Quantum Mechanics Investigation of the Photophysical Properties of Ruthenium(II)-Based Complexes Combined with the Development of their Force Field Parameters Using Molecular Mechanics and Molecular Dynamics Simulation

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Abstract

The focus of this study is to develop a theoretical strategy that can help guide the design of novel organometallics with desirable photophysical properties for molecular engineering. This computational study includes proposed complexes and others for which experimental data are available. The agreement between the computational results and the experimental observations confirms the validity of our procedure and the level of theory we applied in this study. The ground singlet ($S_0$) and excited triplet ($T_1$) electronic states and corresponding optical spectra of a series of cationic complexes —[RuH(CO)L(PPh$_3$)$_2$]$^+$ (L= 2,2’-bipyridyl) (Rubpy), 4,4’-dicarboxylic-2,2’-bipyridyl (Rudcbpy), bis-4,4’-(N-methylamide)-2,2’-bipyridyl (Rudamidebpy), bis-4,4’-(methyl)-2,2’-bipyridyl (RudMebpy), [Ru(CO)$_2$dcbpy(PPh$_3$)$_2$]$^{2+}$ (Ru(2CO)dcbpy), [Ru(H)$_2$dcbpy(PPh$_3$)$_2$] (Ru(2H)dcbpy), and a series of cationic complexes [RuLL(phen)(PPh$_3$)$_2$]$^+$ (phen= 1,10-phenanthroline , L= H, CO, Cl, TFA)— have been studied by combined Density Functional/Time-Dependent Density Functional (DFT/TDDFT) techniques using different combinations of DFT exchange-correlation functionals and basis sets. We demonstrate a correlation between HOMO-LUMO energy gap, Stokes shift, and $T_1$ distortion, which reflects the effects of parent ligand and electron-withdrawing and donating groups. The results of the study of Ru-phen complexes revealed that this correlation is valid only when the metal-to-ligand charge-transfer (MLCT) transition is not isoenergetic with other transitions. In addition, we successfully developed new force field parameters for Ru-bpy based complexes, using molecular mechanics (MM) combined with molecular dynamics (MD), which can help to explain critical aspects of the optical phenomena of Ru-bpy based complexes in solution and biological systems.
I was always told I am lucky that I am a Leo, “You call the shots and hold your own”. Until the day came when I had to leave family, friends, and home. I would wake up under a different sky, and the winds would carry anonymous sounds. I thought I would be fine since “the lion walks alone in the desert”. I left with my parent’s prayers and blessings, my family good wishes. But the path I chose to “seek the buried treasure on the unknown island” was surrounded by rogue waves, black clouds, and peals of thunders. What to do? At one point I thought of giving up and going back home empty-handed. It was then when I realized that a lion’ strength comes from his pride and so do I. I needed support to keep me sailing amidst those rogue waves. That is when I found people that helped me recover my broken ship. “Sandy”, Dr. J. B. Alexander Ross, to whom I am foremost deeply thankful, who showed me the right path and reminded me that “all roads lead to Rome”. I appreciated each minute I spent in his lab, a great environment to learn, and his guidance to be creative. I am grateful to Prof. Francesco Lelj for his time and efforts, and everything he taught me all the way from Rome. To Harmen Steele, Dr. Raquel Arouca, and Michelle Terwilliger the wonderful people and true friends, I thank you for all your supports. I also would like to thank Dr. Ed Rosenberg for giving me the opportunity to learn about new topics. To the rest of Sandy’s lab, past and present, I thank you for all the delightful memories. To strangers I met on the road and become my family during these six years under the big sky, thank you for all the fun, smiles, and laughter. To Imam Abdulrahman Bin Faisal University and the government of Saudi Arabia for the support and giving me this opportunity, I thank you. To my parents, I am sorry for each second I made you worry about your daughter. Seven years ago, I asked my father to study abroad and he said, “I did not let you go to school to stop you now” and my mother said, “My daughter you will be in all my prayers”. If all the seas were ink that wont be enough to write thank you to my parent. To my sisters, brothers, and all my family, may God keep you in his mercy and protection. Finally, thank you God for everything I had, everything I have, and everything I will have.
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Chapter 1. Background

1.1. Introduction

Luminescent techniques are analytical tools that have been developing rapidly, with many new applications in the life sciences. Unique features of these techniques are their sensitivity and selectivity over broad range of wavelengths. Several important parameters can be used as observables, including: luminescence intensity, lifetime, quantum yield, quenching efficiency, and radiative and nonradiative energy transfer [1].

In recent years, organometallic complexes have gained major interest in luminescence spectroscopy because of their exceptional photophysical properties: long lifetimes (ranging from about 100 ns to 10 µs), large Stokes shift, high quantum yields, high intrinsic anisotropies, and a relatively stable triplet excited state associated with metal-to-ligand charge-transfer ($^3\text{MLCT}$) [1]. The second- and third-row transition metal complexes are strong oxidants and ideal for such techniques. One of the most commonly used ligands for forming MLCT complexes, is the polypyridyl ring (e.g., 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen)), because of its strong reductive capacity, which is based on the low-lying π* acceptor level of the ligand. Upon absorption of light in the UV-Vis range, an intramolecular electronic charge transfer from $t_{2g}$ orbitals of the metal to this level will occur causing the formation of the singlet excited state ($^1\text{MLCT}$).

$$A_nM - L \rightarrow h\nu \rightarrow A_nM^+ - L^-$$ (1)

where A is a spectator ligand that is not directly involved in the electronic transition process. Strong spin-orbit coupling, due to the heavy metal, causes the system to undergo a rapid and efficient intersystem crossing to the triplet excited state, the 'phosphorescent state' ($^3\text{MLCT}$), with a quantum efficiency close to unity [1-3].
Once the $^3\text{MLCT}$ state is populated, different deactivation processes can take place. First, phosphorescence is a spontaneous radiative decay that brings the complex back to its ground singlet state ($S_0$) by dissipating energy as a photon. This decay is described by a radiative rate constant ($k_r$). Second, nonradiative decay can bring the complex back to $S_0$ by dissipating the energy through thermal processes such as vibrational relaxation and/or collisional quenching. This decay is characterized by the rate constant ($k_{nr}$). In addition to formation of the $^3\text{MLCT}$ by intersystem crossing (ISC), based on the interaction between the metal and the ligand, a triplet metal-centered ($^3\text{MC}$) state, which will weaken the emission, can be formed by either thermal activation of the $^3\text{MLCT}$ state or directly by ISC from the $^1\text{MLCT}$ state [4-8].

The careful selection of metal and ligand is the critical step toward attaining desirable properties for specific applications. Ruthenium-polypyridyl based complexes have been of considerable interest after the first report of the excited-state electron transfer by $[\text{Ru(bpy)}_3]^{2^+}$ in 1959 [9]. Since then, this complex and its derivatives have been extensively used in applications such as dye-sensitized solar cells (DSSC) [10-11], potential agents for the detection of different biological analytes of clinical and environmental interest [12-14], and DNA diagnostics [15-16].
Recently, due to the limitations of platinum-based antitumor drugs, there are ongoing efforts to develop Ru-based anticancer complexes and some of these complexes have reached phase II clinical trials [17-22]. The following section briefly describes several applications based on the photophysical behavior of Ru-polypyridyl complexes.

1.2. Applications

1.2.1. Ruthenium Complexes as Sensitizers in Dye-Sensitized Solar Cells (DSSC)

The DSSC cell is made of three main parts: a photoanode, cathode (counter electrode), and liquid electrolyte separating them. The photoanode is made of glass that is covered with a conductive oxide. This glass is covered with mesoporous layers of semiconductor, most frequently nano-crystalline TiO$_2$ that is covered with a monolayer of dye molecules (Ru-complexes). The dye has to have anchoring group like carboxylic acid to immobilize the dye on the TiO$_2$ surface. The cathode is made of the same conductive glass as in the photoanode, and particles of a solid catalyst, typically platinum metal, are deposited on the surface. The electrolyte is made of a solution of oxidized redox mediator that contains various species of ions [11, 23-24].

After the dye molecules are excited by absorbing the incident photons, the excited electrons are injected into the conduction band of the semiconductor. Then, the oxidized dye

![Figure 2. A diagram illustrating charge transfer process in DSSC.](image-url)
molecules are reduced by a redox mediator such as (I) in the electrolyte, creating a hole (I$_3^-$). Then, the electrons flow through the external circuit to the counter electrode. At the counter electrode, the electrons reduce the I$_3^-$ to regenerate iodide, which completes the circuit [11, 23-24].

For efficient DSSC, the dye molecule has to fulfill several requirements. The most efficient Ru-bpy-based dye complexes that have been demonstrated to date have been developed by the Grätzel group: the N3, N719 and ‘black’ dyes [25-26].

![Figure 3. Structures of the Ru-based dyes N3, N719 and ‘black dye’ [25,26].](image)

In addition to the excellent photophysical properties described earlier [1-3], Ru-bpy-based dye complexes have ultrafast rates of charge injection with a near unity quantum yield [27-28] and long-term dye stability under various environmental conditions [29-30]. When designing DSSC, it is important to consider the arrangement of the energy levels. In particular, the highest
occupied molecular orbital (HOMO) should be spatially separated from the lowest unoccupied molecular orbital (LUMO). Specifically, the LUMO should be close to the oxide surface for efficient charge injection, while the HOMO should be far away from the oxide surface to reduce the rate of the recombination between the injected charges with either the oxidized dye, or the oxidized redox couple(17) [23-24].

1.2.2. Ruthenium-based anticancer drugs.

Ru(II)-polypyridyl complexes show a unique reactivity that differentiates them from other organometallic compounds, specifically, their ability to photosubstitute ligands. The discovery of this reactivity was for [Ru(bpy)3]2+ in 1976 by Van Houten and Watts [31]. In this process, a triplet metal-centered state ($^3\text{MC}$) is formed either by thermal activation of the $^3\text{MLCT}$ state or direct intersystem crossing from $^1\text{MLCT}$ state [4-8]. In this state, an electron from one of the Ru nonbonded orbitals ($t_{2g}$) is promoted into a Ru-ligand $\pi^* e_g$ orbital. Consequently, the Ru-ligand bond becomes weaker, which facilitates the substitution of a ligand by a solvent molecule. Either of the two parts, the Ru-containing part, or the ligand-containing part, or both, can have biological activity [32-33].

![Figure 4. Photosubstitution of a ligand L bound to a Ru(II) center.](image)

The light-induced cleavage of a chemical bond is very important in designing a drug with high selectivity that is sufficiently reactive to only bind the biological target and not other biomolecules encountered on the way. This gives an advantage for Ru-based antitumor drugs compared to the Pt-based drugs. Regardless of the achievements of the latter, one of their major drawbacks is the ability to interact with other biomolecules thereby causing severe side-effects.
such as bone marrow suppression and kidney toxicity [32-33]. Ru-based anticancer drugs that have reached phase I or II clinical trials are KP1019 and NAMI-A (Figure 5).

![Chemical structures of KP1019 and NAMI-A](image)

**Figure 5.** The structure of KP1019 (A) and NAMI-A (B). Abbreviation: DMSO, dimethyl sulfoxide [34].

The critical consideration in the development of such compounds for photopharmacology is achieving activation ($^1$MLCT formation) in the visible range of the spectrum because visible light is less toxic to cells and infiltrates further into biological tissues, compared to UV light that poorly penetrates through tissues and causes significant damage to cells [32-33]. Thus, the importance to control the HOMO and LUMO energy levels to the desired range of the spectrum arises in this application as well.

One can conclude that for phosphorescence applications, the need for fundamental understanding of the redistribution of the electronic density in response to light excitation, the energy of $T_1$, and the structural parameters that control the energy levels are key factors for improving the design of optically active organometallic complexes. However, proceeding directly to synthesis and experimental characterization is not necessarily the most effective strategy. For example, designing new materials and testing their applicability is costly and involves time-consuming synthesis procedures. In addition, the failure to design a dye for DSSC
with the desirable properties can occur at a late-stage in the synthesis process. Thus, it is critical step to first investigate and understand the molecular levels of these complexes. Another issue is the possibility of generating several excited states that lie in a narrow energy range and that have short lifetimes or small quantum yields. Furthermore, some excited states are optically forbidden (dark) states (e.g., $^3\text{MC}$ or $^3\text{LC}$) and experimentally difficult to detect because they involve photochemical reactions or ultrafast relaxation processes. These states have significant influence on the dynamics of the electronically excited system, and thus it is critically important to find computational procedures to investigate such phenomena [4-8, 35-36].

To overcome this bottleneck in the development of new organometallics with desirable photophysical properties, state-of-the-art computational methods need to be employed. Today, major improvements in computational methods are advancing the study of photophysical and photochemical properties of organometallic complexes, contributing to a fundamental understanding of the dynamics of their excited states [35-39]. The power of new-generation supercomputers facilitates the utilization of large-scale quantum chemical calculations. Specifically, these calculations provide reliable information that can be used to design and screen new compounds prior to synthesis. With this power, a rational design of new materials and a systematic chemical modification of their structures can be achieved.

The widely applied computational approach for modeling ground-state properties is Density Functional Theory (DFT), while Time-Dependent DFT (TD-DFT) calculations are used because of their ability to describe precisely the geometrical features and energies of excited states [35-54]. The use of the TDDFT for computing the optical spectral properties has increased markedly during the past years. For example, in 1997, there were 37 publications, that exceeded 1000 by 2011 [35-39, 45-49, 53-54]. In general, these calculations are validated by their ability
to reproduce the experimental data (e.g., absorption spectra, vibrational frequencies), based on which further interpretation of subtle spectroscopic properties can strategically be made. In the following section, an overview of the basic concepts of DFT and TD-DFT theories is provided.

1.3. Theoretical overview

1.3.1. DFT

In the mid-1960s, Hohenberg and Kohn set down the basic foundation of modern DFT [43]. The Hohenberg-Kohn theorem states that the ground-state energy and other properties are defined by a one-body ground-state density $\rho(r)$. In other words, the energy ($E$) of the system in the ground state is described as a functional of $\rho(r)$ [44-50].

$$E[\rho(r)] = \int V_{\text{ext}}(r) \rho(r) dr + F[\rho(r)]$$

(2)

where the first term describes the electron interaction with an external potential $V_{\text{ext}}(r)$ (this term arises from the Coulomb interaction between electrons and nuclei). The second term is the sum of the electrons’ kinetic energy and their inter-electronic interaction. However, the description of this term is unknown. In particular, it is not known whether the electron is located in occupied or virtual orbitals (orbital-free theory).

In 1965, Kohn and Sham (KS) solved the Hohenberg-Kohn theorem for an interacting system by suggesting an approximation for the kinetic energy in which the density of the interacting many-electron system is obtained as the density of a non-interacting reference system [50]. Thus, the KS orbitals can be described as single Slater determinant of single-particle spin-orbitals. The full expression for the energy $E[\rho(r)]$ of an $N$-electron system with $M$ nuclei that is giving by KS equations will be:

$$\sum_{i=1}^{N} \int \psi_i(r) \left( -\frac{\nabla^2}{2} \right) \psi_i(r) dr + \frac{1}{2} \int \rho(r_1) \rho(r_2) \frac{1}{|r_1 - r_2|} dr_1 dr_2 + E_{xc}[\rho(r)] - \sum_{A=1}^{M} \frac{Z_A}{|r - R_A|} \rho(r) dr$$

(3)
The first term is the kinetic energy of a system of non-interacting electrons that have the same density (charge) as the real system. The second and fourth terms are the electron-electron Coulombic (Hartree electrostatic) energy, and electron-nuclear interaction, respectively. $E_{xc}[\rho(r)]$ is the exchange-correlation energy functional and will be further discussed later. The electron density $\rho(r)$ for non-interacting electrons is the sum over all occupied KS orbitals $\psi_i(r)$ and is giving by:

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (4)

The issue that arises is that molecular orbitals are used as input to calculate the electron density, yet the goal is to calculate the molecular orbitals that best determine the electronic structure. For this, the variation theorem is introduced. It states that “the energy calculated from an approximation to the true wavefunction will always be greater than the true energy” [44]. In other words, when the energy is a minimum, the best wavefunction is obtained. Thus, since the true density corresponds to the lowest energy, the energy and density of the interacting reference can be optimized by variational procedures. The method is based on the linear combinations of atomic orbitals approach (LCAO). The KS molecular orbitals $\psi_i$ are expressed as a linear combinations of atomic orbitals $\varphi_v$ (e.g., the basis function):

$$\psi_i(r) = \sum_{v=1}^{K} c_{vi} \varphi_v$$  \hspace{1cm} (5)

Where $c_{vi}$ is a coefficient. In equation (5) there are K basis functions, and thus a total of K molecular orbitals should be derived. In addition, there are different forms for the basis functions; DFT mostly employs Gaussian functions. The resultant equation is variational in the wavefunction. Thus, it will find the coefficients that minimize the energy and give the best wavefunction. In other words, the coefficients will be changed for a given set of orbitals in the direction that minimizes the energy ($\partial E/\partial c_{iv} = 0$).
KS equations also include the exchange-correlation energy functional $E_{xc}[\rho(r)]$.

Electron-exchange energy refers to the Pauli Exclusion Principle, where no two electrons with the same spin can exist in the same orbital. The electron-correlation energy refers to the fact that the electrons tend to avoid each other (their motions are correlated), resulting in lower energy (Hund’s multiplicity rule) [51]. It is worth mentioning that the remarkable success of DFT to describe the intricate many-body system compared to other methods, such as Hartree-Fock theory, is its treatment of the exchange-correlation functional $V_{xc}[\rho]$ using the electron density.

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$ (6)

The Kronecker delta ($\delta$) is introduced to ensure the orthogonality of the wavefunctions (KS orbitals) and the normalization conditions. The problem is that the exact mathematical expression of the exchange-correlation term is unknown; therefore, different forms of approximate functionals are used (explained below). By introducing eq. 5 and 6 into the KS equations and applying the variational condition, the KS orbitals $\psi_i$ and their energies $\varepsilon_i$ are obtained from the one-electron KS equations as solutions of the Schrödinger equation:

$$\left\{-\frac{\hbar^2}{2m_e} \nabla_i^2 - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(r_2)}{r_{12}} d r_2 + V_{xc}[\rho_i] \right\} \psi_i(r_i) = \varepsilon_i \psi_i(r_i)$$ (7)

To solve KS, the self-consistent field (SCF) strategy is applied. In this strategy, an initial guess of density will be used from which a set of new molecular orbitals that improve the value of the density is derived. The new value of density will then be fed into the second iteration, and so on until convergence is achieved. Therefore, calculating the properties that best describe the ground state is achieved by deriving the wavefunction that has the lowest energy. Specifically, the choice of functional forms (approximation) that describe the exchange-correlation term is a critical step for the success of DFT calculation.
There are several exchange-correlation functionals that have been developed. The most popular functional is the hybrid Becke, three-parameter, Lee-Yang-Parr exchange-correlation functional B3LYP [52]. The three parameters are the Hartree-Fock exact exchange, the local spin-density approximation exchange, and the gradient-corrected exchange and gradient-corrected correlation. This functional provides data that correspond well with experiment [35-39]. Thus, this functional was used extensively in this project.

The remarkable performance of DFT in describing structural and electronic properties in a vast class of materials with high quality calculations for large molecules is undeniable. In addition, DFT is computationally relatively simple, and increasing the number of atoms or the size of the basis sets does not affect the calculation time significantly when compared to the Hartree-Fock method [43-52]. Most importantly, DFT results can be interpreted in the familiar terms of molecular orbital theory.

1.3.2. **TD-DFT**

Twenty years after introducing DFT, Hohenberg, Kohn, and Sham, Runge and Gross extended the theory to include time-dependent systems, the Time-Dependent Density Functional Theory (TD-DFT) [53]. It is based on the same concept of DFT that the density of interacting many-electron system is obtained as the density of a non-interacting reference system inside a one-body potential. In other words, the time-dependent wavefunction is equivalent to the time-dependent electronic density. Deriving the effective potential of the non-interacting system will return the same density of the many-electron interacting system. Thus, TD-DFT is used to investigate the properties and dynamics of many-particle systems in the presence of time-dependent potentials, such as electromagnetic fields, to extract features like excitation, absorption, and emission energies. The evolution of the development of TD-DFT is very
complicated and beyond the scope of this study, so only the conclusive equations are described here essentially following Martin [45], Onida [46], Casida et al. [47,54], Vlček Jr et al [48], and Runge et al [53].

This theorem is based on the linear-response approximation, where the changes of the electron density $\rho(r, t)$ are proportional to the changes of the external potential, $\nu_{\text{ext}}(r,t)$ (time-dependent external perturbation). The time-dependent electron density is:

$$\rho(r, t) = \sum_{i=1}^{N} |\psi_i(r, t)|^2$$  \hspace{1cm} (8)

which is determined by solving the time-dependent KS equations:

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(r_2,t)}{r_{12}} dr_2 + V_{XC}[r_1,t] + V_{\text{ext}}(t) \right\} \psi_i(r_1,t) = i\hbar \frac{\partial}{\partial t} \psi_i(r_1,t)$$  \hspace{1cm} (9)

This will yield the frequency-dependent dynamic polarizability $\alpha(\nu)$, which can be expanded in terms of electronic transitions energies (denoted $n$), and the corresponding oscillator strengths $f_n$:

$$\alpha(\nu) = \frac{4\pi^2 e^2}{m_e} \sum_n \frac{f_n}{(\nu_n - \nu_0)^2 - \nu^2}$$  \hspace{1cm} (10)

$$\alpha(\nu) = \frac{\hbar^2 e^2}{m_e} \sum_n \frac{f_n}{(E_n - E_0)^2 - \nu^2}$$  \hspace{1cm} (11)

$E_0$ and $E_n$ are the energies of the ground and $n$th excited states, respectively, while $\nu_0$ and $\nu_n$ are the corresponding frequencies. The oscillator strength determines the intensity of the absorption band and is obtained as:

$$f_n = \left( \frac{4\pi m_e}{3\varepsilon_0^2 \hbar} \right) \nu_n |\mu_n|^2 = \left( \frac{2m_e}{3\varepsilon_0^2 \hbar^2} \right) E_n |\mu_n|^2$$  \hspace{1cm} (12)

where $\mu$ is the transition dipole moment. So, by solving these equations, the excitation energies along with the oscillator strength can be obtained from the DFT framework.

Today, TD-DFT has become one of the most prominent methods for the investigation of excited states of medium to large molecules [35-39,45-49,53-54]. Based on these computational successes and the ability to explain critical aspects of the optical phenomena of organometalllics,
the two main objectives of this study are: 1) provide a strategy to control the HOMO-LUMO energy gap and the optoelectronics properties in a series of Ru-bpy and Ru-phen complexes by altering the geometrical structures using a combination of DFT and TD-DFT; 2) develop force field parameters for Ru-bpy based complexes using molecular mechanics (MM) combined with energy minimization and molecular dynamics (MD) to obtain insight into the photophysical properties, specifically how these properties depend on the intermolecular interactions with solvents and nearby molecules [55-58]. The procedures developed in this project can help guide the design of novel organometallics with desirable properties for molecular engineering.
References


2.1. Introduction

Ruthenium (II) poly-diimine complexes have received significant attention in recent years [1-4], particularly in applications such as dye-sensitized solar cells, artificial photocatalysis, DNA diagnostics, and as potential agents for the detection of different biological analytes of clinical and environmental interest [1, 5-12]. Additionally, ruthenium diimine (2,2′-bipyridyl) complexes containing hydride, carbonyl and triphenylphosphine (PPh₃) ligands have been used as catalysts for hydrogenation of unsaturated organic compounds [13-17]. The importance of these complexes comes from their unique photophysical and photochemical properties.

The push-pull from ruthenium as a strong reductant that donates an electron from the t₂g orbital to the bpy low-lying π* molecular orbital, results in a singlet ground-state (S₀) to singlet metal-to-ligand charge-transfer (¹MLCT) transitions. The emission after excitation of the ¹MLCT band has a large Stokes shift, typically greater than 150 nm in the visible-to-near IR region of the spectrum, and has a long decay time, ranging from 100 ns to 10 µs; the Stokes shift and long-lived intensity decay are characteristic of triplet state (³MLCT) emissions [1-4]. Additionally, ruthenium complexes exhibit reversible redox behavior with adjustable potentials [18-20].

Tuning the emission wavelength of the transition metals complexes over the visible range is desirable for applications such as organic light-emitting devices (OLEDs) [21], luminescence-based sensors [22], and photocatalysis [23]. Therefore, several modification strategies have been applied to control the HOMO-LUMO energy gap: taking advantage of the substituent effects on the ligand parent by changing the ligand parent entirely or by varying the ligands *trans* to the
ligand parent [21-27]. For example, tuning molecular orbital energies with a variety of substitutes has been reported for Ir (III), Pt (II), and dyes for dye-sensitized solar cells [25-27].

Density functional theory (DFT) combined with the time-dependent DFT (TD-DFT) calculations have been employed to study the photophysical properties of different transition metal systems, and the calculated excitation energies agree well with the experimental data [25, 28-29]. This agreement between theory and experiment demonstrates the power of these calculations to provide reliable predictions about the nature of the molecular orbitals, electronic transitions, and conformational changes that can occur upon excitation. Most previous computational studies have been limited to the description of the trans-influence, the extent to which a ligand weakens the bond trans to itself in the equilibrium ground state of a complex [30], and most have been more concerned with square planar rather than octahedral complexes [31-35].

The purpose of our study is to extend the previous computational studies to include octahedral Ru (II) complexes, and thereby establish, qualitatively, a broader screening protocol for evaluating the correlation between the HOMO-LUMO energy gap and the Stokes shift in transition metal complexes. Here, we are investigating the spectroscopic effects of i) different ligands trans to bpy (hydride as a good σ-donor in comparison to carbonyl as a good π-acceptor), and ii) introducing different electron-withdrawing or electron-donating substituents in derivatives of the Ru(bpy)(PPh₃)₂ moiety.

Our laboratory has been interested in using the photophysical properties of Ru hydride complexes to study dynamics in biological membranes and for applications as catalysts and sensors [36-37]. Here, we report computational results for the photophysical, and photochemical properties of Ru (II) complexes of bpy, carbonyl and PPh₃ and their derivatives, which
previously have been shown to display long excited-state lifetimes with high quantum yields [36-37]. We also report a different synthesis procedure for [RuH(CO)bpy(PPh$_3$)$_2$]PF$_6$ (Rubpy) and [RuH(CO)dcbpy(PPh$_3$)$_2$]PF$_6$ (Rudcbpy) complexes, both of which have been studied previously in our laboratory [36-37], as well as synthesis of the new complex [RuH(CO)bis-4, 4’-(methyl)bpy(PPh$_3$)$_2$]Cl (RudMebpy) (including spectral data).

The good agreement between the experimental data for the former Ru(II) complexes and these calculations, encouraged us to extend the study to include theoretical predictions of three other Ru(II) complexes of interest: [RuH(CO)bis-4, 4’-(N-methylamide)bpy(PPh$_3$)$_2$]$^+$ (Rudamidebpy), [Ru(H)$_2$dcbpy(PPh$_3$)$_2$] (Ru(2H)dcbpy), and [Ru(CO)$_2$dcbpy(PPh$_3$)$_2$]$^{2+}$ (Ru(2CO)dcbpy) (see Fig. 1).

2.2. Experimental section

2.2.1. Preparation of complexes

It was found that the previously synthesized Rubpy and Rudcbpy complexes could be made in one step from Ru(PPh$_3$)$_3$(H)(CO)Cl and the appropriate ligand by following the method of Malecki and Maroń [38]. Each complex was combined with the appropriate ligand in equimolar amounts followed by reflux in methanol for 2h. The IR, $^1$H and $^{31}$P NMR were in
agreement with previously published data [36]. This same method was then applied to the synthesis of the new complex, RudMebpy. Details of the crystal structure analysis with crystal structure of [RuH(CO)bis-4, 4’-(methyl)bpy(PPh3)2]Cl and NMR data are provided in Appendix A.

2.2.2. Spectroscopy

Absorption, excitation and emission spectra for Rubpy, Rudcbpy, and RudMebpy (solution in ethanol) were recorded on a Molecular Devices Spectra Max M2 (Fig. 2 and 3).

Figure 2. Experimental absorption spectra of Rubpy, Rudcbpy, and RudMebpy in ethanol. The intensity is normalized for the comparison.

2.3. Computational Methods

2.3.1. DFT/TDDFT
To select the appropriate functional for describing the photophysical properties for all complexes, we employed DFT using six different exchange-correlation potentials: B3LYP [39], PBE0 [40], CAM-B3LYP [41], M06 [42], B2PLYP coupled with D3 dispersion correction [43] and hybrid meta-GGA with functional wB97XD [44]. All calculations were performed with the Gaussian 09 suite of programs [45] to determine the equilibrium structure of Rudcbpy in the $S_0$ state. M06, B2PLYP, and wB97XD were included for better description of noncovalent interactions. To compare the basis sets, we employed two commonly used effective core potentials (ECPs) for Ru: the Los Alamos pseudopotential (LANL2DZ) [46] and the Stuttgart-Dresden pseudopotential (SDD) [47]. The former are shape-consistent, have no adjustable parameters, and are derived by calculation of the spatial distributions of the valence orbital of the isolated atom. The latter are energy-consistent and include empirical parameters derived from observable data for a single atom, such as ionization energy. For all other atoms, we used the 6-
31G* basis set. In addition, to improve the angular description of the valance orbitals of the central atoms, a one-set-f-polarization function (exponent: 1.235) and a one-set-d-polarization function (exponent: 0.371) [48] were added to Ru and to P [49], respectively. All geometries were optimized, as described below, starting from the crystal structure of Rubpy (Cambridge Crystallographic Data Center Code CCDC 704327) [36], neglecting the PF$_6^-$ counterion in the model. The carboxylic groups were added to the 4 and 4’ positions of the bpy group. The most stable conformation of the carboxyl groups in $S_0$ state was determined by scanning the potential energy surfaces (PES) as a function of -COOH torsion angle and optimizing the remaining non-scanned coordinates (relaxed PES scan). We found that the most stable ground state conformation has both -COOH groups coplanar with bpy, Ru, carbonyl, and the hydride (Fig. 4).

Figure 4. Energy level diagrams of energy-minimized structures of Rudcbpy
To assess the performance of the computations, we used several statistical measures [50]: the mean error $\overline{\Delta}$, the standard deviation in the errors $\Delta_{\text{std}}$, the mean absolute error $\overline{\Delta}_{\text{abs}}$, and the maximum absolute error $\Delta_{\text{max}}$, where the experimental values used for comparison were taken from the crystal structure of Rubpy.\(^1\) A total of six Ru-ligand and six P-C bond-lengths, and 15 ligand-Ru-ligand, six C-P-C, and six C-P-Ru angles were considered. Solvation effects were modeled by using the “Polarizable Continuum Model” (PCM) [51-52] and the Onsager reaction-field model [53]. Normal-mode analysis confirmed that all optimized geometries were in minima. From the optimized $S_0$, the lowest 22 singlet-singlet transitions, and their corresponding oscillator strengths were determined using TDDFT in combination with B3LYP/LANL2DZ, B3LYP/LANL2Z with inclusion of $f,d$-polarization functions to Ru and P, and M06/LANL2DZ [54]. B3LYP and M06 generated similar excitation and absorption spectra that correlated well with the experimental data. We determined the nature of each band by calculating the orbital energies and the composition in terms of atom contributions using electron density difference maps (EDDMs) implemented in GaussSum 2.2 [55].

The lowest energy $T_1$ states were optimized starting from the $S_0$ geometry using two approaches: the linear-response TDDFT and the difference in the self-consistent field (SCF) energies of the $S_0$ and $T_1$ spin states ($\Delta\text{SCF}$) [56-57]. The later was used to ensure the stability of the calculated $T_1$ states by TDDFT. For both methods, the spin-unrestricted Kohn-Sham (UKS) orbitals were used. The analytic gradients and frequencies were calculated for $T_1$ optimized to its minimum energy configuration via TDDFT using Gaussian 16 [58]. $T_1$ was modeled using seven different combinations of methods and basis sets as explained in the discussion. The emission energies were calculated as the energy difference between $S_0$ and $T_1$ with the zero-point (ZP)\(^1\)

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\(^1\) The details of the statistical methods can be found in Appendix A.
vibrational energy correction included. For this, the emission energy was determined as the difference of the ZP of $S_0$ and the ZP of $T_1$ calculated using $\Delta$SCF and TDDFT approaches.

The data suggested that B3LYP/LANL2DZ/6-31G* is sufficient for describing the Ru mono-diimine system and its photophysical properties. Therefore, at lower computational cost, we used this level of theory to describe the other systems. To model RudMebpy and Rudamidebpy, the -COOH groups were substituted by -CH$_3$ and -CONHCH$_3$, respectively. The Ru(2CO)dcbpy and Ru(2H)dcbpy complexes were modeled starting from the optimized Rudcby ground-state geometry. Energy minima were then obtained by optimizing all the geometrical parameters.

2.3.2. QTAIM/NBO

To rationalize the effects of the trans influence and substituent groups, we determined the atomic charges of the optimized structures in the $S_0$ and $T_1$ states using two different approaches: NBO analysis implemented in Gaussian 09 with and QTAIM implemented in the AIMAll program package [59-61]. The wave functions were generated first by a single-point calculation on the optimized structures of the complexes in $S_0$ and $T_1$ using the UKS orbitals. Both methods provided similar trends for the atomic charge changes between $S_0$ and $T_1$, (Appendix A, Table A1).

2.4. Results and Discussion

2.4.1. The optimized $S_0$ geometry of Rudcby and performance of functionals

Table 1 compares selected bond distances and angles from the experimental data for Rubpy (Cambridge Crystallographic Data Center Code CCDC 704327) [36] with the calculated values obtained using B3LYP/LANL2DZ/PCM. The calculations predicted a deviation in the range of 1.20-11.15 pm in the bond length for the different Ru-ligand and a total mean error of
7.07 pm. The table also shows the calculated parameters of Rudcbpy using the same level of theory. Introducing -COOH into the bpy ligand did not significantly affect the core coordination of the parent complex (Appendix A, Tables A2-A5). For example, the total mean error associated with the calculated Ru-ligand bond-lengths of Rudcbpy is 7.14 pm. Additionally, the total mean error for the calculated P-C bond-lengths for Rudcbpy compared to Rubpy differs by 0.09 pm. In the following, we compare the performance of the different combinations of density functional/basis set/PCM in terms of the calculated Ru and P bond-lengths and bond-angles that describe the Rudcbpy S₀ geometry (Fig. 5, Appendix A, Tables A2-A5).

Figure 5. Mean errors $\bar{\Delta}$ relative to experiment in the calculated Ru bond distances (pm) of Rudcbpy.
Table 1. Selected bond lengths (Å), bond angles (°), and torsion angles (°) optimized for complexes in $S_0$ and $T_1$ using TDDFT in ethanol except for Ru(2H)dcbpy where ∆SCF data are reported.

<table>
<thead>
<tr>
<th></th>
<th>Rubpy</th>
<th>Rudcbpy</th>
<th>Rudamidebpy</th>
<th>RudMebpy</th>
<th>Ru(2H)dcbpy</th>
<th>Ru(2CO)dcbpy</th>
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<td>-2.769</td>
<td>4.195</td>
<td>3.189</td>
<td>-2.046</td>
<td>0.114</td>
<td>-0.874</td>
</tr>
</tbody>
</table>

*N1 is trans to CO and N2 is trans to H.

*a Experimental data taken from ref. [36].
The total mean errors of the bond lengths were, on average, larger for Ru-ligand than for P-C bonds. We noted that in all methods the maximum error was associated with Ru-N bonds. As expected, the functionals that were constructed to account for dispersion (M06, B2PLYPD3, and wB79xD) yielded geometric parameters that were closest to the crystal structure parameters. The performance of the different DFT methods followed the ‘Jacobs ladder’ classification scheme with total mean errors of the bond lengths decreasing in the series double-hybrid (B2PLYPD3) < meta-hybrid (M06) < hybrid-GGA (wB79xD) [62]. The methods, however, show no trend in evaluation of bond-angles. With all methods, the Ru bond-angles were smaller (0.01-0.20º) than in the crystal structure of the parent complex Rubpy; the P bond-angles varied over a range of +0.02/-0.04º. It should be noted that the PBE0/LANL2DZ performance was superior to B3LYP/LANL2DZ. Both functionals use a fraction of exact exchange energy, but B3LYP includes empirical parameters determined from the correlation energy of the He atom [63]. Additionally, PBE0 performance was comparable to that of the functionals that include dispersion. Including the long-range corrected exchange correlation functional (CAM-B3LYP) provided a better description compared to that obtained with B3LYP alone.

We found that increasing the basis set size did not provide significant improvement in the geometric parameters. For instance, adding \( f,d \)-polarization functions slightly decreased the mean error of the bond-lengths of Ru-ligand, but not of P-C. The performance of the basis sets that include ECPs is tested with B3LYP and M06 level of theory (Fig. 5, Table A2-A5). The results show better improvements in the determination of Ru-ligand bond-lengths using SDD with both B3LYP and M06 functionals (total mean errors are 5.4 pm and 4.1 pm, respectively) compared to LANL2DZ (7.1 pm and 5.5 pm, respectively). However, LANL2DZ provides a better description of the bond angles, see Table A4 and A5.
To determine the $S_0$ geometry of Rudcbpy, we initially used functionals that did not include dispersion (i.e., B3LYP, PBE0, and CAM-B3LYP). The calculations were performed first without symmetry constraints and then applied the constraints. In all cases, there was lack of symmetry in the calculated structure (i.e., $C_1$). However, using functionals that include dispersion (i.e., B2PLYPD3, M06, and wB79xD), $S_0$ for Rudcbpy was fully optimized with $C_s$ symmetry (i.e., the bpy rings were coplanar with Ru, CO, and H), without any constraints and it was a true minimum.

To assess solvent effects, we optimized the structure using B3LYP first in vacuum and then applying the Onsager model [53]. This procedure produced a minimum geometry with $C_s$ symmetry. The lower symmetry obtained when using the hybrid functionals B3LYP, PBE0 and CAM-B3LYP, as described above, is due to the integral equation approach formalism model (PCM) not accounting accurately for the solute-solvent interaction [64]. In addition, the absence of the dispersion correction in these methods affects the conformation and stability of the system, particularly, the interaction between the phenyl rings.

Regardless of the inability of B3LYP/PCM to adequately describe the geometry of Rudcbpy, it reproduced the experimentally observed absorption and emission energies at a relatively low computational cost compared to other methods. As will be discussed in the following, the excitation energies predicted by B3LYP/LANL2DZ are superior compared to those obtained by other methods. In fact, it has been reported that the functionals that provide the most precise geometries, M06-2X, underestimated the triplet gaps of Ru(II) complexes [65]. With these considerations, we chose B3LYP/LANL2DZ/6-31G*/PCM to evaluate the conformational changes and photophysical properties computed for the other compounds.

2.4.2. *Ru coordination geometry and molecular orbital energies*
2.4.2.1. Substituent effects

In general, the deviations of the Ru-ligand bond lengths upon introducing substituents in Rubpy are not significant (< 1.00 pm, see Table 1). The significant changes are in the electronic distributions and orbital energies. The negative charges over the bpy and phenyl rings decreased as the donor strength of the substituents decreased and the positive charge on the Ru atom increased (Table 2). It should be noted that the charges on the P atoms did not correlate well with the expected trends of the substituents, (i.e., larger positive charge with electron-withdrawing substituents and larger negative charge with electron-donating substituents). The positive charge over the P atoms increased in the series: 1.71 e, 1.78 e, and 1.80 e for Rudcbpy, Rubpy, RudMebp, respectively.

Table 2. The change in the electron density distribution between optimized S₀ and T₁ estimated by calculating the partial atomic charges e using QTAIM.

<table>
<thead>
<tr>
<th>Complex</th>
<th>S₀</th>
<th>T₁</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru</td>
<td>bpy</td>
</tr>
<tr>
<td>Rubpy</td>
<td>0.639</td>
<td>0.064</td>
</tr>
<tr>
<td>Rudcbpy</td>
<td>0.669</td>
<td>0.301</td>
</tr>
<tr>
<td>Rudamidebpy</td>
<td>0.669</td>
<td>0.119</td>
</tr>
<tr>
<td>RudMebp</td>
<td>0.626</td>
<td>-0.011</td>
</tr>
<tr>
<td>Ru(2H)dcbpy</td>
<td>0.474</td>
<td>0.123</td>
</tr>
<tr>
<td>Ru(2CO)dcbpy</td>
<td>0.869</td>
<td>0.365</td>
</tr>
</tbody>
</table>

* X is the substituent and (Ph) is the phenyl rings for both ligands.

In general, the atomic contributions to the molecular orbitals are similar for Ru complexes with different substituents (Table 3 and 4, Fig. 6). In all complexes, more than 90% of the electron density of the HOMO and HOMO-1 is delocalized between the Ru atom and the (PPh₃)₂ groups. HOMO and HOMO-1 can be described as a combination of the Ru dₓz orbitals.
and the bonding π orbitals of the phenyl rings; one phenyl ring from each PPh₃ ligand does not contribute to the HOMO (Fig. 6). HOMO-2 is Ru dₓᵧ with no contribution from the phenyl rings, while HOMO-3 is a combination of Ru dᵧz, π bpy, and π (PPh₃). The calculations showed that more than 80% of the electron density of the LUMO in all ions has π* character and is localized on the bpy rings bearing the substituent with a fractional contribution from the Ru dₓz orbital (Fig. 6).

The changes in the relative energies of the frontier molecular orbitals are based on the different mesomeric effects of the substituents and are plotted in Fig. 6. Introducing the electron withdrawing substituents (-COOH), decreased the electron density and stabilized the LUMO level; the energy is lower by 0.58 eV compared to that of Rubpy. The weaker negative mesomeric behavior for (-CONHCH₃)₂ groups also stabilized the LUMO but by 0.35 eV compared to Rubpy. However, the electron releasing groups (-CH₃) destabilized the LUMO level by only 0.09 eV.

2.4.2.2. Trans influence

The following comparisons are made relative to Rudcbpy. Replacing the carbonyl by hydride increased the σ donation strength along x and y axes reducing the partial positive charge over Ru (Table 2). Thus, the increase of the electron density increases the electrostatic repulsion between Ru dₓzᵧ₂ orbitals and the two hydride ions. The Ru-H bond lengths showed the largest increase (~2.59 pm) compared to the other complexes. The HOMO orbital is destabilized by 1.54 eV and is 95% Ru dₓᵧ. On the other hand, the Ru-N and Ru-P bond lengths decreased by ~5.76 and ~9.02 pm, respectively, suggesting that introducing a σ donor ligand will push more electron density toward Ru, thereby increasing back-bonding from Ru toward other ligands. Additionally, we found that the MLCT band originates from the HOMO-1-HOMO-2 orbitals,
Table 3. Computed absorption, excitation and electronic transitions for complexes using B3LYP/LANL2DZ.

<table>
<thead>
<tr>
<th>complex</th>
<th>λabs$^a$ (nm)</th>
<th>λabs$^b$ (nm)</th>
<th>λexit. (nm)</th>
<th>f</th>
<th>major contribution</th>
<th>% composition</th>
<th>character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubpy</td>
<td>400</td>
<td>394.9</td>
<td>387.7</td>
<td>0.06</td>
<td>H → L (95%)</td>
<td>H: Ru 47%, (PPh$_3$)$_2$ 46%</td>
<td>Ru,(PPh$_3$)$_2$ → bpy</td>
</tr>
<tr>
<td></td>
<td>277$^c$</td>
<td>287.0</td>
<td>288.9</td>
<td>0.36</td>
<td>H-1→ L+2 (46%)</td>
<td>H-1: Ru 50%, (PPh$_3$)$_2$ 45%</td>
<td>Ru → (PPh$_3$)$_2$</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>285.9</td>
<td>286.7</td>
<td>0.19</td>
<td>H-1→ L+3 (34%)</td>
<td>L+3: (PPh$_3$)$_2$ 13%, bpy 85%</td>
<td>Ru,(PPh$_3$)$_2$ → bpy</td>
</tr>
<tr>
<td></td>
<td>300$^c$</td>
<td>326.1$^c$</td>
<td>328.5</td>
<td>0.06</td>
<td>H → L+3 (57%)</td>
<td>H-1→ L+3 (20%)</td>
<td>Ru,(PPh$_3$)$_2$ → bpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>328.5$^c$</td>
<td></td>
<td>H-1→ L+3 (20%)</td>
<td></td>
<td>Ru,(PPh$_3$)$_2$ → bpy</td>
</tr>
<tr>
<td>Rudcbpy</td>
<td>422</td>
<td>455.3</td>
<td>446.1</td>
<td>0.09</td>
<td>H→ L (94%)</td>
<td>H: Ru 42%; (PPh$_3$)$_2$ 52%</td>
<td>Ru,(PPh$_3$)$_2$ → dcbpy</td>
</tr>
<tr>
<td></td>
<td>310$^c$</td>
<td>320.3</td>
<td>309.5</td>
<td>0.29</td>
<td>H-15→ L (82%)</td>
<td>H-15: bpy 81%; (PPh$_3$)$_2$ 18%</td>
<td>bpy,(PPh$_3$)$_2$ → (COOH)$_2$</td>
</tr>
<tr>
<td></td>
<td>270$^c$</td>
<td>322.5</td>
<td>349.6</td>
<td>0.08</td>
<td>H→ L+3 (55%)</td>
<td>H-3: (PPh$_3$)$_2$ 83%, Ru 12%</td>
<td>Ru,(PPh$_3$)$_2$ → dcbpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>328.5</td>
<td>328.5$^c$</td>
<td>0.08</td>
<td>H→ L+3 (57%)</td>
<td>H-9: bpy 14%; (PPh$_3$)$_2$ 85%</td>
<td>Ru,(PPh$_3$)$_2$ → dcbpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>325.9$^c$</td>
<td></td>
<td>H-1→ L+3 (20%)</td>
<td></td>
<td>Ru,(PPh$_3$)$_2$ → bpy</td>
</tr>
<tr>
<td>RudMebpy</td>
<td>390</td>
<td>390.6</td>
<td>382.7</td>
<td>0.07</td>
<td>H→ L (96%)</td>
<td>H: Ru 50%, (PPh$_3$)$_2$ 42%</td>
<td>Ru, (PPh$_3$)$_2$ → dMebpy</td>
</tr>
<tr>
<td></td>
<td>290$^c$</td>
<td>286.4</td>
<td>290.1</td>
<td>0.30</td>
<td>H-1→ L+1 (46%)</td>
<td>H-1: (PPh$_3$)$_2$ 46%, Ru 48%, bpy 8%</td>
<td>Ru → (PPh$_3$)$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>295.5</td>
<td>0.24</td>
<td>H→ L+1 (61%)</td>
<td>H-6: (PPh$_3$)$_2$ 34%, bpy 55%, Ru 9%</td>
<td>Ru, (PPh$_3$)$_2$ → dMebpy</td>
</tr>
<tr>
<td></td>
<td>310$^c$</td>
<td>328.3$^c$</td>
<td>328.3$^c$</td>
<td>0.13</td>
<td>H→ L+1 (64%)</td>
<td>L+2: bpy 88%, (CH$_3$)$_2$ 1%</td>
<td>Ru, (PPh$_3$)$_2$ → dMebpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>325.9$^c$</td>
<td>0.06</td>
<td>H→ L+2 (61%)</td>
<td></td>
<td>Ru, (PPh$_3$)$_2$ → dMebpy</td>
</tr>
</tbody>
</table>

$^a$ Experimental data for Rudcbpy, Rubpy, and RudMebpy from this work. $^b$ calculated absorption. $^c$ excitation observed at the shoulder.
<table>
<thead>
<tr>
<th>complex</th>
<th>λ_{abs} (nm)</th>
<th>λ_{exit.} (nm)</th>
<th>f</th>
<th>major contribution</th>
<th>% composition</th>
<th>character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rudamidebpy</td>
<td>428.1</td>
<td>420.8</td>
<td>0.09</td>
<td>H → L (95%)</td>
<td>H: Ru 45%; (PPh₃)₂ 49%</td>
<td>Ru, (PPh₃)₂ → damidebpy</td>
</tr>
<tr>
<td></td>
<td>320.1</td>
<td>297.2</td>
<td>0.19</td>
<td>H-17 → L (31%)</td>
<td>H-17: (PPh₃)₂ 46%; bpy 42%; (CONHCH₃)₂ 12%</td>
<td>(PPh₃)₂,(CONHCH₃)₂ → bpy</td>
</tr>
<tr>
<td></td>
<td>324.3</td>
<td>316.9</td>
<td>0.07</td>
<td>H-8 → L (27%)</td>
<td>H-8: (PPh₃)₂ 89%</td>
<td>Ru → (PPh₃)₂</td>
</tr>
<tr>
<td></td>
<td>310.5</td>
<td>326.8</td>
<td>0.06</td>
<td>H → L+1 (76%)</td>
<td>H-9: (PPh₃)₂ 62%; bpy 19%; (CONHCH₃)₂ 17%</td>
<td>(PPh₃)₂,(CONHCH₃)₂ → bpy</td>
</tr>
<tr>
<td>Ru(2H)dcbpy</td>
<td>454.6</td>
<td>502.6</td>
<td>0.20</td>
<td>H-1 → L+1 (97%)</td>
<td>H-1: (PPh₃)₂ 25%, Ru 57%, bpy 17%</td>
<td>Ru,(PPh₃)₂→ dcbpy</td>
</tr>
<tr>
<td></td>
<td>444.0</td>
<td>457.5</td>
<td>0.11</td>
<td>H-2 → L+1 (75%)</td>
<td>L-1: bpy 82%, (COOH)₂ 16%</td>
<td>Ru,(PPh₃)₂→ dcbpy</td>
</tr>
<tr>
<td></td>
<td>576.3</td>
<td>351.2</td>
<td>0.12</td>
<td>H-1 → L (67%)</td>
<td>L-1: bpy 78%, (COOH)₂ 8%</td>
<td>Ru,(PPh₃)₂→ dcbpy</td>
</tr>
<tr>
<td></td>
<td>357.1</td>
<td>360.8</td>
<td>0.23</td>
<td>H-1 → L+3 (83%)</td>
<td>L-3: (PPh₃)₂ 91%, Ru 8%</td>
<td>Ru → (PPh₃)₂</td>
</tr>
<tr>
<td>Ru(2CO)dcbpy</td>
<td>436.0</td>
<td>428.5</td>
<td>0.34</td>
<td>H → L (99%)</td>
<td>H: Ru 10%, (PPh₃)₂ 89%</td>
<td>Ru,(PPh₃)₂→ dcbpy</td>
</tr>
<tr>
<td></td>
<td>332.8</td>
<td>341.5</td>
<td>0.99</td>
<td>H → L+2 (91%)</td>
<td>L+2: Ru 36%, (PPh₃)₂ 55%</td>
<td>(PPh₃)₂→ (2CO), Ru</td>
</tr>
<tr>
<td></td>
<td>331.9</td>
<td>333.5</td>
<td>0.58</td>
<td>H → L+2 (92%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6. HOMO and LUMO representations of the optimized ground states of the complexes calculated using B3LYP/LANL2DZ. Left: isodensity plots of the frontier orbitals of LUMO of the complexes arranged as the energies increase along with schematic representation of LUMOs energies. Right: isodensity plots of the frontier orbitals of HOMO of the complexes arranged as the energies increase along with schematic representation of HOMOs energies.
which have been both destabilized by ~1.82 eV. The HOMO-1 and HOMO-2 orbitals have Ru \(d_{xz}\) and \(d_{yz}\) contributions (57%, and 83% respectively) with less \(\pi\) bonding from the phenyl rings. In addition, the HOMO-1 orbital has 17% \(\pi\) bonding from dcbpy. The three lowest LUMOs, lying 2.53 eV above the HOMO, are largely localized on the dcbpy, and have minor Ru \(d_{xz}\) and \(d_{yz}\) character. Introducing hydride destabilized the LUMO by 0.64 eV and the charge on the bpy is more negative, -0.052 \(e\) compared to the Ru(dcbpy).

Replacing the two hydride ions by two CO \(\pi\)-acceptors resulted in depopulation of the orbitals between the x and y axes (\(d_{xz}\) and \(d_{yz}\)), which stabilized the HOMO and LUMO by 0.65 and 0.63 eV, respectively. Consequently, the contributions of the Ru \(d_{xz}\) and \(d_{yz}\) to the HOMO orbital are significantly reduced and become smaller (<10%). The major contribution to the HOMO up to HOMO-3 comes from the bonding \(\pi\) orbitals of the phenyl rings (89%). Introducing the \(\pi\)-acceptors increased the positive partial charges on the Ru and both P atoms, thereby reducing the back-bonding from Ru toward P atoms, and the Ru-P bond length increased by ~10.0 pm compared to Ru(dcbpy). The LUMO and LUMO+1 are mainly localized on the dcbpy with a contribution from the antibonding \(\pi^*\) CO, while LUMO+2 has antibonding contribution from Ru \(d_z^2\), \(\pi^*\) phenyl rings, and \(\pi^*\) CO.

2.4.3. Absorption spectra

TDDFT/B3LYP/LANL2DZ/PCM calculations were employed to calculate the 22 lowest singlet-singlet transitions starting from the \(S_0\) geometry, optimized in ethanol. In all complexes, two maxima are observed in the calculated absorption spectra (Fig. 2, 7). The results reveal that the lowest energy band is composed of several electronic transitions that have the HOMO as the initial state and the LUMO as the final state. Thus, this band, which is in the visible region of the spectrum, is the MLCT transition with a contribution from (PPh\(_3\))\(_2\) that varies from 25%
(Ru(2H)dcbpy) to 89% (Ru(2CO)dcbpy) (see Table 4). Most notably, our calculations predicted a forbidden HOMO → LUMO transition in Ru(2H)dcbpy. The MLCT band for this complex is due to transitions from lower HOMOs (HOMO-1 to HOMO-3) to the lower LUMOs (LUMO to LUMO+3).

The next higher energy absorption maximum observed in the near-UV region of the experimental spectra is composed of several overlapping bands that are not well resolved (Fig. 2). The calculations show that these are the intra-ligand π-π* and n-π* electronic transitions of PPh₃ and bpy with the substituents that occur in the same region. This band is due to excitation either from lower HOMOs to LUMO or from HOMO to higher LUMOs (Table 3 and 4). Moreover, the calculations reveal that the low-energy side of this band, which ranges from 300 to 330 nm (Table 3 and 4), includes MLCT transitions from Ru to both PPh₃ and bpy for all complexes except Ru(2H)dcbpy and Ru(2CO)dcbpy. The appearance of an additional near-UV MLCT band (300-350 nm) has also been observed for other Ru (II) systems [66]. To confirm the theoretical findings, excitation spectra were measured over the range 300-500 nm, and electronic transitions that correspond to the predicted MLCT transitions were observed. The molecular orbital contributions and maxima of the computed absorption spectra and electronic transitions compared with the corresponding experimental data are listed in Tables 3 and 4. The computational results agree well with the overall features of the experimentally determined absorption spectra of Rubpy and RudMebpy (Figs. 2 and 7).

The calculated MLCT band of Rudcbpy is red shifted by ~28 nm compared with the experimental absorption spectrum which has a maximum at 422 nm. It should be noted that the calculation does not take into account the possibility of hydrogen bond formation with solvent molecules. However, we anticipated that hydrogen bonding will affect the molecular orbital
energies in the Rudcbpy compared to Rubpy and RudMebpy because of the solvent interaction with the carboxylic groups. To test this hypothesis, we modeled a system with four explicit methanol molecules with their hydroxyl groups interacting with the carboxylic groups of Rudcbpy. This interaction elongated the O-H bond length of the -COOH groups by 3.70 pm and rotated the –COOH by ~15º with respect to the plane of the bpy ring. In addition, the LUMO orbital was destabilized by 0.10 eV, which blue shifted the MLCT band ~9 nm. We then explored the possible effect of the counterion by including PF$_6^-$ with the methanol molecules, and the MLCT band was further blue shifted by another 13 nm (Fig. 8). The calculated shift suggests the role of the solvent and counterion in controlling the HOMO-LUMO energy gap which can be studied further by applying combined quantum mechanics/molecular mechanics (QM/MM) methods.

Figure 7. The absorption spectra for the complexes calculated using B3LYP/LANL2DZ. The intensities are optimized to the highest intensity for each complex.
We also computed the UV/Visible absorption spectra for Rudcbpy using M06/LANL2DZ and CAM-B3LYP/LANL2DZ (Fig. A1). Overall, all methods predicted similar shapes for the optical spectra, and the atomic orbital contributions involved in the excitations. B3LYP and M06 provided comparable excitation energies. However, a large blue-shift is observed with TDDFT/CAM-B3LYP (>100 nm). This overestimate of the HOMO-LUMO energy gap when using CAM-B3LYP combined with PCM has been observed for other Ru(II) systems [67].

2.4.3.1. Substituent effects

The shift in the MLCT bands correlated well with the changes in the conformational and MO energies described above. In the experimental data, the MLCT band of Rudcbpy was red shifted by 22 nm when compared to Rubpy, whereas the MLCT band of RudMebpy was blue.
shifted by 14 nm (Fig. 2). The computations using the continuum model predicted the same trends but different magnitudes for the shifts. The MLCT band of the Rudcbpy was red shifted by 60 nm when compared to Rubpy. Converting -COOH to -CONHCH₃ resulted in a smaller red shift of 33 nm, whereas the MLCT band of RudMebpy was blue shifted by 4 nm (Fig. 7).

2.4.3.2. Trans influence

Calculations show that the carbonyl groups in the Ru(2CO)dcbpy stabilize both HOMO and LUMO, but the overall energy gap increases resulting in a 19 nm blue shift of the MLCT band when compared to Rudcbpy. In addition, in Ru(2CO)dcbpy, the intra-dcbpy π-π* transitions are weak while strong electronic excitations from PPh₃ to Ru and CO are observed in the higher energy bands. Replacing the two carbonyls with hydrides decreases the energy gap and destabilizes all occupied orbitals causing a red shift in the MLCT. Interestingly, this band has greater intensity and is much broader than the MLCT bands of the other complexes. This is because it is characterized by a larger (97%) weight from a transition involving HOMO-1 and LUMO+1 with a significant contribution of orbitals both localized on the bpy ligand (17% and 82%, respectively). This composition enhances the transition dipole and also causes a large bathochromic shift in excitation when compared to the excitation of the other complexes. Notably, it has a high intensity peak at 455 nm and shoulder at 576 nm.

2.4.4. Triplet excited-state geometries

The T₁ state geometry was optimized for Rudcbpy using TDDFT/B3LYP and ΔSCF/B3LYP with combinations of LANL2DZ, LANL2DZ(f), and LANL2DZ(f,d), CAM-B3LYP/LANL2DZ, M06/LANL2DZ, and M06/SDD (Table A6). The corresponding TDDFT and ΔSCF calculations characterized the optimized geometry as a ³MLCT state. Furthermore, the analysis of the T₁ molecular orbital showed that the highest singly occupied molecular orbital
(HSOMO) centered on the bpy (Fig. 9). To quantify the geometric changes, we calculated the root-mean-square deviation (RMSD) of T₁ compared to S₀ using the method of Kabsch as implemented in the Visual Molecular Dynamics (VMD) program [68] (Table A6). All methods yielded similar pattern of geometric parameter changes in T₁ using both ΔSCF and TDDFT. For example, the difference in the RMSD between ΔSCF and TDDFT is in the range 0.001-0.239; CAM-B3LYP gave the higher deviation.

Upon excitation, the symmetry and planarity between Ru and the other ligands are broken and the bpy rings are twisted. The most significant change is reduction in the bend observed in the P1-Ru-P2 angle for all complexes (24.66-32.25°). This reduction is asymmetric and is accompanied by an increase in the distance between the phenyl rings and bpy, which likely reduces the steric crowding that could arise from an increase in the π*-LUMO orbital population.
on bpy. N1 is \textit{trans} to CO and N2 is \textit{trans} to H. Both Ru-N bonds lengths decrease, but because of the trans influence, Ru-N2 decreases the most. The increase of the Ru-P bond length in the \textsuperscript{3}MLCT state, which is observed when using ∆SCF with all levels of theory, is due to the depopulation of the HOMO orbitals and reduction of the bond strength. However, the optimized \textit{T}\textsubscript{1} by TDDFT/B3LYP and TDDFT/CAM-B3LYP predicted an increase of only one Ru-P bond length. Regardless of the method used, accompanying the electron migration from Ru and PPh\textsubscript{3} to the bpy, there is an overall reduction in CPRu angles and increase in CPC angles. The changes in the phenyl ring twist angles (Fig. 10) are presumably due to decreased repulsion between rings that occurs upon electron migration. The largest twist (30.05\textdegree) is observed for the phenyl rings that do not contribute to the HOMO.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Overlaying \textit{S}\textsubscript{0} and \textit{T}\textsubscript{1} calculated using B3LYB/UB3LYP, respectively, for Rudcbpy (left) and Ru(2CO)dcbpy (right).}
\end{figure}

The \textit{T}\textsubscript{1} geometries for Rudamidebpy and Ru(2CO)dcbpy were minimized successfully using TDDFT/B3LYP and UKS/B3LYP. However, different approaches were required to minimize \textit{T}\textsubscript{1} geometries of the other complexes. For example, when optimizing Ru(2H)dcbpy \textit{T}\textsubscript{1} state, TDDFT/B3LYP produced oscillatory minima. This is due to a small HOMO-LUMO gap that caused the states to cross during the optimization. By using UKS/B3LYP, optimization was achieved. However, this approach was inadequate for Rubpy and RudMebpy. Minimization of
these complexes was achieved using the PBE0 level of theory with ∆SCF and TDDFT. The calculated RMSD for all minimized geometries correlated well with HOMO-LUMO gap — the larger energy gap in S₀ is accompanied by less distortion and smaller RMSD in T₁. The changes between the S₀ and optimized T₁ geometries, due to the substituent effects and the trans influence, were evaluated comparing ∆SCF with TDDFT (Table 1). A comparison of selected parameters, emission energies, and RMSD using ∆SCF and TDDFT for all complexes is in Fig. 11 and Table A7.

2.4.4.1. Substituent effects

The T₁ of RudMebpy, which has the largest energy gap, showed the smaller RMSD while Rudcbpy had the larger RMSD (Fig. 11). As explained above for Rudcbpy, the changes in the Ru-ligand bond lengths for the different substituents show similar trends. Specifically, increases in the Ru-P bond lengths were observed for all complexes except for one Ru-P bond in Rudamidebpy, and Ru-N bond lengths decreased with RudMebpy having the shortest Ru-N bond lengths. This reduction in the Ru-N bond is associated with greater localization of the electron density on the N atoms compared to other complexes for which the electron density is distributed over the entire bpy ring. On the other hand, Ru-H and Ru-CO bonds lengths in all complexes increased. Moreover, as a result of the electron migration, the Ru and PPh₃ charges became more positive. The positive charge on Ru increased the most in the RudMebpy complex, indicating that more electron density moves toward bpy. This unexpected trend of increased positive charge on Ru in T₁ when in the presence of an electron-donating group has been noted previously in platinum(II) biphenyl 2,2’-bipyridine complexes, where Pt was found to have the largest positive charge upon binding the strongest electron-donating group (–NH₂) [25]. Finally, in T₁, the same change in the relative rotation of the phenyl rings was observed for all complexes, the largest
twist being $\sim 41^\circ$ in RudMePy.

2.4.4.2 Trans influence

The Ru(2H)dcbpy has the smallest $S_1 \leftarrow S_0$ energy gap and its $T_1$ shows the largest distortion. By contrast, Ru(2CO)dcbpy has the largest $S_1 \leftarrow S_0$ energy gap and its $T_1$ shows the

Figure 11. The calculated RMSD of $T_1$ compared to the HOMO-LUMO energy gap for the complexes with respect to the substitutions using TDDFT (a), and trans influence using $\Delta$SCF (b). The calculated emission energies using TDDFT compared to the HOMO-LUMO energy gap for the complexes with respect to the substitutions (c), and trans influence using $\Delta$SCF (d).
smallest distortion (Fig. 11). The variations in the Ru-ligand bond lengths in T1 with respect to S0 of the two complexes had opposite trends. While the Ru-P and Ru-N bond lengths increased in Ru(2H)dcbpy, both bond types decreased in Ru(2CO)dcbpy. In addition, the Ru-CO bond increased in Ru(2CO)dcbpy while the Ru-H bond length decreased in Ru(2H)dcbpy (Table 1). There was no change in either the P-Ru-P bond angle or phenyl ring twist angles in Ru(2CO)dcbpy, while the P-Ru-P bond angle increased by 9° and the phenyl ring twist angle changed by 18° in Ru(2H)dcbpy.

2.4.5. Excitation and Emission Energies

The ΔSCF approach (ΔE = E (T1) - E (S0)) was used to calculate the emission energies, as explained previously. To assess the quality of the DFT models of the T1 for Rudcbpy, we compared the experimental and calculated emission energies using different methods, as explained above. In general, including the zero-point energy vibrational correction yielded emission energies that agreed well with experiment. We further noted that the emission energies obtained by TDDFT are comparable to those from ΔSCF, and both B3LYP and M06 provided similar emission energies (Fig. 12). In addition, CAM-B3LYP overestimated the emission energy (2.36 eV or 525 nm) when compared to B3LYP (1.94 eV or 639 nm), the latter which predicted an energy more similar to the experimental value of 2.04 eV (609 nm). On this basis, we concluded that B3LYP/LANL2DZ predicted a reasonable T1. Moreover, increasing the basis set size by adding f and then f,d-polarization functions neither improved the description of S0, as explained earlier, nor the prediction of the T1 emission energy (Fig. 12).
The calculated emission energies for Rubpy and RudMebpy using TDDFT/PBE0/LANL2DZ were also overestimated (2.35 eV (528 nm) and 2.41 eV (514 nm), respectively) compared to the experimental values (2.09 eV (593 nm) and 2.20 eV (563 nm), respectively). Nevertheless, all complexes showed the expected shift that correlated with the HOMO-LUMO gap (Fig. 11). The trend in the Stokes shifts calculated for the two complexes reproduced their relative order (including the parent compound), but not the absolute energies observed experimentally (Fig. 2), where the maximum of RudMebpy emission is at 563 nm while that of Rudcbpy is at 609 nm.

Experimentally, the observed Stokes shift is largely determined by the Coulomb energy difference between S₁ and T₁ as well as contributions from radiationless processes such as vibrational relaxation. Theoretically, we are relating the radiationless processes to the amount of distortion of the T₁ (RMSD). The system that undergoes minimal conformational reorganization between the two states will emit higher energy photons. Our calculations estimated Stokes shifts that agreed well with the calculated energy gap and RMSD (Fig. 11). To estimate the Stokes shift, the molecular orbital energies of each complex were calculated using the same level of
theory at which the emission energy has been calculated. Because Ru(2H)dcbpy has the smallest HOMO-LUMO gap compared to Rudcbpy and Ru(2CO)dcbpy, its emission spectra was shifted to the far infrared (0.88 eV or 1,409 nm). Comparing complexes with different substituents, the emission energy was increasingly red shifted with decreasing the electron-donor strength: RudMebpy (2.41 eV or 514 nm), Rubpy (2.35 eV or 528 nm), Rudamidebpy (2.13 eV or 582 nm), and Rudcbpy (1.94 eV or 639 nm) (Fig. 11). The shifts observed in the emission spectra of other Ru systems constructed from imidazole, phenanthroline, and other derivatives with various ligands, are in accord with our calculations [25-27, 69-70]. Furthermore, based on the energy gap law, the rate of the radiationless decay of T1 will increase as the energy gap between the two states decreases [71]. Consequently, we predict that Ru(2H)dcbpy should exhibit the shorter triplet decay time.
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Chapter 3. Computational Study of the Emission Energy in Ru-Phenanthroline-Based Complexes: Control of the HOMO-LUMO Energy Gap, Influence of Electronic Delocalization, and Formation of the Triplet Metal-Centered State

3.1. Introduction

Ru (II) polypyridyl complexes exhibit metal-to-ligand charge transfer (1MLCT) transitions in the UV-vis spectrum where an electron is transferred from one of the Ru t_{2g} orbitals (d_{xy}, d_{yz}, and d_{xz}) to a ligand π* molecular orbital (MO) [1-3]. Highly efficient intersystem crossing from 1MLCT to 3MLCT occurs due to the strong spin-orbit coupling of second-row transition metals. The large Stokes shift and long-lived intensity decay are characteristic of the 3MLCT [4-7]. Because of their unique photophysical properties, Ru(II) polypyridyl complexes have been extensively used in applications such as dye-sensitized solar cells, DNA diagnostics, artificial photocatalysis, and recently as anticancer drugs [8-20].

In our previous combined experimental and theoretical study of Ru(bpy)(PPh_3)_2 derivatives, we have proposed strategies to tune the emission energy for these complexes and we observed correlations between the HOMO-LUMO energy gap, Stokes shift, and triplet excited state (T_1) distortion, as a function of different substituent electron-withdrawing and donating groups [21]. Here, we extend our study toward establishing a broader screening protocol for estimating the photophysical properties of organometallic complexes to include the new series of Ru(phen)(PPh_3)_2. The structure of the acceptor ligand plays an important role in determining the quantum yield (Φ) and excited-state lifetime (τ) [22]. Specifically, the more rigid ligand reduces the nonradiative rate (k_{nr}) and thus the complex has a higher quantum yield and longer lifetime. This has been confirmed in Os(II) complexes that have lower k_{nr} when constructed from 1,10-phenanthroline (phen) compared to 2,2’-bipyridine ligand (bpy) [23-24].
In this report, we are investigating the effects of i) the rigidity of the ligand on the HOMO-LUMO gap energy, the shift of the spectra, and the quantum yield; and ii) different ligands trans to phen (different strength of σ-donor groups (hydride, chloride, and trifluoroacetate (TFA)) in comparison to carbonyl as a good π-acceptor).

In addition, the nature of excited state can affect the stability of ligand coordination [25-28]. If the ligand-field splitting is small, the energy of the σ*(e^g*) Ru—ligand orbital is reduced, and excitation to this orbital can result in sufficient electron-electron repulsion that one or two of the coordination bonds weaken, facilitating ligand dissociation, and allowing substitution by another molecule. This new state is known as triplet metal-centered state (3MC). It has one singly occupied orbital of d_{xy}, d_{yz}, or d_{xz} and one of d_{x^2-y^2} or d_{z^2}, and relaxes back to S_0 through nonradiative processes, including photosubstitution [25-28]. Because of the potential for excited-state photosubstitution, generation of the 3MC state is avoided in the design of dye-sensitized solar cells, but becomes critically important in the design of tumor-selective Ru-based drugs [19-20].

In this study, we further explore the effects of ligand coordination on the stability and emission of T_1 (creation of 3MC state). Therefore, we are including two ligands: Cl, which induces metal-ligand cleavage in analogous Ru(II) systems [16-18], and TFA as an alternative ligand that behaves similarly to Cl. Based on the successful of our previous computational approach using Density functional theory (DFT) combined with the time-dependent DFT (TD-DFT) calculations combined with experimental data, we follow the same approach in this study. The calculations reproduced the experimental data of [Ru(CO)(TFA)phen(PPh_3)_2]PF_6 (Ru(TFA)phen) (reported in the earlier study [29]) and [RuH(CO)phen(PPh_3)_2]Cl (Ruphen) (this work). Here we are using Ruphen to investigate the effect of ligand rigidity by making
comparison to the previously studied complex [RuH(CO)bpy(PPh\textsubscript{3})\textsubscript{2}]PF\textsubscript{6} (Rubpy) [21], and we included theoretical predictions of four other Ru(II) complexes of interest – [RuCl(CO)phen(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{+} (Ru(Cl)phen), [Ru(TFA)\textsubscript{2}phen(PPh\textsubscript{3})\textsubscript{2}] (Ru(2TFA)phen), [Ru(H)\textsubscript{2}phen(PPh\textsubscript{3})\textsubscript{2}] (Ru(2H)phen), [Ru(CO)\textsubscript{2}phen(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{2+} (Ru(2CO)phen), and [RuH(2Cl)phen(PPh\textsubscript{3})\textsubscript{2}] (Ru(2Cl)phen) (Fig.1) – to investigate the \textit{trans} influence.

![Figure 1. Optimized molecular structures of Ruphen (left) and RuTFAphen (right) complexes. Hydrogen atoms are omitted for clarity.](image)

3.2. Experimental section

3.2.1. Preparation of complexes

We were able to synthesize Ruphen [29] complex in one step from Ru(PPh\textsubscript{3})\textsubscript{3}(H)(CO)Cl and 1,10-phenanthroline two hydrate following the method of Malecki et al. [30]. We applied the same method in the synthesis of Rubpy [21]. Details of the crystal structure analysis with crystal structure of Ruphen, IR and NMR data are provided in the supplementary materials.

3.2.2. Spectroscopy

Absorption, excitation and emission spectra for Ruphen and Rubpy (solution in acetonitrile) were recorded on a Molecular Devices Spectra Max M2 (Fig. 2 and 3). The quantum yields (Φ) were calculated by the following equation [31-32]:

$$\Phi = \frac{I_{em}}{I_{ex}}$$
\[ \Phi^i = \frac{F^i f n_i^2}{F^s f n_s^2} \Phi^s \]  \hspace{1cm} (1)

Where \(\Phi^i\) and \(\Phi^s\) are the photoluminescence quantum yield of the sample and the standard, respectively. \(F^i\) and \(F^s\) are the integrated intensities of sample and standard spectra, respectively, \(n\) is refractive index, and \(f\) is the absorption factor, the fraction of the light impinging on the sample that is absorbed:

\[ f = 1 - 10^{-A} \]  \hspace{1cm} (2)

Where \(A\) is absorbance. The complexes were dissolved in acetonitrile and Rhodamine 123 was dissolved in ethanol. For all fluorescence measurements the excitation was at 420 nm and the emission scans were from 450 to 750 nm with 2-nm step size.

Figure 2. Experimental absorption and emission spectra of Ruphen in acetonitrile. The intensity is normalized for the comparison.

Figure 3. Experimental absorption spectra of Ruphen and Rubpy in acetonitrile. The intensity is normalized for the comparison.
3.3. Computational details

From our previous theoretical study of the photophysical properties of Ru diimine (2,2′-bipyridyl) complexes containing hydride, carbonyl and triphenylphosphine (PPh₃) ligands [21], we found that using the hybrid exchange-correlation density functional B3LYP [33-34] combined with Los Alamos pseudopotential (LANL2DZ) [35] as the effective core potentials (ECPs) for Ru and using the 6-31G* basis set for all other elements, yielded geometries and excitation energies that correlated well with the experimental data. Thus, B3LYP/LANL2DZ/6-31G* implemented in Gaussian 16 suite of programs was used in this study [36]. The geometries were optimized in acetonitrile solvent using the polarizable continuum model (PCM) [37]. No symmetry restrictions were applied during optimization. To confirm that all optimized geometries are true minima on the potential energy surface, the second-order force constant matrix was calculated for each structure. In addition, we used meta-hybrid M06 for better description of the noncovalent interactions [38], specifically, the electrostatic and dispersion interactions between the phenyl rings and Cl in RuClphen and Ru(2Cl)phen.

No crystal structures were available for any of the complexes when we started the calculations, and the ground states (S₀) for all geometries were optimized starting from the crystal structure of [Ru(X)₂phen(PPh₃)₂][PF₆][NO₃] (X=Cl or CO)(Cambridge Crystallographic Data Center Code CCDC 704326) [29], neglecting the counter ion in the structure model. To make models of Ruphen, RuClphen or RuTFAphen, respectively, one of the carbonyl groups in the crystal structure was replaced by H, Cl, or TFA (Fig. 1). Then, both CO groups were replaced by H, Cl, or TFA. Later, we synthesized Ruphen, and solved its crystal structure (Appendix B). The experimental parameters agreed well with our calculation. In Table 1, selected parameters for the optimized S₀ of all complexes are compared to the available experimental data.
Table 1. Selected bond lengths (Å), bond angles (º), and torsion angles (º) optimized for complexes in $S_0$, $^3$MLCT, $^3$MC states using ΔSCF approach in acetonitrile.

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</tr>
<tr>
<td>P1-Ru-P2</td>
<td>146.445</td>
<td>173.733</td>
<td>177.035</td>
<td>169.372</td>
<td>176.505</td>
<td>176.389</td>
<td>177.517</td>
</tr>
<tr>
<td>N1-Ru-N2</td>
<td>78.428</td>
<td>78.917</td>
<td>77.475</td>
<td>75.940</td>
<td>76.932</td>
<td>66.758</td>
<td>69.706</td>
</tr>
<tr>
<td>N1-C-C-N2</td>
<td>0.228</td>
<td>0.003</td>
<td>0.006</td>
<td>0.000</td>
<td>0.060</td>
<td>1.080</td>
<td>0.008</td>
</tr>
</tbody>
</table>

$^*N1$ is trans to CO and N2 is trans to H.

$^a$ Experimental data taken from this work, $^b$ experimental data taken from ref. [29].
Time-dependent density functional theory (TD-DFT) was used for excited-state calculations [39]. 22 singlet-singlet transitions were computed based on the corresponding optimized $S_0$ in acetonitrile. The molecular orbital energies were determined and each transition was characterized using electron density difference maps (EDDMs) implemented in GaussSum 2.2 [40].

For modeling the lowest-lying triplet states ($T_1$), we used the $\Delta$SCF and TDDFT approaches [41-42], each with spin-unrestricted Kohn-Sham (UKS) orbitals. Normal-mode analysis confirmed that all optimized $T_1$ geometries were in minima. We applied two approaches to compute the emission energies shown in Fig. 4: first, by using the difference between the energy of the $T_1$ computed at $T_1$ equilibrium geometry using TDDFT and the energy of the $S_0$ computed at $T_1$ equilibrium geometry (no minimization for $S_0$); and second, by including the zero-point energy vibrational correction where the emission energy is the difference between the energy of the lowest vibrational state of $T_1$ computed at $T_1$ equilibrium geometry and the ground vibrational state of $S_0$ computed at $S_0$ equilibrium geometry ($S_0$ is minimized). To determine the nature of the electronic state, $^3$MLCT or $^3$MC, Mulliken spin-density analysis was used. A net spin of one on Ru is associated with $^3$MLCT state while a net spin of two is associated with the $^3$MC state.

![Figure 4. Diagram summarizing the calculated emission energy with two approaches. The vertical blue arrow corresponds to emission energy including the zero-point energy vibrational correction and the vertical red arrow without the correction.](image)
In addition, in this study, we used two computational approaches to rationalize the effects of different ligands on the electronic distribution around Ru, the π back-bonding interaction (Ru → ligand), and the molecular orbital energies. The natural bond orbital (NBO) method [43-45], as implemented in Gaussian 16, was used to estimate the energy stabilization of the interaction between Ru (donor) and ligand (vacant acceptor) orbitals (π back-bonding interaction). The NBO method uses perturbation theory to estimate the stabilization energy $E(2)$ as

$$E(2) = \Delta E_{ij} = q_i \times F(i, j)^2/(\varepsilon_j - \varepsilon_i),$$

where, $q_i$ is the donor orbital occupancy, $\varepsilon$ is the respective donor (i) and acceptor (j) orbital energies, and $F(i, j)$ is the off-diagonal Fock matrix element expressed in the NBO basis [46].

It should be pointed out that although NBO theory provides an excellent approximation of the localized electron-pair bonding units, it failed to obtain the Ru—N bond interaction in Ruphen, Ru(2H)phen, Ru(2Cl)phen, and Ru(2TFA)phen. Therefore, we evaluated the π back-bonding stabilization energy for only the Ru—P bond. One critical step to obtain meaningful results is the choice of the reference orbitals (acceptors and donors) for the NBO analysis. For this, the donor orbitals that we included are: i) the highly occupied NBOs (valence orbitals) of Ru which are idealized Lewis structure that described as lone pair (LP) on Ru center; ii) all two-center (bonding) orbitals that involved $\sigma$ (Ru—P), $\sigma$ (Ru—H), $\sigma$ (Ru—Cl), and $\sigma$ (Ru—C); and iii) the nonbonding orbitals in the subshells below the valance shell, which are referred to as core orbitals for Ru (4s, 4p$_x$, 4p$_y$, and 4p$_z$ orbitals). The phosphorus acceptor orbitals are $\sigma$ (Ru—P), $\sigma^*$ (Ru—P), and the Rydberg-type molecular orbitals, (3d and 4p).

The second approach to evaluate the Ru → N back-bonding for all complexes is analyzing the frontier orbitals of the atomic contributions as explained in the discussion. Tables
2-4 show the partial atomic charges and the NBO back-bonding interaction energies. We defined the z axis as lying along the Ru—P bond, the x axis along Ru—CO bond, and the y axis along Ru—H bond.

3.4. Results and Discussion

3.4.1. S₀ geometry optimization and molecular orbital analysis.

The discussion in this section follows in two parts. First, to understand the effects of the different ligands (bpy versus phen) on the Ru center dependent coordination, we compare the crystal and the optimized S₀ structures for [RuH(CO)bpy(PPh₃)₂]PF₆ (Rubpy) (Cambridge Crystallographic Data Center Code CCDC 704327) [29] and Ruphen (this work). Second, we analyze the effects of different ligands (H, CO, Cl, TFA) trans to the phen on the geometry and molecular orbitals.

Rubpy and Ruphen. The largest deviation for Ru—ligand bond lengths between the two crystals is observed for the Ru—H bond, which is 10 pm shorter than in Rubpy. The largest discrepancies in the bond angles between the two crystals were associated with N1, trans to the carbonyl (deviation ± 2-4°). The deviation was reduced in the optimized structures, and the optimized structures had comparable parameters and partial charges over the Ru and P atoms (Table 1 and 2). The total atomic charge over the phen ligand (0.54 e) was similar to that over the bpy ligand (0.55 e).

Hydride replacement of Ruphen and trans influence. The molecular point group for the optimized S₀ for all complexes was found to be C₁. As discussed below, we note that introducing identical ligands trans to the phen does not produce a recognizable trend in the energy gap and the shift of the MLCT compared to the case when mixed ligands are used. Thus, we will discuss the trans influence in two groups; mixed ligand: Ruphen, RuClphen and
RuTFAphen, and analogue ligands: Ru(2H)phen, Ru(2CO)phen, Ru(2Cl)phen, and Ru(2TFA)phen. In addition, to assess the *trans* influence on the Ru-phen push-pull stabilization interaction (the increase of the electron density over Ru improves the back bonding toward the phen ring and maximizes the push-pull interaction), we compared the changes in the atomic partial charges and the Ru—N bond length.

**Table 2. The change in the electron density distribution of *S*₀ with different *trans* ligands estimated by calculating the partial atomic charges *e* using NBO analysis.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru</th>
<th>phen</th>
<th>2P</th>
<th>(PPh₃)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(phen)</td>
<td>-1.055</td>
<td>0.541</td>
<td>2.589</td>
<td>1.159</td>
</tr>
<tr>
<td>RuTFAphen</td>
<td>-0.526</td>
<td>0.654</td>
<td>2.524</td>
<td>1.151</td>
</tr>
<tr>
<td>RuClphen</td>
<td>-0.731</td>
<td>0.654</td>
<td>2.578</td>
<td>1.203</td>
</tr>
<tr>
<td>Ru(2H)phen</td>
<td>-1.222</td>
<td>0.368</td>
<td>2.580</td>
<td>0.861</td>
</tr>
<tr>
<td>Ru(2TFA)phen</td>
<td>-0.088</td>
<td>0.543</td>
<td>2.423</td>
<td>0.901</td>
</tr>
<tr>
<td>Ru(2Cl)phen</td>
<td>-0.437</td>
<td>0.545</td>
<td>2.507</td>
<td>0.948</td>
</tr>
<tr>
<td>Ru(2CO)phen</td>
<td>-0.960</td>
<td>0.739</td>
<td>2.623</td>
<td>1.448</td>
</tr>
</tbody>
</table>

The Ru coordination geometry undergoes similar transformations upon replacing the H (the strongest σ-donor) in Ru(phen) with TFA or Cl. The Ru—N₂ bond lengths (N₂ *trans* to the H) were reduced by ~ 14 pm in both RuClphen and RuTFAphen. Both Ru—P bond lengths increased in the series Ru(phen) < RuClphen < RuTFAphen, which follows the decrease in the ligand σ-donor strength in this series (see Table 1). The elongation correlated with the reduction to the π* (Ru—P) back-bonding found in RuClphen and RuTFAphen (Table 3 and 4). As can be seen from Table 2, the positive charges over Ru increased in the series Ru(phen) < RuClphen < RuTFAphen. One would expect that the electron density will be localized on the Ru when Cl or TFA is introduced due to repulsion between the Cl or O lone pair (p₂) and the Ru filled dₓz or dᵧz electron (filled- filled) interactions [47]. However, an increase in the Ru positive charge is observed that is associated with an increase of the PPh₃ negative charges (Table 2). NBO
analysis revealed that the Ru d<sup>2</sup> orbital decreased (1.18 e) in both RuTFAphen and RuClphen compared to Ruphen (1.70 e), which was accompanied by a 2% increase in the bond localization on P atom, thereby increasing the positive charge over Ru. In other words, the σ (Ru—P) bond polarity increases more toward the P atom due to the filled-filled repulsion interaction causing a reduction in Ru electron density and an increase in back-bonding from the P atoms to the phenyl rings (see Appendix B, Table B1), which will minimize the push-pull interaction and weaken the MLCT transition.

Table 3. Second-order perturbation interaction energy (E(2)) (kcal/mol) from the donation from metal to ligand for complexes with mixed ligands at the B3LYP/LANL2DZ level obtained by NBO analysis.

<table>
<thead>
<tr>
<th>donor</th>
<th>occupancy (e)</th>
<th>acceptor</th>
<th>occupancy (e)</th>
<th>E(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR(1)Ru&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.988</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>0.97</td>
</tr>
<tr>
<td>LP*(4)Ru&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.214</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>32.18</td>
</tr>
<tr>
<td>LP*(5)Ru&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.196</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>0.59</td>
</tr>
<tr>
<td>σ(Ru-P)</td>
<td>1.835</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>1.56</td>
</tr>
<tr>
<td>σ(Ru-H)</td>
<td>1.843</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>22.57</td>
</tr>
<tr>
<td>σ(Ru-C)</td>
<td>1.935</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>10.96</td>
</tr>
<tr>
<td>σ(Ru-P)</td>
<td>1.835</td>
<td>σ*(Ru-P)</td>
<td>0.156</td>
<td>6.6</td>
</tr>
<tr>
<td>CR(1)Ru</td>
<td>1.989</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>1.74</td>
</tr>
<tr>
<td>σ(Ru-Cl)</td>
<td>1.912</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>0.95</td>
</tr>
<tr>
<td>σ(Ru-C)</td>
<td>1.921</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>9.81</td>
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<tr>
<td>σ(Ru-P)</td>
<td>1.822</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>7.05</td>
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<td>CR(1)Ru</td>
<td>1.989</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>0.95</td>
</tr>
<tr>
<td>LP*(4)Ru&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.230</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>16.9</td>
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<tr>
<td>σ*(Ru-Cl)</td>
<td>0.103</td>
<td>σ*(Ru-P)</td>
<td>0.147</td>
<td>22.82</td>
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</table>

<table>
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<tr>
<td>σ(Ru-P)</td>
<td>1.830</td>
<td>σ*(Ru-P)</td>
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<td>1.57</td>
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<tr>
<td>σ(Ru-C)</td>
<td>1.926</td>
<td>σ*(Ru-P)</td>
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<td>9.11</td>
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<tr>
<td>σ(Ru-P)</td>
<td>1.828</td>
<td>σ*(Ru-P)</td>
<td>0.145</td>
<td>8.48</td>
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<td>CR(1)Ru</td>
<td>1.989</td>
<td>σ*(Ru-P)</td>
<td>0.145</td>
<td>0.82</td>
</tr>
</tbody>
</table>

<sup>a</sup> CR(1)Ru is 4s, <sup>b</sup> LP*(4) is sp<sup>3</sup> (s(21.80%)p 3.40(74.05%)d 0.19(4.15%)), <sup>c</sup> LP*(5) p(s(2.79%)p31.42(87.81%)d 3.36(9.40%)), <sup>d</sup> LP*(4) is sp<sup>3</sup> (s(15.14%)p 5.14(77.83%).
Table 4. Second-order perturbation interaction energy (E(2)) (kcal/mol) from the donation from metal to ligand for complexes with analogues ligands at the B3LYP/LANL2DZ level obtained by NBO analysis.

<table>
<thead>
<tr>
<th></th>
<th>donor</th>
<th>occupancy (e)</th>
<th>acceptor</th>
<th>occupancy (e)</th>
<th>E(2)</th>
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<tbody>
<tr>
<td><strong>Ru(2H)phen</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CR(1)Ru(^a)</td>
<td>1.991</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>1.32</td>
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<tr>
<td>LP*(4)Ru(^b)</td>
<td>0.202</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>0.73</td>
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<td>LP*(5)Ru(^c)</td>
<td>0.189</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>15.58</td>
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</tr>
<tr>
<td>(\sigma)(Ru-P)</td>
<td>1.847</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>4.73</td>
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</tr>
<tr>
<td>(\sigma)(Ru-H)</td>
<td>1.859</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>19.38</td>
<td></td>
</tr>
<tr>
<td>(\sigma)(Ru-H)</td>
<td>1.858</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.148</td>
<td>17.38</td>
<td></td>
</tr>
<tr>
<td><strong>Ru(2Cl)phen</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma)(Ru-P)</td>
<td>1.864</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.192</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>(\sigma)(Ru-P)</td>
<td>1.864</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.192</td>
<td>10.40</td>
<td></td>
</tr>
<tr>
<td>CR(1)Ru</td>
<td>1.994</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.192</td>
<td>2.70</td>
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</tr>
<tr>
<td>CR(2)Ru(^d)</td>
<td>1.994</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.192</td>
<td>0.75</td>
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<tr>
<td>LP*(5)Ru(^e)</td>
<td>0.298</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.192</td>
<td>30.23</td>
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<tr>
<td><strong>Ru(2TFA)phen</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(\sigma)(Ru-P)</td>
<td>1.851</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.185</td>
<td>13.99</td>
<td></td>
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<tr>
<td>CR(1)Ru</td>
<td>1.993</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.185</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td>CR(2)Ru</td>
<td>1.997</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.185</td>
<td>0.61</td>
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<tr>
<td><strong>Ru(2CO)phen</strong></td>
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<td>(\sigma)(Ru-P)</td>
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<tr>
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<td>1.930</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.159</td>
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</tr>
<tr>
<td>(\sigma)(Ru-C)</td>
<td>1.883</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.159</td>
<td>4.30</td>
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</tr>
<tr>
<td>CR(1)Ru</td>
<td>1.988</td>
<td>(\sigma^*)(Ru-P)</td>
<td>0.159</td>
<td>0.57</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) CR(1)Ru is 4s, \(^b\) LP*(4) is sp\(^\dagger\) (s(25.60%)p 2.81(71.88%)d 0.10(2.52%)),
\(^c\) LP*(5) is s(0.18%)p99.99(86.30%)d77.28(13.53%), \(^d\) CR(2)Ru is 4p, \(^e\) LP*(4) is s(77.88%)p 0.16(12.36%)d 0.13(9.77%).

In addition, we noted that the Ru atom is carrying the highest positive charge when bound to TFA. This is because the –CF\(_3\) moiety withdraws electron density via induction from the carboxylate due to the electronegativity of fluoride. Because the electron density moves in the direction of electron-withdrawal, the Ru—O bond polarity increases toward the oxygen atom. Interestingly, the total atomic charges over the phen ligand in RuClphen and RuTFAphen are similar and more positive compared to Ruphen. This reduction of the electron density over Ru and phen upon binding Cl or TFA confirmed the expected minimization of the push-pull
interaction as is seen in the calculations.

Similar transformation with Ru—P bond length and P atomic charge is observed when introducing analogous ligands (Table 1 and 2). The Ru—P bond length increases in the series Ru(2H)phen < Ru(2Cl)phen < Ru(2TFA)phen < Ru(2CO)phen following the strength of electron-withdrawal. The strong π-acceptor (CO) increases the back-donation from Ru to CO and decreases it toward the P atoms, thereby increasing both the Ru-P bond length and the positive charge over Ru and PPh₃. The P atomic positive charge decreases in the series Ru(2CO)phen > Ru(2H)phen > Ru(2Cl)phen > Ru(2TFA)phen. A similar increase of the σ (Ru—P) polarity toward P atom is observed in Ru(2Cl)phen and Ru(2TFA)phen due to the filled-filled repulsion interaction, where in the latter the positive charge over P atom decreased the most and the localization of the σ (Ru—P) bond over the P atom increased by 6%. This is also accompanied by an increase in the back bonding from the P atoms to the phenyl rings (Appendix B, Table B2). We would anticipate that the Ru positive charge would increase the most upon introducing the strong π-acceptor ligands (CO). However, the Ru positive charge increases in the series Ru(2H)phen < Ru(2CO)phen < Ru(2Cl)phen < Ru(2TFA)phen (Table 2). This suggests that repulsion-repulsion interaction between Ru and ligands with lone pairs (TFA and Cl) has a greater effect on the electronic distribution around the metal center than ligands that are strong π-acceptors, which minimize the push-pull interaction.

The maximum electron density over the phen ligand was observed with the two hydrides, whereas the minimum electron density was observed with the two CO ligands (Table 2). Thus, the Ru—phen push-pull stabilization interaction is maximized in Ru(2H)phen compared to other complexes. The smallest Ru—N bond length was observed in Ru(2H)phen, Ru(2Cl)phen, and Ru(2TFA)phen (2.1 Å). This is due to increased back-bonding from Ru dₓᵧ to
the $\pi^*$ (Ru—N) (Fig. 5). Thus, the electron density over phen was greater in Ru(2H)phen, Ru(2TFA)phen, and Ru(2Cl)phen when compared to the corresponding complexes Ruphen, RuTFAphen, and RuClphen, respectively (Table 2). Although the increased strength of the Ru—N bond in the ground state in Ru(2TFA)phen and Ru(2Cl)phen suggests a larger push-pull interaction, this bond is not stable upon excitation as discussed below.

**Molecular orbitals contributions and energies.** The atomic contributions to the molecular orbitals in Rubpy and Ruphen are similar, where HOMO and HOMO-1 are mainly composed of Ru d$_{yz}$ and bonding $\pi$ orbitals of the phenyl rings. More than 90% of the electron density of the LUMO is localized over the ligands (bpy or phen). Consequently, similar energy gaps are observed, 3.93 eV and 3.97 eV for Rubpy and Ruphen, respectively. The small difference arose from LUMO orbitals, -2.35 and -2.28 eV for Rubpy and Ruphen, respectively. The increase of the number of conjugated $\pi$-bonds in the phen will increase the negative charge over the ligand and thus its energy. Table 5 shows the contributions of the individual atomic orbitals to the molecular orbitals and the corresponding energies.

The rearrangement in the electronic distribution when Ru binds TFA or Cl in RuTFAphen or RuClphen correlated with the changes in the HOMO and LUMO energies (Table 5). When TFA or Cl combined with CO in RuTFAphen and RuClphen, the electron density decreases over both Ru and phen and increases over PPh$_3$, thus a stabilization of both the HOMO and LUMO in these complexes is observed (Tables 2 and 5, and Fig. 7). When compared to Ruphen, the HOMO is stabilized by 0.30 eV and 0.37 eV, while the LUMO is stabilized by 0.13 eV and 0.24 eV in RuClphen and RuTFAphen, respectively. Accordingly, both complexes have a similar energy gap (~ 4.10 eV), which is slightly larger than that of Ruphen (3.97 eV).
Figure 5. HOMO representations of the optimized ground states of the Ru(2H)phen, Ru(2Cl), Ru(2CO)phen and Ru(2TFA)phen calculated using B3LYP/LANL2DZ and the back-bonding from d$_{xy}$-Ru to the Ru-N bond.
Table 5. Computed absorption, excitation and electronic transitions for complexes using B3LYP/LANL2DZ.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\lambda_{abs}) (nm)</th>
<th>(\lambda_{abs}) (nm)</th>
<th>(\lambda_{exit}) (nm)</th>
<th>(f)</th>
<th>Major Contribution</th>
<th>% Composition</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuPhen</td>
<td>382</td>
<td>379.0</td>
<td>381.6</td>
<td>0.07</td>
<td>H→L (95%)</td>
<td>H: Ru 47%, (PPh(_3)) 43%, phen 9%</td>
<td>MLCT</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>320.0</td>
<td>326.7</td>
<td>0.13</td>
<td>H→L+2 (61%)</td>
<td>L+2: Ru 21%, (PPh(_3)) 75%</td>
<td>Ru, phen→(PPh(_3))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>324.4</td>
<td>315.2</td>
<td>0.06</td>
<td>H→L+2 (57%)</td>
<td>H-1: Ru 45%(PPh(_3)): 50%, phen 4%</td>
<td>MLCT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1→L+1 (64%)</td>
<td>0.05</td>
<td>H-2→L (30%)</td>
<td>H-2: Ru 21%(PPh(_3)): 21%, phen 50%</td>
<td>(PPh(_3))→phen, H</td>
</tr>
<tr>
<td></td>
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<td>292.4</td>
<td>289.1</td>
<td>0.25</td>
<td>H-1→L+2 (25%)</td>
<td>L+1: phen 86%, H 12%</td>
<td>MLCT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-8→L (25%)</td>
<td>0.09</td>
<td>H-10→L (39%)</td>
<td>H-10: (PPh(_3)): 69%, phen 27%</td>
<td>(PPh(_3))→phen, H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-7→L+1 (22%)</td>
<td>0.09</td>
<td>H-8→L (43%)</td>
<td>H-7: Ru 9%(PPh(_3)): 86%, phen 4%</td>
<td>MLCT, (PPh(_3))→phen, H</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>H-2→L+1 (70%)</td>
<td>0.08</td>
<td>H-2→L+1 (70%)</td>
<td>H-2→L+1 (70%)</td>
<td>(PPh(_3))→phen, H</td>
</tr>
<tr>
<td>RuTFAphen</td>
<td>420</td>
<td>-</td>
<td>366.1</td>
<td>0.04</td>
<td>H→L (75%)</td>
<td>H: Ru 35%(PPh(_3)): 44%, TFA 11%, phen 10%</td>
<td>MLCT, TFA→phen</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>H-12→L (29%)</td>
<td>H-12: Ru 57%(PPh(_3)): 18%, TFA 12%, CO 11%</td>
<td>MLCT, TFA, CO→phen</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>H-1→L+1 (24%)</td>
<td>H-1: Ru 31%(PPh(_3)): 48%, phen 19%</td>
<td>phen→Ru, (PPh(_3))</td>
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<tr>
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<td></td>
<td>H-1→L+2 (24%)</td>
<td>L+2: Ru 39%(PPh(_3)): 53%, phen 4%</td>
<td>(PPh(_3))→phen</td>
</tr>
<tr>
<td></td>
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<td>H-7→L (23%)</td>
<td>H-7: (PPh(_3)): 88%, phen 10%</td>
<td>(PPh(_3))→phen</td>
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<tr>
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<td></td>
<td>H-4→L+1 (22%)</td>
<td>H-4: Ru 13%(PPh(_3)): 49%, phen 33%</td>
<td>MLCT</td>
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<td></td>
<td>L+1: phen 97%</td>
<td>L+1: phen 97%</td>
<td>MLCT</td>
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<tr>
<td>RuCphen</td>
<td>355.2</td>
<td>365.4</td>
<td>323.2</td>
<td>0.06</td>
<td>H→L+1 (85%)</td>
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<td>MLCT, Cl→phen</td>
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<td>H-1→L (93%)</td>
<td>L+1: phen 97%</td>
<td>(PPh(_3))→phen</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>H-1: Ru 19%(PPh(_3)):(\text{PPh}_2) 75%, phen 6%</td>
<td>MLCT, (PPh(_3))→phen</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L: phen 94%</td>
<td>L+2: Ru 40%(PPh(_3)):(\text{PPh}_2) 45%, phen 7%</td>
<td>(PPh(_3))→Ru, Cl</td>
</tr>
<tr>
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<td></td>
<td>H→L+1 (44%)</td>
<td>L+2: Ru 40%(PPh(_3)):(\text{PPh}_2) 45%, phen 7%</td>
<td>(PPh(_3))→Ru, Cl</td>
</tr>
<tr>
<td></td>
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<td>H-2→L+1 (45%)</td>
<td>H: Ru 47%(PPh(_3)): 4%, Cl 37%, CO 9%</td>
<td>MLCT, Cl→phen, (PPh(_3))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H→L+3 (26%)</td>
<td>L+3: Ru 46%(PPh(_3)):(\text{PPh}_2) 32%, Cl 14%, phen 11%</td>
<td>MLCT, Cl→phen, (PPh(_3))</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>H-3→L+1 (67%)</td>
<td>H-3: Ru 10%(PPh(_3)):(\text{PPh}_2) 54%, phen 34%</td>
<td>MLCT, (PPh(_3))→phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H-3→L+2 (28%)</td>
<td>H-3→L+2 (28%)</td>
<td>(PPh(_3))→phen, Ru, Cl</td>
</tr>
</tbody>
</table>

* Experimental data for RuTFAphen from reference [29] and for RuPhen this work, calculated absorption.
In addition, the HOMOs for all complexes with mixed ligands show contributions from d-Ru, \( \pi \)-PPh\(_3\), and little localization (\( \leq 10\% \)) on the \( \pi \)-phen. The Ru \( d_{xz} \) and \( d_{yz} \) characters in the HOMO orbitals decreased in the series RuClphen (50\%) > Ruphen (47\%) > RuTFAphen (35\%) (see Fig. 6 and Table 5). Because of the strong electron-withdrawing effect of the TFA, the Ru contribution decreased the most in RuTFAphen. Furthermore, the nonbonded \( p_{z}-O \) and \( p_{z}-Cl \) orbitals in RuTFAphen and RuClphen contribute to the HOMO by 11\% and 26\%, respectively.

Interestingly, we noted that the opposing phenyl rings \textit{trans} to the phen and located on the opposite phosphorus ligands, do not contribute to the HOMO orbitals in Ruphen, similar to what is observed for Rubpy (Fig. 6). Nevertheless, due to the increased back-bonding from P toward the phenyl rings, as explained earlier for RuTFAphen and RuClphen, all rings contribute to the HOMO (Fig. 6). In addition, the \( \pi \)-PPh\(_3\) character increases in HOMO-1 for all complexes. However, the HOMOs that lie under HOMO-1 show different contributions. For example, HOMO-2 contributions are 97\% from \( \pi \)-PPh\(_3\) in RuTFAphen, 37\% from \( p_{z}-Cl \) in RuClphen, and 50\% from \( \pi \)-phen in Ruphen (Table 5). The LUMO orbitals in all complexes have 90\% \( \pi^{*} \)-phen character (Fig. 6).

As expected, Ru(2H)phen shows the smallest energy gap (2.85 eV) due to destabilization of both HOMO and LUMO orbitals by 1.69 eV and 0.57 eV, respectively compared to Ruphen. However, although HOMO and LUMO orbitals have the largest stabilization energies in Ru(2CO)phen (0.72 eV and 0.80 eV, respectively compared to Ruphen), due to the strong \( \pi \)-acceptor feature of this ligand, the calculated energy gap is comparable for both of these complexes (3.99 eV and 3.97 eV) and to other complexes that included CO as ligand (RuTFAphen and RuClphen 4.10 eV) (Fig. 7).
Figure 6. HOMO representations of the optimized ground states of the Ruphen, RuClphen, and RuTFAphen calculated using B3LYP/LANL2DZ.
The changes in the orbitals of Ru(2TFA)phen and Ru(2Cl)phen can be compared to RuTFAphen and RuClphen, respectively, to understand the effect of the CO replacement. When 2TFA or 2Cl are introduced, an increase of the filled-filled repulsion between Ru and those ligands increases the electron density over PPh$_3$ and phen. This correlates with the changes in the atomic charges where Ru is more positive while phen and PPh$_3$ are more negative in both Ru(2TFA)phen and Ru(2Cl)phen, when compared to RuTFAphen and RuClphen, respectively (Table 2). Therefore, the LUMO and in particular the HOMO are destabilized significantly (> 1.00 eV for the HOMO) (Table 6).

For theses complexes, the energy gap increases in the series Ru(2H)phen < Ru(2Cl)phen < Ru(2TFA)phen < Ru(2CO)phen (Fig. 7). The HOMO orbitals for all, with the exception of Ru(2CO)phen, are > 70% located on the Ru d$_{\alpha\gamma}$. In Ru(2CO)phen, Ru d orbitals show a small contribution (10%) to the HOMO due to strong $\pi$ back-bonding from Ru to CO; the HOMO mainly has $\pi$-PPh$_3$ character. On the other hand, no $\pi$-PPh$_3$ character is observed in HOMO orbitals of Ru(2TFA)phen, Ru(2Cl)phen, and Ru(2H)phen (Fig. 5 Table 6). However, in Ru(2H)phen, $\pi$-PPh$_3$ orbitals contribute to the HOMO-1, while in Ru(2Cl)phen and Ru(2TFA)phen they do not contribute to the first three HOMOs. Presumably, this is because the filled-filled repulsion pushes more electrons to the P atoms, increases the back-bonding from P to the phenyl rings, and thereby stabilizes these orbitals, which correlates with the increase of negative charge over theses rings (Tables 2 and B2 in Appendix B). In addition, the $p_x$-O and $p_x$-Cl orbitals contribute to the HOMOs in Ru(2TFA)phen and Ru(2Cl)phen. The LUMO orbitals in all complexes have > 90% of $\pi^*$-phen character (Fig. 5).

The first Ru—N antibonding orbitals (with Ru $d_{x^2-y^2}$ contribution) are located more than 5 eV above the HOMO level in complexes with mixed ligands and in Ru(2H)phen. However,
### Table 6. Computed absorption, excitation and electronic transitions for complexes using B3LYP/LANL2DZ.

<table>
<thead>
<tr>
<th>complex</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{exit}$ (nm)</th>
<th>$f$</th>
<th>major contribution</th>
<th>% composition</th>
<th>character</th>
</tr>
</thead>
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<tr>
<td>Ru(2H)phen</td>
<td>490.7</td>
<td>471.8</td>
<td>0.06</td>
<td>H-2→L+1 (81%)</td>
<td>H-2: Ru 84%, (PPh$_3$)$_2$ 11%, phen 5%</td>
<td>MLCT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L+1: phen 98%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>503.0</td>
<td>471.8</td>
<td>0.05</td>
<td>H-1→L (53%)</td>
<td>H-1: Ru 64%, (PPh$_3$)$_2$ 22%, phen 13%</td>
<td>MLCT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L: phen 93%, Ru 5%</td>
<td></td>
</tr>
<tr>
<td>Ru(2CO)phen</td>
<td>331.9</td>
<td>331.9</td>
<td>0.7</td>
<td>H→L+2 (88%)</td>
<td>H: Ru 10%, (PPh$_3$)$_2$ 88%, phen 2%, L+2: phen 4%, Ru 36%, (PPh$_3$)$_2$ 36%</td>
<td>phen→(PPh$_3$)$_2$</td>
</tr>
<tr>
<td>Ru(2Cl)phen</td>
<td>417.6</td>
<td>417.6</td>
<td>0.07</td>
<td>H-2→L (62%)</td>
<td>H-2: Ru 65%, Cl 17%, phen 14%</td>
<td>MLCT, Cl→phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L: phen 93%, Ru 5%</td>
<td></td>
</tr>
<tr>
<td>Ru(2TFA)phen</td>
<td>391.3</td>
<td>391.3</td>
<td>0.10</td>
<td>H-2→L (63%)</td>
<td>H-2: Ru 70%, TFA 7%, phen 7%</td>
<td>MLCT, TFA→phen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L: phen 94%</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 7. The calculated HOMO-LUMO energy gap using B3LYP/LANL2DZ.](image)
they appear below 4.5 eV in both Ru(2Cl)phen and Ru(2TFA)phen. Therefore, the ligand-field splitting is smaller, which facilitates the transition to these orbitals and, thereby, the cleavage of Ru—N bond as we observed and discuss below.

Interestingly, comparing the energy gap for all complexes revealed a pronounced rule for the CO to maintain the gap energy nearly unchanged regardless of the combined ligand. To investigate this finding, we model a system where we used H and Cl as trans ligands (RuHClphen) and the calculated energy gap is 3.02 eV that differs significantly.

3.4.2. Absorbance spectroscopy

The UV–vis spectra of Rubpy and Ruphen, which were collected in acetonitrile, closely matched the theoretical spectra (Fig. 2, 3, and 8). Much like the spectra of the Rubpy complex, the broad MLCT band in the measured Ruphen spectrum was observed in the low energy region around 400 nm.

By comparison, the calculated maximum of the MLCT band of Rubpy is 394 nm whereas that of Ruphen is about 380 nm. Thus, the observed spectra correlate well with the predicted energy gap. In addition, several intense transitions with two maxima below 350 nm are observed for the calculated Ruphen spectra. The low energy band with a maximum at about 320 nm includes π-Ru and π-phen transitions to π-PPh3 and very weak MLCT transitions, while the higher energy band is due to π-PPh3 transitions to π-phen.

As expected, due to the energy gap similarity, both RuClphen and RuTFAphen generated similar shapes and energies for the calculated spectra, and differ significantly from Ruphen (Fig. 8). Neither complex has the broad lower energy absorption and Intensity that characterizes the MLCT band. This is due to the expected minimal push-pull interaction as explained earlier. Instead, one strong band is observed with a
maximum that occurs at 318 nm and 308 nm for RuClphen and RuTFAphen, respectively. This band is composed of several mixed electronic transitions (i.e., each excitation energy is due to multiple electronic transitions) (see Table 5). We will discuss the excitations that have oscillator strength > 0.04 and atomic contribution ≥ 20%. In contrast to the hydride, both TFA and Cl contribute to the HOMO orbitals and participate in electron transition to the phen.

Figure 8. The absorption spectra for the complexes with mixed ligands calculated using B3LYP/LANL2DZ.

Although the calculations did not predict well resolved MLCT bands for RuTFAphen and RuClphen, several transitions were assigned as MLCT. In RuTFAphen, the MLCT transitions at 313 and 303 nm start from lower HOMOs because of the smaller
contribution of the Ru to the HOMO that increased in the sub-HOMO orbitals. Another weak MLCT transition (oscillator strength 0.043) for this complex is observed in the low energy tail of the band (366 nm) with a contribution in the HOMO orbital from TFA. However, in RuClphen, the MLCT transition from HOMO to LUMO is observed because of increased Ru contribution to the HOMO. In addition, several MLCT transitions were noted at 355, 323, 319, and 303 nm, with Cl providing a greater contribution when compared to TFA. Similar weak MLCT excitations were also observed in the low energy tail of the band (365 nm). All previously predicted MLCT transitions for both complexes were blue shifted compared to Ruphen because these transitions started mainly from lower HOMOs to upper LUMOs (larger energy gap) (Table 5).

Ru(2CO)phen, Ru(2TFA)phen, and Ru(2Cl)phen have spectra with shapes similar to those of RuTFAphen and RuClphen (Fig. 9). In Ru(2CO)phen, only one strong transition, mainly from HOMO to LUMO+2, was predicted to occur at about 332 nm. This band is assigned to electron transfer from PPh₃ to Ru and phen with no MLCT transition. In our previous study, we examined the effects of the substituent in Rubpy [21]. The band vanished when two CO were trans to the bpy, generating the same spectra as of Ru(2CO)phen and no Ru → N back-bonding occurred. When two -COOH are substituents of the bpy, the electron density over Ru and bpy is balanced, and as a result the MLCT band and Ru back-bonding to bpy are recovered (Fig. 10).
In contrast to Ru(2CO)phen, the strongest transition calculated for Ru(2TFA)phen at 391 nm and for Ru(2Cl)phen at 418 nm is assigned as a MLCT band. This band, however, is mainly due to a transition from HOMO-2 to the LUMO. In addition, several HOMO to LUMO+2 excitations were observed in both complexes. Since the antibonding Ru—N orbitals contribute to LUMO+2, this excitation is expected to weaken the bond.

Replacing the strong \( \pi \)-acceptor (2CO) in Ru(2CO)phen by the strong \( \sigma \)-donor (H) recovered the spectral line-shape observed for Ru(2H)phen (Fig. 9). As in Ru(2Cl)phen and Ru(2TFA)phen, the observed MLCT is not due to HOMO to LUMO transition (Table 6). However, it is the most red shifted (491 nm) of all the complexes, and correlated well with the calculated energy gap (Ru(2H)pehn has the smallest energy gap).

Figure 9. The absorption spectra for the complexes with analogues ligands calculated using B3LYP/LANL2DZ.
The weaker, higher energy band around 380 nm is due to transitions from the HOMO to the higher LUMOs (LUMO+3 to LUMO+6). All of these transitions are from Ru to the PPh$_3$ and phen, which correlates with the increase in electron density over Ru in this complex (see Table 2). Since both Ru d$_{xy}$ (HOMO) and phen π* (LUMO) orbitals are perpendicular to each other, the HOMO-LUMO transitions are symmetry-forbidden in Ru(2H)phen, Ru(2Cl)phen, and Ru(2TFA)phen.

The results suggest that when the Ru atom binds to a weak σ-donor ligand or has an acceptor trans to the phen ligand, in a system where phen is the parent ligand, the push-pull interaction will be minimized, which weakens the MLCT transition; consequently it is buried among the intra-ligand transitions. Thus, the three combinations of ligands trans to the phen that maximize the push-pull interaction are: i) two strong σ-donors; ii) a strong σ-donor combined with a strong π-acceptor; or iii) a strong π-acceptor combined with an electron-withdrawing substituent such as –COOH. In addition, the correlation between the energy gap and the shift of the MLCT transition is distinct in the complexes with analogue ligands; the larger the gap, the more blue shifted the transition. However, in the complexes with mixed ligands, there was no clear correlation because the MLCT transition is isoenergetic with transitions from one or more other HOMOs to

![Figure 10. HOMO representation of the optimized ground state of the Rudcbpy showing the Ru back-bonding to bpy ligand.](image)
their corresponding LUMOs (see for example, RuClphen in Tables 5 versus Ru(2Cl)phen in Table 6).

3.4.3. Triplet Excited-State Geometries

The optimized excited-state geometries for complexes with mixed ligands were characterized as a $^3$MLCT state for which the highest singly occupied molecular orbital (HSOMO) is centered on the phen (Fig. 11). We also analyzed the lowest singly unoccupied molecular orbital (LSUMO) of T$_1$. The composition of the LSUMO varies considerably among the different complexes; however, it always involves d orbitals of the Ru. For example, in Ruphen, the LSUMO involves π orbitals of both PPh$_3$ and phen. In RuClphen, the loan pair of the p$_z$-Cl orbital is the predominant contribution with a small contribution from π-phen. In RuTFAphen, the LSUMO is largely centered on the π orbitals of PPh$_3$ (Fig. 11).

As observed in the Rubpy derivatives, the Ru—P bond lengths increase while the Ru—N bond lengths decrease (Table 1). This is because migration of the HOMO electron density (which centered on the Ru and PPh$_3$) to populate the LUMO orbitals (centered on phen), both reduces the Ru—P bond strength and increases the Ru—N bond strength. There is marked bending in the P1—Ru—P2 angle (by 23.7°) in Ruphen compared to other complexes to reduce steric crowding that results between the phenyl rings and the phen ring (Table 1 and Fig 11). In addition, there are changes in the twist angles of the phenyl rings, which also occur in Rubpy complexes [21] (Fig. 12). Finally, it is important to consider the conformational stability of the phen ligand upon excitation, which is due to the electron delocalization over the aromatic rings, versus that of the bpy ligand, where the rings are less constrained (Table 1). For example, the two aromatic rings twisted by 3°
in Rubpy compared to 0.2° in Ruphen.

When searching for $T_1$ for Ru(2H)phen using TDDFT, an excessive mixing of frozen-core and valence orbitals occurred. Therefore, we tried the other functionals M06
and PBE0 [49-50], but they did not resolve the issue. Increasing the size of the basis sets is suggested, but computationally is very demanding. Thus, we only reported the $\Delta$SCF results for this complex.

![Figure 12. Overlaying $S_0$ and $T_1$ calculated using B3LYP/UB3LYP for RuTFAphen.](image)

We found that the minimum geometry for Ru(2H)phen was $^3$MLCT state while those for Ru(2Cl)phen and Ru(2TFA)phen were $^3$MC states. We were not able to optimize the $^3$MLCT $\rightarrow$ $^3$MC transition state with the available computational methods. Specifically, we were not able to determine the $^3$MLCT states for the latter complexes. Using $\Delta$SCF approach, we characterized the states by calculating the Mullikan spin density on the Ru, analyzing the HSOMO and LSUMO orbitals, and the change in the geometry with concomitant cleavage of Ru—N bond. In Ru(2H)phen, Ru has a net spin of unity. In addition, Ru $d_{xy}$ contributes to the LSUMO. For this complex, the HSOMO is centered on phen, indicating that the state is $^3$MLCT (Fig. 13). Both Ru—P and Ru—N bond lengths increased as previously observed in Ru(2H)bpy [21]. In addition, the largest phenyl rings twist angle is 16.7°.

By contrast, Ru has a net spin of two in both Ru(2Cl)phen and Ru(2TFA)phen. In addition, the HSOMO is characterized as $\sigma^*$ (Ru—N), $\sigma^*$ (Ru—O), $\sigma^*$ (Ru—P), and the LSUMO centered on the phen, indicating that this state is $^3$MC (Fig. 11). For both complexes, the Ru—N bond length increased by 20% (i.e., it is broken) compared to 2%
change in the bond length of other complexes (Table 1).

To quantify the geometric changes and correlate the HOMO-LUMO energy gap with the expected distortion in $T_1$, the root-mean-square deviation (RMSD) of $T_1$ and $S_0$ were compared using the method of Kabsch as implemented in the Visual Molecular Dynamics (VMD) program (Table 7) [51]. It should be noted that TDDFT and $\Delta$SCF results are comparable for all complexes except for RuClphen (Table 7). Thus, the comparison is made only for complexes for which we were able to determine the $^3$MLCT state using TDDFT. For complexes with mixed ligands, the RMSD decreases in the series $\text{Ru(phen)} > \text{Ru(TFAphen)} > \text{Ru(Clphen)}$, which correlated with the calculated energy gaps (3.97 eV, 4.10 eV, and 4.15 eV, respectively); the smallest energy gap is associated with the largest distortion in $T_1$. Ru(2H)phen has slightly larger RMSD when compared to Ruphen (Table 7), which also correlated with the energy gap.

Figure 13. HSOMO (bottom) and LSUMO (top) representations of the $^3$MC states for Ru(2TFA)phen and Ru(2Cl)phen.
Table 7. RMSD in $^3$MLCT and emission energies (eV) with and without the zero-point energy vibrational correction (ZP) using TDDFT and $\Delta$SCF approaches calculated at B3LYP and M06.

<table>
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<tr>
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<th>RuClphen</th>
<th>RuTFAphen</th>
<th>Ru(2H)phen</th>
</tr>
</thead>
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<td></td>
<td></td>
</tr>
<tr>
<td>RMSD</td>
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<td>0.62</td>
<td>0.70</td>
<td></td>
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<tr>
<td>$E_{\text{Em}}$ (ZP)</td>
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<td>2.1</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
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<td>1.9</td>
<td>2.1</td>
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<tr>
<td>$\Delta$SCF</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>RMSD</td>
<td>0.80</td>
<td>0.17</td>
<td>0.90</td>
<td>0.81</td>
</tr>
<tr>
<td>$E_{\text{Em}}$ (ZP)</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>$E_{\text{Em}}$ (no ZP)</td>
<td>1.9</td>
<td>2.3</td>
<td>2.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

3.4.4. Excitation and Emission Energies.

Based on the calculated energy gap values for Rubpy and Ruphen, both complexes should have similar Stokes shifts. In fact, the experimental data show that Ruphen emits at a maximum about 593 nm (2.09 eV) whereas Rubpy emits at 595 nm (2.08 eV) (Fig. 2). Since both complexes generated similar spectra, we determined the quantum yields, using Rhodamine 123 as a standard, to illustrate how the phen ligand versus the bpy ligand affects the photophysical properties. The quantum yield for both complexes in acetonitrile was small (0.01 and 0.005 for Ruphen and Rubpy, respectively). The higher quantum yield for the phen is due to its rigidity, which decreases nonradiative decay of the excited state.

We note that, contrary to our expectation [21], the calculated emission energies obtained using B3LYP were overestimated compared to the available experimental data when the zero-point energy vibrational correction was included with $\Delta$SCF and TDDFT (Table 7). For example, TDDFT estimated the emission energy to be 539 nm (2.30 eV) for both Ruphen and RuTFAphen. When the correction is excluded, the energies for Ruphen (1.9 eV (653 nm)) and RuTFAphen (2.07 eV (599 nm)) are closer to the experimental data [29].

Notably, while the $\Delta$SCF method predicted an emission energy for Ruphen similar to that obtained by TDDFT, it overestimated the energy by about 0.20 eV for other complexes when
compared to energies obtained by TDDFT. In addition, ΔSCF yielded emission energies for RuTFAphen and RuClphen that were 0.20 eV larger than for Ruphen. This difference can be related to the small increase in the energy gap of these complexes (by 0.10 eV) compared to Ruphen; no trend was observed using TDDFT.

As expected, the emission energy for Ru(2H)phen was shifted to the far infrared (> 900 nm) because it has the smallest $^3$MLCT energy gap. In addition, the $^3$MC emission energies for Ru(2Cl)phen and Ru(2TFA)phen are in the far infrared (the former emits at wavelength > 1500 nm).
References

Chapter 4. Toward Developing Force Fields for Ruthenium Hydride-Carbonyl Complexes of Mono- Diimine and Triphenylphosphine Ligands: The Reproducibility of the Photophysical Properties

4.1. Introduction

Ru complexes have played a crucial role in the development of inorganic photochemistry for the past decades due to their unique excited-state features [1-4]. Intense research efforts toward understanding the photophysical and photochemical properties of the Ru-polypyridyl based complexes (i.e. bipyridine (bpy), and phenanthroline (phen)) have continued to increase. Ru-bpy derivatives complexes have been used for several applications such as organic light-emitting devices (OLEDs), dye-sensitized solar cells (DSCs), biophysical probes for studying the dynamics and interactions on phospholipid membranes, and as catalysts for hydrogenation of unsaturated organic compounds [5-20]. However, the photophysical behavior of these systems depends strongly on understanding the intermolecular interactions and the geometrical features in solution. Thus, molecular mechanics (MM) applications have been recently extended to study the conformational changes and photophysical behaviors in systems including organometallic complexes [21-27].

Computational techniques have successfully been used to explore many aspects of how a molecule behaves in a system. In particular, (MM) combined with energy minimization and molecular dynamics (MD) provide useful knowledge about dynamics and structure of biomolecular systems, the physical properties of nanotechnological devices, the dynamic motions of macromolecules (e.g., proteins and nucleic acids) [28-31]. However, transition metals create a major problem for MM force fields, mainly
because of the nature of metal-ligand bonds. For example, metal ions are able to interact with more ligands than they can through the well-defined number of possible covalent bonds. In addition, the metal-ligand bond is neither covalent nor nonbonded (i.e., hydrogen bonds). Based on these facts, one metal can form several possible geometries. Therefore, no standard MM parameters are available for organometallic complexes. However, several ongoing efforts aim to develop parameters for organometallic systems seemed to be very promising, especially for metallo-proteins, nanosystems, and metal-organic framework (MOF) [32-37].

Although our quantum mechanical studies of the photophysical properties of Ru-bpy based complexes provided new, valuable knowledge, there are unsolved phenomena that need explanation and MM/MD will be suitable for such a task. For example, QM calculations treat the complex in a continuum dielectric medium of the solvent and do not account for explicit solvent-solute interaction such as hydrogen bonds. In addition, we designed [RuH(CO)dcbpy(PPh3)2]PF6 (dcbpy= 4,4´-dicarboxylic-2,2´-bipyridyl) (Rudcbpy) which displayed a long excited-state lifetime of ~720 ns in ethanol with high quantum yield ($\Phi = 0.30$) and an emission maximum at 610 nm. However, when conjugated to a lipid, the luminance in ethanol was quenched. Then to our surprise, emission was observed when incorporated into lipid vesicles, but blue shifted to 505 nm (a Stokes shift that would be expected for singlet emission), and the lifetime decreased to 11 ns [20]. This unanticipated behavior can be investigated using MM/MD procedures when the complex parameters are well defined in proposed models that mimic the systems in organic solvent and biological environment.
In addition, in 2016, Josefsson et al. performed MD simulations to investigate the interaction between [Ru(bpy)$_3$]$^+$ and different counterions ($\text{I}^-$ and $\text{Cl}^-$) in dye-sensitized solar cells (DSCs) in different solvents [28]. The counterion in the DSC acts as redox-couple conductor to regenerate the photo-oxidized dye. They found a correlation between DSC efficiency and the complex-anion interaction in different solvents. This study motivated us to investigate the effects of different counterions on the photophysical properties of Rudcbpy. Thus, we resynthesized Rudcbpy but with $\text{Cl}^-$ as counterion. However, the same spectra were observed for both complexes. Using MM/MD simulation will help to gain insight into the counterion interaction with the complex in a solvent. In particular, this simulation can be used to examine the effects of several ions and solvents on the photophysical behavior of the complex, and to investigate different catalytic chemical reactions.

![Figure 1. Proposed models for Rudcbpy on vesicle (left) and in organic solvent (right).](image)

Therefore, this study is considered as a first stage toward exploring larger systems of Ru-bpy derivatives and complexes. In this study: i) we present the first generation of force-field parameters that describe the Ru-coordination sphere in Rudcbpy, which to the
best of our knowledge have not been developed, by using MM/MD with QM calculations; ii) we use AMBER molecular dynamics software [38] for easy comparison of the output with other analogues systems (e.g., [Ru(bpy)$_3$]$^+$) that were studied using this package [28,31]; and iii) we model systems with different counterions and solvents to study their effects on the photophysical properties of the Rudcbpy.

4.2. Methodology

4.2.1. AMBER Force Filed Parameters Classification

The main step to initialize a molecular dynamic simulation is to select structural parameters; force fields, which can describe the system performance during the simulation. Force fields divide energy calculations into bonded and nonbonded terms. The bonded term defines intramolecular parameters by describing energetic penalties associated with the deviations of the bond, angle, and torsion from their equilibrium. The nonbonded term describes interactions between the nonbonded parts of the system. The AMBER potential energy formula is a function of the inter- and intramolecular forces, and is giving as [39-44]:

$$U (r_{ij}) = U_{bonded} + U_{unbonded}$$

$U_{bonded}(r_{ij}) = \sum_{bonds} k_r (r_{ij} - r_{eq})^2 + \sum_{angles} k_{\theta} (\theta_{ij} - \theta_{eq})^2 + \sum_{torsions} \frac{\gamma_n}{2} \left[ 1 + \cos (n\omega - \gamma) \right] \tag{2}$

$U_{unbonded}(r_{ij}) = \sum_{i \neq j} \left\{ \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} \tag{3}$

where in the first term $k_r$, $r_{ij}$, and $r_{eq}$ are, respectively, the bond force constant, the bond length, and the equilibrium bond length. Next, in the second term, $k_{\theta}$, $\theta_{ij}$, and $\theta_{eq}$ are, respectively, the angle force constant, the angle amplitude, and the equilibrium angle. Both of these terms are described using harmonic equations, while in the third term the
Fourier series is used to describe the torsion potential: $V_n$, $n$, $\omega$, and $\gamma$ are, respectively, the torsion force constant, the angle periodicity (the number of minimum points through $360^\circ$), the torsion angle, and the angle phase. It should be noted that $\gamma$ defines the shift of the torsion angle peak from zero, (has zero value if the maximum is at zero, and 180 if the torsion angle minimum is at zero).

The non-bonded potential energy in eq 3 sums interactions that occur between pairs of atoms, i and j, either within the same molecule and separated by at least three bonds, or pairs of atoms that are in different molecules. The two types of potential energies considered in non-bonded calculations are electrostatic interactions expressed as Coulomb’s law, and van der Waals interactions expressed as the Lennard-Jones (L-J) 6-12 potential [44]. These are explained below.

**The electrostatic interactions:** Deriving the physical properties such as the intermolecular interactions, for a system in molecular mechanics and dynamics, relies on the accuracy of describing the electron distributions. There are several approaches to generate the atomic charge, $q_{i,j}$, in the Coulomb expression: the central multipole expansion, the point-charge model, and the partial-atomic-charge model [44-48]. In this study, the widely used partial-atomic-charge model is applied due to its simplicity. This model includes various classes. We tested the performance of the predominant models used for simulating organometallic systems. Class I charges are generated by partitioning the electron density of a molecule, obtained from high-level quantum calculation, into the atomic population. Hirshfeld population analysis (HPA) and the theory of “atoms in molecule” (AIM) are examples of this class [49-51]. Class II charges are those calculated to reproduce the quantum chemical electrostatic potential (ESP) on a fine grid outside the
van der Waals radius of each atom in the molecule and model the two-body interactions [52]. However, (ESP) suffers from some deficiencies. For example, in a large molecule with embedded (buried) atoms, the ESP charges can fluctuate widely resulting in unrealistic charges. Therefore, the restrained electrostatic potential (RESP) model, in which a penalty function is introduced to reduce this problem [48, 52-56], is used in this study. Class III charges are those calculated to reproduce dipole-moments that either determined by experiment or by high-level quantum calculations. The Charge Model 5 (CM5), that has been developed by Marenich et al. (2012), is an example of this class, and it used in this study [57].

**The van der Waals interactions:** L-J 6-12 function is the model used to simulate van de Waals interactions. \( r_{ij} \) is the nonbonded distance between two atoms i and j, \( \varepsilon_{ij} \) is the well depth, and \( \sigma_{ij} \) is the radius between atoms i and j at which the inter-particle potential is zero [58]. The \( r^{-6} \) term accounts for the attractive London dispersion force, and \( r^{-12} \) term accounts for the repulsive force caused by Pauli exclusion. In the Amber force field, \( \sigma_{ij} \) in eq 3 is replaced by \( r_0 \).

\[
E_{\text{VDW}} = \sum_{i,j \neq i} \varepsilon_{ij} \left[ \left( \frac{r_0}{r_{ij}} \right)^{12} - 2 \left( \frac{r_0}{r_{ij}} \right)^{6} \right] \tag{4}
\]

Where \( r_0 \) is the contact distance between atom i and j at which the potential is at its minimum, and \( r_0 = 6\sqrt{2} \sigma \). This approach is used because of its physically simple interpretation: the equilibrium distance \( r_0 \) is simply the sum of the van der Waals radii of atom i and j [59-61]. L-J parameters for empirical force fields are developed, in part, by using experimental data, such as crystal data, the heat of vaporization and molecular volume, and by using \textit{ab initio} geometries and energies [62-66].
For hydrogen-bonding, the 10-12 L-J function is used.

\[ E_{\text{VDW}} = \sum_{\text{Hbonds}} \left[ \frac{A}{r^{12}} - \frac{C}{r^{10}} \right] \]  

(5)

where A and C are van der Waals parameters and given as \( A = \varepsilon(r_0)^{12} \) and \( C = 2\varepsilon(r_0)^{10} \).

### 4.2.2. Determining the Intramolecular Force Constants for an Organometallic System

As mentioned before, modeling a system that includes a transition metal is challenging. However, there are a number of methods by which the force constant parameters can be obtained. The more broadly applied method, which is used in AMBER, is empirical, but it shows limited accuracy especially for organometallic systems [67]. Another more time-consuming method extracts the parameters from experimental information, (e.g., X-ray or/and NMR) [68-69]. The Seminario method is the most common one used for systems containing transition metals. It extracts force constants from the calculated Hessian matrix and it is what we applied in this study [70-71]. In the following subsection a description of the method.

#### 4.2.2.1. Seminario method

The Seminario method, which was used here to calculate the internal force constants for Ru(II) complexes, extracts force constants via diagonalization of the second derivatives Hessian matrix in Cartesian coordinates. The following is the explanation of the key features of this method [71].

In a molecular system composed of N atoms each that undergo a small displacement, \( \delta x \), the corresponding reaction force, \( \delta F \), can be expressed as

\[ \delta F = -[k] \delta x \]  

(6)
Where \([k]\) is the Hessian matrix, which is symmetric with \(3N \times 3N\) dimensions, and is the second derivatives of the potential energy with respect to the displacements \([k] = \frac{\partial^2 E}{\partial x_i \partial x_j}
\). Therefore, the full form of eq 6 is expressed as

\[
\begin{bmatrix}
\delta F_1 \\
\vdots \\
\delta F_{3N}
\end{bmatrix} = - \begin{bmatrix}
\frac{\partial^2 E}{\partial x_1^2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N}} \\
\vdots & \ddots & \vdots \\
\frac{\partial^2 E}{\partial x_{3N} \partial x_1} & \cdots & \frac{\partial^2 E}{\partial x_{3N}^2}
\end{bmatrix} \times \begin{bmatrix}
\delta x_1 \\
\vdots \\
\delta x_{3N}
\end{bmatrix}
\]

(7)

The Seminario method uses the Hessian to calculate the force constant for each bond, angle, and dihedral angle. For any pair of atoms, \(A\) and \(B\), interacting in a system, the reaction force \(\delta F_A\) on atom \(A\) due to a displacement \(\delta r_B\) of atom \(B\) is expressed as

\[
\delta F_A = -[k_{AB}] \delta r_B
\]

(8)

Where \([k_{AB}]\) is the interatomic bond force constant matrix \([k_{AB}] = \frac{\partial^2 E}{\partial r_B \partial r_A}\), and now it has \(3 \times 3\) paired-interaction dimensions,

\[
\begin{bmatrix}
\delta F_{xA} \\
\delta F_{yA} \\
\delta F_{zA}
\end{bmatrix} = - \begin{bmatrix}
\frac{\partial^2 E}{\partial x_A \partial x_B} & \frac{\partial^2 E}{\partial x_A \partial y_B} & \frac{\partial^2 E}{\partial x_A \partial z_B} \\
\frac{\partial^2 E}{\partial y_A \partial x_B} & \frac{\partial^2 E}{\partial y_A \partial y_B} & \frac{\partial^2 E}{\partial y_A \partial z_B} \\
\frac{\partial^2 E}{\partial z_A \partial x_B} & \frac{\partial^2 E}{\partial z_A \partial y_B} & \frac{\partial^2 E}{\partial z_A \partial z_B}
\end{bmatrix} \times \begin{bmatrix}
\delta x_B \\
\delta y_B \\
\delta z_B
\end{bmatrix}
\]

(9)

The physical interpretation of eq 9 is that the atomic pair \((A, B)\) is considered stably bonded if there is a restoring force that maintains the atomic separation for any displacement of one of the atoms. This is observed if all three eigenvalues for the pair are positive. This ensures that the direction of the reaction force on atom \(A\) is in the same direction of atom \(B\) displacement.

Recall from linear algebra that for a \(d \times d\) matrix \(M\), there are \(d\) eigenvalues \(\lambda_1,..,\lambda_d\), and a set of corresponding \(d\) eigenvectors \(v_1,..,v_d\). Thus, \([k_{AB}]\) has three eigenvalues \(\lambda^{AB}_i\) that are the force constants in the direction of three eigenvectors \(v^{AB}_i\) \((i=1,2,3)\).
However, the aim is to calculate the force constants for the changes in the bond length, stretching and compressing, which may not coincide with any of the eigenvectors. Therefore, to calculate the AB bond force constant, each eigenvector has to be projected onto the direction of the bond vector, \( \hat{\mathbf{u}}^{AB} \), (hence, \( \hat{\mathbf{u}}^{AB} \) is a unit vector). From spectral decomposition theorem, the second derivative for a real and symmetric \( d \times d \) matrix \( \mathbf{M} \) in a specific direction is represented by a unit vector \( \mathbf{v}_l^T \), and can be written as

\[
\mathbf{M} = \sum_{l=1}^{d} \lambda_l \mathbf{v}_l \mathbf{v}_l^T .
\]

Consequently, the bond force constant \( k_{AB} \) will be written as

\[
k_{AB} = \sum_{l=1}^{3} \lambda_l^{AB} \left| \hat{\mathbf{u}}^{AB} \cdot \hat{\mathbf{v}}_l^{AB} \right| \tag{10}
\]

The angle force constant is more complex because the eigenvectors are projected onto directions perpendicular to two bonds AB and BC (Fig. 2).

![Figure 2. The unit vectors perpendicular to the bonds and within ABC plane.](image)

Similar to the previous definitions, the bonds AB and BC have bond vectors \( \hat{\mathbf{u}}^{AB} \) and \( \hat{\mathbf{u}}^{CB} \) respectively. The interatomic force constant matrices, \([k_{AB}]\) and \([k_{BC}]\), have eigenvalues \( \lambda_l^{AB} \) and \( \lambda_l^{CB} \), and eigenvectors \( \hat{\mathbf{v}}_l^{AB} \) and \( \hat{\mathbf{v}}_l^{CB} \). The unit vectors, \( \hat{\mathbf{u}}^{PA} \) and \( \hat{\mathbf{u}}^{PC} \) that describe the direction of the displacements of atom A and C upon opening or closing the angle (\( \theta \)) are perpendicular to the bonds and within the ABC plane. If \( R_{AB} \) and \( R_{BC} \) are the bonds lengths, then the angle force constant (\( k_{\theta} \)) is given by an expression analogous to two springs connected in a series.
The force constant for a dihedral angle \((k_\phi)\) defined by A, B, C, and D atoms is expressed using an approach similar to that used for the bond angle (eq. 11). Let the bonds AB, BC, and CD have unit vectors \(\hat{u}^{AB}\), \(\hat{u}^{BC}\), and \(\hat{u}^{DC}\), and let \(\hat{u}^{N_{ABC}}\) and \(\hat{u}^{N_{BCD}}\) be the unit vectors perpendicular on the ABC and BCD planes. So

\[
\hat{u}^{N_{ABC}} = \frac{\hat{u}^{CB} \times \hat{u}^{AB}}{|\hat{u}^{CB} \times \hat{u}^{AB}|}
\]

(12)

\[
\hat{u}^{N_{BCD}} = \frac{\hat{u}^{DC} \times \hat{u}^{BC}}{|\hat{u}^{DC} \times \hat{u}^{BC}|}
\]

(13)

Then the dihedral angle force constant \((k_\phi)\) is

\[
\frac{1}{k_\phi} = \frac{1}{R_{AB}^2} \sum_{i=1}^{3} \lambda_i^{AB} |\hat{r}^{PA} \cdot \hat{\varphi}_i^{AB}| + \frac{1}{R_{CB}^2} \sum_{i=1}^{3} \lambda_i^{CB} |\hat{r}^{PC} \cdot \hat{\varphi}_i^{CB}|
\]

\[
\frac{1}{k_\phi} = \frac{1}{R_{CD}^2} \sum_{i=1}^{3} \lambda_i^{DC} |\hat{r}^{DC} \cdot \hat{\varphi}_i^{DC}|
\]

(14)

The Seminario method provides fast parameterization and has been used by many research groups, especially for the simulation of metalloproteins, metal-organic framework (MOF), and nanosystems [25-26, 32-33, 36-37, 71-76]. Although this method helped to define and incorporate Ru(II) into the AMBER force field, there are drawbacks associated with calculation of some of the metal bonds and angles force constants.

Double counting is the most common problem. In the calculated Hessian matrix, the bonded and nonbonded interactions are not isolated, and consequently, the Seminario method does not decouple the two contributions [76-77]. In other words, the nonbonded force constants are included twice, (calculating by Seminario and Amber in eq 3), causing an overestimation of the force constant. Therefore, we recalculated some of the force constants using harmonic functions (eq 2), as explained in the following subsection.

4.2.2.2. Harmonic functions
Stretching a bond or bending an angle in the force field is described by Hooke’s law as simple motion of a harmonic oscillator: near the equilibrium position,

\[ E = \frac{1}{2} k(q_{ij} - q_{eq})^2. \]

The potential energy curve that corresponds to this motion is quadratic, and the harmonic force constant is the second derivative of the potential energy with respect to the displacement, \([k] = \frac{\partial^2 E}{\partial x^2}\). If a bond stretched furthermore, the deformation will not be reversible (non-elastic) and the potential energy will deviate (Fig. 3). Thus, the harmonic force constant is determined around the equilibrium value (within the elastic limit) by solving the second-order polynomial of the differentiable expression.

![Quadratic curve near equilibrium](image)

![Deviation from harmonic motion](image)

**Figure 3.** The potential energy variation of stretching the Ru-P1 bond distance using B3LYP/LANL2DZ/6-31G*.
To ensure elastic behavior, we varied each bond distance from its equilibrium by stretching and compressing the bond by ± 2.0 %, while the bond angle was bent by ± 7%, as suggested in the literature [27,78]. In this way, we redefined the forces for Ru-ligand and -COOH bond lengths and angles. We selected these parameters because their normal modes, calculated after MM minimization, deviated significantly from the QM equilibrium geometry (see results and discussion). A total of ten bond lengths and nine bond angle force constants were determined using the B3LYP/LANL2DZ/6-31G* level of theory (Table 1). We performed a relaxed potential energy scan for each bond by compressing and stretching a bond by a maximum of 2.0 % of its equilibrium geometry for several steps to determine the potential function near equilibrium (Fig. 3). Then by using XMGRACE software [79], we fitted the results (potential energies that correspond to variation of bond lengths) to the expression \( E = \frac{1}{2} k_b (r_{ij} - r_{eq})^2 \) to obtain the force constant. We used the same procedure to determine the harmonic force constant for bond angles.

4.2.3. Workflow

The workflow can be illustrated as the following main steps:

1. Geometry optimization (QM calculation, Gaussian 09 software) \([80]\) \(\rightarrow\) Building the solvent box (Packmol software) \([81]\) \(\rightarrow\) Generate frcmod and mol2 files for each molecule in the system (AMBERTools16 software) \([38]\) \(\rightarrow\) Create library files, solvate the complex in the center of the solvent box, determine the desired concentrations and box size (tleap program) \([38]\) \(\rightarrow\) Create two separate sets of files for Ru and all other ligands: pdb, frcmod, and mol2 (AMBERTools16 software) \(\rightarrow\) Build Ru-ligands bonds, Create input Gaussian files for RESP calculations (MCPB.py program) \([30]\) \(\rightarrow\) Calculate
RESP charge (Gaussian 09 software) [80] → Extract the force constants for Ru coordination (MCPB.py program) → Build the AMBER topology and coordinate files (Tleap program) → MM energy minimization and short MD simulation (AMBERTools16 software) → Structure validation: Calculate the vibrational frequencies and UV-Vis (Gaussian 16) → production simulation → Analysis (VMD, ParmEd, CPPTRAJ) [38, 82].

First, we minimized the Ru[COH(PPh$_3$)$_2$dcbpy]$^+$ complex and determined the equilibrium geometry using the B3LYP/LANL2DZ level of theory. We prepared five systems: 1) The complex solvated in 95% ethanol with PF$_6^-$ counterion, 2) The complex solvated in 95% ethanol with Cl$^-$ counterion, 3) The complex solvated in acetonitrile with PF$_6^-$ counterion, 4) The complex solvated in acetonitrile with Cl$^-$ counterion, and 5) [(H)Ru(CO)(PPh$_3$)$_2$4,8-(dimethyl)bpy]$^+$ (RudMebpy) solvated in 95% ethanol with Cl$^-$ counterion. To attempt to mimic experimental conditions and to eliminate any possibility of intermolecular interaction between nearby Ru complexes, we added only one Ru complex giving a concentration of $3 \times 10^{-3}$ M, which was the concentration used to determine the absorption spectra. Each simulation box is a cube with sides of 85.0 Å. The number of solvent molecules, (concentration), were calculated based on their pure densities at 298 K ($\rho_{\text{ethanol}} = 0.79$ g/cm$^3$, $\rho_{\text{acetonitrile}} = 0.79$ g/cm$^3$, $\rho_{\text{water}} = 1.00$ g/cm$^3$). Thus, the ethanol box contained 6017 ethanol molecules, 317 water molecules, one complex, and one counterion to balance the system charge, while the acetonitrile box contained 6971 acetonitrile molecules, one complex, and one counterion. We included only one counterion to avoid salt precipitation. To model a metal ion, there are different strategies such as the bonded model, nonbonded model, and cationic dummy atom approach [83-
The AMBER force field uses the bonded approach as explained in eq 1-3. The Seminario method, implemented in the metal-center parameter builder software (MCPB.py) was used for Ru parameterizations while the Generalized AMBER Force Field (GAFF) was applied for the ligands, counterion, and solvent molecules. RESP charges from QM calculations were used for all complex atoms. We used the AMBER default TIP3P model for water molecules [87], and we used Ru van der Waals parameters as reported in the literature [88].

We used the first system to benchmark the accuracy of the parameters. We applied the steepest descent algorithm for minimizations to provide the needed output files for conformational validation and production simulation. The calculations were run with the sander module in the AMBER16, using the geometry pre-optimized by QM as the starting structure. The system was subjected to three rounds of 2000-step minimizations under constant volume. To gradually release the internal strain energy, all complex atoms were kept restrained in the first two steps to their positions in the QM equilibrium geometry by using a harmonic force constant of 500 and 250 kcal. mol\(^{-1}\).Å\(^{-2}\). In the third step, only nonhydrogen atoms were restrained by 100 kcal. mol\(^{-1}\).Å\(^{-2}\). For box equilibration, 200 ps of six rounds of MD simulations were carried out under constant volume and pressure. The restraints were reduced sequentially by 100, 70, 40, 20, 5, and zero kcal. mol\(^{-1}\).Å\(^{-2}\). After this step, the quality of the equilibration was checked first by analyzing a variety of system properties: box volume, density, temperature, pressure, and energies (Fig. 4). Before running the production MD simulation, the minimized structure was analyzed and validated based on the deviation in the geometry of the MM calculation
from that calculated by QM. We considered three criteria: the mean error associated with Ru-ligand bond lengths and angles, the vibrational frequencies, and the UV-Vis spectra.

Based on the results, we redefined several parameters as explained in the discussion, and all steps have been repeated with respect to each new parameter until the deviation was reduced and the system reproduced comparable UV-Vis spectra to the experiment and QM calculations.

Finally, we ran a series of 200-ns production simulations under constant temperature \((T = 298 \text{ K})\) and pressure \((P = 1 \text{ atm})\) and without restraints. The distance cutoff for nonbonded interactions was 12 Å. The Langevin thermostat was used to regulate the temperature of the entire system with a collision frequency \(\gamma = 3.0 \text{ ps}^{-1}\), and the system pressure was controlled by the Monte Carlo barostat [89-90]. Bond stretching involving hydrogen atoms was removed using the SHAKE algorithm [91]. Finally, the periodic boundary condition was enabled during the simulation. For each simulation, the starting point of the counterion was from different position and within 5.0 Å of the complex. The modified parameters obtained for this system were then used for the four other systems.

The radial distribution functions (RDFs), (also denoted \(g(r)\)), from the MD trajectories was calculated in order to analyze the counterion and the solvent molecules fluctuating near the complex. RDFs implemented in VMD program, provide information about the density probability of finding specific molecule or atom at distance \(r\) around the given central atom, Ru in this case.
4.3. Results and Discussion

4.3.1. System minimization and relaxation

The results showed that the entire system is relaxed under the applied conditions. All energy terms (potential energy (EP), kinetic energy (EK), total energy = potential energy + kinetic energy) increased during the first few ps, due to heating the system from 100 K to 298 K then remained constant during the constant pressure stage (Fig. 4a). This behavior indicates that the temperature thermostat worked correctly, and the relaxation was completed and equilibrium was reached. The temperature behaved properly as expected under regulation by Langevin dynamics. It initially increased with heating the system then reminded constant (Fig. 4b). From Fig. 4c, it can be seen that the pressure dropped sharply negative during the first 10 ps before it started to stabilize around 1 atm after ~35 ps of simulation, indicating successful equilibration. The negative pressure implied that the box size needed to shrink slightly from its initial volume (614,125 Å³).

The reduction of the solvent box volume was followed by oscillation around a mean value of ~ 601,817 Å³, indicating that equilibrium volume was reached (Fig. 4d). Finally, the density increased then equilibrated at approximately 0.789 g/cm³ (Fig. 4e).

4.3.2. Validation of the derived parameters

**Bonded parameters:** Initially, the MM minimization was run using the force constants determined by the Seminario method for Ru-ligand bond lengths and angles and AMBER force fields for the rest of the complex (dcbpy and PPh₃). To validate the Ru parameters derived by Seminario, we used three criteria: i) measuring the mean errors

\[
\bar{\Delta} = \frac{1}{n} \sum_{i=1}^{n} (R_{i}^{\text{MM}} - R_{i}^{\text{QM}})
\]

associated with Ru-ligand bond lengths and angles, ii) calculating the vibrational frequencies, and iii) calculating the UV-Vis spectra. To the
best of our knowledge, using UV-Vis spectra to evaluate the structure has not been considered in any study. All results were compared to that of the QM optimized geometry.

First, the calculation of the mean errors. The total mean error associated with the

![Figure 4](image-url)

Figure 4. Variations of some properties of the equilibrated system during 200 ps long simulation: 4a) for all energies, 4b) for temperature, 4c) for pressure, 4d) for volume, and 4e) for density.
calculated Ru-ligand bond lengths is 7.81 pm and for Ru-ligand bond angles is 0.50°. This small deviation indicates that Ru parameters were reproduced very well.

Second, the vibrational frequencies of the minimized MM geometry were calculated using QM. From Fig. 5, it is clear that although most of the vibrational frequencies match well with their counterparts calculated from the QM optimized geometry, some notable discrepancies are observed. The stretching motions of the X-H bonds (X = C, or O) is largely responsible of the disagreements at high frequencies (> 3000 cm⁻¹). Different motions associated with the Ru, N, CO, hydride vibrations cause the deviations that are observed over the range 1000-1700 cm⁻¹. The appearance of the imaginary frequencies is due to several motions mainly related to the dcbpy and phenyl rings with contributions from Ru-P stretching mode.

Figure 5. Vibrational frequencies computed at the B3LYP/LANL2DZ level for the optimized QM geometry (black) and for MM minimized geometry (red).
Finally, we evaluated the reproducibility of the UV-Vis spectra of the QM equilibrium geometry. We found that the shape, intensity, and electronic transitions for MM model were different from that of QM geometry (Fig. 6). The analysis for the atomic orbital contributions showed that all three main transitions are from Ru and PPh₃ to dcbpy (MLCT). No intraligand transitions were calculated, and the spectral intensity is three times weaker. The failure to reproduce the accurate UV-Vis spectra indicates insufficient descriptions of the molecular orbitals energies (HOMOs and LUMOs).

**Figure 6.** The calculated UV-Vis spectra at the B3LYP/LANL2DZ level for the optimized QM geometry (left) and for MM minimized geometry (right).

It is worth mentioning that refinement parameters and keeping the existing one unchanged is a decision made based on the desired goal to be achieved. Since we are interested in photophysical properties of the Rudcbpy, we concluded, from the discrepancies of the vibrational frequencies and the failure to reproduce UV-Vis spectra that the parameters of Ru-ligands and –COOH have to be redefined. In addition, we concluded that calculating the mean errors alone would not quantify the behavior of the complex in a system despite other studies [71-76]. In order to develop more efficient parameters that describe the system photophysical properties more accurately, the
vibrational frequencies for the normal modes and the UV-Vis spectra have to be considered.

We redefined the force constants for six Ru-ligand bond lengths, O-H bond, C-H and C-C bonds of dcbpy. Based on the observed errors, further force constants for nine bond angles were also redefined (Table 2). It should be noted that there was not a specific pattern to indicate which Ru-ligand bond to start with because it is hard to specify which atom is responsible for the observed inconsistencies in the normal modes and UV-Vis spectra. First, we determined the harmonic force constant for Ru-P1 stretching bond. We then replaced the initial force constant with the new value from which the topology and coordinates files were generated and used for MM minimization. The structure was evaluated by analyzing the three criteria: mean errors, vibrational frequencies, and UV-Vis. Then, the force constant for Ru-P2 was determined and included along with the corrected one for Ru-P1 followed by the same steps, and so on for each new force constant. Scheme 1 describes the repeated workflow for each new force constant.

**Scheme 1**

**Determine harmonic force constant**  
\[ E = \frac{1}{2} k (q_{ij} - q_{eq})^2 \]

**Build the topology and coordinate files**

**Perform MM energy minimization and short MD simulation**

**Validate the structure: mean errors, vibrational frequencies, UV-Vis**

In the following we explain the improvement of the Ru parameters using the proposed three criteria. First, remarkable improvement is observed upon correcting the
force constants when calculating the mean errors. Figure 7 shows the order of correcting the force constants with the calculated mean errors for Ru-ligand bond lengths and angles. The total mean errors for Ru-ligand bond lengths and angles are reduced from 7.81 pm and 0.50° to 0.13 pm and 0.14°, respectively, when including all corrected force constants (Fig. 7). Three main observations of the calculated mean errors have to be considered. First, each attempt of introducing new force constant did not necessarily improve the geometry. For example, when we included the new k(Ru-H), the mean error of the Ru-ligand bond lengths increased but then decreased when adding the new k(Ru-C). Second, as can be seen from Fig. 7, the mean errors associated with Ru-ligand bond angles have the smallest value after introducing the new k(Ru-P2), which increased when all new force constants were included. Finally, the mean errors associated with modifying Ru-ligand bond angles and –COOH parameters are not shown, and instead the results of including all new data in the last attempt are reported (Fig. 7). With all above considerations, the structure defined with the nonbonded parameters in Table 1 and the new force constants listed in Table 2 was used to perform the production simulation. The new defined force constants for Ru-ligand bond angles and –COOH parameters are not shown, and instead the results of including all new data in the last attempt are reported (Fig. 7). With all of the above considerations, the structure defined with the nonbonded parameters in Table 1 and the new force constants listed in Table 2 were used to perform the production simulation.

Second, calculation of the vibrational frequencies provides general improvements. A reduction in the imaginary frequencies is observed from -138 cm\(^{-1}\) to –67 cm\(^{-1}\) (Fig. 8).
The frequencies over the range 900 – 1700 cm\(^{-1}\) agree better with their counterparts produced by the QM optimized geometry.

A significant improvement of the UV-Vis spectra can be seen from Fig. 9. Including all redefined new force constants (Fig. 9 (7)) generates spectra with shapes and electronic excitations that agree with the QM optimized geometry. However, the calculated MLCT band is red shifted (450 nm and 550 nm for the optimized QM and MM geometries, respectively). The orbital energy analysis of the minimized geometry by MM calculation revealed destabilization of the HOMO by 0.22 eV combined with stabilization of the LUMO by 0.32 eV, and thereby the energy gap is decreased and the spectra red shifted.
Figure 8. Vibrational frequencies computed at the B3LYP/LANL2DZ level for the optimized QM geometry (black), MM minimized geometry with no corrections of force constants (red), and MM minimized geometry with all new force constants (green).

Figure 9. The calculated UV-Vis spectra at the B3LYP/LANL2DZ level for the optimized QM geometry and for MM minimized geometries with different parameters in ethanol. (7) is the result of including all new force constants.
To test the ability of the modified parameters to reproduce the properties of analogue Ru(II) systems, they were used to calculate the UV-Vis spectra of [RuH(CO)bis-4, 4’-(methyl)bpy(PPh$_3$)$_2$]$^+$ (RudMebpy). From our combined experimental data and QM calculations of this complex$^1$, we observed a blue shift of the MLCT band (maximum about 390 nm) compared to that of Rudcbpy, which is due to the electron-donating nature of the methyl groups. To examine the ability of our modified parameters to reproduce the same UV-Vis shift trends, we applied them to RudMebpy and then calculated the UV-Vis spectra. The minimized MM RudMebpy geometry provides the expected shift. However, the calculated spectra from the minimized MM geometry were red shifted compared to those from the QM geometry (see Fig.10). The shape and trends of the calculated UV-Vis spectra from the minimized MM geometries were reproduced for both Rudcbpy and RudMebpy but with a large red shift (>60 nm).

Figure 10. The calculated UV-Vis spectra of RudMebpy at the B3LYP/LANL2DZ level for the optimized QM geometry (right) and for MM minimized geometry (left).

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$^1$ All results for this complex reported in chapter 2.
The origin of the large shift in the spectra is not clear. It needs further investigation, which is one of our future goals. We considered the possibility that the stretching motions of the C-H and O-H bonds contribute to this issue and PPh₃ ligands parameters need to be redefined. To explore the former effect, we restrained the bonds by doubling the values of the corresponding force constants. The results showed a reduction of the shift by 40 nm (see Fig. 11 verses Fig. 9). This approximation is valid under the presumption that it is not critical to determine precisely the bond and angle force constants. In fact, Brandt and Norrby [27] point out that “… some simplified descriptions go as far as to use totally rigid bonds and angles.”

In summary, the modified force fields for Ru(II) complex that we developed were able to provide quantitative data for the photophysical properties. In particular, characterizing the MLCT band and the relative shift with different substituents was successfully achieved. We anticipate that these modified force fields can be used for other Ru mono-dimine complexes that include PPh₃ ligands.

**Nonbonded parameters:** To assess the role of the electrostatic potential in describing the photophysical behavior of Rudcbpy, three other applications of partial atomic charges were studied: AIM, CM5, and HPA, which were explained earlier.
Gaussian 09 was used to calculate the atomic charges for the optimized QM geometry for each approach using the B3LYP/LANL2DZ level of theory. Considering the final successful parameters, the previous (RESP) charges were replaced in the mol2 file (the file in which the atomic charges are defined) by the new values. The structure was minimized by MM and UV-Vis spectra were calculated. The structure that was described by the AIM charge model failed to converge. Both HPA and CM5 provided UV-Vis spectra to close that obtained using the RESP charge model (Fig. 12). Interestingly, the calculated spectra using the CM5 model reduced the large shift that was observed earlier. In fact, it has been reported by Wang et al. (2014) that the CM5 charge model yields more accurate charge distributions for small inorganic molecules when compared with various other charge models [92].

![Image](image.png)

**Figure 12.** The calculated UV-Vis spectra of Rudcbpy at the B3LYP/LANL2DZ level for the MM minimized geometry using RESP (left), CM5 (middle), and HPA (right) methods of calculating atomic charges.

4.3.3. *Rudcbpy interaction with different counterions*

Rudcbpy with two different counterions, PF$_6^-$ and Cl$,^-$, were synthesized and their UV-Vis absorption spectra were measured in ethanol. Both systems produced similar UV-Vis spectra with an MLCT band at about 422 nm (Fig. 13). This indicates that both
ions interact with the complex in a similar way, and thus the HOMO-LUMO energy gap remains unaffected.

![Figure 13. UV-Vis absorption spectra of Rudcbpy with Cl\(^-\) (dashed) and PF\(_6^-\)](image)

Table 1. Nonbonded parameters for Rudcbpy.

<table>
<thead>
<tr>
<th></th>
<th>$Q^b$</th>
<th>$\sigma_{ij}(\text{Å})$</th>
<th>$\varepsilon_{ij}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>0.0004</td>
<td>2.96$^a$</td>
<td>0.56$^a$</td>
</tr>
<tr>
<td>N1</td>
<td>-0.0207</td>
<td>1.82</td>
<td>0.17</td>
</tr>
<tr>
<td>N2</td>
<td>0.0128</td>
<td>1.82</td>
<td>0.17</td>
</tr>
<tr>
<td>P1</td>
<td>-0.0266</td>
<td>2.10</td>
<td>0.20</td>
</tr>
<tr>
<td>P2</td>
<td>-0.0093</td>
<td>2.10</td>
<td>0.20</td>
</tr>
<tr>
<td>C</td>
<td>0.1749</td>
<td>1.91</td>
<td>0.210</td>
</tr>
<tr>
<td>H</td>
<td>-0.1497</td>
<td>0.60</td>
<td>0.016</td>
</tr>
</tbody>
</table>

$^a$ From ref. [62]. $^b$ Charges obtained by RESP.
Table 2. Selection of force constants, and comparison between the QM and MM minimized geometries for bond lengths (Å) and bond angles (°) for the central structure.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$k_b$(kcal/(mol.Å²))</th>
<th>QM</th>
<th>MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-N1</td>
<td>102</td>
<td>2.168</td>
<td>2.169</td>
</tr>
<tr>
<td>Ru-N2</td>
<td>70</td>
<td>2.244</td>
<td>2.177</td>
</tr>
<tr>
<td>Ru-P1</td>
<td>63</td>
<td>2.454</td>
<td>2.543</td>
</tr>
<tr>
<td>Ru-P2</td>
<td>66</td>
<td>2.453</td>
<td>2.430</td>
</tr>
<tr>
<td>Ru-H</td>
<td>170</td>
<td>1.610</td>
<td>1.573</td>
</tr>
<tr>
<td>Ru-C</td>
<td>236</td>
<td>1.865</td>
<td>1.893</td>
</tr>
<tr>
<td>bpyC-COOH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>325</td>
<td>1.497</td>
<td>1.435</td>
</tr>
<tr>
<td>bpyC-COOH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>326</td>
<td>1.496</td>
<td>1.384</td>
</tr>
<tr>
<td>O-H</td>
<td>439</td>
<td>0.973</td>
<td>0.973</td>
</tr>
<tr>
<td>C-H</td>
<td>408</td>
<td>1.084</td>
<td>1.084</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle</th>
<th>$k_\theta$(kcal/(mol.rad²))</th>
<th>QM</th>
<th>MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Ru-N2</td>
<td>120</td>
<td>167</td>
<td>166</td>
</tr>
<tr>
<td>P-Ru-N2</td>
<td>80</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>N1-Ru-N2</td>
<td>102</td>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td>N-C-C</td>
<td>69</td>
<td>123</td>
<td>121</td>
</tr>
<tr>
<td>C-O-H</td>
<td>50</td>
<td>108</td>
<td>109</td>
</tr>
<tr>
<td>C-C-OH</td>
<td>18</td>
<td>113</td>
<td>117</td>
</tr>
<tr>
<td>O-C-O</td>
<td>75</td>
<td>124</td>
<td>118</td>
</tr>
<tr>
<td>N-C-H</td>
<td>49</td>
<td>116</td>
<td>123</td>
</tr>
<tr>
<td>C-C-H</td>
<td>66</td>
<td>122</td>
<td>121</td>
</tr>
</tbody>
</table>

<sup>a</sup> COOH trans to CO. <sup>b</sup> COOH trans to H.
We applied MD simulation for two systems with Cl$^-$ and PF$_6^-$, first to validate the
developed parameters and second to understand the electrostatic interaction between the
complex and the counterions. After 200 ps for equilibration, we performed several 200-ns
production runs for each system. To help ensure evaluation of all possible complex-
counterion interactions, we started each simulation from randomly selected positions of
the counterion which were 10.0 Å from the Ru.

To assess the suitability of the developed parameters, the HOMO-LUMO energy
gap should not change regardless of counterion type or interaction. Thus, from the
trajectory files, we selected 25 structures with different counterion locations. Both
ParmEd and CPPTRAJ programs were used to extract the distance between Ru and the
counterion (Cl$^-$ or P in PF$_6^-$) from the trajectory file and the output was plotted using
XMGRACE (Fig. 14) [38,79]. Two considerations have been taken into account to select
a structure: 1) the counterion is located 10.0 Å from the Ru, and 2) the complex-
counterion interaction persists for at least 1 ns at each position.

![Figure 14. Trajectory data showing Ru-Cl distance fluctuating over 200 ns production simulation.](image)
After selecting the structures that met these criteria, we performed a single-point energy calculation for each structure without solvent or counterion to determine the orbitals energies for each structure. Regardless of the counterion position, we found that averaging the HOMO-LUMO energy gap of the 25 structures produced a similar value for both systems (the difference is < 0.03 eV) (Fig 15). Thus, the calculated UV-Vis for Cl$^-$ in ethanol is the same as for PF$_6^-$ (Fig. 9), consequently, the parameters reproduced the experimental observation.

![Figure 15. The calculated HOMO-LUMO energy gap for 25 selected structures with different counterions.](image)

The complex-counterion interactions show interesting behaviors. First, from RDF analysis, no Cl$^-$ was found within 7.0 Å of Ru, while the smallest Ru-PF$_6^-$ separation was ~ 4.5 Å (Fig. 16). That means that PF$_6^-$ can come closer to Ru than Cl$^-$. In addition, both anions can penetrate the solvation shells and approach the complex regardless of the starting point of the simulation, indicating that anion-complex interaction is stronger than anion-solvent (Fig 16).

In addition, the positions at which the anions interact with the complex differ. As seen in Fig 16, a maximum peak is observed for Cl$^-$ at separation distance of 10-11 Å from Ru. This corresponds to the anion interacting mostly with the carboxylic groups.
specifically, the proton (Fig. 17). In other words, during the simulation, Cl\(^-\) was found located near the proton of the carboxylic group for long periods (> 1 ns). The two protons of the carboxylic groups have the most positive charges compared to other carbon or hydrogen atoms in the system. The reason that Cl\(^-\) is more easily captured by the protons is probably due to its small size compared to PF\(_6\)\(^-\). The smaller the counterion, the more concentrated the negative charge over its surface. Thus, we anticipated that Cl\(^-\) would strongly interact with the proton.

Figure 16. Radial distribution functions (RDFs), g(r), for Ru-PF\(_6\)\(^-\) (left) and Ru-Cl\(^-\) (right) separation.

Figure 17. Illustration of the locations where high concentration of Cl\(^-\) in blue (right) and PF\(_6\)\(^-\) in purple (left) are found during simulations.
On the other hand, PF$_6^-$ shows a broad, oscillating peak (Fig. 16). The analysis reveals that this anion, in contrast to Cl$^-$, is moving between ligands and tends to interact with the aromatic rings (Fig. 17). This interaction has been observed and defined as noncovalent anion-π interaction [92-94]. Apparently, an association will occur between neutral π-moieties (also called π-electron-deficient aromatic rings, e.g., hexafluorobenzene) and negatively charged groups (i.e. PF$_6^-$).

Fully understanding the different behaviors of the complex-anion interaction needs further investigation. Including other anions with different sizes and applying DFT calculations to derive the electrostatic potentials and the structural features of the complex upon interacting with the anions are in consideration.

4.3.4. Solvent effects

The measured UV-Vis absorption spectra of Rudcbpy with the two counterions, PF$_6^-$ and Cl$^-$, were similar (MLCT peak at about 422 nm) for both anions in ethanol. However, a blue shift of ~10 nm is observed in acetonitrile when PF$_6^-$ is the counterion (Fig 18). Modeling a system with PF$_6^-$ in acetonitrile using MD simulation reproduced the observed blue shift (see Fig. 9 verses Fig. 19). Furthermore, the calculated MLCT band

![Figure 18. The observed UV-Vis spectra of Rudcbpy with Cl$^-$ (right) and PF$_6^-$ (left) in different solvents.](image-url)
for the complex with Cl\(^-\) as counterion was the same in both solvents (Fig. 9 and Fig. 19). Thus, the modified parameters that we developed reproduced successfully the experimental observations.

In addition, from RDFs analysis, Cl\(^-\) was found to be localized near the proton of either carboxylic acid of the complex in acetonitrile and remained bound to the proton for the duration of the simulation (200 ns). A single, narrow peak is observed for the distribution in acetonitrile (Fig. 20) compared to that in ethanol where there is broad localization of the counterion (Fig. 16). On the other hand, PF\(_6^\)- was found to behave as in ethanol and moves between ligands (compare Figs. 16 and 20).

**Figure 19.** The calculated UV-Vis spectra of Rudcbpy using B3LYP/LANL2DZ for the MM minimized geometry for PF\(_6^\)- (left) and Cl\(^-\) (right), both in acetonitrile.

**Figure 20.** Radial distribution functions (RDFs), g(r), for Ru-PF\(_6^\)- (left) and Ru-Cl\(^-\) (right) separation in acetonitrile.
This finding suggests that in the absence of solvent hydrogen bonds (as in acetonitrile), the stability is high for the interaction of an anion that has smaller surface area (Cl\textsuperscript{−}) with the proton of the carboxylic group. This interaction when changing solvent properties from polar protic (i.e. Ethanol) to polar aprotic (i.e. Acetonitrile) suggests that Cl\textsuperscript{−} might acts as better redox conductor for regenerating the photo-oxidized dye in the dye-sensitized solar cells.

4.4. Conclusion

In our initial computations, we used the Seminario method to extract the Ru-ligands force constants from our high-level QM calculations (B3LYP/LANL2DZ). However, the computational results did not agree well with experimental data because of the double counting problem (nonbonding interactions). Our approach toward resolving this issue was to redefine the Ru-ligand parameters by solving the harmonic potential functions described by Hooke’s law for different bonds and angles. Although the modified Ru force fields were adequate to describe the photophysical properties for a system of Ru(II) constructed from bpy and PPh\textsubscript{3} ligands, slight deviations were observed. We hypothesized that the observed discrepancies were due to the ligands parameters (bpy and PPh\textsubscript{3}), which were defined by AMBER force fields (AMBER uses low-level QM calculations). The goal toward resolving this issue is redefining the ligands parameters at the same level of theory, which is one of our future goals. We showed that the electrostatic term calculated by AMBER can be improved by using a different model of atomic charge. The results show that CM5 gives a better description compared to RESP. In addition, performing dynamic simulation with two different anions in two different solvents demonstrates that neither counterion nor solvent significantly affect the spectra.
However, the interesting behavior of the anions with respect to the solvent will be investigated further, and the results are anticipated to be useful in other fields such as developing solar cell with high efficiency.
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Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.;
Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.;
Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi,
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5.1. Conclusions

5.1.1. Quantum Mechanics Study

The structural, HOMO-LUMO gap, and spectroscopic properties of the ground-state singlet and lowest lying triplet excited states of derivatives of Ru(bpy)(PPh$_3$)$_2$ with different electron-withdrawing and donor substituents and $\sigma$-donor and $\pi$-acceptor ligands trans to the bpy have been investigated by combined DFT/TDDFT calculations [1-3]. The statistical measurements of the performance of ten combinations DFT/basis sets used to describe $S_0$ geometry for [(H)Ru(CO)(PPh$_3$)$_2$(dcbpy)]$^+$, followed the ‘Jacobs ladder’ classification scheme and decreased in the series double-hybrid (B2PLYPD3) > meta-hybrid (M06) > hybrid-GGA (PBE0, B3LYP, CAM-B3LYP, wB79xD) [4]. The PBE0/LANL2DZ performance was superior compared to that of B3LYP/LANL2DZ. To accurately assess the symmetry of these systems, it is essential to use methods that include the dispersion correction. Although B3LYP did not produce the most accurate geometry for the ground state, it reproduced well the experimental singlet absorption and triplet emission energies, which suggests that it will likely yield reliable predictions for the spectroscopy of other complexes. Also, we have shown with Rudcbpy that when solvent and counterions are included, the calculated excitation energies are closer to those observed in the experimental spectra.

The calculations showed that introducing electron-withdrawing groups stabilizes the bpy $\pi^*$ LUMOs, shifts the absorption and emission spectra to lower energies, and increases the distortion in the $T_1$ geometry. The opposite was observed with electron-donating substituents. The bpy $\pi^*$ LUMOs were destabilized, the absorption and emission spectra shifted to higher energies, and there was less distortion in the $T_1$ geometry. In addition, when the two ligands $trans$
to bpy are strong $\sigma$-donors, the calculated $T_1$ is much closer to $S_0$, which predicts an unusually red-shifted luminescence and lower quantum yield. This suggests that to generate complexes with less red-shifted emission and higher quantum yields, it is desirable to use weaker electron donors such as halogens or better $\pi$ acceptors such as CO. In summary, this computational study revealed a general trend: increased HOMO-LUMO energy gaps correlate with a blue shift in both the excitation and emission energies and less geometric distortion in $T_1$.

We then extended our previous study of the relationships between the HOMO-LUMO energy gap and the photophysical properties for Ru-bpy to include a new series of Ru-phen-based complexes. The results obtained confirmed our earlier findings for Ru(bpy)(PPh$_3$)$_2$ and revealed new aspects that can be summarized by four major conclusions. First, the excited electron is delocalized over $\pi^*$ of the phen acceptor ligand, which decreases the geometrical distortion and $k_{nr}$, thereby increasing the quantum yield compared to bpy ligand. Second, a general trend is observed: increased HOMO-LUMO energy gaps correlate with a blue shift in both the excitation and emission energies and less geometric distortion in $T_1$ only when no other transitions are present that are isoenergetic with the MLCT transition. Third, this study suggests two ligands (Cl and TFA) as potential candidates for investigating the photo-substitution mechanism in Ru-phen based complexes. When the strong $\pi$-acceptor ligand (CO) is replaced by Cl or TFA, the splitting-ligand field is reduced and induces excitation to the $\sigma^*$ (Ru—N). The occupation of this orbital causes electron-electron repulsion that weakens the bond strength and results in formation of a $^3$MC state. Fourth, when CO is used as a trans ligand, Ru-phen-based complexes can be designed that have similar energy gaps regardless of the other trans ligand.

In conclusion, we have proposed a strategy to tune the HOMO and LUMO energy level by either changing the substituents or the ligand in the trans position. The correlation and the
computational approach we outlined here can be used to design complexes rationally and screen other organometallic candidates that may have desirable excited-state properties.

5.1.2. MM/MD Study

In this study, we developed successfully new force-field parameters for Ru-bpy based complexes. These parameters are the first to be reported for such system. We showed that calculation of the mean errors to validate the proposed MM geometry is not a sufficient benchmark for the accuracy of the developed parameters. In other words, the mean errors will not ensure that the structure represents the ground state. Thus, we suggest that the calculated UV-Vis spectra be used as the standard for validating the parameters.

Although the Seminario method implemented in the AMBER package facilitates extracting the Ru-ligand force constants from QM output, the double counting problem (nonbonded interactions) causes a large distortion in the minimized geometry. For this reason, we redefined all Ru-ligand bond lengths using Hooke’s law. This approach yields a more accurate description of the geometry and spectra. Furthermore, we showed that our developed parameters reproduced successfully the expected shift of the spectra when comparing Rudcbpy and RudMebpy. This indicates that the newly developed Ru force fields are adequate to describe the photophysical behavior for analogue systems constructed from bpy and PPh₃ ligands.

5.2. Future Work

5.2.1. Optimizing the $^3$MLCT $\rightarrow$ $^3$MC Transition State of Ru(2Cl)phen and Ru(2TFA)phen and Tuning the HOMO-LUMO Energy Gap

For a more comprehensive and quantitative understanding of the quenching process (the formation of non-emissive $^3$MC state) in the proposed complexes (Ru(2Cl)phen and Ru(2TFA)phen), calculation of the potential energy curves (PECs) along the Ru—N reaction
coordinate starting from both $^1$MLCT and $^3$MC geometry is suggested. Several questions need to be addressed: i) Does $^3$MC state come from the $^3$MLCT state or directly from the $^1$MLCT state? ii) What is the energy difference between $^3$MC and $^3$MLCT, and is it positive or negative? iii) Does the activation energy correspond to the zero-point energy difference between $^3$MC and $^3$MLCT ($\Delta E^0$) or at the barrier crossing ($E^a$).

![Potential energy diagram](image)

**Figure 1.** Potential energy diagram showing the energies of the different states and the activation energies of the transition between $^3$MLCT and $^3$MC states.

First, we would optimize $^1$MLCT state to investigate the nature of the Ru—N bond length (stably bonded or dissociated in this state). From the PEC surface, we would locate the $^3$MLCT state, and then calculate the activation energy. If the value of the activation energy is positive, this indicates that the $^3$MC state is located above $^3$MLCT state and thus it is thermally populated (Fig.1).

In addition, we have shown that these complexes undergo photo-substitution, which makes them promising candidates for use as anti-cancer drugs that require photo-activation. However, they have to be activated in the visible region. Thus, to reduce the HOMO-LUMO
energy gap, (red shift the spectra), we will tune the LUMO energy by introducing electron-withdrawing groups (e.g., -COOH) to the phen ligand that stabilizes the LUMO orbitals as we have previously observed for Rudcbpy\(^1\).

5.2.2. Investigation of the photophysical properties of the 
\[(H)Ru(CO)(PPh_2C_2H_4C(O)OH)_2(bpy))PF_6 \text{ in solution and on the silica polyallylamine surface (PAA)}\]

Recently, Abbott et al. developed silica PAA surfaces as useful metal separation materials that could be easily modified [5]. These surfaces provide an opportunity for the development of a heterogeneous platform for luminescent complexes for use as either catalysts or sensors [6-7]. The \([(H)Ru(CO)(PPh_2C_2H_4C(O)OH)_2(bpy))]PF_6 \text{ (1)} \text{ complex has the same MLCT spectrum in solvent and on the surface. The } \[(H)Ru(CO)(PPh_3)_2(dcbpy))]PF \text{ (Rudcbpy) (2) complex also has the same MLCT spectrum in solvent and on the surface. While 1 has the same emission spectrum whether in solvent or on the surface, the emission of 2 was red shifted upon binding to the surface [5].}

The observed different spectroscopic behaviors of these complexes motivated us to explore at a theoretical level how the nature of the surface influences the photophysical properties and the excited states of the immobilized complexes. We first modeled \([(H)Ru(CO)(PPh_2C_2H_4C(O)OH)_2(bpy))]PF_6 \text{ and Rudcbpy to calculate their spectra in solution. Because each has two propionic acid groups and no crystal structures were available, several conformational geometries were modeled (Fig. 2). The calculated MLCT band was near 400 nm, which is blue shifted compared to the reported experiment value of 460 nm [8].}

\(^1\) See chapter 2 for details.
Therefore, we would determine the most stable conformation for the complex first in solution at the room temperature by performing MM/MD simulation using the force-field parameters that we developed. When the UV-Vis spectra are reproduced, we will attach the complex to the PAA surface and investigate its photophysical properties, which to the best of our knowledge has not been investigated theoretically. However, the PAA surface must be modeled first. To do so, we will use the plane-wave wavefunctions implemented in the Quantum ESPRESSO program [9-10]. Then, we will attach the Ru complex and study its photophysical properties by employing a combined DTF/TDDFT approach (Fig. 3).

Figure 2. Different calculated conformational geometries of [(H)Ru(CO)(PPh₂C₂H₄C(O)OH)₂(bpy)]PF₆ using B3LYP/LANL2DZ.

Figure 3. Proposed model for the complex binds to the PAA surface.
5.2.3. Improving the Developed Force-Field Parameters

To improve the minimized MM/MD geometry, we first will redefine the parameters of both bpy and PPh\textsubscript{3} at the same level of theory as done previously to determine the Ru-ligand parameters. The next step is to investigate the intermolecular interaction effects on the geometry and spectra. Thus, we plan to include more complexes. Once the geometry is enhanced, further investigation of the complex-counterion interaction can be performed. Understanding the ion-ion dependence in the solar cell efficiency and catalyzed reactions is very important [11]. Thus, we will examine the behavior of the complex-anion interaction using anions with different sizes. For each system, the complex (cation)-anion interaction energy ($\Delta E$), which is defined as the difference between the energy of the system $E_{CA}$ and the sum of the energies of the pure compositions ($E_A + E_C$), will be calculated for different positions of the anion. In addition, the anion distribution around a complex is affected by solvent. Because the polarity and the ability of the solvent to form hydrogen bonds will control the local concentration of the anions in the first solvation shell, we will also include solvents with different dielectric and hydrogen bonding properties.

5.2.4. Investigation of the acid-base behavior of [RuH(CO)dcbpy(PPh\textsubscript{3})\textsubscript{2}]PF\textsubscript{6} (Rudcbpy) and the effects of the pH on its photophysical properties

Proton-coupled electron-transfer (PCET) reaction is an important step in different chemical and biological processes such as water splitting, nitrogen fixation, proton reduction, and ribonucleotide reductase reactions [12-17]. In addition, Ru-bpy based complexes have been reported as water oxidation catalysts to produce a fuel source [18-19]. Thus, we examined the possibility of PCET in Rudcbpy in the excited state. We calculated the change in the acid-base
behavior between $S_0$ and $T_1$ states by calculating their $pK_a$ values. The $pK_a$ value is determined for the acid-dissociation reaction

$$HA_{(s)} \rightarrow H^+_{(s)} + A^-_{(s)}$$

(1)

$$pK_a = \frac{\Delta G^o_a}{2.303 RT},$$

(2)

where $\Delta G^o_a = G^o(H^+_{(s)}) + G^o(A^-_{(s)}) - G^o(HA_{(s)})$

(3)

where the first, second and third terms are the standard-state free energies of the proton, the deprotonated form of the complex (monoanion), and the protonated form of the complex, respectively. The $S_0$ of $[\text{RuH(CO)dcbpy(PPPh}_3)_2]^+$ (HA) and its deprotonated form (A⁻) were optimized using B3LYP and then a vibrational frequency calculation in ethanol was performed using PCM to obtain the structures free energy. The values obtained were inserted in eqs. 2 and 3 and used to calculate the $pK_a$ in $S_0$. We repeated the steps for the optimized complex in $T_1$ and obtained $pK_{a,T^*}$. Our calculations revealed an increase of 5 for $pK_{a,T^*}$ in the excited state indicating an increase in its basicity. This finding agrees well with Parker’s observation that the aromatic carboxylic acids become stronger bases in the triplet excited state as well as other studies of Ru(II) complexes [20-23]. This is a direct result of a charge transfer to the bpy and, consequently, the increased strength of the OH bond.

We applied another approach to study the stability (increased basicity) of the complex in $T_1$ by performing a relaxed potential energy surface scan as a function of the OH bond length for $[\text{RuH(CO)dcbpy(PPPh}_3)_2]^+$. We found that the energy required to break the OH bond in $T_1$ is twice that required in $S_0$ (Fig. 4). This also confirms our finding of increased basicity of the complex in the $T_1$ state. Thus, we conclude that no proton transfer coupled with electron transfer will occur in $\text{Rudcbpy}$. 

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We then studied the possibility of tuning the spectral properties of complex through changing pH with ethanol as solvent, comparing experiment and computation. Upon deprotonation, computation predicts a blue shift in the MLCT band of Rudcbpy (Fig. 5).

The blue shift is due to the increase of HOMO-LUMO energy gap. When carboxylic acid group loses a proton, the negative charge over the carboxylate increases. This destabilizes the LUMO orbitals and blue shift the spectra. Because the ligand is pH dependent, this could provide a useful control mechanism. We then investigated the shift experimentally by adding base (pH=11), and a small blue shift was observed (Fig. 6). The preliminary experimental data and theoretical data revealed the same trend. This indicates that the complex reactivity can be controlled by changing pH. Therefore, for more understanding of the complex behavior in different pH environments, we would perform MM/MD simulation over a range of pH and study
the change in the photophysical properties.

Figure 6. UV-Vis absorption spectra of Rudebpy in two different pH.
References


Appendix A: Equations, Figures, and Tables for Chapter 2

The statistical measures used in this study.

Mean error $\bar{\Delta}$

$$\bar{\Delta} = \frac{1}{n} \sum_{i=1}^{n} \Delta_i$$

Were the error $\Delta_i = R_i^{calc} - R_i^{exp}$

Standard deviation $\Delta_{std}$

$$\Delta_{std} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\Delta_i - \bar{\Delta})^2}$$

Mean absolute error $\bar{\Delta}_{abs}$

$$\bar{\Delta}_{abs} = \frac{1}{n} \sum_{i=1}^{n} |\Delta_i|$$

Maximum error $\Delta_{max}$

$$\Delta_{max} = max|\Delta_i|$$

Crystal structure analysis for RudMebpY

X-ray diffraction data for $[\text{RuH(CO)bis-4, 4'-}(\text{methyl})\text{bpy}(\text{PPh}_3)_2]\text{Cl}$ were collected at 100 K on a Bruker D8 Venture using MoKα-radiation ($\lambda=0.71073$ Å). Data have been corrected for absorption using SADABS1 area detector absorption correction program. Using Olex22, the structure was solved with the SHELXT3 structure solution program using Direct Methods and refined with the SHELXL4 refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to heteroatoms were found from the residual density maps, placed, and refined with isotropic thermal parameters. All other hydrogen atoms in the investigated structure were located from difference Fourier maps but finally their positions were placed in geometrically calculated positions, and refined using a riding model. Isotropic thermal parameters of the placed hydrogen
atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). The structure was found to contain indistinguishable solvent molecules within voids within the lattice. Attempts at modeling this solvent were not able to produce a suitable model. The SQUEEZE5 routine within PLATON6 was utilized to account for the residual, diffuse electron density and the model is refined against these data. A total of 185 electrons per unit cell were corrected for. This corresponds to roughly 10 methanol molecules per unit cell (180 electrons). All calculations and refinements were carried out using APEX27, SHELXTL8, Olex2, and PLATON, (Fig. A2). A comparison between selected experimental and calculated parameters listed in Table A8.

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Figure A1. The absorption spectra for Rudcbpy calculated with different methods.

Figure A2. Solid state structure of [RuH(CO)bis-4, 4’-(methyl)bpy(PPh3)2]Cl, showing the 50% probability thermal ellipsoid and the hydride position, hydrogen atoms omitted for clarity.
Figure A3. $^1$H NMR (top) and $^{31}$P NMR (bottom) spectra of [RuH(CO)bis-4, 4’-(methyl)bpy(PPh$_3$)$_2$]Cl.
Table A1. Selected atomic natural charges, q (e), in computed $S_0$ and $T_1$ for $[\text{RuH(CO)dcbpy(PPh}_3)_2]^+$

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<th>H</th>
<th>C</th>
<th>O</th>
<th>P1</th>
<th>P2</th>
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$^a$ obtained by QTAIM analysis; $^b$ obtained by NBO analysis

Table A2. Statistical measures of errors in calculated Ru-coordination bond lengths for Rubpy and Rudcbpy. (pm)

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<th>Rubdcby B3LYP</th>
<th></th>
<th>CAM-B3LYP</th>
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<th>B2PLYP3D</th>
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<td>LANL2DZ (f)</td>
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Table A3. Statistical measures of errors in calculated P-coordination bond lengths for Rubpy and Rudcbpy. (pm)

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<td>LANL2DZ (f)</td>
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Table A4. Statistical measures of errors in calculated Ru-coordination bond angles for Rubpy and Rudcbpy. (degree)

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Table A5. Statistical measures of errors in calculated P-coordination bond angles for Rubpy and Rudcbpy. (degree)

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Table A6. Selected bond lengths (Å), bond angles (º), and torsion angles (º) optimized for Rudcbpy in \( S_0 \) using different methods and for \( T_1 \) using TDDFT and \( \Delta \)SCF approaches all in ethanol, emission energies, and the calculated root mean square deviation (RMSD).

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<th></th>
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<tr>
<td>( S_0 )</td>
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<td>( T_1 ) (TDDFT)</td>
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<td></td>
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<tr>
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<td>0.767</td>
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<td>0.852</td>
<td>0.844</td>
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<td>2.134</td>
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<td>2.160</td>
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<td>1.618</td>
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<tr>
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<td>1.886</td>
<td>1.909</td>
<td>1.883</td>
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Table A7. Selected bond lengths (Å), bond angles (º), and torsion angles (º) optimized for the complexes in T₁ using TDDFT and ∆SCF orbitals all in ethanol and the calculated root mean square deviation (RMSD.)

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<td>B3LYP</td>
<td>PBE0</td>
<td>B3LYP</td>
<td>B3LYP</td>
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<td>2.406</td>
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<td>2.130</td>
<td>2.094</td>
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<td>2.138</td>
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<td>PBE0</td>
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<td>B3LYP</td>
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<td>2.144</td>
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<td>2.149</td>
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<td>1.636</td>
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Table A8. Selected bond lengths (Å), bond angles (º), and torsion angles (º) optimized for RudMebpy in $S_0$ using B3LYP/LANL2DZ and PBE0/LANL2DZ compared to X-ray data

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<td>1.854</td>
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Appendix B: Additional Figures and Tables for Chapter 3

Crystal structure analysis for RuHphen

Diffraction quality crystals were grown by slow evaporation of a methanol solution of RuHphen. The crystal selected was a yellow plate with dimensions of 0.19mm x 0.08 mm x 0.03 mm. X-ray diffraction data were collected at 100 K on a Bruker D8 Venture using MoKα-radiation (λ=0.71073 Å). Data have been corrected for absorption using SADABS1 area detector absorption correction program. Using Olex22, the structure was solved with the SHELXT3 structure solution program using Direct Methods and refined with the SHELXL4 refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to heteroatoms were found from the residual density maps, placed, and refined with isotropic thermal parameters. All other hydrogen atoms in the investigated structure were located from difference Fourier maps but finally their positions were placed in geometrically calculated positions, and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to.

The structure was found to have void space within the lattice and are observed when viewing a packing diagram down the crystallographic b axis. The voids are centered over the twofold rotation axis of the C2/c, space group, further complicating unsuccessful attempts at modeling the solvent and anion. The presence of chloride in this void is known, to account for charge balance. However, the void contains additional unknown solvent molecules that are believed to be methanol as the crystals were grown from a slow evaporation of a methanol solution. The SQUEEZE5 routine within PLATON6 was utilized to account for the residual, diffuse electron density within the void and the model is refined against these data. A total of 376 electrons per unit cell were corrected for. All calculations and refinements were carried out using APEX27, SHELXTL8, Olex2, and PLATON, (Fig. B1). 1

Figure B1. Solid state structure of [RuH(CO)phen(PPh$_3$)$_2$]Cl, (RuHphen) showing the 50% probability thermal ellipsoid, hydrogen atoms omitted for clarity.
Figure B2. $^1$P NMR (top) and IR (bottom) spectra of RuHphen.
Table B1. Second-order perturbation interaction energy ($E(2)$) (kcal/mol) from the donation from P atom to PPh$_3$ and Ru for complexes with mixed ligands at the B3LYP/LANL2DZ level obtained by NBO analysis.

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<th>acceptor</th>
<th>occupancy (e)</th>
<th>$E(2)$</th>
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<td>$\sigma^*(C-C)$</td>
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<td>0.59</td>
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<td>$\sigma^*(C-C)$</td>
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$^a$CR(2)P is 2s.
Table B2. Second-order perturbation interaction energy (E(2)) (kcal/mol) from the donation from P atom to PPh₃ and Ru for complexes with analogues ligands at the B3LYP/LANL2DZ level obtained by NBO analysis.

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a CR(2)P is 2s, c RY*(1)C28 (s(0.36%)p99.99(92.20%)d20.61(7.44%))