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Changing the Role of 2,2′-Bipyridine from Secondary Ligand to Protagonist in [Ru(bpy)$_2$(N−N)]$^{2+}$ Complexes: Low-Energy, Red Emission from a Ruthenium(II)-to-2,2′-Bipyridine ^{3}MLCT State

Samik Nag,[†,‡] Janaina G. Ferreira,[†] Ludwig Chenneberg,[†] Philippe Dauphin Ducharme,[†] Garry S. Hanan,[*,†] Giuseppina La Ganga,[§] Scolastica Serroni,[§] and Sebastiano Campagna[*,§]

[†]*Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada,* [‡]*Department of Chemical Sciences, Sikkim University, Sixth Mile, Tadong, Gangtok, Sikkim, India 737102, and* [§]*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Via Sperone 31, I-98166 Messina, Italy*

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Two new bidentate ligands (**1** and **2**) with bicyclic guanidine moieties were synthesized and attached to a Ru^{II}(bpy)$_2$ core (bpy = 2,2′-bipyridine) to afford complexes **3** and **4**, which were characterized by spectroscopic and electrochemical methods. Complex **4** was further characterized by X-ray crystallography. In cyclic voltammetric studies, both complexes show a Ru$^{II/III}$ couple, which is 500 mV less positive than the Ru$^{II/III}$ couple of Ru(bpy)$_3$$^{2+}$. The ^{1}MLCT and ^{3}MLCT states of **3** (560 nm/745 nm) and **4** (550 nm/740 nm) are significantly red-shifted with respect to Ru(bpy)$_3$$^{2+}$ (440 nm/620 nm). Compounds **3** and **4** exhibit emission from a Ru^{II}-to-bpy ^{3}MLCT state, which is rarely the emitting state at $\lambda > 700$ nm in [Ru(bpy)$_2$(N−N)]$^{2+}$ complexes.

Ruthenium(II) complexes of polypyridyl ligands have long been of intense interest.[1] The archetypical complex, Ru^{II}(bpy)$_3$ (bpy = 2,2′-bipyridine), has stable ground- and excited-state properties[1a] and can be modified to afford complexes with absorption and emission energies that span the UV, visible, and near-infrared regions.[2] New red-emitting photosensitizers that maintain relatively long excited-state lifetimes have potential applications in biological systems,[3] because of the penetration of red light into tissues, and as low-lying energy traps in multichromophore arrays, reminiscent of the special pair in photosystem II.[4] Mononuclear ruthenium(II) complexes are of particular interest because their ground- and excited-state optical and electrochemical properties can be tuned by judicious selection of their heterocyclic ligands (ring size; functionalization; nature, number, and position of the heteroatoms), and they are relatively easy to synthesize compared to multinuclear species. The two main approaches toward red-emitting species are the incorporation of either a better acceptor ligand or a better donor ligand in place of one bpy in Ru(bpy)$_3$$^{2+}$.

The better acceptor ligand functions by contributing the lowest unoccupied molecular orbital (LUMO) to the new Ru(bpy)$_2$(acceptor)$^{2+}$ species. Several red-emitting ruthenium(II) complexes have focused on the functionalization of bpy with various substituents in order to lower the LUMO as compared to unsubstituted bipyridines, which, in turn, give rise to lower-energy absorptions and emissions.[5,6] Other complexes incorporate diazine ligands because their LUMO energies are lower than that of bpy.[7−10] Even fused polyaromatic ligands have been used because their ruthenium(II) complexes emit at much longer wavelengths (e.g., isoeilatin, 994 nm;[11] tetrazacoronene, 880 nm[12]), although their ligands

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[*] To whom correspondence should be addressed. E-mail: garry.hanan@umontreal.ca (G.S.H.), campagna@unime.it (S.C.). Tel: +1 514 343 7056 (G.S.H.), +39 090 676 5737 (S.C.). Fax: +1 514 343 2468 (G.S.H.), +39 090 393 756 (S.C.).

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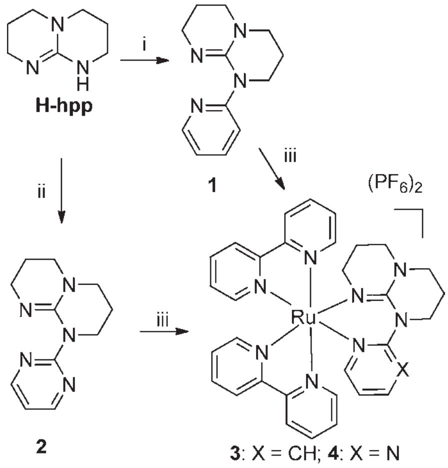
Scheme 1. Synthesis of Ligands **1** and **2** and Complexes **3** and **4**[a]



[a] (i) Pd(OAc)$_2$, BINAP, 2-bromopyridine, *t*-BuOK in dry toluene at 90 °C; (ii) neat, 2-bromopyrimidine at 130 °C; (iii) *cis*-Ru(bpy)$_2$Cl$_2$ in *n*-butanol at reflux followed by the addition of NH$_4$PF$_6$.

are not readily available. Thus, the newly introduced bidentate ligand is always involved in the emitting triplet ligand-to-metal charge-transfer (^{3}MLCT) state.

The alternate approach, introducing a better donor ligand, functions by raising the energy of the highest occupied molecular orbital (HOMO) in the new Ru(bpy)$_2$(donor)$^{2+}$ species. In the case of [Ru(bpy)$_2$(N−N)]$^{2+}$ complexes (where N−N is a neutral, bpy-like ligand), donor bidentate ligands have rarely given very large spectral shifts compared to the incorporation of bidentate acceptor ligands. For example, the Ru^{II}(bpy)$_2$ complexes of 2-pyridylazole ligands, such as 3-(pyrid-2′-yl)-1,2,4-triazole and 2-(pyrid-2′-yl)imidazole, exhibit a lower-energy emission than Ru(bpy)$_3^{2+}$, albeit with emission maxima at λ < 690 nm.[13−15] Although replacement of the N−N ligand in [Ru(bpy)$_2$(N−N)]$^{2+}$ complexes with a weak acceptor ligand would also lead to a Ru-to-bpy MLCT state, the red shift would be far less than that generated by the incorporation of a strongly donating N−N ligand moiety.

Herein, we report the synthesis of two new, neutral bidentate ligands and their ruthenium complexes in which a hexahydropyrimidopyrimidine unit is coupled with pyridine or pyrimidine to complete the bidentate chelate ligand. The electrochemical and photophysical consequences of the presence of strong donor ligands are also reported.

The two N-heterocyclic ligands **1** and **2** (Scheme 1) were synthesized by the reaction of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (**H-hpp**) with 2-bromopyridine and 2-bromopyrimidine, respectively, taking advantage of C−N bond-forming reactions. While the synthesis of **1** requires a palladium-catalyzed Buchwald C−N coupling reaction,[16] **2** was synthesized by the direct reaction of the reactants at 130 °C. Attaching a heterocycle to the guanidine N*H* position of **H-hpp** renders the six annular methylene units nonequivalent by NMR spectroscopy, in contrast to free **H-hpp**, in which the tautomerization of the guanidine proton leads to only three proton resonances in its ^{1}H NMR at 400 MHz. Similar observations were reported by Coles and co-workers for a methylene-linked bis(guanidine) compound, H$_2$C{hpp}$_2$.[17]

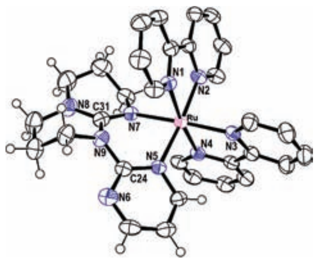


Figure 1. ORTEP view of the cation in **4**. The anions and protons on the bipyridines have been omitted for clarity.

The stoichiometric reaction of **1** with *cis*-Ru(bpy)$_2$Cl$_2$ in refluxing 1-butanol, followed by the addition of an aqueous NH$_4$PF$_6$ solution, affords [Ru(bpy)$_2$(**1**)](PF$_6$)$_2$ (**3**) as a dark-red crystalline powder (Scheme 1). The most interesting feature in the ^{1}H NMR spectra of **3** in CD$_3$CN is that now 10 different methylene signals are found due to the bis-bpy Ru^{2+} moiety, 9 of them integrating for one proton each while the other three protons are at the same chemical shift.

A similar reaction of **2** with *cis*-Ru(bpy)$_2$Cl$_2$ in a refluxing 1:1 (v/v) 1-butanol−H$_2$O mixture, followed by the addition of an aqueous NH$_4$PF$_6$ solution, affords a brown precipitate from which [Ru(bpy)$_2$(**2**)](PF$_6$)$_2$ (**4**; Scheme 1) is obtained as a wine-red powder after column chromatography on SiO$_2$. Complex **4** also exhibits a similar restriction in the exchange of methylene protons, as revealed by ^{1}H NMR spectroscopy.

Slow diffusion of isopropyl ether into an acetonitrile solution of **4** furnished single crystals suitable for X-ray crystallography. The X-ray crystal structure reveals that the Ru center in **4** has a distorted octahedral geometry with a RuN$_6$ core (Figure 1).

The distortion from a regular octahedron arises from the smaller bite angles of the two bpy ligands with the metal center [78.88(9)° and 78.77(8)°]. The bicyclic pyrimidopyrimidine ligand **2** forms a six-membered chelate ring with a bite angle of 84.98(8)°. The six Ru−N distances range between 2.051(2) and 2.090(2) Å.

The longest bond is the Ru−N5 bond, while the shortest one is the Ru−N3 bond trans to the guanidine moiety. The Ru−N7 bond is 2.087(2) Å long. The N9−C24 [1.392(3) Å] and N9−C31 [1.408(3) Å] bond distances clearly suggest that there is delocalization between the pyrimidine ring and guanidine to some extent, whereas N7−C31 seems to be a localized C−N double bond with a distance of 1.314(4) Å. The alkyl chains are directed away from the Ru^{II} center, and thus the conformation of the saturated ring does not appear to have any noticeable influence on the structure, as opposed to other coordination complexes incorporating CH$_2$-bridged donor atoms.[18]

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The electrochemical behavior of complexes **3** and **4** has been examined by cyclic voltammetry using a glassy carbon electrode in purified acetonitrile under a dry argon atmosphere. At positive potentials, complex **3** shows a quasi-reversible $Ru^{III/II}$ couple at 0.73 V vs SCE with a peak-to-peak separation (ΔE_p) of 100 mV at 200 mV/s. This value is 0.54 V less positive than that observed for the same $Ru^{III/II}$ couple in $[Ru(bpy)_3]^{2+}$, which appears at 1.27 V vs SCE;[19,20] i.e., **3** is much easier to oxidize than $[Ru(bpy)_3]^{2+}$, confirming that **1** is a stronger donor than bpy. Complex **4** also shows a quasi-reversible $Ru^{III/II}$ couple at 0.75 V vs SCE (ΔE_p = 90 mV). This marginal increase in the $Ru^{III/II}$ couple in **4** in comparison to **3** may be attributed to substitution of the pyridine donor in **1** with a pyrimidine in **2**. Because pyrimidine is a weaker donor ligand, the Ru center in **4** is more difficult to oxidize.[21]

Both complexes display three quasi-reversible ligand-based reduction peaks. For complex **3**, the first two reduction peaks are centered at −1.41 and −1.66 V vs SCE, whereas those for complex **4** are at −1.42 and −1.63 V vs SCE. Both of these reduction peaks are assigned as bpy-based by comparing them to those for $Ru(bpy)_3^{2+}$ (−1.35, −1.55, and −1.76 V vs SCE),[14,19,20] and although they are not perfectly reversible, i.e., $\Delta E_p > 59$ mV, at 60 mV for **4** and 80 mV for **3**, these small differences are similar to those found in most ruthenium(II) complexes.[14] The third reduction peak for **3** had an anodic peak potential of −2.30 V vs SCE, whereas that for **4** is more well-defined and is centered at −1.96 V vs SCE. These peaks can be designated as reductions occurring at **1** and **2**, respectively. Because pyrimidine is a better π acceptor than pyridine, it is easier to reduce ligand **2** in complex **4** than ligand **1** in complex **3**. The observation of reduction peaks at such negative potentials in both ligands may be attributed to the loss of electron delocalization in **1** and **2** compared to bpy-type ligands.

The UV−vis spectra of **3** and **4** in an acetonitrile solution display singlet metal-to-ligand charge-transfer (^{1}MLCT) bands in the 400−600 nm region. The UV region is dominated by the $\pi \rightarrow \pi^*$ transition in the ligand (bpy) moieties centered around 293 nm for **3** and 290 nm for **4**.[14,22,23] The most noticeable feature in the visible region is that the lowest-energy ^{1}MLCT maxima (560 and 550 nm for **3** and **4**, respectively) are red-shifted with respect to that of $Ru(bpy)_3^{2+}$ for both complexes. As discussed above, with ligands **1** and **2** being stronger donors than bpy, they are expected to interact with the d orbitals of ruthenium more strongly than bpy, raising the metal-based HOMO energy. On the other hand, the LUMO is still bpy-based, as revealed by the first reduction potentials of **3** and **4**, which results in a lowering of the energy of the $d\pi \rightarrow \pi^*$ MLCT transition and, hence, a red shift. With ligand **1** being a stronger donor than **2**, complex **3** displays a more pronounced red shift in its ^{1}MLCT compared to **4**. Moreover, both complexes show an additional band at approximately 350 nm, which receives contributions from a MLCT transition involving a higher-energy orbital of bipyridine.[24] It may be noted that such a band is usually observed for $Ru(bpy)_2(diamine)^{2+}$ chromophores.[25]

Complexes **3** and **4** exhibit room temperature emission in an acetonitrile solution. The emission maximum for **3** is at 745 nm, while that for **4** is at 740 nm, with associated excited-state lifetimes of 30 and 40 ns, respectively. The emission wavelength for **3** and **4** is significantly red-shifted compared to that of $Ru(bpy)_3^{2+}$, which is observed at 620 nm,[22] and still remains Ru-to-bpy charge transfer in nature. These are, to the best of our knowledge, the lowest-energy emissions for $Ru(bpy)_2(N{-}N)^{2+}$ compounds, where N−N is a neutral ligand, and demonstrate that anionic ligands are not strictly required for obtaining a large red shift of MLCT emissive states involving bpy. The red shift in the emission energy is accompanied by a sharp decrease in the emission quantum yield and lifetime (see data in the Supporting Information) compared to $Ru(bpy)_3^{2+}$, as expected on the basis of the energy gap law.[14,22,23] Moreover, vibrations due to the aliphatic component of **hpp** can contribute to radiationless decay.

In conclusion, we have synthesized two N_{amine}-substituted guanidine−pyridine/pyrimidine ligands that can coordinate to a Ru^{II} center, forming a six-membered chelate ring. From the $Ru^{III/II}$ potentials of the two new complexes, it is found that both ligands **1** and **2** possess strong donating ability compared to common polypyridyls, e.g., bpy or phenanthroline. In fact, the ligands reported in this work are even more electron-donating than 2-(2′-aminoethyl)pyridine (AEtPy) or ethylenediamine (en) as revealed by the $Ru^{III/II}$ couples of the complexes $Ru(bpy)_2(AEtPy)^{2+}$ (1.12 V vs SCE) and $Ru(bpy)_2(en)^{2+}$ (0.96 V vs SCE).[25−27] As a result of strong σ donation from **1** and **2**, complexes **3** and **4** have low-energy ^{1}MLCT absorption in the visible region in comparison to $Ru(bpy)_3^{2+}$. The 298 K fluid solution emission maxima for the two complexes are also red-shifted by ~100 nm with respect to that for $Ru(bpy)_3^{2+}$.

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Supporting Information Available: X-ray structural data for **4** in CIF format, synthetic details of all compounds, absorption and emission spectra of **4**, and a table collecting full photophysical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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