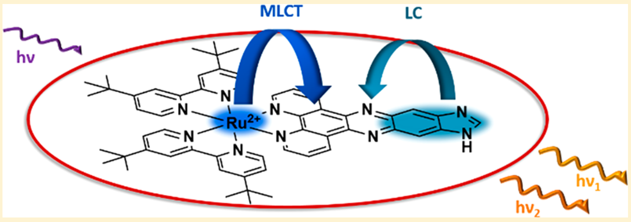
Supporting Information



ABSTRACT: A ruthenium(II) polypyridine-type complex based on the dipyridophenazine ligand with a directly fused imidazole unit (**L1**, dipyrido[3,2-*a*:2′,3′-*c*]phenazine-10,11-imidazole) has been synthesized, and its electrochemical and photophysical properties have been studied. The cyclic voltammogram of $[\mathrm{Ru(tbbpy)_2}(\mathbf{L1})]^{2+}$ (**C1**) (tbbpy is 4,4′-*tert*-butyl-2,2′-bipyridine) shows a cathodic shift of the phenazine-based reduction process compared to similar molecules, while the first detected reduction wave (−1.34 V vs $\mathrm{Fc/Fc^+}$) is assigned to the imidazole unit within the molecule. On the basis of the TD-DFT calculations, the strong visible absorption band exhibited by **C1** is assigned to a metal-to-ligand charge transfer (MLCT) transition with a concurrent ligand-centered (LC) transition. At room-temperature, **C1** features emission ($\Phi = 0.04$) from its lowest excited states with time constants of 1.2 and 18.3 μs. These lifetimes are assigned to emission processes from the ^{3}MLCT and ^{3}LC state, respectively. This is the first time that a long-lived dual emission has been observed for a ruthenium(II) complex bearing a directly fused extended π-system. Furthermore, the emission of **C1** is quenched upon water addition. In contrast to related compounds based on a dipyridophenazine ligand, the excited state energy is not shifted, and the lifetime is drastically decreased to 169 ns.

INTRODUCTION

Ruthenium polypyridine complexes play a prominent role in functional molecular assemblies in solar energy conversion, photodynamic therapy, and sensing.[1,2] Tuning of excited state properties of Ru(II) complexes, among others, plays a pivotal role within all light driven applications. A crucial factor determining the usability of ruthenium polypyridine complexes is the lifetime of the excited state, since it determines the time span where interactions with reactants may occur during photocatalysis or photodynamic therapy. Adjusting these properties may be accomplished by manipulating the ligand sphere,[3] immediate environment,[4,5] or introduction of additional functional units that stabilize the triplet states.[6,7]

In that regard, ruthenium dipyridophenazine (dppz) complexes are of particular interest. The principal dynamics in the prototype complex $[\mathrm{(bpy)_2Ru(dppz)}]^{2+}$ are associated with the accessibility of several excited states. This causes the *light switch* effect,[8] that is, a strong dependence of the luminescence characteristics on the solvent properties.[9] Emission is not observed when these complexes are dissolved in water, but the addition of DNA switches the luminescence back on again. This effect can be explained by the existence of two particular excited states known as the *bright state* and the *dark state*, residing on the phenanthroline and phenazine part of the dppz ligand, respectively. In protic solvents, the dark state is stabilized to a certain extent, which favors radiationless deactivation from the dark state over thermal depopulation of the bright state.[10−12] In presence of DNA, intercalation occurs via the extended oligoaromatic units of the dppz ligand; hence, the thermal depopulation of the *bright state* to the *dark state* is reduced. Extensive studies were made in the past 30 years to unravel the principle mechanism behind this *light switch* effect.[8−25] Besides the ability to function as a reversible DNA light switch sensor,[26−28] the extension of the dppz ligand by an imidazole moiety should be also considered to provide long-lived charge excited states in different solvents. Notably, the extension of the dppz ligand, leads to strong effects on the photochemistry. For instance, the loss of water sensitivity in the excited state by fused pyrazine moieties[29] or long-lived dark charge separated states in fused benzene moieties (20 μs)[30] and in substituted dppz ligands with electron-donating triarylamine in 11-position (11 μs).[31] Especially the long-lived excited states of Ru(II) complexes of dppn (dppn is benzo[*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine)derivatives have resulted in interesting properties like efficient light-driven ligand dissociation and singlet oxygen formation[30,32] and applications as highly efficient photodynamic therapy agent.[33] Instead, the Ru(II) complex with a pyridoquinolinone unit fused to the dppz ligand results in an emissive state with sub nanosecond lifetimes.[34,35]

However, dual emission in ruthenium complexes is mainly known for asymmetric substituted 1,10-phenanthroline,[3,36] terpyridine,[37] or triazineligands[38,39] and for dinuclear complexes.[40−42] In many cases, the dual emission is only observable under 77 K[38,39,43,44] or the emission decays in a

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few nanoseconds.[36,40] One prominent example with a long-lived dual emission of 11 μs is the Ru(II) complex where an electron-rich *p*-methoxyphenyl unit was attached to the 4-position of the 1,10-phenanthroline ligand via an alkynyl bridge.[45] Glazer et al. reasoned dual emission with the prerequisite of having large deviations of the excited state with respect to the ground state, which should only be possible with asymmetric ligands.[45] To the best of our knowledge, a dual emission with microsecond lifetimes at room temperature for a Ru(II) dppz complex and, thus, for a symmetric complex, is unknown so far.

This study presents the electrochemical and photophysical properties of a ruthenium complex with a modified dppz ligand that contains a conjugated imidazole unit at the distal end. The corresponding heteroleptic complex $[(\text{tbbpy})_2\text{Ru}(\textbf{L1})]^{2+}$ (**C1**) (tbbpy is 4,4′-*tert*-butyl-2,2′-bipyridine and **L1** is dipyrido[3,2-*a*:2′,3′-*c*]phenazine-10,11-imidazole) (Figure 1) was prepared and investigated using mass spectrometry, NMR, absorption, and emission spectroscopy and cyclic voltammetry.

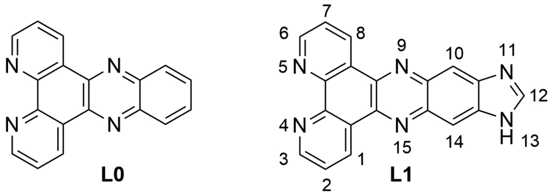


Figure 1. General structure of the ligands **L0** and **L1** with the applied numbering scheme.

Supportive time-dependent DFT (TD-DFT) calculations were also performed. The properties of **C1** were compared with **C0**, which is an analogous complex containing the unsubstituted dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand **L0** instead of **L1** (Figure 1).

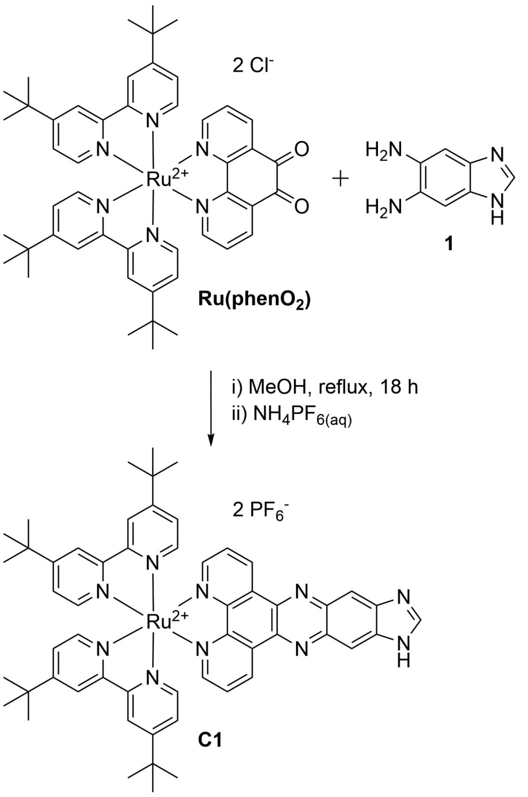
Furthermore, the behavior of the triplet excited states of **C1** were investigated in more detail via transient absorption spectroscopy and emission lifetime measurements on the nanosecond time scale. These measurements allowed the nature of the triplet excited states to be characterized and the impact of the incorporated imidazole unit on the underlying processes to be elucidated.

■ RESULTS AND DISCUSSION

Synthesis. The π-extended dipyridophenazine complex **C1** comprising an imidazole unit was obtained from the condensation reaction of $[(\text{tbbpy})_2\text{Ru}(\text{phenO}_2)]^{2+}$ (**Ru(phenO$_2$)**; phenO$_2$ is 1,10-phenanthroline-5,6-dione) with 5,6-diaminobenzimidazole (Scheme 1). Performing the reaction at the complex circumvented the formation of the free ligand, which would have required sophisticated purification of the target molecule due to intermolecular π–π stacking.[46–48] Complex **C0** was synthesized for comparison following literature procedures.[47] Additionally $[(\text{MeCN})_2\text{Zn}(\textbf{L1})](\text{BF}_4)_2$ (**ZnL1**) was synthesized, allowing the characterization of the poorly soluble ligand **L1**. Calculation of the ground state structure of **C1** confirmed that the ligand has an almost planar structure in the complex. The details from this calculations and the full characterization data for **C1** and **L1** are given in the Supporting Information.

Electrochemical Properties. The cyclic voltammogram of **C1** recorded in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile displays a reversible redox couple assigned to Ru$^{\text{II}}$/Ru$^{\text{III}}$ and several LC redox processes at more negative potentials (Figure 2 and Table 1). For **C1** the Ru$^{\text{II}}$/Ru$^{\text{III}}$ redox couple is centered at 0.82 V vs Fc/Fc$^+$, while the parent complex **C0** has an analogous redox couple at 0.85 V vs Fc/Fc$^+$.[47] Usually the stepwise reduction of $[(\text{bpy})_2\text{Ru}(\text{L})]^{2+}$ complexes, where L is a dppz derivative, follows the order: (i) phenazine part of L, (ii)/(iii) bpy ligands, and (iv) phenanthroline part of L.[49] Therefore, four LC reversible reductions are expected for **C1**. By comparing the voltammetry recorded for **C1** with that

Scheme 1. Synthetic Route for $[(\text{tbbpy})_2\text{Ru}(\textbf{L1})]^{2+}$ C1



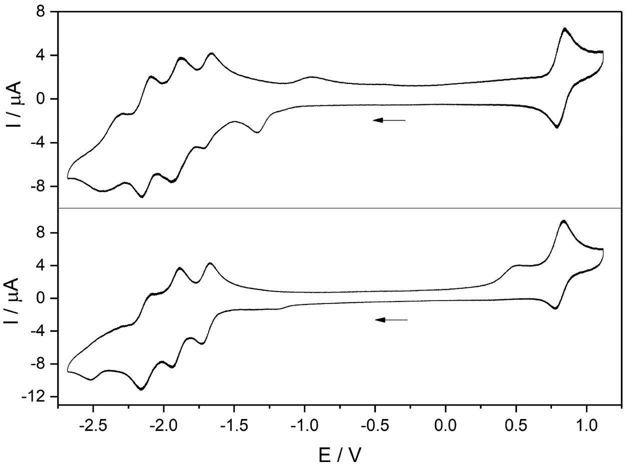


Figure 2. Cyclic voltammograms of solutions of **C1** at room temperature in acetonitrile (top) and acetonitrile with an excess of sodium hydride (bottom), both referenced vs ferrocene/ferricenium (Fc/Fc$^+$) couple, respectively. Scan rate: 200 mV s^{-1}. Supporting electrolyte: 0.1 M Bu$_4$NPF$_6$.

Table 1. Summary of the Electrochemical Properties of the Compounds C0, C1, and the Deprotonated Form of C1 ($C1_{depr}$)[a]

	E^0_{ox} [V]	E^0_{red} [V]
C0[b]	0.85	−1.34, −1.86, −2.11, −2.48
C1	0.82	−1.34,[c] −1.69, −1.91, −2.12, −2.38
$C1_{depr}$	0.81	−1.70, −1.91, −2.12, −2.52[c]

[a] The data were obtained from deaerated, anhydrous acetonitrile solution at room temperature versus the ferrocene/ferricenium (F/Fc$^+$) couple. For reversible processes, $E^0 = (E_{pc} + E_{pa})/2$. [b] From literature.[47] [c] Cathodic peak potential for irreversible processes.

recorded for **C0** and similar compounds in the literature, one can assign the reductions at −1.91, −2.12, and −2.38 V vs Fc/Fc$^+$ to the reduction of the tbbpy ligands and the phenanthroline part of **L1**, respectively.[47,50,51] Accordingly, the reversible reduction wave at −1.69 V vs Fc/Fc$^+$ is attributed to the phenazine part of the molecule. However, the voltammetry of **C1** shows a fifth reduction process at −1.34 V vs Fc/Fc$^+$ that is not reversible and occurs at a more positive potential than the other ligand-centered redox couples. The irreversibility of the process led us to believe that the redox couple at −1.34 V vs Fc/Fc$^+$ was due to the reduction of the imidazole moiety on **L1** in the **C1** complex. Since imidazole moieties are known to undergo protonation/deprotonation processes affecting the reversibility of the corresponding redox couple,[52,53] an excess of sodium hydride was added to **C1** in the electrolyte solution to deprotonate the imidazole moiety. This led to complete disappearance of the irreversible reduction process at −1.34 V vs Fc/Fc$^+$ (Figure 2), while the remaining reduction steps remained almost unaffected during the in situ deprotonation.

Absorption and Emission Properties. The absorption spectrum of **C1** in acetonitrile (Figure 3 and Table 2) exhibits two distinct maxima at 289 and 315 nm. These absorption bands in the UV region have a high intensity and are typical for ligand centered transitions of ruthenium polypyridine complexes.[54] TD-DFT calculations showed that these bands do indeed belong to several ligand centered (LC) transitions of the tbbpy and the **L1** ligand of **C1** (compare Figure 3 and Table S6.1 for details). A broad absorption band between 350 and 400 nm also emerges for **C1**, which is red-shifted compared to the corresponding transition for **C0**. The reason for this pronounced red-shift is that interligand $\pi-\pi^*$ transitions occur from the benzimidazole unit of the **L1** ligand to the bpy ligand (Table S6.1).

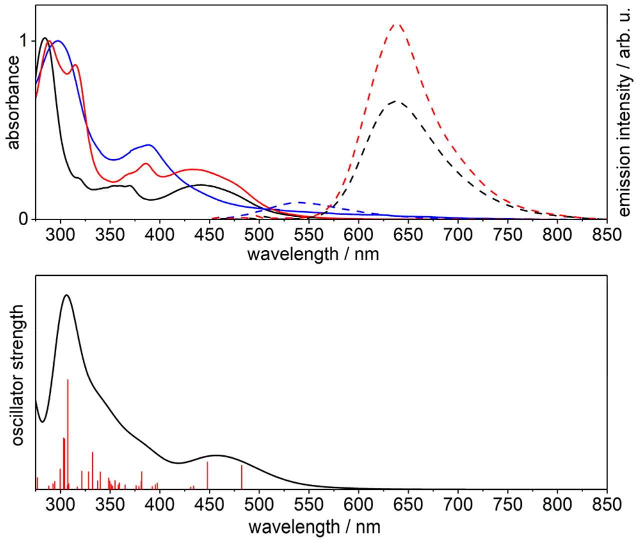


Figure 3. Top: Normalized absorption (solid line) and emission (dashed line) spectra of **C0** (black), **ZnL1** (blue), and **C1** (red) in deaerated, anhydrous acetonitrile; emission spectra were recorded at excitation wavelengths of the maximum of the lowest energy absorption band, respectively (see Table 2). Bottom: Calculated absorption spectrum (B3LYP-D3(BJ)/def2-TZVP) of complex **C1** (solid line), resulting from the convolution of the transitions above 560 nm (vertical bars) with a Gaussian function.

Table 2. Summary of the Photophysical Properties of the Compounds C0, C1, and ZnL1[a]

	λ_{abs} [nm]	ε_{MLCT} [$\times 10^3$ M^{-1} cm^{-1}]	Φ[c]	λ_{em}[d] [nm]
C0	441[b]	17.6	0.02	638
C1	433[b]	20.9	0.04	638
ZnL1	298, 389			542

[a] Data were obtained from deaerated, anhydrous acetonitrile solution at room temperature. [b] ^{1}MLCT absorption maximum. [c] Quantum yields were determined, using $[Ru(bpy)_3](PF_6)_2$ as reference.[57] [d] Recorded at excitation wavelength of the maximum of the lowest energy absorption band.

The broad absorption between 400 and 575 nm displays a maximum at 433 nm and a weakly pronounced shoulder at approximately 478 nm. Remarkably, the extinction coefficient of **C1** at 433 nm is 20.9 × 10^3 M^{-1} cm^{-1}, which is significantly higher than the corresponding absorption value for **C0** of 17.6 × 10^3 M^{-1} cm^{-1}. The increased absorption coefficient for **C1** at this wavelength is a result of overlaying MLCT and LC transitions based on the **L1** ligand. This is corroborated by TD-DFT calculations, showing a contribution located at the distal part of **L1** that stems from the benzimidazole and pyrazine unit, as depicted in the differential density plots (Figure 4). Such LC transitions in the MLCT transitions range are unknown for complexes with the **L0** ligand. Nevertheless, such overlay behavior is comparable to metal complexes with ligands bearing an extended π-system such as 3,6-dimethyldipyrido[3,2-*a*:2′,3′-*c*]anthracene-9,10-dinitrile,[55] 12-bromo-14-ethoxydipyrido[3,2-*a*:2′,3′-*c*]quinolino[3,2-*h*]-phenazine,[34] or benzo[*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine.[56]

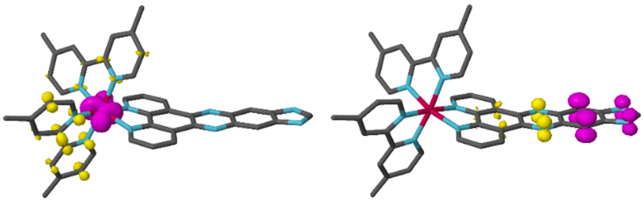


Figure 4. Differential density of **C1** between the ground state and the singlet excited state S_8 (left) and S_9 (right), respectively. Yellow corresponds to a positive isovalue in the density difference between the single-electron matrices of the ground and excited state. A decline in electron density is shown in purple color corresponding to a negative isovalue. More details about the transitions are summarized in SI, section 6.

In addition to the TD-DFT calculations the absorption spectrum of $[(MeCN)_2Zn(L1)](BF_4)_2$ (**ZnL1**) was recorded (Figure 3). **L1** is insoluble in most solvents, but coordination of the ligand to the redox inactive zinc(II) cation promotes the solubility of **L1**. Spectra recorded for **ZnL1** in solution only display the electronic transitions in the ligand **L1**.[58] The absorption spectrum of **ZnL1** in acetonitrile solution shows two maxima at 298 and 389 nm (Figure 3), which correlate with the LC $\pi-\pi^*$ transitions of **C1**. Further, a very broad contribution to lower energy is detected for **ZnL1**. These experimental results and the TD-DFT calculations for **C1** confirm that the LC transitions occur above 400 nm.

The excitation of **C1** dissolved in degassed, anhydrous acetonitrile solution at 433 nm results in an emission with a maximum at 638 nm and a quantum yield of 0.04. While the absorption properties of **C1** are barely altered by changing the solvent to dichloromethane or methanol (Figure S4.1), the emission maxima and overall intensities vary with changing solvent polarity (Figure S4.1 and Table S4.1). In dichloromethane and methanol, the emission of **C1** occurs at a slightly higher energy than in acetonitrile (Table S4.1). Similar observations have been made for related complexes, such as $[(bpy)_2Ru(\mathbf{L1})]^{2+}$, which emits at 625 nm in a water-based buffer solution (pH 7), and $[(phen)_2Ru(\mathbf{L1})]^{2+}$, which emits at 610 nm in pure water.[26,27] **C0** and **C1** display nearly the same emission maxima in acetonitrile at 639 and 638 nm, respectively. This indicates that the imidazole unit has a weak influence on the bright state emission initiated from the bpy part of the **L0** scaffold.[59]

For **C0** and related complexes, the light switch mechanism has been investigated in detail by quenching the emission with the addition of water and, then, causing the emission to return by adding DNA.[59,60] We carried out a similar quenching experiment to compare the *light switch* mechanisms of **C1** and **C0**. The emission of **C0** is, in accordance to literature,[24] clearly quenched and shifted to higher energy due to addition of water (Figure 5 and S4.9). **C1** showed comparable behavior during water addition, with the emission intensity considerably quenched. The Stern−Volmer plots of **C0** and **C1** (Figure S4.11) show similar slopes, but the quenching effect is more pronounced in case of **C1**. Additionally, the shift of the emission maximum due to water content is less pronounced for **C1** (Figure 5 top) compared to **C0**.

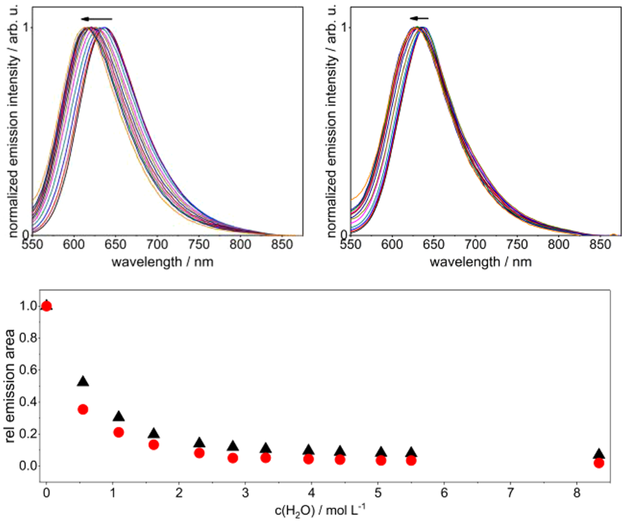


Figure 5. Top: Emission spectra of **C0** (left) and **C1** (right) in degassed acetonitrile−water mixtures. Arrows indicate the shift of emission maximum, upon increasing water concentrations. All spectra were recorded at excitation wavelengths of the maximum of the lowest-energy absorption band, respectively (see Table 2), and are normalized to the respective emission maximum intensity. For experimental details see SI, section 4.3. Bottom: Relative emission area of **C0** (black, triangles) and **C1** (red, dots) as a function of water concentration in deaerated acetonitrile solution.

Properties of Long-Lived Triplet Excited States. To further investigate the excited state properties and the underlying excited state deactivation processes of **C1** in more detail, time-resolved spectroscopy was performed on the nanosecond time scale. **C1** was excited at 355 nm in dry acetonitrile under an argon atmosphere, and the decay of the emission at 638 nm clearly revealed two long-lived emissive states with lifetimes of 1.19 μs, τ_1, and 18.25 μs, τ_2 (Figure 6 top and Table 3). The emission decay was also detected at several other wavelengths between 570 and 700 nm, which allowed a homogeneous kinetic emission map to be obtained (Figure S7.1). Global analysis of the respective emission decays resulted in amplitudes for the two time constants which are almost same in energy (Figure 6 bottom). Comparable results were obtained with an excitation wavelength of 532 nm (Figure S7.6−8). This means that **C1** possesses two excited states which are deactivated via emissive radiation of comparable energy. To the best of our knowledge this is the first experimental evidence for long-lived *dual emission* in mononuclear ruthenium complexes at room temperature, bearing a dppz scaffold with a directly fused π-extension. The short-lived component (1.19 μs, τ_1) is in the same energy range (630 nm) and time regime as reported for related $[Ru(N{\wedge}N)\mathbf{L0}]^{2+}$ complexes, such as $[Ru(phen)_2\mathbf{L0}]^{2+}$[10] with

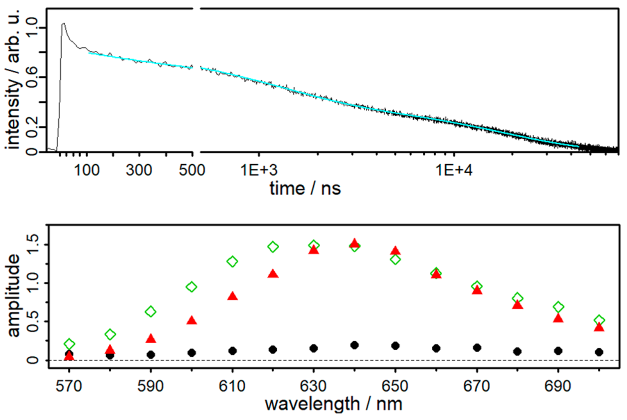


Figure 6. Top: Time-resolved emission spectra of **C1** in dry acetonitrile under inert conditions after excitation at λ_{ex} = 355 nm. The cyan line represents a biexponential fit with the time constants τ_1 = 1.19 μs ($\pm$0.01 μs) and τ_2 = 18.25 μs ($\pm$0.18 μs). Bottom: Decay-associated spectra of the biexponential fit with τ_1 = 1.07 μs and τ_2 = 13.40 μs. The amplitudes of the fit function $F(\lambda, t) = \sum_i^2 c_i(\lambda)\cdot\exp(-t/\tau_i) + c_0$ are displayed in green squares (c_1), red triangles (c_2), and black dots (c_0, long-living component).

Table 3. Summary of the Excited State Lifetimes of C1 in Acetonitrile and Acetonitrile/H_2O (10% v/v) Solution at Room Temperature after Excitation at λ_{ex} = 355 nm

water [% v/v]	emission, τ_{em} [μs]	transient absorption, τ_{tA} [μs]
0	1.19 ($\pm$0.01), 18.25 ($\pm$0.18)	18.0
10	0.17 ($\pm$0.01)	0.16

660 ns and $[Ru(bpy)_2\mathbf{L0}]^{2+}$ with 740 ns.[61] Therefore, this emission in **C1** is also originated from a ^{3}MLCT state located on the bipyridine scaffold of **L1**, as assigned previously in $[Ru(N\wedge N)\mathbf{L0}]^{2+}$ complexes.[11] As a second emissive state in transition metal complexes is highly uncommon, there are only a few reports of such peculiar characteristics. For example, Glazer et al. investigated a system where an additional chromophoric unit was attached to the 4-position of the phenanthroline ligand via an alkynyl bridge.[41,45] In this and related cases,[44] the second emissive state was attributed to be a MLCT process in nature. The time constant τ_2 of **C1** is, however, unusually long-lived to be assigned to a pure ^{3}MLCT state. Similar observations were made for Ru(II) complexes of dppn and pydppn (dppn is benzo[*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine, pydppn is 3-(pyrid-2′-yl)-4,5,9,16-tetraaza-dibenzo[*a*,*c*]naphthacene), where the remarkably long lifetimes were attributed to a ^{3}LC excited state, which was accessible through absorption into the ^{1}LC or ^{1}MLCT state.[30,56,62] Supporting TD-DFT calculations for **C1** indicated the presence of low-lying LC transitions are also responsible for this emission (Figure 4 and Table S6.1). This is also corroborated by electrochemical measurements and calculations performed on **L0** and its derivatives, highlighting that such electronically separated subunits within complexes bearing π-extended diimine ligands are not uncommon.[47,63−65] Similar behavior has recently been reported for heteroleptic Cu(I) complexes with an extended π-system based on an anthracene moiety.[55] Although the excited states of the Cu(I) complexes underwent nonradiative decay, this example highlights the possibility of having ^{3}MLCT and ^{3}LC excited states in parallel on one coordinated ligand with an extended π-system.

Additionally, measurements of **ZnL1** (Figure S7.5) were performed to verify that all emission features originate from **C1** and not from uncoordinated ligand in the solution. However, no emission with time constants in the microsecond range could be detected, confirming that the results of **C1** described above stem from the complex.

To corroborate the emission lifetime measurements, transient absorption spectroscopy was performed. Here, the spectra of **C1** in deaerated acetonitrile were probed from 420 to 660 nm (Figure 7). The resulting spectra displayed a strong and broad excited state absorption feature between 430 and 660 nm, which was rather structureless. Single kinetic-traces were recorded with freshly prepared samples (to avoid photodegradation) at characteristic bands (470, 500, and 570 nm) and fitted with a monoexponential decay where τ_1 = 18.0 μs (Figure S8.2 and S8.4). This is in good agreement with the long-lived emission lifetime as discussed above. The strong ground state bleach is only weakly visible below 425 nm because of the overlapping broad excited state absorption. In contrast, $[(bpy)_2Ru(\mathbf{L0})]^{2+}$ and **C0** exhibit a strong ground-state MLCT absorption at 452 nm and a broad signal at $\lambda >$ 500 nm.[47,66] Such dominating excited state absorption of ^{3}LC excited states have already been described in the literature by Dietzek et al. and Castellano et al.[34,67] The shape of the amplitude spectra (Figure S8.1) is surprisingly well represented by the long-lived component alone. This implies that, when compared to the ^{3}LC state, the ^{3}MLCT state has either (i) a much higher absorption cross section or (ii) a much higher population following excitation at 355 nm. Notwithstanding, it is presumed that the ^{3}LC state largely decays by radiationless pathways due to the −NH bond on the imidazole ring and the N-acceptor atoms on the phenazine moiety. Both moieties offer an efficient pathway for radiationless deactivation processes, for example, hydrogen-bonding to adjacent complex or solvent molecules.

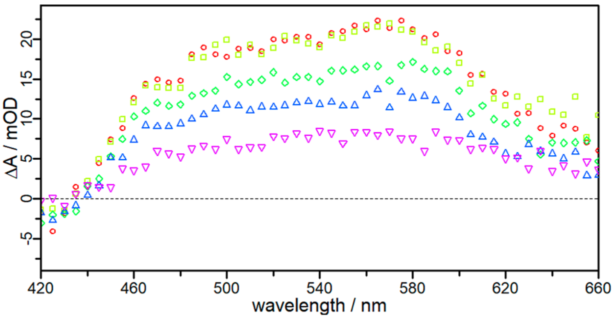


Figure 7. Transient absorption spectra of **C1** in acetonitrile excited at 355 nm after 0.5 (red), 1.0 (yellow), 5.0 (green), 10.0 (blue), and 20.0 μs (magenta). The decay-associated amplitude spectra can be found in the Supporting Information.

As stated above, upon addition of water (10% v/v), the steady-state emission of **C1** is considerably quenched (Figures 5 and S4.10). The emission signal decays monoexponentially with a time constant of 169 ns (Figure S7.4), which is most likely due to hydrogen bonding of the water molecules with the pyrazine or imidazole nitrogen atoms leading to stabilization of the ^{3}LC state. Thus, it seems that the ^{3}LC deactivates nonradiatively (c.f., Figure S7.2). Therefore, it may be concluded that the shortened lifetime is associated with the proximal ^{3}MLCT state instead of the ^{3}LC state. This contrasts the known *light switch* mechanism, where the *dark state* (^{3}MLCT$_{dist}$) is populated from the *bright state* (^{3}MLCT$_{prox}$).[10,59,68] Because of the unincisive hypsochromic shift in the emission spectra with addition of water it seems that the distal and proximal ^{3}MLCT states are only slightly affected by the described hydrogen bonding. Thus, it is not definite that the relaxation process of the light switch is present in **C1** as it is described for a Ru(II) complex bearing a 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-l:2‴,3‴]-pentacene (tatpp) by MacDonnell and Coworkers.[69] However, this also implies that there is, if any, only weak coupling of the two states. The nanosecond-transient absorption measurements in acetonitrile/water (10% *v*/*v*) at λ = 470, 500, and 570 nm mirror the same behavior as observed in the emission measurements: The intensity is strongly quenched and the decay signal can be fitted monoexponentially with τ_1 = 170 ns (Figure S8.3).

■ CONCLUSIONS

The aim of this study was to investigate the electrochemical and photophysical behavior of a complex bearing a dipyridophenazine ligand with a directly fused imidazole unit. For this purpose, a Ru(II) complex bearing a dipyrido-[3,2-*a*:2′,3′-*c*]phenazine-10,11-imidazole ligand (**C1**) was synthesized and structurally characterized. The cyclic voltammetry of **C1** showed five ligand based redox couples. The redox couple at the most positive potential belongs to the imidazole unit and disappears upon deprotonation with a base. Compared to the parent complex **C0** bearing a dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand, the absorption of **C1** is red-shifted and the extinction coefficient of the lowest lying absorption band is increased. This is due to the overlay of metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) transitions. Thus, following excitation of **C1**, either a ^{1}MLCT or a ^{1}LC state will be populated in the molecule (Figure 8). The respective ^{3}MLCT and ^{3}LC states are populated by transfer processes that occur faster than the ns time-scale explored here. Unlike other reported Ru(II) complexes of dipyrido[3,2-*a*:2′,3′-*c*]phenazine derivatives, both triplet excited states discussed, herein, are emissive at room temperature with time constants of 1.2 and 18.3 μs (λ_{ex} = 355 nm). In this study, there was no indication of conversion between this ^{3}MLCT and the slightly energetically lowered ^{3}LC state. Up to now, it is unclear if **C1** exhibits several other low-lying ^{3}MLCT states similar to **C0**. However, the ^{3}MLCT and ^{3}LC states are very similar in energy and lie spatially close together, and thus, for such a symmetric and conjugated system, it is not foreseen that the emission does not occur from the lowest excited state.

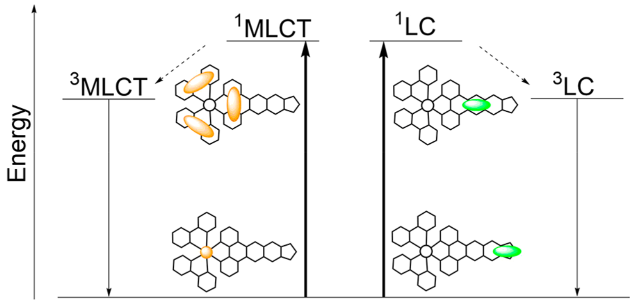


Figure 8. Simplified Jablonski diagram for the concurrent formation of two different long-lived emissive excited states of **C1** in acetonitrile solution at room temperature. The green area indicates LC transition, while the orange part corresponds to the ^{3}MLCT state. It is unclear whether a coupling between the respective MLCT and the LC states exists.

Furthermore, the impact of water addition on the excited state properties of **C1** was analyzed, resulting in an obvious emission quenching. In contrast to related Ru(II) complexes (like **C0**), only a very slight hypsochromic shift of the steady-state emission spectra occurs. Also, the relaxation to the ground state is drastically accelerated with 10% v/v water in acetonitrile so that only one time-constant (169 ns) could by analyzed in this study. These results demonstrate that **C1** is an attractive building block for extended π-systems and for use as a photosensitizer in catalysis. However, extended investigations of the nature of the excited states are crucial.[70,71] Methods, such as temperature-dependent emission,[11,12] time-resolved resonance Raman,[16,72] or ultrafast transient absorption spectroscopy[10,47,66] with supporting calculation of the singlet and triplet excited states via time-dependent DFT methods, would allow the interactions between the different excited states to be characterized. Further targeted design principles could then be applied to new analogues of **C1**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01372.

General information on the experimental and synthetic details, NMR, UV−vis spectra, and the results of the (TD)DFT calculations. (PDF)

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Notes

The authors declare no competing financial interest.

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