

**Polyazine-Bridged Ru(II),Pt(II) Trimetallic and Tetrametallic Supramolecular Complexes
Exhibiting Unusual Excited State Dynamics Important in Catalysis and PDT Drug Development**

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Abstract

The goal of this research was to develop structurally diverse polyazine-bridged Ru(II),Pt(II) trimetallic and tetrametallic supramolecular complexes and study the impact of component variation on the redox, spectroscopic, and excited state properties that influence photoinduced charged separation and multielectron reduction. These complexes are active photocatalysts for H₂O reduction to H₂. Tetrametallic complexes with the supramolecular architecture $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$ (Ru₃Pt; TL = phen = 1,10-phenanthroline or Ph₂phen = 4,7-diphenyl-1,10-phenanthroline; BL' = dpp = 2,3-bis(2-pyridyl)pyrazine or dpq = 2,3-bis(2-pyridyl)quinoxaline) feature a trimetallic dpp-bridged Ru(II) light absorber coupled to a *cis*-PtCl₂ reactive metal center. Trimetallic complexes with one less Ru-based light absorbing unit, $[\{(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL')PtCl_2\}^{4+}$ (Ru₂Pt; BL' = dpp or dpq), represent a new supramolecular architecture that was designed and synthesized to provide less complex systems for excited state analysis. Both the Ru₃Pt and Ru₂Pt systems have a remote Ru center separated from the reactive Pt site designed to provide extended ³MLCT lifetimes relative to directly coupled $[(TL)_2Ru(BL)PtCl_2]^{2+}$ systems.

The building block synthetic method used in constructing supramolecules provides the ability to purify and analyze the properties following each synthetic step, allowing sub-unit variation and structural diversity. Building a knowledge base about the properties of smaller, less complicated structures is critical in understanding the electrochemistry, spectroscopy, and excited state dynamics of multi-metallic, multi-ligand complexes. Electrochemical analysis of the $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$ complexes suggests a HOMO localized on the terminal Ru centers ($E_{1/2}$ (Ru^{II/III}) = 1.56-1.63 V vs. Ag/AgCl) and a LUMO localized on the remote BL' coordinated to the reactive Pt site, with the energy dictated by the BL' identity ($E_{1/2}$ = -0.32 or -0.33 V for BL' = dpp or $E_{1/2}$ = -0.02 or -0.05 V for BL' = dpq). This provides

spatially separated HOMOs and LUMOs which predict lowest-lying charge separated states. The complexes are robust UV and visible light absorbers due to multiple broad, overlapping ligand centered and metal-to-ligand charge transfer (MLCT) transitions. The lowest energy $^1\text{MLCT}$ absorption is centered around 540-550 nm for the four tetrametallic complexes with high molar absorptivity (31,000-42,000 $\text{M}^{-1}\text{cm}^{-1}$). BL' variation has only a small impact on the electronic absorption spectroscopy, while the TL variation greatly enhances the absorptivity between 350 nm and 500 nm from 29,000 to 42,000 $\text{M}^{-1}\text{cm}^{-1}$ for complexes with TL = phen and Ph₂phen, respectively.

The tetrametallic $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes exhibit unusual excited state dynamics as well as spatially separated HOMOs and LUMOs. The lowest lying optically populated state is a terminal $\text{Ru} \rightarrow \mu\text{-dpp}$ MLCT in all the Ru₃Pt and Ru₂Pt systems reported herein. The terminal $\text{Ru}(\text{d}\pi)$ based HOMO and $\text{BL}'(\pi^*)$ based LUMO suggests a lower lying terminal $\text{Ru} \rightarrow \text{BL}'$ CS state in all systems. Because the lowest lying terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS (charge separated) state is optically inaccessible, indirect population occurs. The tetrametallic $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes have similar excited state lifetimes (τ) of 75-83 ns, and they exhibit quantum yields of emission (Φ^{em}) of 7.1×10^{-4} (when BL' = dpp) and $3.2\text{-}3.7 \times 10^{-4}$ (when BL' = dpq). The lifetimes are shortened and the emission quantum yields are quenched in comparison to the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')]\text{PtCl}_2]^{6+}$ models which possess the same emissive terminal $\text{Ru} \rightarrow \mu\text{-dpp}$ $^3\text{MLCT}$ state with $\tau = 110$ ns and $\Phi^{\text{em}} = 1.0\text{-}1.1 \times 10^{-3}$. In marked contrast to the large number of Ru polyazine systems studied, both monometallic and supramolecular complexes, the lowest lying $^3\text{MLCT}$ state of the Ru₃Pt complexes is not populated with unit efficiency due to ^3CS state population from the emissive terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT state and a higher energy $^3\text{MLCT}$ state, likely the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CT state. The degree of population of this state is strongly dependent on the LUMO energy or driving force for population. Stabilization of the BL' = dpq(π^*) compared to higher energy dpp(π^*) provides a larger driving force for intramolecular electron transfer to populate the ^3CS state, resulting in ca. 40 % and 95 % population of the emissive state when BL' = dpq and dpp, respectively. This suggests ca. 60 % and 5 % indirect population of the non-

emissive ^3CS state via a higher-lying $^3\text{MLCT}$ state and the terminal $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ emissive state when $\text{BL}' = \text{dpq}$ and dpp , respectively. These complexes violate Kasha's rule, an unusual occurrence for Ru(II) polypyridine complexes, as the emissive state is not populated with unit efficiency. Instead, the degree of population of the emissive state is dependent on the excitation wavelength.

The Ru_3Pt complexes are active photocatalysts for H_2O reduction to H_2 . In the presence of light and the sacrificial electron donor, DMA (*N,N*-dimethylaniline), the tetrametallic complexes collect electrons on the ligand π^* orbitals of the central Ru to serve as photoinitiated electron collectors. The photocatalytic activity in H_2 production is drastically impacted by BL' identity, consistent with the enhanced driving force for charge separation to move electrons toward the *cis*- PtCl_2 moiety. After photolysis for 10 h, $15 \pm 1 \mu\text{mol}$ ($66 \pm 4 \text{ TON}$) and $4 \pm 1 \mu\text{mol}$ ($18 \pm 1 \text{ TON}$) of H_2 were produced using $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, respectively. Varying TL to Ph_2phen serves to enhance light absorptivity and subsequently increase H_2 production to $21 \pm 1 \mu\text{mol}$ ($94 \pm 6 \text{ TON}$) and $5 \pm 1 \mu\text{mol}$ ($23 \pm 2 \text{ TON}$) using $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, respectively. The identity of BL' greatly influences the ability to direct the flow of charge through the supramolecular architecture impacting photocatalysis, while the identity of TL serves to fine tune the light absorbing and excited state properties.

Due to the complicated excited state properties imparted by the large number of MLCT transitions in the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes, the analogous $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ complexes were designed and a synthetic scheme developed. The trimetallics possess similar electronic absorption spectroscopy with fewer terminal metal-based transitions due to removal of one $(\text{TL})_2\text{Ru}^{\text{II}}(\text{dpp})$ sub-unit and allow for distinguishable spectroscopic shifts resulting from perturbation of specific sub-units and the related molecular orbitals. The trimetallic complexes exhibit similar redox properties with the HOMO localized on the terminal Ru and the LUMO localized on the remote BL' , providing a low lying ^3CS state. Similar degrees of emission quenching are observed with the trimetallic complexes and their $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')]\text{PtCl}_2^{4+}$ models as was

observed in the tetrametallic complexes. The values of τ and Φ^{em} measured for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2]^{4+}$ were 90 ns and 1.1×10^{-3} , respectively, and these values were 100 ns and 5.2×10^{-4} for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$. Similar to the Ru_3Pt systems, the lifetimes are shortened and the emission is quenched compared to the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')]^{4+}$ models ($\tau = 120$ ns and $\Phi^{\text{em}} = 1.50 \times 10^{-3}$, regardless of BL' identity). These values provide ca. 98 % and 45 % population of the emissive state in the Ru_2Pt systems for BL' = dpp and dpq, respectively, suggesting ca. 2 % and 55 % population of the non-emissive ^3CS state for BL' = dpp and dpq, respectively. This supports the use of this new Ru_2Pt motif as models to study the excited state dynamics. A substantial difference was observed between the excitation and absorption spectra for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$, consistent with non-unity population of the emissive $^3\text{MLCT}$ excited state. The simplified electronic absorption spectroscopy allowed the use of nanosecond transient absorption (TA) spectroscopy to analyze the excited state, and strong evidence of violation of Kasha's rule through partial population of the terminal $\text{Ru}(\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS state ($\tau = 25$ ns) in addition to the emissive terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ state ($\tau = 120$ ns) was observed through excitation-based emission spectroscopy and time-resolved TA spectroscopy.

The synthesis, electrochemistry, electronic absorption spectroscopy, and steady-state and time-resolved emission spectroscopy for the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ complexes as well as photocatalytic H_2 production with $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ and transient absorption spectroscopy of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$, are reported herein. The work discussed within this dissertation provides in depth knowledge about the effects of component modification on the excited state dynamics and photocatalytic activity of structurally diverse Ru_3Pt and Ru_2Pt supramolecular complexes that is important in developing photochemical molecular devices. Unusual excited state dynamics make it clear that much remains to be uncovered about structure-property relationship in these complex mixed-metal, mixed-ligand supramolecular motifs. These supramolecular motifs also have applications in

photodynamic therapy drug development and are currently under investigation by members of the Brewer research group.

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List of Abbreviations

^1ES = singlet excited state
 ^1GS = singlet ground state
 $^1\text{MLCT}$ = singlet metal-to-ligand charge transfer
 ^3ES = triplet excited state
 $^3\text{MLCT}$ = triplet metal-to-ligand charge transfer
 A = absorbance
 b = pathlength
 BAS = bioactive site
 BL = bridging ligand
 bpm = 2,2'-bipyrimidine
 bpy = 2,2'-bipyridine
 c = concentration
 CCD = charge-coupled device
 CH_3CN = acetonitrile
 cm = centimeter
 CS = charge separated state
 CT = charge transfer
 CV = cyclic voltammetry
 DMA = *N,N*-dimethylaniline
 DMF = *N,N*-dimethylformamide
 dmgBF_2 = (difluoroboryl)dimethylglyoximate
 DMSO = dimethylsulfoxide
 dpb = 2,3-bis(2-pyridyl)benzoquinoxaline
 dpp = 2,3-bis(2-pyridyl)pyrazine
 dpq = 2,3-bis(2-pyridyl)quinoxaline
 ED = electron donor
 EDTA = ethylenediaminetetraacetic acid
 ER = electron relay
 Et_2O = diethyl ether
 EtOH = ethanol
 eV = electron volt
 f = oscillator strength
 FeCp_2 = ferrocene
 HOMO = highest occupied molecular orbital
 IL = intraligand
 J = joule
 k_{d-d} = rate constant for population of ligand field state
 k_{et} = rate constant for intramolecular electron transfer
 k_{ic} = rate constant for internal conversion

k_{isc} = rate constant for intersystem crossing
 k_{nr} = rate constant for non-radiative decay
 k_q = rate constant for excited state quenching
 k_r = rate constant for radiative decay
 k_{rxn} = rate constant for photochemical reaction
 K_{SV} = Stern-Volmer constant
 LA = light absorber
 LED = light emitting diode
 LF = ligand field
 L-pyr = (4-pyridine)oxazolo-[4,5-*f*]phenanthroline
 LUMO = lowest unoccupied molecular orbital
 m = meter
 M = molarity
 MeOH = methanol
 MV^{2+} = methyl viologen
 NAD^+ = nicotinamide adenine dinucleotide
 NHE = normal hydrogen electrode
 OD = optical density
 OPO = optical parametric oscillator
 pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine
 PEC = photoinitiated electron collector
 Ph₂phen = 4,7-diphenyl-1,10-phenanthroline
 phen = 1,10-phenanthroline
 PMD = photochemical molecular device
 PMT = photomultiplier tube
 py = pyridyl
 pz = pyrazine
 qn = quinoxaline
 RM = reactive metal
 RT = room temperature
 SWV = square wave voltammetry
 tatpp = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2'3'-*c*:3'',2''-1:2''',3'''-*n*]pentacene
 tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2'3'-*c*:3'',2''-1:2''',3'''-*n*]pentacene-10,21-quinone
 TBAH = tetra-*n*-butylammonium hexafluorophosphate
^tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine
 TL = terminal ligand
 TON = turnover number
 tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine
 V = volt
 ϵ = extinction coefficient
 λ = wavelength
 τ = excited state lifetime

Φ^{em} = quantum yield

Φ^{pop} = quantum yield of population of a state

Ψ_{ES} = excited state wavefunction

Ψ_{GS} = ground state wavefunction

Thesis Statement

The goal of this research is to develop structurally diverse Ru(II),Pt(II) mixed-ligand supramolecular complexes with remote and long-lived Ru→BL ³MLCT states and study how their redox, spectroscopic, and photophysical properties imparted by component variation impact their photoinitiated electron collection and excited state dynamics with applications in solar energy conversion.

List of Publications

“A new paradigm for photodynamic therapy drug design: multifunctional, supramolecular DNA photomodification agents featuring Ru(II)/Os(II) light absorbers coupled to Pt(II) or Rh(III) bioactive sites” Knoll, J. D.; Brewer, K. J., Invited chapter in *Progress in Inorganic Chemistry* **2013**, submitted for publication.

“Terminal and bridging ligand variation in structurally diverse polyazine-bridged Ru(II),Pt(II) supramolecules with low lying charge separated states providing insight into the functioning as H₂O reduction photocatalysts to produce H₂.” Knoll, J. D.; Higgins, S. L. H.; White, T. A.; Brewer, K. J. *Inorganic Chemistry* **2013**, accepted for publication.

“Supramolecular complexes as photochemical molecular devices for solar energy conversion via water reduction to produce hydrogen.” White, T. A.; Manbeck, G.; Whitaker, B.; Quinn, K.; Zhou, R.; Dent, E.; Knoll, J.; Wang, J.; Higgins, S.; Arachchige, S.; Brewer, K. J. *From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry* **2012**, 57, 581-582.

“A series of supramolecular complexes for solar energy conversion via water reduction to produce hydrogen: an excited state kinetic analysis of Ru(II),Rh(III),Ru(II) photoinitiated electron collectors.” White, T. A.; Knoll, J. D.; Arachchige, S. M.; Brewer, K. J. *Materials* **2012**, 5, 27-46.

“Supramolecular complexes as photochemical molecular devices for solar energy conversion via water reduction to produce hydrogen fuel,” Brewer, K. J.; White, T. A.; Arachchige, S.; Tsui, H.-M.; Knoll, J.; Gardner, P.; Shaw, R. *American Solar Energy Society – Proc. ASES Annual Conference*, **2011**.

“Electrochemical, spectroscopic, and photophysical properties of structurally diverse polyazine-bridged Ru(II),Pt(II) and Os(II),Ru(II),Pt(II) supramolecular motifs.” Knoll, J. D.; Arachchige, S. M.; Wang, G.; Rangan, K.; Miao, R.; Higgins, S. L. H.; Okyere, B.; Zhao, M.; Croasdale, P.; Magruder, K.; Sinclair, B.; Wall, C.; Brewer, K. J. *Inorganic Chemistry* **2011**, 50 (18), 8850-8860.

“A structurally diverse Ru^{II},Pt^{II} tetrametallic motif for photoinitiated electron collection and photocatalytic hydrogen production.” Knoll, J. D.; Arachchige, S. M.; Brewer, K. J. *ChemSusChem* **2011**, 4 (2), 252-261.

1. Introduction

1.1. Solar-to-Chemical Energy Conversion

The quest for clean, renewable fuels is a critical issue as the demand for energy rapidly increases and the earth's supply of fossil fuels decreases.¹ Carbon-based fuels such as oil, natural gas, and coal provide the majority of the energy used in the world today. These resources are non-renewable, and their combustion by-products have negative environmental impacts. Renewable energy research is currently focused on sources such as solar, wind, geothermal, and hydroelectric energy. Solar-to-chemical energy conversion in which water splitting is driven by energy from the sun to produce chemical fuels will be discussed in the context of this dissertation.

1.1.1. Light Absorption

The absorption of radiation in the form of ultraviolet (UV) and visible light is needed for solar-to-chemical energy conversion. The electromagnetic spectrum which features the approximate energy, frequency, wavelength, and wavenumber for each type of radiation as well as the process promoted by each type is given in **Figure 1.1**.² The relationships between energy, frequency, and wavelength of a photon are discussed in **Equations 1.1-1.3**. The energy of a photon, E , is related to its frequency, ν , by **Equation 1.1**,

$$E = h\nu \quad (1.1)$$

where h is the Planck constant (4.136×10^{-15} eV·s). The photon's frequency and wavelength, λ , are inversely related by **Equation 1.2**,

$$\nu = \frac{c}{\lambda} \quad (1.2)$$

where c is the speed of light (3×10^8 m/s). Using **Equations 1.1** and **1.2** to relate the energy and wavelength of a photon gives **Equation 1.3**.

$$E = \frac{hc}{\lambda} \quad (1.3)$$

The typical wavelength range for UV light is 10-400 nm and that of visible light is 400-700 nm. UV and visible light typically contain the appropriate energy to promote electronic transitions (1.7-3.0 eV). Other common transitions in molecules include vibrational transitions (promoted by infrared radiation) and rotational transitions (promoted by microwave radiation). Electronic transitions are useful in solar-to-chemical energy conversion as they provide a method to control the motion of electrons in a molecule in a desired direction, i.e. toward a substrate at a localized catalytic site. The ability to drive electronic transitions makes solar energy an attractive resource.

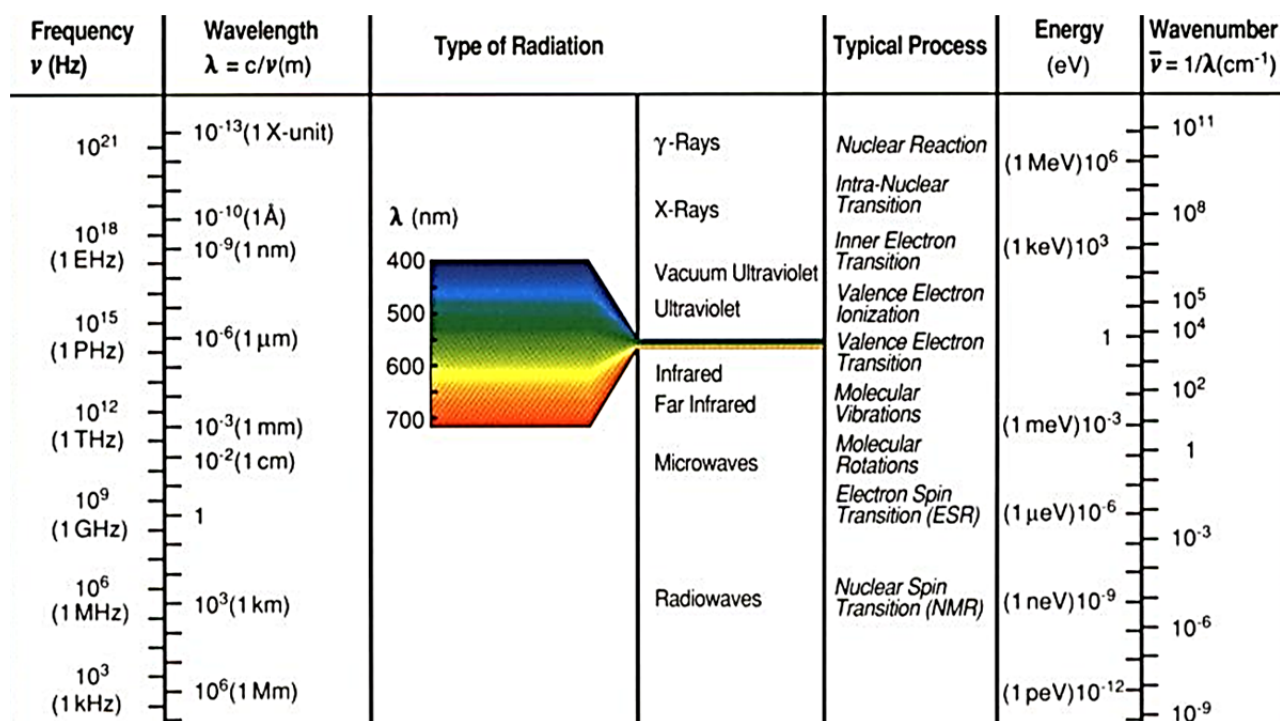


Figure 1.1: The electromagnetic spectrum highlighting the frequency, wavelength, energy, wavenumber, and typical processes resulting from each type of radiation. Figure adapted from reference 2.

1.1.2. Solar Energy

The sun provides an abundant amount of energy to the earth. More energy reaches the earth's surface in one hour (4.3×10^{20} J) than the amount consumed on the planet in one year (4.1×10^{20} J).³⁻⁶ The solar spectrum is pictured in **Figure 1.2**, displaying the intensity of light at each wavelength absorbed by a 1 m^2 surface as a function of wavelength.⁷ The majority of the energy delivered to the surface of the earth is between 280 nm and 2500 nm, corresponding to 4.4 eV and 0.5 eV.³ Despite the sun's potential as an abundant, globally available source of inexhaustible energy, an efficient and commercially viable means of harnessing solar energy and transforming it into a usable fuel is still elusive.

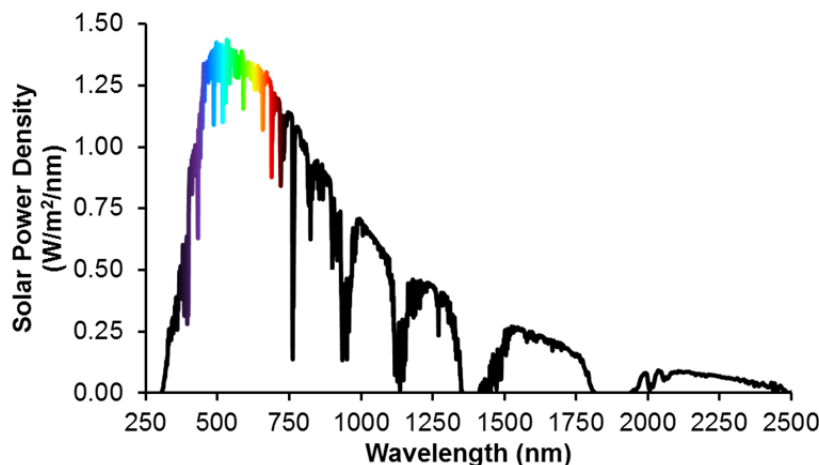


Figure 1.2: Solar spectrum depicting the solar power density as a function of wavelength. The solar power density is the intensity of light absorbed by a 1 m^2 surface at each wavelength. Figure adapted from reference 7.

1.1.3. H_2O Splitting

The search for clean, renewable fuels directs much research toward the production of H_2 which has the highest power density of any non-nuclear based fuel (**Table 1.1**),⁶ providing great potential in this arena. H_2 combustion in air is a clean process as it produces H_2O rather than environmentally harmful byproducts.⁸ Because H_2O is also a source of H_2 , this process is cyclic. H_2O can be split into its components through two processes: a single electron process that produces $\text{H}^\bullet$ and $\text{OH}^\bullet$ and requires ca. 5 eV, or a multielectron process which produces H_2 and O_2 and only requires ca. 1.23 eV.⁹ The overall

multielectron water splitting reaction and the reduction and oxidation half reactions at pH = 7 and 25 °C (potentials vs. NHE) are given below in **Equations 1.4-1.6**.



The half reaction potentials are dependent on the pH. At pH = 0, the half reaction potential is 0.00 V vs. NHE, and the potential changes by -0.059 V per pH unit, as described by the Nernst equation. The H_2O oxidation half reaction also changes with pH so that the overall reaction potential is a constant -1.23 V . Conveniently, the majority of the solar spectrum (ca. 75 %) provides sufficient energy to drive the uphill, multielectron water splitting reaction; however, a photocatalyst that can efficiently harness the sun's energy and convert it to chemical energy is necessary for solar driven water splitting to occur.

Table 1.1: Energy Densities of Non-Nuclear Based Fuels ^a

Fuel	Energy Density (kWh/kg)
Sucrose	4.6
Methanol	6.2
Coal	9.0
Gasoline	13.3
Hydrogen	30.1

^a Data from reference 6.

Many challenges arise in the design and development of an efficient photocatalyst for H_2O splitting. First, light from the sun must be efficiently absorbed and stored in the form of a long-lived excited state with sufficient energy to drive the reaction. Charge separation should occur to create a potential gradient on the molecular level, and multiple reducing/oxidizing equivalents must be collected to enable the multielectron process. Finally, the reducing equivalents must be delivered to H_2O to

produce H_2 and the oxidizing equivalents must be utilized to produce O_2 .^{6,10-12} Splitting of H_2O by **Equation 1.4** is complicated, as it involves several bond breaking and bond forming steps. Designing systems which successfully carry out each of these processes is a major challenge. Much research focuses on the reduction half reaction (**Equation 1.5**),^{8,10,13,14} and recently an increased effort is evolving that focuses on the oxidation half reaction (**Equation 1.6**).^{15,16}

1.2 Ru(II)-Polyazine Complexes as Light Absorbers

Ru(II) coordination complexes with three bidentate polyazine ligands, $[\text{Ru}(\text{TL})_3]^{2+}$ (TL = terminal ligand), exhibit suitable properties for efficient solar energy harvesting that if coupled to catalysts can result in conversion to chemical energy. These properties include potent UV and visible light absorption, sufficiently long-lived excited states, and strongly reducing/oxidizing excited states that display excited state electron transfer reactions with properties tuned by ligand variation.^{17,18} The excited state properties of these complexes are tuned through ligand variation, providing them as interesting and useful candidates for light absorbers in solar energy conversion schemes. The most well-studied homoleptic Ru(II)-polyazine complex is $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine).¹⁸⁻²² $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline and Ph_2phen = 4,7-diphenyl-1,10-phenanthroline), **Figure 1.3**, are analogues with redox and photophysical properties that reflect the TL identity.

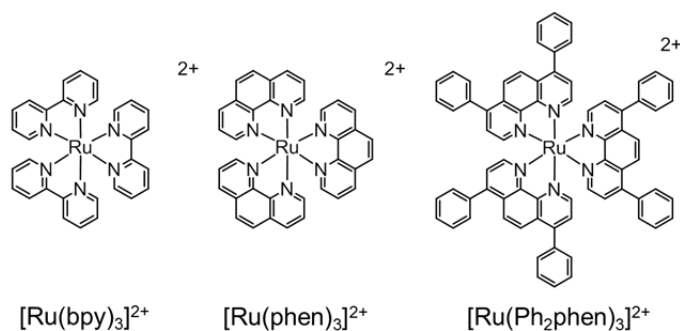


Figure 1.3: Structural representations of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$. bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline.

1.2.1. Redox Properties

Analysis of the potential of redox couples provides relative frontier orbital energies and analysis of the reversibility suggests whether a species undergoes a chemical reaction following the redox event.^{23,24} Cyclic voltammetry is an electrochemical technique that analyzes redox active species using a potential sweep method. The waveform (**Figure 1.4A**) and cyclic voltammogram (**Figure 1.4B**) for the $\text{Fe}(\text{C}_5\text{H}_5)_2/\text{Fe}(\text{C}_5\text{H}_5)_2^+$ redox couple are provided below as an example to explain this analytical tool. Beginning at the initial potential (E_i) of 0.30 V vs. Ag/AgCl, the potential is increased at a fixed scan rate of 0.1 V/s. When the switching potential (E_s) is reached at 0.60 V, the scan direction is reversed until the final potential (E_f) of 0.30 V. Oxidation of $\text{Fe}(\text{C}_5\text{H}_5)_2$ to produce $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ occurs while scanning in the positive direction (anodically), and reduction of the oxidized species back to the original $\text{Fe}(\text{C}_5\text{H}_5)_2$ species occurs while scanning in the opposite direction (cathodically). In the case of $\text{Fe}(\text{C}_5\text{H}_5)_2$, the anodic peak current (i_p^a) and the cathodic peak current (i_p^c) are equivalent ($i_p^a/i_p^c = 1$), indicating that the process is reversible. A reversible redox process does not involve bond forming or breaking following the oxidation or reduction. The separation (ΔE_p) between the cathodic and anodic peak potentials (E_p^c and E_p^a , respectively) is independent of scan rate and provides the number of electrons transferred (n) in the redox process (**Equation 1.7**).

$$\Delta E_p = E_p^c - E_p^a = \frac{59 \text{ mV}}{n} \quad (1.7)$$

The half wave potential ($E_{1/2}$) of a reversible couple is calculated using **Equation 1.8**.

$$E_{1/2} = \frac{E_p^c + E_p^a}{2} \quad (1.8)$$

The half wave potential for the $\text{Fe}(\text{C}_5\text{H}_5)_2/\text{Fe}(\text{C}_5\text{H}_5)_2^+$ couple is 0.46 V vs. Ag/AgCl. Redox couples are considered quasi-reversible if $i_p^a/i_p^c \neq 1$ and irreversible if either i_p^a or $i_p^c = 0$. In the case of an irreversible couple, the E_p^a or E_p^c is reported in lieu of $E_{1/2}$. In the context of this dissertation, Ru-centered and

polyazine ligand-centered redox couples are generally reversible or quasi-reversible and Pt-centered redox couples are generally irreversible.

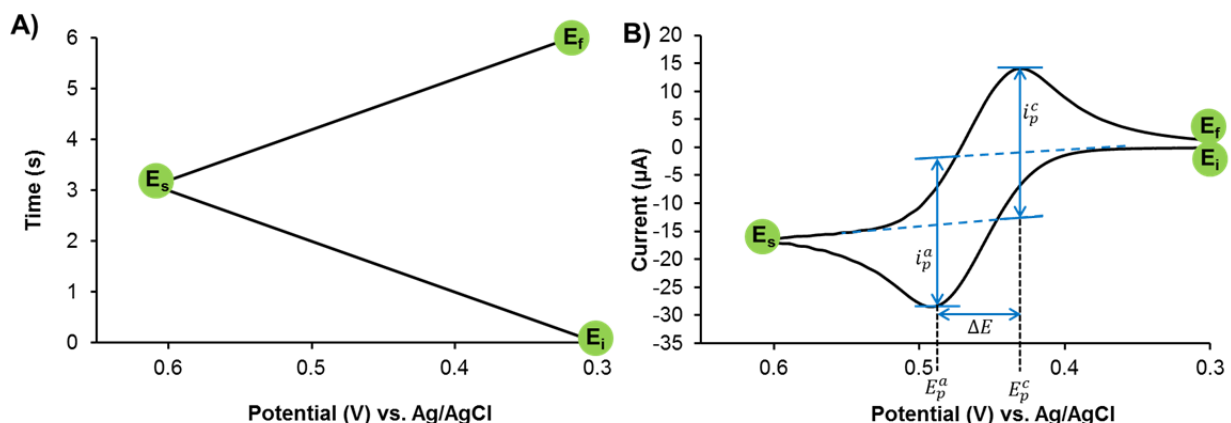


Figure 1.4: A) Potential waveform and B) cyclic voltammogram of the $\text{Fe}(\text{C}_5\text{H}_5)_2^+/\text{Fe}(\text{C}_5\text{H}_5)_2$ couple. E_i = initial potential, E_s = switching potential, E_f = final potential, E_p^a = anodic peak potential, E_p^c = cathodic peak potential, ΔE_p = potential separation between the anodic and cathodic peak potentials, i_p^a = anodic peak current, i_p^c = cathodic peak current.

Electrochemical analysis of Ru(II)-polyazine complexes provides information about the redox properties of molecules related to the frontier orbital energetics.^{23,24} $[\text{Ru}(\text{TL})_3]^{2+}$ complexes exhibit Ru-based oxidations when scanned anodically and ligand-based reductions when scanned cathodically. The cyclic voltammogram for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in CH_3CN is given in **Figure 1.5**. Anodic scanning reveals one reversible couple in the electrochemical window at 1.31 V vs. Ag/AgCl, corresponding to the $\text{Ru}^{\text{II/III}}$ oxidation. This complex features three equivalent bpy ligands that are electronically coupled through the Ru center, resulting in the reduction of each ligand to occur sequentially. The three $\text{bpy}^{0/-}$ reductions occur at -1.30 V, -1.49 V, and -1.74 V vs. Ag/AgCl.²⁵ The electrochemical properties are consistent with a $\text{Ru}(\text{d}\pi)$ -based HOMO (highest occupied molecular orbital) and a $\text{bpy}(\pi^*)$ -based LUMO (lowest unoccupied molecular orbital) for $[\text{Ru}(\text{bpy})_3]^{2+}$.

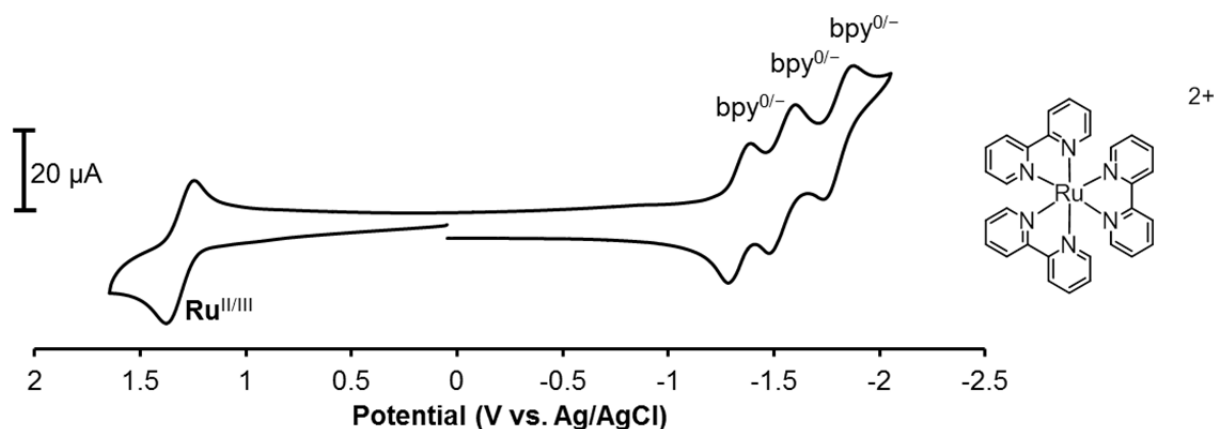


Figure 1.5: Cyclic voltammogram of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in RT deoxygenated CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte and a glassy carbon working electrode, Ag/AgCl reference electrode, and Pt wire auxiliary electrode. bpy = 2,2'-bipyridine.

Ligand variation in homoleptic Ru(II)-polyazine complexes from bpy to phen or Ph_2phen does not significantly impact the electrochemical properties. The $\text{Ru}^{\text{II/III}}$ oxidation occurs at 1.31 V and 1.29 V for $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$, respectively, suggesting that this ligand variation does not change the electronics enough to significantly impact the $\text{Ru}(\text{d}\pi)$ orbital (HOMO) energy.^{25,26} The LUMO also exhibits very similar energies upon variation from bpy to phen to Ph_2phen , as the first reduction occurs at -1.31 V and -1.27 V for $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$, respectively. Altering the skeletal backbone of bpy to produce phen and Ph_2phen does not have a significant impact on the σ -donating or π -accepting abilities of the ligand, and subsequently the redox properties are maintained across this series. Interestingly, this ligand variation does impact light absorbing and excited state properties (discussed below).

1.2.2. Light Absorbing Properties

Electronic absorption spectroscopy provides information about the light absorbing capabilities of a photoactive species. Absorption of a photon is necessary for population of an electronic excited state, and the HOMO-LUMO energy gap (ΔE) must match the energy of the incident photon ($h\nu$). In order for an electronic transition to occur, the ground state and excited state wavefunctions (Ψ_{GS} and Ψ_{ES}) must

overlap.²⁷⁻²⁹ The electronic transition should also obey symmetry and spin selection rules.²⁹ In **Equation 1.9**, the transition moment operator ($\hat{\mu}_e$) dictates the intensity of the transition from the GS to ES.

$$\langle \Psi_{GS} | \hat{\mu}_e | \Psi_{ES} \rangle = \int \Psi_{GS} \hat{\mu}_e \Psi_{GS} d\nu \quad (1.9)$$

For an electronic transition to occur, the symmetry selection rule requires that the integral of the transition moment ($\Psi_{ES} \hat{\mu}_e \Psi_{GS} d\nu$) must be nonzero (a change in dipole must occur). The square of the transition moment is directly proportional to the probability that a transition will occur from the GS to the ES, and this is also directly proportional to the oscillator strength of the transition, f , **Equation 1.10**.

$$f = 4.32 \times 10^{-9} \int_{-\nu}^{\nu} \varepsilon(\nu) d\nu \quad (1.10)$$

The strength of the transition is expressed in the extinction coefficient at a given energy, $\varepsilon(\nu)$. The Beer-Lambert law provides a relationship between ε and the absorption of the species in **Equation 1.11**,

$$A_\lambda = \varepsilon_\lambda bc \quad (1.11)$$

where A_λ is the absorption of the species at a given wavelength, ε_λ is the extinction coefficient of the species at that wavelength, b is the pathlength of the sample through which light passes, and c is the concentration of the species. According to the spin selection rule, a transition in which the spin is maintained between the GS and ES ($^1\text{GS} \rightarrow ^1\text{ES}$) is allowed and a transition that results in a spin flip ($^1\text{GS} \rightarrow ^3\text{ES}$) is forbidden. Spin-orbital coupling, often observed in heavy metal complexes, provides exceptions to the spin selection rule, allowing formally spin-forbidden transitions to occur. The value of ε gives information into the spin-allowedness of the transition, as spin-forbidden transitions have ε between 1 and $10^2 \text{ M}^{-1}\text{cm}^{-1}$ and spin-allowed transitions have ε between 10^2 and $10^5 \text{ M}^{-1}\text{cm}^{-1}$.

A general description of electronic transitions in octahedral metal complexes is necessary to understand the electronic absorption spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$. A block molecular orbital (MO) diagram for a d^6 octahedral (O_h) metal complex with π -backbonding ligands is depicted in **Figure 1.6**. Although $[\text{Ru}(\text{bpy})_3]^{2+}$ has D_3 symmetry, the Ru center is in a pseudo-octahedral environment. The block MO diagram for an O_h complex is given for simplification. This MO diagram is constructed by a linear

combination of atomic orbitals (LCAO) in which each MO is a combination of more than one atomic orbital. The MOs are labeled “M” when they receive more contribution from metal AOs than ligand AOs and “L” when they receive more contribution from ligand AOs than metal AOs. Each block represents a set of orbitals of similar energy, and the black blocks represent filled or partially filled orbitals while the white blocks represent unfilled orbitals. Four types of electronic transitions are commonly discussed in such complexes.³⁰ A metal-to-ligand charge transfer (MLCT) transition occurs when an electron moves from an orbital that is predominantly localized on a metal to one predominantly localized on a ligand. A ligand-to-metal charge transfer (LMCT) transition is the opposite, in which an electron is promoted from a largely ligand-based orbital to a largely metal-based orbital. An intraligand (IL) transition occurs when an electron is promoted from a π orbital to a π^* orbital within the same ligand, and a ligand field (LF) transition occurs when an electron is promoted from one metal-based orbital to another in the same metal. The energies of these transitions are dictated by the metal and the ligand set.

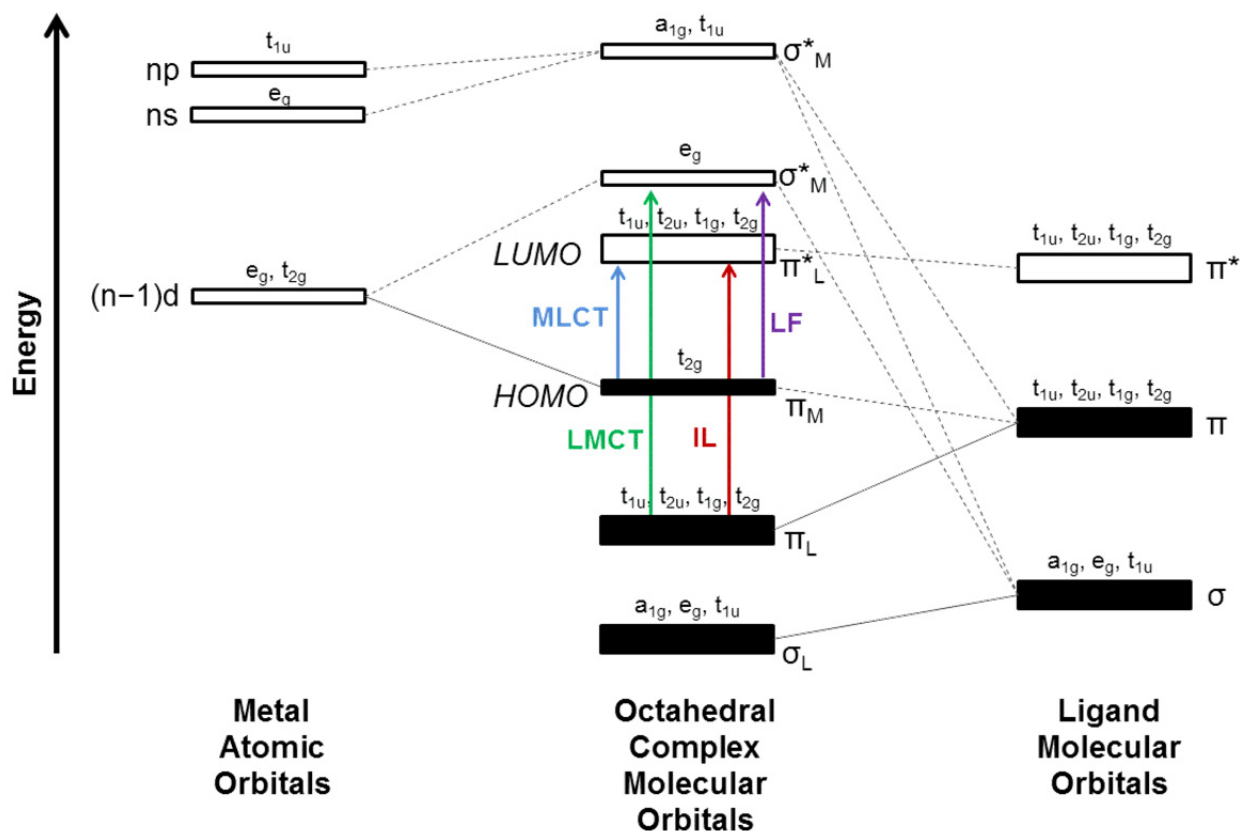


Figure 1.6: Block molecular orbital diagram for a d⁶ octahedral metal complex with a π-backbonding ligand. Black blocks indicate filled or partially filled orbitals and white blocks indicate unfilled orbitals. HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital, MLCT = metal-to-ligand charge transfer transition, LMCT = ligand-to-metal charge transfer transition, IL = intraligand transition, LF = ligand field transition. Figure adapted from reference 30.

The electronic absorption spectroscopy of [Ru(bpy)₃]²⁺ (**Figure 1.7**) is well studied.^{17-20,22,27,28,31,32} The sharp, intense absorption band centered at 286 nm ($\epsilon = 8.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) is a result of bpy $\pi \rightarrow \pi^*$ transitions, and the broad absorption band centered at 450 nm ($\epsilon = 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) is due to Ru(d π) $\rightarrow$ bpy(π^*) ¹MLCT transitions. The magnitude of ϵ suggests that these transitions are spin-allowed. The low energy absorption ($\lambda > 500 \text{ nm}$, $\epsilon \sim 5 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$) is a result of the spin-forbidden Ru(d π) $\rightarrow$ bpy(π^*) ³MLCT absorption which gains intensity due to the large degree of spin-orbit coupling imparted by Ru.²²

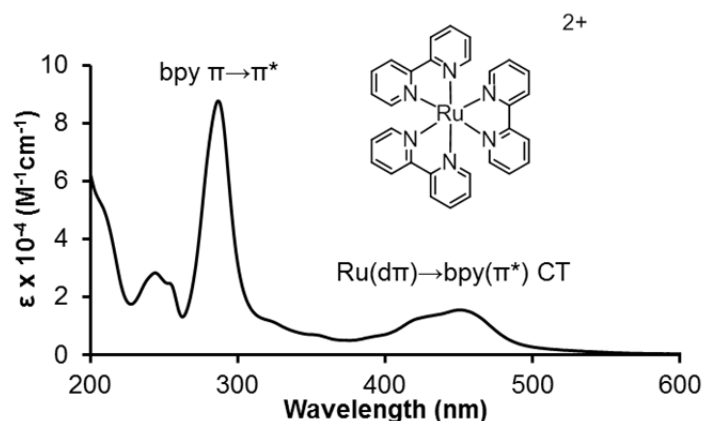


Figure 1.7: Electronic absorption spectrum of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in RT CH_3CN . bpy = 2,2'-bipyridine. Spectrum is consistent with data reported in reference 32.

While no significant differences in the redox properties of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ were observed, the light absorbing properties display differences that are dictated by the ligand identity. The overlaid electronic absorption spectra of these three complexes are given below in **Figure 1.8**. In the UV region, the IL $\pi \rightarrow \pi^*$ transition in $[\text{Ru}(\text{phen})_3]^{2+}$ occurs at 262 nm ($\epsilon = 1.02 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$), blue-shifted compared to $[\text{Ru}(\text{bpy})_3]^{2+}$.²⁵ The IL transition for $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ was not reported. The most dramatic impact of ligand variation is observed in the visible region. The $\text{Ru}(\text{d}\pi) \rightarrow \text{phen}(\pi^*)$ CT transition occurs at a maximum of 443 nm ($\epsilon = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), quite similar to that of $[\text{Ru}(\text{bpy})_3]^{2+}$,²⁵ however, the visible light absorption is greatly enhanced in the case of $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$, with $\epsilon = 3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 460 nm, a value nearly twice that of the bpy or phen analogues.³³ This observation indicates that the overlap between the GS and ES wavefunctions for $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ is larger than for TL = bpy or phen, therefore increasing the oscillator strength corresponding to the $\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi)$ ^1CT transition. Contribution from the Ph_2phen MOs to the formally $\text{Ru}(\text{d}\pi)$ orbital set strongly impacts the allowedness of this ^1CT transition. Analysis of the electronic absorption spectroscopy of these complexes highlights that the proper selection of bidentate polyazine ligands provides control over the light absorbing properties of $\text{Ru}(\text{II})$ complexes.

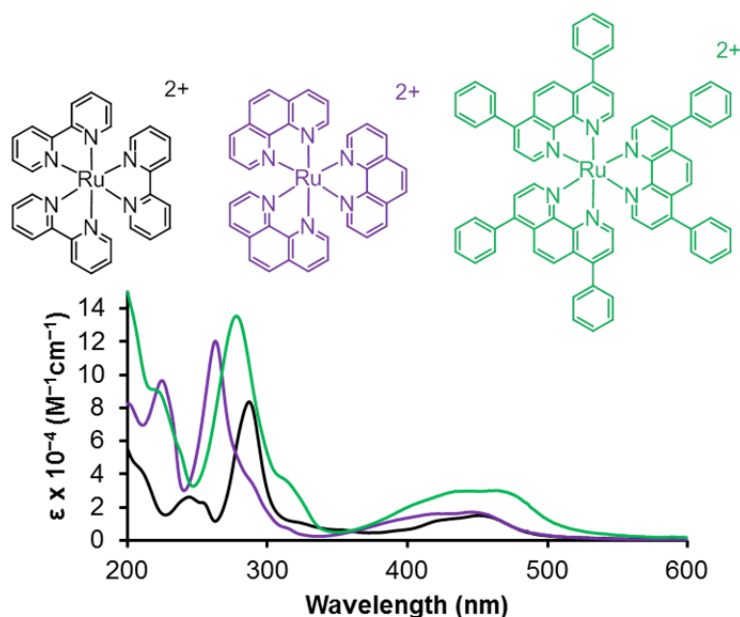


Figure 1.8: Electronic absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ measured in spectral grade CH_3CN . bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline. Spectra are consistent with data reported in references 25 and 33.

1.2.3. Excited State Properties

Electronic excited states must be understood to elucidate the photophysical or photochemical processes that occur in a molecule following the absorption of a photon. In a very simple scheme in **Figure 1.9**, an electron occupying a low energy orbital in the ^1GS is promoted to a previously unoccupied higher energy orbital to provide the ^1ES species as a result of photon absorption. The ^3ES is then populated through intersystem crossing in which the excited electron undergoes a spin flip.

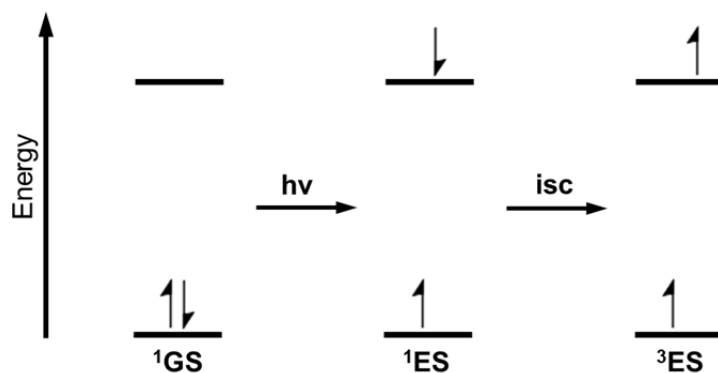


Figure 1.9: Simplified molecular orbital diagrams showing the electronic configuration of a singlet ground state (^1GS), singlet excited state (^1ES), and triplet excited state (^3ES). $h\nu$ = excitation with a photon, isc = intersystem crossing.

These electronic excited states can be more deeply understood with a Morse potential energy surface diagram (**Figure 1.10**) that depicts the energy of the electronic and vibrational states as a function of the internuclear distance axis for a Ru(II) polyanine complex.^{27,29} In the case of $[\text{Ru}(\text{TL})_3]^{2+}$ complexes, the lowest lying ^1ES and ^3ES are $^1\text{MLCT}$ and $^3\text{MLCT}$ in nature. Excitation of the ^1GS complex results in population of any of the numerous vibrational states within the $^1\text{MLCT}$ state. Through vibrational relaxation (k_{vr}) the lowest energy vibrational state of the $^1\text{MLCT}$ state is populated. Population of a vibrational state of the $^3\text{MLCT}$ excited state occurs through intersystem crossing (k_{isc}) with unit efficiency (quantum yield, $\Phi = 1$) when there is sufficient overlap between vibrational states in each of the electronic states. This ultrafast process occurs on the order of 10^2 fs.³⁴ The excited state then undergoes vibrational relaxation (k_{vr}') to populate the thermally equilibrated excited state from which radiative decay (emission of a photon, k_r) and nonradiative decay (relaxation without emission of a photon, k_{nr}) occurs to result in population of the ^1GS . Emission from this $^3\text{MLCT}$ state follows Kasha's rule which states that emission only occurs from the lowest energy excited state regardless of excitation energy.³⁵

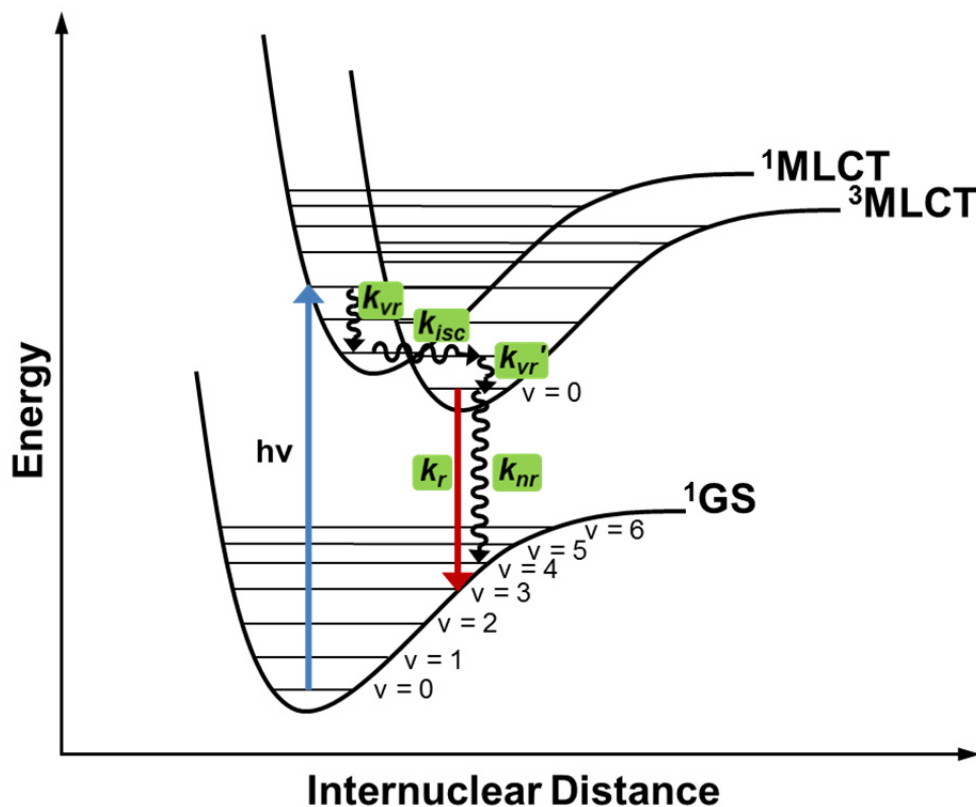


Figure 1.10: Morse potential energy surface diagram depicting the excited state processes in vibrational and electronic states in a $[\text{Ru}(\text{TL})_3]^{2+}$ complex. Straight arrows represent radiative processes and wavy arrows represent nonradiative processes. ^1GS = singlet ground state, $^1\text{MLCT}$ = singlet metal-to-ligand charge transfer state, $^3\text{MLCT}$ = triplet metal-to-ligand charge transfer state, $h\nu$ = photoexcitation, k_{isc} = rate constant for intersystem crossing, k_{vr} = rate constant for vibrational relaxation, k_r = rate constant for radiative decay, k_{nr} = rate constant for nonradiative decay.

The Jablonski diagram in **Figure 1.11** is a simplified version of the Morse potential energy surface diagram, in which the bold horizontal lines correspond to the thermally equilibrated vibrational level of the ^1GS , $^1\text{MLCT}$, and $^3\text{MLCT}$ and the stacked thin lines correspond to higher energy vibrational states within each electronic excited state. State diagrams such as that depicted in **Figure 1.12** are further simplifications to the previously discussed excited state diagrams. The vibrational levels are omitted, and it should be noted that the diagonal intersystem crossing (labeled k_{isc}) depicted in the state diagram is the sum of the horizontal k_{ixc} and vertical k_{vr}' to populate the thermally equilibrated $^3\text{MLCT}$ state, and the nonradiative decay from the $^3\text{MLCT}$ state to the ^1GS (labeled k_{nr}) is the sum of intersystem crossing from

the $^3\text{MLCT}$ state to the ^1GS and vibrational relaxation. These simplified state diagrams are necessary as Ru(II) complexes are constructed to be larger and their photophysical processes become more complex.

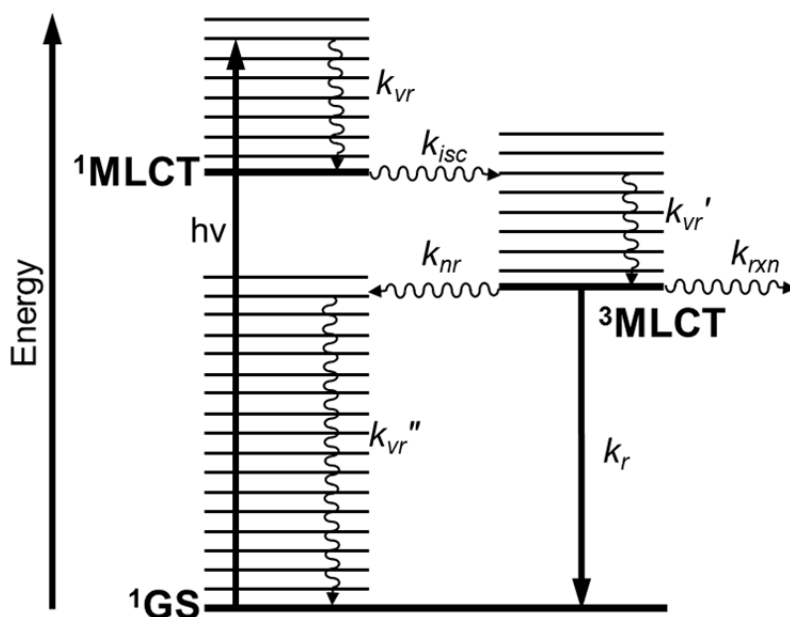


Figure 1.11: Jablonski diagram depicting the excited state processes of a $[\text{Ru}(\text{TL})_3]^{2+}$ complex. Straight lines represent radiative processes and wavy lines represent nonradiative processes. ^1GS = singlet ground state, $^1\text{MLCT}$ = singlet metal-to-ligand charge transfer state, $^3\text{MLCT}$ = triplet metal-to-ligand charge transfer state, k_{vr} = rate constant for vibrational relaxation, k_{isc} = rate constant for intersystem crossing, k_r = rate constant for radiative decay, k_{nr} = rate constant for nonradiative decay, k_{rxn} = rate constant for a photochemical reaction.

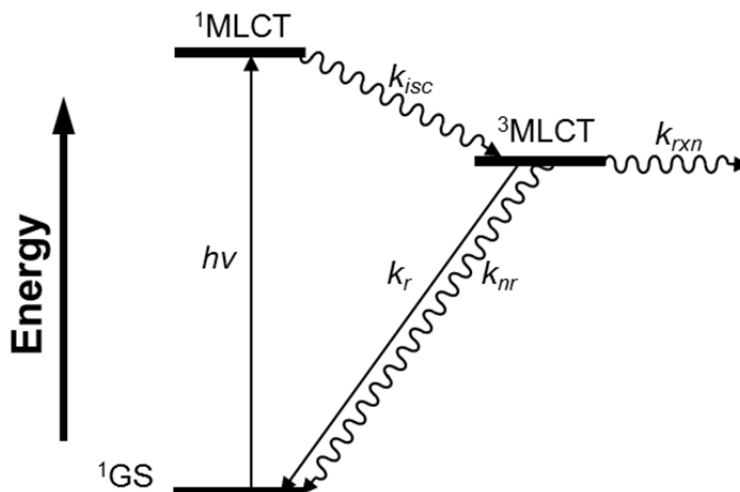


Figure 1.12: Simplified state diagram for a $[\text{Ru}(\text{TL})_3]^{2+}$ complex. Straight lines represent radiative processes and wavy lines represent nonradiative processes. TL = bidentate polyazine terminal ligand, ^1GS = singlet ground state, $^1\text{MLCT}$ = singlet metal-to-ligand charge transfer, $^3\text{MLCT}$ = triplet metal-to-ligand charge transfer, k_{isc} = rate constant for intersystem crossing, k_r = rate constant for radiative decay, k_{nr} = rate constant for non-radiative decay, k_{rxn} = rate constant for photochemical reaction.

The emissive nature of the $^3\text{MLCT}$ excited state in $[\text{Ru}(\text{TL})_3]^{2+}$ complexes (TL = bpy, phen, Ph_2phen) provides a convenient probe into the excited state dynamics. The excited state lifetime (τ) and the quantum yield of emission (Φ^{em}) provide insight into the rate constants for various excited state processes. The inverse of the sum of all rate constants for the processes which deactivate the $^3\text{MLCT}$ excited state constitutes τ (**Equation 1.12**). The value for τ for a complex in the absence of a photochemical reaction is represented as

$$\tau = \frac{1}{k_r + k_{nr}} \quad (1.12)$$

where k_r and k_{nr} are the rate constants for radiative and non-radiative decay, respectively. The quantum yield of emission, Φ^{em} , provides a ratio of the number of photons emitted to the number of photons absorbed (**Equation 1.13**).

$$\Phi^{\text{em}} = \frac{\# \text{ photons emitted}}{\# \text{ photons absorbed}} \quad (1.13)$$

The values of k_r and k_{nr} are also related to Φ^{em} and the quantum yield of population of the $^3\text{MLCT}$ state (Φ^{pop}) as shown in **Equation 1.14**.

$$\Phi^{em} = \Phi^{pop} \frac{k_r}{k_r + k_{nr}} \quad (1.14)$$

Typically in Ru(II)-polyazine complexes, population of the ³MLCT ES occurs with unit efficiency ($\Phi^{em} = 1$), which allows the following relationship between τ and Φ^{em} (**Equation 1.15**) to be true.

$$\Phi^{em} = k_r \tau \quad (1.15)$$

If the lifetime of the emissive state and the quantum yield of emission are known, the value of k_r calculated from **Equation 1.15** can be inserted into **Equations 1.12** to determine a value for k_{nr} .

Analysis of the excited state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, and $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$ reveals that the ligand set has a dramatic impact on Φ^{em} and τ . In deoxygenated RT CH_3CN , $[\text{Ru}(\text{bpy})_3]^{2+}$ emits from the ³MLCT excited state at 603 nm with $\Phi^{em} = 0.07$ and $\tau = 850$ ns.^{28,32} Substituting bpy for phen to afford $[\text{Ru}(\text{phen})_3]^{2+}$ results in a blue-shifted emission (585 nm), decreased Φ^{em} (0.020) and shortened τ (400 ns).²⁵ This trend violates the energy gap law which states that k_{nr} increases as the energy gap between the emissive ES and the GS (ΔE) decreases.³⁶ The reduced Φ^{em} and τ of $[\text{Ru}(\text{phen})_3]^{2+}$ is due to the restricted bending of phen vs. bpy providing reduced d-orbital splitting, leading to more efficient population of the thermally accessible ³LF state which results in the decreased Φ^{em} and shortened τ .¹⁹ Use of Ph_2phen to produce $[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+}$, in addition to dramatically enhancing visible light absorption, provides an excited state species with a much larger Φ^{em} (0.366) and a drastically longer-lived excited state (4680 ns) with a slightly red-shifted emission (610 nm) compared to the phen and bpy analogues.³⁷ While this enhanced emission using Ph_2phen is not well understood, it may be attributed to a smaller degree of population of a ³LF state or less perturbation of the internuclear distance between the ground state and the excited state which would result in less efficient nonradiative decay (k_{nr}). The large differences in light absorption and excited state properties as a function of ligand variation and the minor impact on redox properties of $[\text{Ru}(\text{TL})_3]^{2+}$ provides important information to be considered in designing larger assemblies of molecules for photocatalysis and other light induced applications.

1.3. Extending the Molecular Architecture through Supramolecular Chemistry

1.3.1. Supramolecular Chemistry Defined

Incorporating $[\text{Ru}(\text{TL})_3]^{2+}$ -type light absorbers (LA) into larger molecular assemblies is employed to construct photocatalysts for H_2O reduction. The coupling relies on the $[\text{Ru}(\text{TL})_3]^{2+}$ type unit to retain desirable and tunable redox and excited state reactivity characteristic of these chromophores. Supramolecular chemistry is an appropriate arena for building such systems. In the scope of this dissertation, a supramolecular complex is described as an assembly of components that each execute a distinct task and work together to perform a complicated function, as proposed by Vincenzo Balzani in 1987.³⁸ When this function such as intramolecular electron or energy transfer is initiated by light, the complex is known as a photochemical molecular device (PMD).^{4,38-40} The ability to complete this function is governed by the selection of individual components and the order in which they are assembled. Incorporation of Ru(II)-polyazine LAs into multimetallic supramolecular assemblies requires the use of bridging ligands. This perturbs the properties of the sub-units used to build the supramolecule. Understanding and controlling the perturbations of sub-units' properties upon incorporation into supramolecular assemblies is paramount to these applications and a major focus of this research.

1.3.2. Bridging Ligands

The ability to covalently link multiple metal centers and control properties is critical in building PMDs to facilitate directional energy or electron transfer. TLs (discussed above) such as bpy, phen, and Ph_2phen possess only one bidentate site for metal coordination, while bridging ligands (BLs) feature two or more metal coordination sites.^{32,41} The commonly employed bis-bidentate BLs bpm (2,2'-bipyrimidine), dpp (2,3-bis(2-pyridyl)pyrazine), dpq (2,3-bis(2-pyridyl)quinoxaline), and dpb (2,3-bis(2-pyridyl)benzoquinoxaline), are shown in **Figure 1.13**.

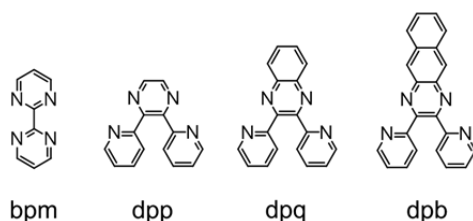


Figure 1.13: Bis-bidentate polyazine bridging ligands. bpm = 2,2'-bipyrimidine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, dpb = 2,3-bis(2-pyridyl)benzoquinoxaline.

Replacing TLs with BLs in monometallic Ru(II)-polyazine complexes has important ramifications on the redox, spectroscopic, and photophysical properties. Replacing bpy TL(s) in $[\text{Ru}(\text{bpy})_3]^{2+}$ with one or more dpp BL to form $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ or $[\text{Ru}(\text{dpp})_3]^{2+}$ (**Figure 1.14**, **Table 1.2**) gives insight into the impacts of BL vs. TL on the properties of the supramolecular assembly.^{32,42} It is important to first consider the energetics of the uncoordinated bpy and dpp ligands. The electrochemistry of the two ligands in DMF gives reduction potentials of -2.05 V and -1.89 V vs. Ag/AgCl for bpy and dpp, respectively, suggesting that the dpp π^* orbitals are stabilized compared to bpy π^* orbitals.⁴³ This trend is also observed in Ru(II) complexes where the dpp reductions occur prior to bpy reductions. The cyclic voltammograms of the tris-homoleptic complexes $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dpp})_3]^{2+}$ each exhibit three consecutive reduction processes that correspond to reduction of each bpy or dpp.^{32,42} The first reduction in both $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[\text{Ru}(\text{dpp})_3]^{2+}$ is assigned as $\text{dpp}^{0/-}$ ($E_{1/2} = -1.01$ V and -0.91 V vs. Ag/AgCl, respectively, **Table 1.2**). The 100 mV difference is attributed to the nature of the ligands coupled to the dpp through the Ru center. Coupling of two dpp BLs in $[\text{Ru}(\text{dpp})_3]^{2+}$ that are more electron withdrawing than two bpy TLs in $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ results in a slightly more easily reduced dpp. The impact of the ligand set has a significant impact on the $\text{Ru}(\text{d}\pi)$ orbitals, as observed in the 420 mV difference in $\text{Ru}^{\text{II/III}}$ oxidation for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dpp})_3]^{2+}$ ($E_{1/2} = 1.30$ V and 1.72 V, respectively). The more electron withdrawing nature of dpp vs. bpy stabilizes the $\text{Ru}(\text{d}\pi)$ orbitals, requiring a larger potential to oxidize $[\text{Ru}(\text{dpp})_3]^{2+}$ compared to its bpy analogue. The potential for the $\text{Ru}^{\text{II/III}}$ oxidation in the heteroleptic $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ complex falls between that of the two homoleptic analogues ($E_{1/2} = 1.38$ V), as the $\text{Ru}(\text{d}\pi)$ orbitals are influenced by coordination of two bpy TLs and one dpp BL.

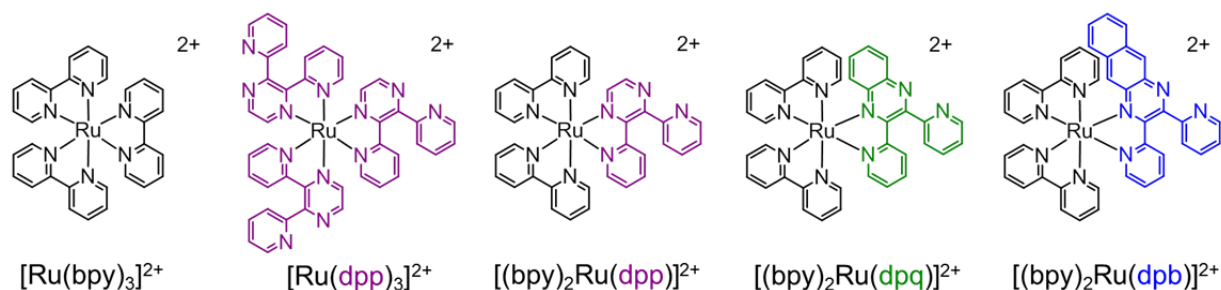


Figure 1.14: Structural representations of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dpp})_3]^{2+}$, $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$, $[(\text{bpy})_2\text{Ru}(\text{dpq})]^{2+}$, and $[(\text{bpy})_2\text{Ru}(\text{dpb})]^{2+}$. bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, dpb = 2,3-bis(2-pyridyl)benzoquinoxaline.

Table 1.2: Electrochemical and Spectroscopic Data for Ru(II) Monometallic Complexes

Complex	$E_{1/2}^{\text{ox}}$ (V) ^a	$E_{1/2}^{\text{red1}}$ (V) ^a	$E_{1/2}^{\text{red2}}$ (V) ^a	λ^{abs} (nm) ^b	λ^{em} (nm) ^b	τ (ns) ^b
$[\text{Ru}(\text{bpy})_3]^{2+ \text{ c}}$	1.30	-1.30	-1.49	450	603	850
$[\text{Ru}(\text{phen})_3]^{2+ \text{ d}}$	1.31	-1.31	-1.42	443	585	400
$[\text{Ru}(\text{Ph}_2\text{phen})_3]^{2+ \text{ e}}$	1.29	-1.27		460	610	4680
$[\text{Ru}(\text{dpp})_3]^{2+ \text{ c}}$	1.72	-0.91	-1.08	455	636	270
$[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+ \text{ f}}$	1.38	-1.01	-1.46	430, 470(sh) 430 ^g	675 680 ^g	135 380 ^g
$[(\text{bpy})_2\text{Ru}(\text{dpq})]^{2+ \text{ h}}$	1.43	-0.74	-1.41	517 ^g	760 ^g	< 20 ^g
$[(\text{bpy})_2\text{Ru}(\text{dpb})]^{2+ \text{ i}}$	1.48	-0.62	-1.25	550	^j	^j
$[(\text{phen})_2\text{Ru}(\text{dpp})]^{2+ \text{ f}}$	1.39	-1.07	-1.35	435, 465(sh)	654	252
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]^{2+ \text{ k}}$	1.39	-1.04	-1.38	474	664	820

^a Potentials vs. Ag/AgCl. Measured in deoxygenated RT CH_3CN with 0.1 M TBAH supporting electrolyte. ^b Measured in deoxygenated RT H_2O unless otherwise noted. ^c From references 28 and 32. ^d From reference 25. ^e From reference 33. ^f From reference 32. ^g Measured in deoxygenated RT CH_3CN . ^h From reference 44. ⁱ From reference 44. ^j Emission not detected. ^k From reference 26.

The spectroscopic properties of this series of Ru(II) homoleptic and heteroleptic complexes are dictated by the ligand set and are presented in **Table 1.2**. The lowest energy absorption bands are similar for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dpp})_3]^{2+}$ in H_2O , with $\lambda^{\text{max}} = 452$ and 455 nm assigned as $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT and $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT transitions, respectively.^{32,42} The almost identical absorption maxima are a result of the stabilized $\text{Ru}(\text{d}\pi)$ orbitals and ligand(π^*) orbitals of $[\text{Ru}(\text{dpp})_3]^{2+}$ compared to $[\text{Ru}(\text{bpy})_3]^{2+}$, resulting in very similar HOMO-LUMO gaps ($\Delta E = 2.61$ V for $[\text{Ru}(\text{bpy})_3]^{2+}$ and 2.63 V for $[\text{Ru}(\text{dpp})_3]^{2+}$). The HOMO-LUMO gap for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ is 2.39 V and the lowest energy absorption band is red

shifted to 470 nm, due to the relatively destabilized Ru(d π) orbitals and stabilized dpp(π^*) orbitals compared to [Ru(dpp)₃]²⁺. The emission from the lowest-lying ³MLCT excited states for [Ru(bpy)₃]²⁺, [Ru(dpp)₃]²⁺, and [(bpy)₂Ru(dpp)]²⁺ in RT deoxygenated CH₃CN decreases in energy in this series, with λ^{max} = 603 nm, 636 nm, and 675 nm, respectively, consistent with the absorption energies.^{32,42} The excited state lifetimes also decrease with the emission energy, consistent with the energy gap law. Because [(bpy)₂Ru(dpp)]²⁺ and [Ru(dpp)₃]²⁺ serve as common subunits in supramolecular Ru(II)-polyazine complexes, understanding these properties is important in careful design of larger assemblies.

The impact of BL variation in [(bpy)₂Ru(BL)]²⁺ is critical in designing PMDs for directional energy or electron transfer, as MLCT excitation moves an electron to the BL that will be attached to a reactive metal. Replacing dpp with dpq and dpb (**Figure 1.14**) provides a means of tuning the LUMO energy in Ru(II)-polyazine LAs. The most prominent effect of BL variation in this motif is observed in the first reduction potential, assigned as BL^{0/-} reduction ($E_{1/2}$ = -1.01 V (dpp), -0.74 V (dpq), and -0.62 V (dpb) vs. Ag/AgCl), resulting from the increased aromaticity which enhances stabilization of the BL(π^*) orbitals.^{44,45} A small positive shift in the Ru^{II/III} oxidation is observed ($E_{1/2}$ = 1.38 V, 1.43 V, and 1.48 V for BL = dpp, dpq, and dpb, respectively) owing to the enhanced electron withdrawing ability from dpp to dpq to dpb. The lowest energy absorption, Ru(d π)→BL(π^*) ¹CT, shifts from 430 nm to 517 nm to 550 nm as the BL aromaticity increases, consistent with the decreasing HOMO-LUMO gaps of 2.39 V, 2.17 V, and 2.10 V obtained from the electrochemical analysis.^{44,45} Emission from the lowest-lying ³MLCT excited state is sensitive to BL identity. The emission of [(bpy)₂Ru(dpq)]²⁺ occurs with a maximum of 760 nm and a < 20 ns lifetime, red-shifted about 80 nm compared to the dpp analogue.⁴⁵ Emission from the Ru(d π)→dpb(π^*) CT excited state in [(bpy)₂Ru(dpb)]²⁺ was not detectable, but it is expected to occur at λ^{max} > 760 nm.⁴⁴ Incorporating an appropriate combination of these bis-bidentate BLs into larger supramolecular assemblies can provide a means of directing electron or energy flow from ligands with higher energy acceptor orbitals to those with lower energy acceptor orbitals.

Varying TL in Ru(II) monometallic complexes has a significant impact on the excited state properties. This is somewhat surprising given the formally $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ nature of the emissive state. In a series of complexes of the form $[(\text{TL})_2\text{Ru}(\text{dpp})]^{2+}$ where TL = bpy, phen, or Ph_2phen (**Table 1.2**), the electrochemistry suggests a $\text{Ru}(\text{d}\pi)$ -based HOMO and a $\text{dpp}(\pi^*)$ -based LUMO.^{26,32} The very small impact of TL identity on the $\text{Ru}(\text{d}\pi)$ orbitals is similar to that observed in the $[\text{Ru}(\text{TL})_3]^{2+}$ complexes, and the $\text{dpp}(\pi^*)$ orbitals are weakly coupled to the TLs, as dpp reduces at -1.01 V, -1.07 V, and -1.04 V for TL = bpy, phen, and Ph_2phen . The three complexes exhibit a lowest energy absorption around 470 nm assigned as a $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^1CT transition. The remarkable difference in these complexes is observed in the excited state lifetimes of the emissive $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT excited states ($\lambda^{\text{max}} = 680$ nm, 654 nm, and 664 nm for TL = bpy, phen, and Ph_2phen).^{26,32} Despite the lowest lying excited state being largely localized on the Ru and the dpp ligand, τ greatly varies from 380 ns to 252 ns to 820 ns for TL = bpy, phen, and Ph_2phen . This suggests that the TL-based orbitals significantly contribute to the HOMO which is largely localized on the $\text{Ru}(\text{d}\pi)$ orbitals. Knowledge of the effects of TLs and BLs on the redox and spectroscopic properties aids in the selection of suitable components in designing efficient PMDs.

Expanding the supramolecular architecture through coordination of a second Ru(II) center to the BL open coordination site to produce the $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{TL})_2]^{4+}$ bimetallic complexes has a significant impact on the orbital energetics leading to light absorbing and excited state properties quite different from the parent $[(\text{TL})_2\text{Ru}(\text{dpp})]^{2+}$ complexes. A series of $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{TL})_2]^{4+}$ complexes, where TL = bpy, phen, or Ph_2phen , are depicted in **Figure 1.15** and the redox, spectroscopic, and photophysical data are compiled **Table 1.3**. Cyclic voltammograms of $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ are provided in **Figure 1.16** to highlight the change in orbital energetics. The $\mu\text{-dpp}(\pi^*)$ orbitals are stabilized in the bimetallic complex compared to the uncoordinated $\text{dpp}(\pi^*)$ orbitals in the monometallic complex, and the $\text{dpp}^{0/-}$ couple shifts 0.40 V positive from -1.01 V to -0.61 V vs. Ag/AgCl .³² This stabilization is commonly observed upon electropositive metal coordination to a polyazine ligand. The

bimetallic complex exhibits a dpp^{-2-} couple at -1.09 V which is then followed by reduction of each of the bpy TLs. The presence of a second $\text{Ru}^{\text{II}}(\text{bpy})_2$ unit results in two separate $\text{Ru}^{\text{II/III}}$ couples at 1.43 V and 1.61 V. While the two Ru centers are in equivalent coordination environments and are expected to have identical redox potentials, they are electronically coupled through dpp so oxidation of one Ru impacts the other Ru center, making it more difficult to oxidize. Additionally, the $\text{Ru}^{\text{II/III}}$ couple shifts 50 mV more positive from 1.38 V to 1.43 V for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$, respectively, as the coordination of a second electropositive metal center slightly stabilizes the $\text{Ru}(\text{d}\pi)$ orbitals.

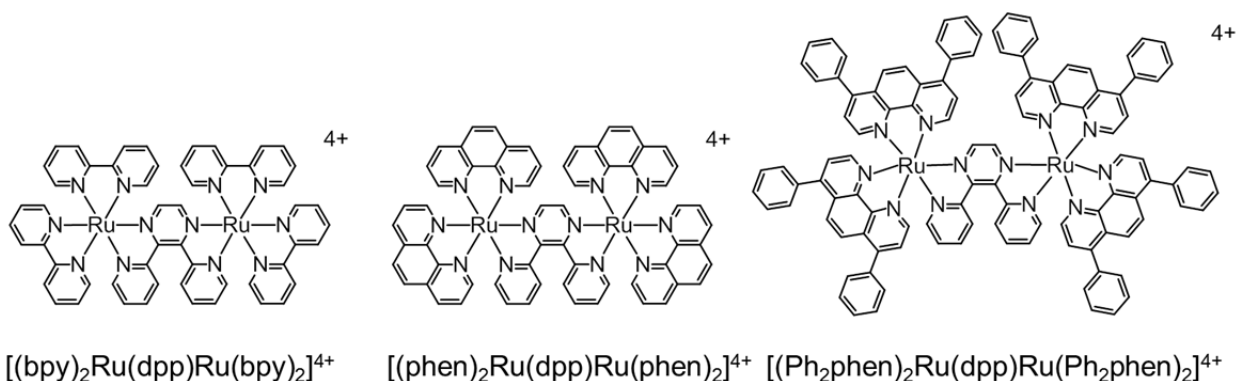


Figure 1.15: Structural representations of Ru(II),Ru(II) bimetallic complexes. bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

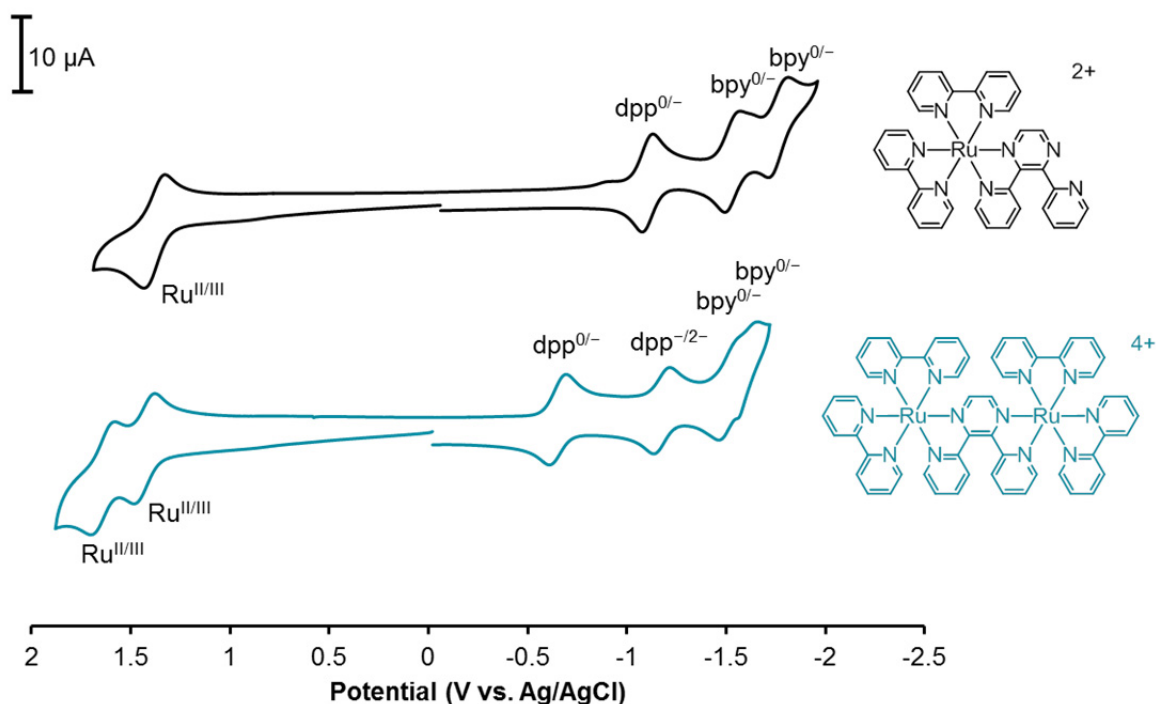


Figure 1.16: Cyclic voltammograms of $[(bpy)_2Ru(dpp)](PF_6)_2$ (—) and $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ (—) measured in RT CH_3CN with a glassy carbon working electrode, silver wire auxiliary electrode, and Ag/AgCl reference electrode. Voltammograms are consistent with data from reference 32.

The changes observed in the orbital energetics have significant impacts on the light absorbing and photophysical properties of the metal complexes when comparing $[(bpy)_2Ru(dpp)]^{2+}$ and $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$.⁴⁶ The overlaid electronic absorption spectra of these two complexes in CH_3CN are featured in **Figure 1.17** and the spectroscopic data are compiled in **Table 1.3**. The lowest energy MLCT transition shifts from 465 nm for the monometallic complex to 523 nm for the bimetallic complex, a result of the smaller HOMO-LUMO gap (2.04 V vs. 2.39 V for $[(bpy)_2Ru(dpp)]^{2+}$ and $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$, respectively) due to significant $dpp(\pi^*)$ stabilization. The $dpp \pi \rightarrow \pi^*$ IL transition is also red-shifted from underneath the intense $bpy \pi \rightarrow \pi^*$ transitions in $[(bpy)_2Ru(dpp)]^{2+}$ to a more prominent shoulder centered around 340 nm for $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$. The number of bpy TLs doubles upon coordination of a $Ru^{II}(bpy)_2$ moiety to the $[(bpy)_2Ru(dpp)]^{2+}$ complex and the $bpy(\pi^*)$ orbitals are relatively unaffected between the monometallic and bimetallic complexes. As a result, the

transitions involving bpy (bpy $\pi \rightarrow \pi^*$ and Ru(d π) $\rightarrow$ bpy(π^*) CT) occur at similar energies for the two complexes with ϵ values approximately doubled for the bimetallic complex, suggesting that ϵ is additive for these transitions. The emissive Ru(d π) $\rightarrow$ dpp(π^*) ^{3} CT excited state is also impacted by dpp(π^*) stabilization with emission occurring at 758 nm for [(bpy) $_2$ Ru(dpp)Ru(bpy) $_2$] $^{4+}$ compared to 680 nm for [(bpy) $_2$ Ru(dpp)] $^{2+}$.⁴⁷ This lower energy emission results in a shorter excited state lifetime with τ = 126 ns for the bimetallic compared to 380 ns for the monometallic complex, consistent with the energy gap law.³⁶ While coordination of a second metal center extends light absorption further into the visible region, the excited state lifetime is significantly shortened by virtue of the low energy Ru(d π) $\rightarrow$ dpp(π^*) ^{3} CT excited state.

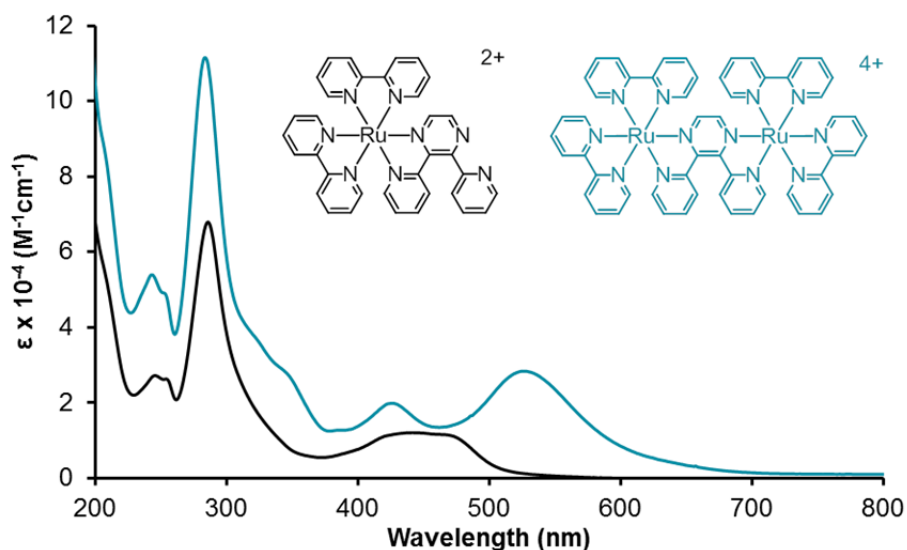


Figure 1.17: Electronic absorption spectra of [(bpy) $_2$ Ru(dpp)](PF $_6$) $_2$ (—) and [(bpy) $_2$ Ru(dpp)Ru(bpy) $_2$](PF $_6$) $_4$ (—) measured in RT CH $_3$ CN. Spectra are consistent with data from references 32.

TL variation in [(TL) $_2$ Ru(dpp)Ru(TL) $_2$] $^{4+}$ complexes from bpy to phen or Ph $_2$ phen provides similar impacts on the redox and spectroscopic properties as observed in the [(TL) $_2$ Ru(dpp)] $^{2+}$ monometallic complexes.^{32,46,48} The frontier orbital energetics are relatively unaffected by TL identity, with the first Ru $^{II/III}$ couple occurring at 1.50 V and 1.45 V vs. Ag/AgCl for TL = phen and Ph $_2$ phen, respectively, and the dpp $^{0/-}$ couple occurring at -0.64 and -0.61 V vs. Ag/AgCl.^{46,48} This is reflected in

the electronic absorption spectroscopy with the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^1CT transitions centered at 526 nm ($\epsilon = 23,000 \text{ M}^{-1}\text{cm}^{-1}$) and 540 nm ($\epsilon = 29,000 \text{ M}^{-1}\text{cm}^{-1}$) for $[(\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{phen})_2]^{4+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{Ph}_2\text{phen})_2]^{4+}$, respectively. The enhancement in absorptivity of this transition when $\text{TL} = \text{Ph}_2\text{phen}$ results from the overlapping, strongly absorbing $\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ ^1CT transition centered at 436 nm ($\epsilon = 38,000 \text{ M}^{-1}\text{cm}^{-1}$).⁴⁶ Emission from the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT excited state occurs at similar energies for this series of $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{TL})_2]^{4+}$ complexes, with $\lambda^{\text{max}} = 758 \text{ nm}$, 750 nm and 754 nm for $\text{TL} = \text{bpy}$, phen , and Ph_2phen , respectively. The excited state lifetimes, however, are influenced by TL identity despite the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT nature of the lowest lying excited state. The observed lifetimes are reported as 126 ns, 170 ns, and 192 ns for $\text{TL} = \text{bpy}$, phen , and Ph_2phen , respectively. This suggests that the TL orbitals have a significant contribution to the lowest lying excited state in Ru_2Ru bimetallic complexes that is similar to that observed in the $[(\text{TL})_2\text{Ru}(\text{dpp})]^{2+}$ complexes.

The effect of coordinating a *cis*- $\text{Pt}^{\text{II}}\text{Cl}_2$ moiety to the open coordination site of $[(\text{TL})_2\text{Ru}(\text{BL})]^{2+}$ complexes is important in the context of this dissertation. A series of $[(\text{TL})_2\text{Ru}(\text{BL})\text{PtCl}_2]^{2+}$ bimetallic complexes, where $\text{TL} = \text{bpy}$, phen , or Ph_2phen and $\text{BL} = \text{dpp}$ or dpq , is depicted in **Figure 1.18** and the redox, spectroscopic, and photophysical data are compiled **Table 1.3**. In comparison to the parent $[(\text{TL})_2\text{Ru}(\text{BL})]^{2+}$ monometallic complexes, coordination of *cis*- $\text{Pt}^{\text{II}}\text{Cl}_2$ to the open BL coordination site generally has a larger stabilizing effect on the $\text{BL}(\pi^*)$ orbitals than coordination of $\text{Ru}^{\text{II}}(\text{TL})_2$.⁴⁹ The $\mu\text{-dpp}^{0/-}$ couple occurs at -0.50 V for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ and -0.45 V for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ which is stabilized ca. 100 mV compared to the $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{TL})_2]^{4+}$ complexes.^{50,51} Consistent with the $\text{BL}(\pi^*)$ stabilized when $\text{BL} = \text{dpq}$ compared to dpp , the $\text{dpq}^{0/-}$ couple occurs at -0.20 V , -0.20 V , and -0.19 V vs. Ag/AgCl for $[(\text{bpy})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$, $[(\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$, respectively.^{44,50} The anodic electrochemistry of Ru_2Pt complexes is not well understood. The $\text{Ru}^{\text{II/III}}$ couple for each of these complexes is reported to occur at 1.61-1.63 V vs. Ag/AgCl when $\text{BL} = \text{dpp}$ and at 1.67 V when $\text{BL} = \text{dpq}$, consistent with the enhanced π -accepting ability of dpq vs. dpp . An irreversible couple at 1.51 V vs. Ag/AgCl was reported for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ as

a $\text{Pt}^{\text{II/III}}$ oxidation⁵¹ and for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$ as a $\text{Pt}^{\text{II/IV}}$ oxidation.⁵⁰ No Pt-based oxidation is reported for $[(\text{bpy})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$ or $[(\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$. In this series of bimetallic complexes, BL has the most significant impact on frontier orbital energetics while TL fine tunes the $\text{Ru}(\text{d}\pi)$ orbital energy.

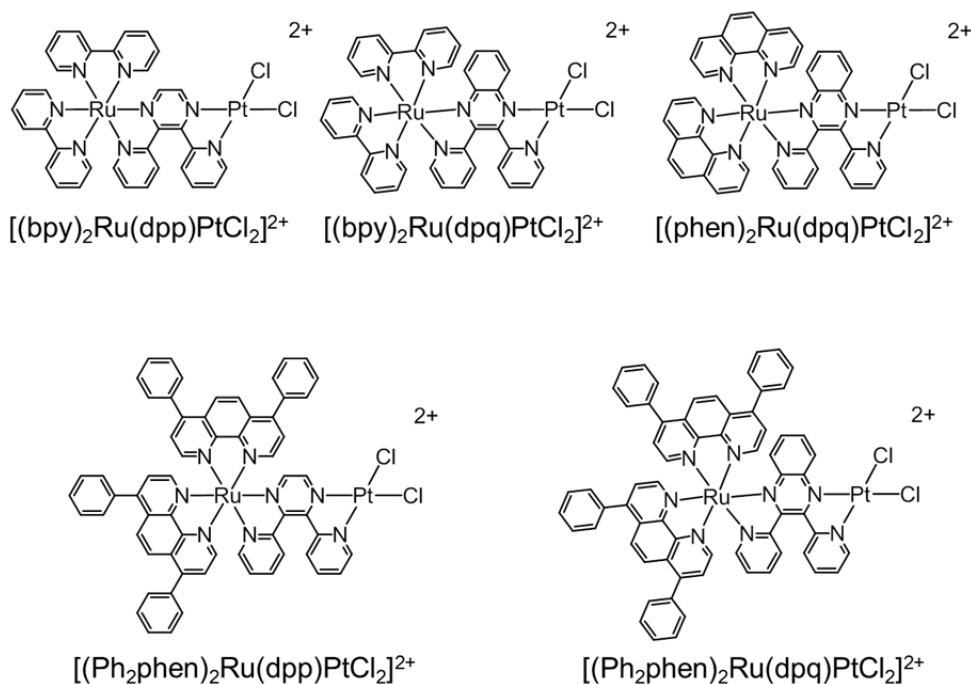


Figure 1.18: Structural representations of Ru(II),Pt(II) bimetallic complexes. bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The impact of TL and BL on the frontier orbital energetics of $[(\text{TL})_2\text{Ru}(\text{BL})\text{PtCl}_2]^{2+}$ complexes is reflected in the photophysical properties. In the electronic absorption spectroscopy, BL identity influences the lowest lying MLCT transition, with the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^1CT transitions centered at 509 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ and 517 nm for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ while the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ ^1CT transitions are centered at 590 nm for $[(\text{bpy})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$ and $[(\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$ and 600 nm for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{2+}$.^{44,50,51} This is consistent with the smaller HOMO-LUMO gap for the BL = dpq complexes (1.82-1.87 V) compared to BL = dpp (1.96-2.01 V). As described in the $[(\text{TL})_2\text{Ru}(\text{BL})]^{2+}$ and $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{TL})]^{4+}$ complexes, TL = Ph_2phen greatly enhances visible light

absorption between 350 and 450 nm compared to TL = phen or bpy.⁵⁰ Few reports of the emissive properties of Ru,Pt complexes are present, so the photophysical properties of these complexes are not well understood. The lowest lying excited state, $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}(\pi^*)$ ^3CT in nature, is expected to be populated with unit efficiency upon photoexcitation. Emission from this excited state for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ was first reported to occur at 800 nm ($\tau = 450$ ns).⁵¹ This emission wavelength seems too long for this transition compared to other $\text{Ru} \rightarrow \text{dpp}$ ^3CT transitions and the excited state lifetime is expected to be much shorter for this low energy emission. This complex was recently reported to emit at 760 nm with a more appropriate lifetime of 46 ns which is similar to the values reported for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ ($\lambda^{\text{em}} = 740$ nm, $\tau = 44$ ns).⁵² No emission data are reported for the BL = dpq complexes as emission from the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ ^3CT excited state is expected to occur at long wavelengths (> 800 nm) that are not detectable due to low PMT response in this region. While *cis*- $\text{Pt}^{\text{II}}\text{Cl}_2$ coordination and use of dpq as the BL extends light absorption further into the visible region, the resulting low energy $^3\text{MLCT}$ excited state results in an emission that is short lived or undetectable.

Table 1.3: Electrochemical and Spectroscopic Data for Ru(II),Ru(II) and Ru(II),Pt(II) Complexes ^a

Complex	E _{1/2} ^{ox} (V) ^b	E _{1/2} ^{red} (V) ^b	λ ^{abs} (nm) (ε, M ⁻¹ cm ⁻¹)	λ ^{em} (nm)	τ (ns)
[(bpy) ₂ Ru(dpp)Ru(bpy) ₂] ⁴⁺ ^c	1.43 (Ru ^{II/III})	-0.61 (dpp ^{0/-})	523 (23,000)	758	126
	1.61 (Ru ^{II/III})	-1.09 (dpp ⁻²⁻)			
[(phen) ₂ Ru(dpp)Ru(phen) ₂] ⁴⁺ ^d	1.50 (Ru ^{II/III})	-0.64 (dpp ^{0/-})	525 (23,000)	750	170
	1.65 (Ru ^{II/III})	-1.13 (dpp ⁻²⁻)			
[(Ph ₂ phen) ₂ Ru(dpp)Ru(Ph ₂ phen) ₂] ⁴⁺ ^e	1.45 (Ru ^{II/III})	-0.61 (dpp ^{0/-})	540 (29,000)	754	192
	1.64 (Ru ^{II/III})	-1.11 (dpp ⁻²⁻)			
[(bpy) ₂ Ru(dpp)PtCl ₂] ²⁺ ^f	1.51 (Pt ^{II/III}) ^g	-0.50 (dpp ^{0/-})	509 (15,240)	760 ^h	46 ^h
	1.61 (Ru ^{II/III})	-1.07 (dpp ⁻²⁻)			
		-1.45 (bpy ^{0/-})			
[(bpy) ₂ Ru(dpq)PtCl ₂] ²⁺ ⁱ	1.67 (Ru ^{II/III})	-0.20 (dpq ^{0/-})	590 (9,500)	^j	< 10
		-0.82 (dpq ⁻²⁻)			
[(phen) ₂ Ru(dpq)PtCl ₂] ²⁺ ⁱ	1.67 (Ru ^{II/III})	-0.20 (dpq ^{0/-})	590 (9,500)	^j	< 10
		-0.95 (dpq ^{0/-})			
[(Ph ₂ phen) ₂ Ru(dpp)PtCl ₂] ²⁺ ^k	1.51 (Pt ^{II/IV}) ^g	-0.45 (dpp ^{0/-})	517 (11,400)	740	44
	1.61 (Ru ^{II/III})	-1.15 (dpp ⁻²⁻)			
		-1.33 (Ph ₂ phen ^{0/-})			
[(Ph ₂ phen) ₂ Ru(dpq)PtCl ₂] ²⁺ ^k	1.51 (Pt ^{II/IV}) ^g	-0.19 (dpq ^{0/-})	600 (9,800)	^j	< 10
	1.63 (Ru ^{II/III})	-0.95 (dpq ⁻²⁻)			
		-1.33 (Ph ₂ phen ^{0/-})			

^a Measured in RT CH₃CN unless otherwise noted. bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. ^b Potentials vs. Ag/AgCl. ^c From references 32 and 47. ^d From references 32, 47, and 48. ^e From reference 46. ^f From reference 51. ^g Potential corresponds to E_p^a. ^h From reference 52. ⁱ From reference 44. ^j No detectable emission. ^k From reference 50.

1.3.3. Excited State Dynamics of Multimetallic dpp-Bridged Ru(II) Supramolecules

A variety of multimetallic Ru(II)-polyazine complexes have been reported in the development of light harvesting antenna systems to study the impacts of supramolecular architecture and electronic coupling on intramolecular energy transfer and electron transfer processes.^{39,40} The multi-Ru(II) complexes discussed herein provide information about the importance of component selection and arrangement in designing PMDs.

1.3.3.1. Ru(II)-Polyazine Trimetallic Complexes

The trimetallic complex $[\{(bpy)_2Ru(dpp)\}_2RuCl_2]^{4+}$ (**Figure 1.19**) is an important building block in the construction of larger Ru(II) supramolecular complexes, as the labile Cl^- can be replaced by a free BL or a metal complex with an open bidentate chelating site.⁵³ The electrochemical and spectroscopic properties of this complex are compiled in **Table 1.4**. The HOMO is localized on the central Ru(II) unit, a result of destabilization of the $d\pi$ orbitals due to the σ -donating Cl^- ligands in the $(dpp)_2Ru^{II}Cl_2$ unit compared to the lower energy $d\pi$ orbitals in the $(bpy)_2Ru^{II}(dpp)$ peripheral units. The LUMO is localized on the μ -dpp ligands, resulting in a lowest lying central $Ru(d\pi) \rightarrow dpp(\pi^*)$ CT excited state with a ^1MLCT absorption centered at 625 nm. Emission from the ^3MLCT state occurs at 904 nm, consistent with participation of the destabilized central *cis*- $Ru^{II}Cl_2$ unit. Localization of the HOMO is shifted to the terminal Ru(II) by stabilizing the central Ru(II) through bpy coordination to provide the trimetallic complex $[\{(bpy)_2Ru(dpp)\}_2Ru(bpy)]^{6+}$, **Figure 1.19**. Subsequently, the lowest energy terminal $Ru(d\pi) \rightarrow dpp(\pi^*)$ ^1MLCT absorption is centered at 545 nm, and emission is blue-shifted to 802 nm with a lifetime of 125 ns.⁵³ Simple ligand substitution in this motif controls the direction of excitation energy transfer which is important in designing light harvesting antennae.

1.3.3.2. Ru(II)-Polyazine Tetrametallic Complexes

Variation of BL and TL in the series of $[Ru\{(BL)Ru(TL)_2\}]^{8+}$ tetrametallic complexes (where BL = dpp or bpm and TL = bpy or phen, **Figure 1.19**) is important in understanding the impacts of electronic coupling and ligand set in large Ru(II) LAs.^{48,54} Similar to the previously discussed $[\{(bpy)_2Ru(dpp)\}_2Ru(bpy)]^{2+}$, the HOMO is localized on the terminal Ru(II) in the $(TL)_2Ru^{II}(\mu-BL)$ units. Oxidation of the more electron deficient central Ru(II) in the $Ru^{II}(\mu-BL)_3$ unit requires a greater potential because TLs such as bpy and phen are better electron donors than BLs such as dpp and bpm. The lowest energy absorptions, emission energies, and excited state lifetimes (**Table 1.4**) are quite similar for $[Ru\{(dpp)Ru(bpy)_2\}_3]^{8+}$ ($\lambda^{abs} = 534$ nm, $\lambda^{em} = 772$ nm, $\tau = 89$ ns) and $[Ru\{(dpp)Ru(phen)_2\}_3]^{8+}$ ($\lambda^{abs} = 539$ nm, $\lambda^{em} = 760$ nm, $\tau = 87$ ns). This similarity is expected due to the terminal $Ru(d\pi) \rightarrow dpp(\pi^*)$ CT nature

of the lowest energy excited state in which TL does not participate, but this is in stark contrast to the comparison of $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$. The BL selection has a significant impact on electronic coupling of the central and terminal Ru centers, as no detectable emission is observed from $[\text{Ru}\{(\text{bpm})\text{Ru}(\text{bpy})_2\}_3]^{2+}$.⁵⁴ The dpp ligand maintains the light absorbing and photophysical properties of the individual building blocks, making it a popular choice for designing Ru(II)-polyazine PMDs.

1.3.3.3. Ru(II)-Polyazine Heptametallic Complex

Interesting excited state dynamics are observed in the heptametallic complex $[\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{12+}$ (**Figure 1.19**) in which 100 % population of the lowest energy excited state localized on the $(\mu\text{-dpp})_2\text{Ru}^{\text{II}}\text{Cl}_2$ core (formally $\text{Cl}_2\text{Ru}(\text{d}\pi) \rightarrow \text{inner } \mu\text{-dpp}(\pi^*)$ CT) occurs from excitation of the terminal $(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-dpp})$ LAs despite a high energy $\text{Ru}^{\text{II}}(\mu\text{-dpp})_3$ barrier.⁵⁵ The lowest energy absorption band is broad between 460 and 800 nm ($\lambda^{\text{max}} = 560$ nm, $\epsilon = 50,900 \text{ M}^{-1}\text{cm}^{-1}$) due to many different types of overlapping $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ CT transitions resulting from multiple Ru centers and dpp BLs (**Table 1.4**). Ultrafast transient absorption spectroscopic analyses of the smaller analogous complexes $[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ and $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$ were performed to predict the spectral signatures of the $(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-dpp})$ terminal LAs and the $(\mu\text{-dpp})_2\text{Ru}^{\text{II}}\text{Cl}_2$ center. The transient absorption spectrum of $[\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{12+}$ at 600 fs following excitation features two maxima at 560 nm (consistent with the $\text{bpy}_2\text{Ru} \rightarrow \mu\text{-dpp}$ CT bleach in $[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+}$) and 620 nm (consistent with the $\text{Cl}_2\text{Ru} \rightarrow \mu\text{-dpp}$ CT bleach in $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$), suggesting an intermediate charge separated state in which the hole is localized on central Ru and the electron is localized on the outer $\mu\text{-dpp}$ which gives rise to bleaching of the $\text{bpy}_2\text{Ru} \rightarrow \text{outer dpp}$ CT and $\text{Cl}_2\text{Ru} \rightarrow \text{inner dpp } ^3\text{CT}$ transitions. Within a few ps, the bleach at 560 nm is recovered leaving only the 620 nm bleach, suggested to be a result of ligand-to-ligand electron hopping from outer $\mu\text{-dpp}$ to inner $\mu\text{-dpp}$, populating the lowest lying $\text{Cl}_2\text{Ru} \rightarrow \text{inner } \mu\text{-dpp } ^3\text{CT}$ excited state from which emission occurs with a lifetime of ca. 1 ns. This study is important in understanding supramolecular excited state dynamics as transient absorption studies of multimetallic Ru(II)-polyazine

complexes are rare. Excitation energy is frequently transferred from one subunit to another over a high energy barrier in large Ru(II)-polyazine complexes, and this study provides insight into the ultrafast processes involved.

1.3.3.4. Ru(II)-Polyazine Complexes with 10 or More Metal Centers

A series of branched dpp-bridged Ru(II) supramolecular complexes with 10, 13, and 22 metal centers has been reported in an effort to produce efficient light harvesting antenna. The 10 metal system $[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3]^{20+}$ (**Figure 1.19**) also contains nine dpp BLs and 12 bpy TLs.^{56,57} The HOMO is localized on the terminal Ru(II) orbitals as evidenced by the oxidation at 1.48 V corresponding to six overlapping, one electron processes (**Table 1.4**). The reductive electrochemistry is expectedly complicated with one broad couple at -0.45 V corresponding to reduction of the nine μ -dpp ligands. The lowest lying excited state, terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT in nature, emits at 809 nm with a lifetime of 55 ns. The lack of excitation wavelength dependence on the emission suggests efficient deactivation of higher lying excited states to the emissive state according to Kasha's rule. This efficient center-to-periphery excitation energy transfer is also observed in extended systems such as $[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3]^{26+}$ ($\lambda^{\text{em}} = 800 \text{ nm}$, $\tau = 62 \text{ ns}$)⁵⁸ and $[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_2]_2\}_3]^{44+}$ ($\lambda^{\text{em}} = 786 \text{ nm}$, $\tau = 45 \text{ ns}$)^{59,60} which also have emissive excited states localized on the terminal LA units, terminal $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3CT in nature. Despite the rich light absorbing properties of these complexes ($\epsilon = 100,000\text{-}200,000 \text{ M}^{-1}\text{cm}^{-1}$), these complexes are not desirable as light harvesting antennae because the excitation energy is not transferred to and concentrated at one single unit, rather it is transferred to one of many terminal $(\text{bpy})_2\text{Ru}^{\text{II}}(\mu\text{-dpp})$ units.

Component variation in the decametallic $[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3]^{20+}$ complex provides a species which inverts the direction of energy flow to produce an efficient periphery-to-center light harvesting antenna. The mixed-metal complex $[\text{Os}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{PtCl}_2]_2\}_3]^{8+}$ (**Figure 1.19**) replaces the greatly stabilized Ru(II) core with a destabilized Os(II) and the terminal $(\mu\text{-dpp})\text{Ru}^{\text{II}}(\text{bpy})_2$ units with higher energy $(\mu\text{-dpp})\text{PtCl}_2$ units, reversing the energy gradient.⁶¹ The complex emits from the lowest

energy $\text{Os}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3CT excited state at 875 nm (**Table 1.4**). The related tetrametallic complex $[(\text{bpy})_2\text{Os}(\text{dpp})\text{Ru}\{(\text{dpp})\text{PtCl}_2\}_2]^{4+}$ also exhibits the same transfer of excitation energy toward the Os center from the higher energy terminal and central units, with emission occurring from the $\text{Os}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3CT excited state at 975 nm. This red shift compared to the decametallic is due to the destabilization of the $\text{Os}(\text{d}\pi)$ orbitals from substitution of two electron withdrawing $(\text{dpp})\text{Ru}^{\text{II}}[(\text{dpp})\text{Pt}^{\text{II}}\text{Cl}_2]_2$ units with two electron donating bpy TLs. This set of complexes highlights the ability to control directional energy or electron transfer by component substitution (in this case, metal variation). Incorporating BLs with different acceptor orbital energies provides an additional means to direct the flow of charge through a Ru(II) supramolecular complex; however, this arena is relatively unexplored.

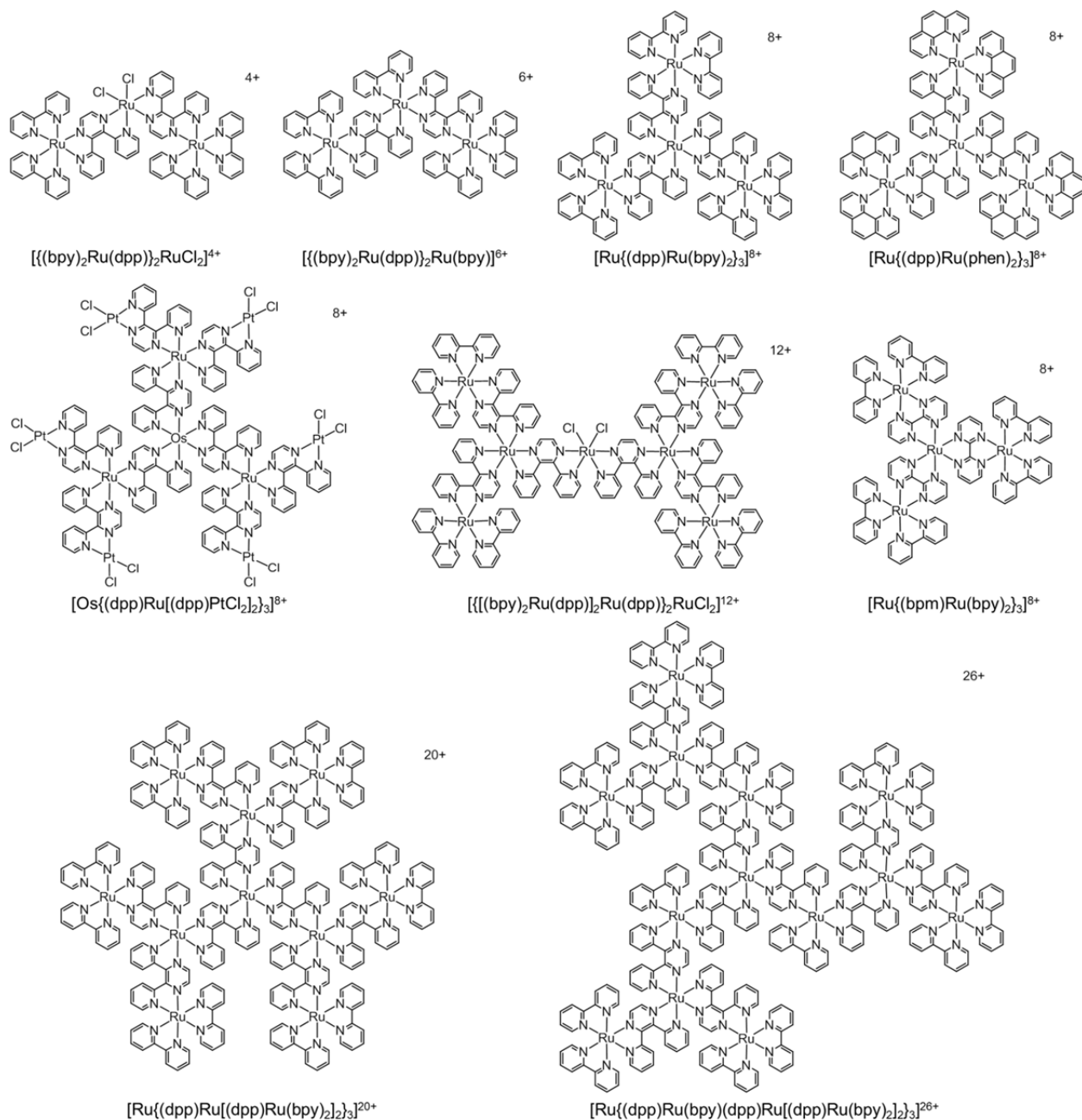


Figure 1.19: Structural representations of multimetallic Ru(II)-polyazine supramolecular complexes. bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpm = 2,2'-bipyrimidine.

Table 1.4: Electrochemical and Spectroscopic Data for Ru(II) Supramolecular Complexes^a

Complex	$E_{1/2}^{\text{ox}}$ (V) ^b	$E_{1/2}^{\text{red}}$ (V) ^b	λ^{abs} (nm) (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	λ^{em} (nm)	τ (ns)
$[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+ c}$	0.87 (1) 1.62 (2)	−0.67 (1) −0.83 (1)	625 (26,100)	904	< 10
$[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{bpy})]^{6+ c}$	1.56 (2) 2.00 (1)	−0.47 (1) −0.61 (1)	545 (23,500)	802	125
$[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+ d}$	1.55 (3)	−0.51 (1) −0.69 (1) −0.84 (1)	534 (36,400)	772	89
$[\text{Ru}\{(\text{dpp})\text{Ru}(\text{phen})_2\}_3]^{8+ d}$	1.48 (3)		539 (35,700)	760	87
$[\text{Ru}\{(\text{bpm})\text{Ru}(\text{bpy})_2\}_3]^{8+ e}$			613 (17,400)		< 10
$[\text{Os}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{PtCl}_2]_2\}_3]^{8+ f}$			520 (67,100)	875	<10
$[\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{12+ g}$	0.91 (1) 1.61 (4)	−0.46 (2) −0.57 (2) −0.71 (2) −1.11 (2)	560 (50,900)	895	< 10 ^h
$[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3]^{20+ i}$	1.48 (6)	−0.45 (9)	541 (125,000)	809	55
$[\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3]^{26+ j}$	1.55 (6)		544 (133,000)	800	62
$[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_2\}_3]^{44+ k}$			542 (202,000)	786	45

^a Measured in RT CH_3CN unless otherwise noted. bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline, bpm = 2,2'-bipyrimidine. ^b Potentials vs. Ag/AgCl. Number in parentheses corresponds to the number of exchanged electrons. ^c From reference 53. ^d From reference 48. ^e From reference 54. ^f From reference 61. ^g From reference 55. ^h Ultrafast transient absorption suggests a lifetime close to 1 ns. ⁱ From references 56 and 57. ^j From reference 58. ^k From references 59 and 60.

The majority of multimetallic Ru(II)-polypyridyl supramolecular complexes feature only dpp BLs as the resulting complexes have attractive light absorbing properties and appropriate excited state dynamics that provide an emissive probe, but these complexes generally possess a lowest-lying $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ CT excited state localized at the periphery and a series of high energy $\text{Ru}^{\text{II}}(\mu\text{-dpp})_3$ subunits in the center of the complex. Application of these supramolecules in photocatalytic systems is limited to intermolecular excited state electron or energy transfer processes.^{17-19,28,62,63} For efficient intramolecular electron transfer toward a catalytic site within a supramolecular architecture, the proper components must be selected to concentrate electrons near or at the catalytic site.

1.4. Photocatalysts for Reduction of H_2O to H_2

1.4.1. Multicomponent Systems

Given the rich light absorbing properties and strong oxidizing/reducing power of the long-lived $^3\text{MLCT}$ excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ and related Ru(II)-polyazine LAs, these complexes have found an important role in photocatalytic H_2O reduction schemes to harness energy from visible light. One of the earliest reported multicomponent photocatalytic systems for reduction of H_2O to H_2 , **Figure 1.20**, utilizes a $[\text{Ru}(\text{bpy})_3]^{2+}$ LA with a $^3\text{MLCT}$ excited state which provides an appropriate driving force for intermolecular electron transfer to a methyl viologen (MV^{2+}) electron relay (ER) to give an oxidized LA, $[\text{Ru}(\text{bpy})_3]^{3+}$ and a reduced ER, $\text{MV}^{\bullet+}$.^{64,65} In the presence of a heterogeneous Pt catalyst, the electrons are transferred from multiple $\text{MV}^{\bullet+}$ Ers to the H_2O substrate to produce H_2 and OH^- . A sacrificial electron donor (ED), in this case EDTA (ethylenediaminetetraacetic acid), regenerates the $[\text{Ru}(\text{bpy})_3]^{2+}$ LA through another intermolecular electron transfer event to avoid undesirable back electron transfer from $\text{MV}^{\bullet+}$ to $[\text{Ru}(\text{bpy})_3]^{3+}$. This catalytic cycle occurs with an efficiency of ca. 10 % in aqueous solution. Related systems utilize a $[\text{Rh}(\text{bpy})_3]^{3+}$ ER.⁶⁶⁻⁶⁸

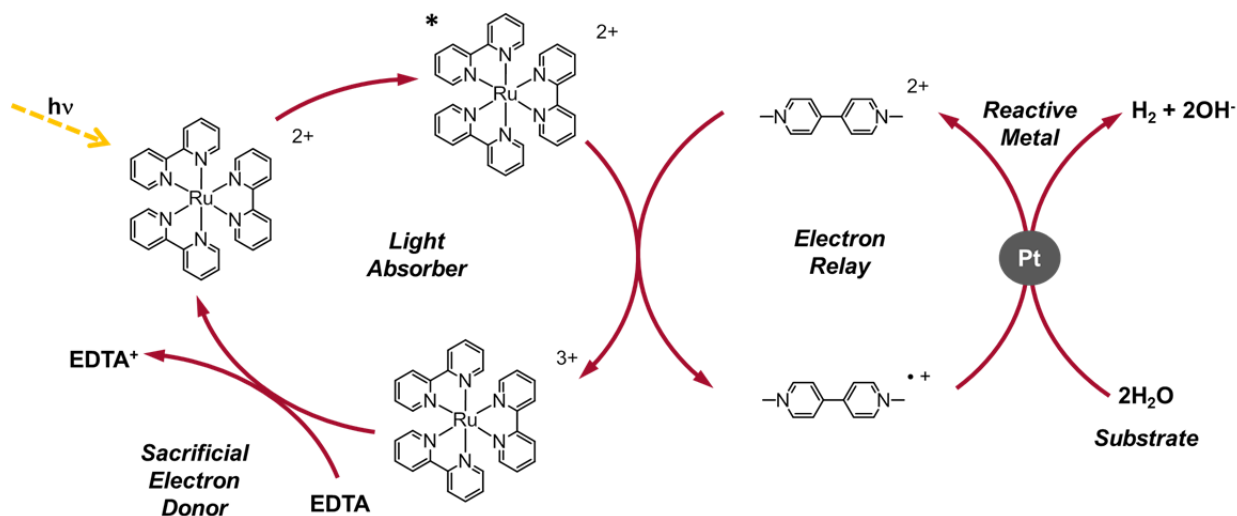


Figure 1.20: Scheme depicting the catalytic cycle in the multi-component photocatalysis system with a $[\text{Ru}(\text{bpy})_3]^{2+}$ light absorber, MV^{2+} electron relay, EDTA sacrificial electron donor, Pt colloid reactive metal, and H_2O substrate. bpy = 2,2'-bipyridine, MV^{2+} = methyl viologen, EDTA = ethylenediaminetetraacetic acid.

The multicomponent system for H₂O reduction to produce H₂ poses two major limitations. First, the efficiency of the catalytic cycle relies on collision of the excited state LA with the ER within the LA's excited state lifetime. This is followed by the necessity for the ED to efficiently reduce the oxidized LA back to its original state so it can participate in the next cycle. Additionally, the use of a heterogeneous colloidal Pt catalyst is economically undesirable, as only the Pt atoms on the surface of a particle can be utilized in catalysis, and the atoms on the interior are unused. Photocatalysts with the LA, ER, and reactive metal (RM) incorporated into a single molecule provide the ability to circumvent the diffusion limited LA to ER electron transfer, and each Pt atom is utilized in the catalytic cycle.

1.4.2. Single Component Systems

Supramolecular complexes can be designed to incorporate the LA, ER, and RM into single molecules to act as catalysts to drive the less thermodynamically demanding multielectron H₂O reduction to produce H₂. These complexes must be able to absorb light, collect multiple electrons, and utilize the electrons to reduce H₂O by breaking and forming bonds while regenerating the supramolecular photocatalyst to its original state for continued participation in the cycle.¹⁴

1.4.2.1. Photoinitiated Electron Collection

A variety of Ru(II)-polyazine complexes possess ligand π^* acceptor orbitals capable of collecting reducing equivalents in the presence of visible light and an ED (**Figure 1.21**). Achieving photoinitiated electron collection (PEC) is complicated by a coulombic barrier which prevents the localization of more than one electron on the same ligand, rendering most [(TL)₂Ru(BL)Ru(TL)]⁴⁺ complexes unable to collect more than one electron (for example, where BL = dpp, dpq, dpb, or bpm). Design considerations for PMDs to undergo PEC necessitate separating the LA and electron collector (EC) to circumvent this coulombic barrier. The first reported PMD to act as a PEC, [{(bpy)₂Ru(dpb)}₂IrCl₂]⁵⁺, collects two reducing equivalents on the low lying dpb(π^*) orbitals, one on each ligand.⁶⁹ Later the bimetallic supramolecules of the form [(phen)₂Ru(BL)Ru(phen)₂]⁴⁺ (BL = tatpp = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]pentacene or tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-

a:2'3'-c:3'',2''-1:2''',3'''-n]pentacene-10,21-quinone) were reported to collect two (BL = tatpp) or four (BL = tatpq) electrons on the BL π^* orbitals.^{70,71} A Ru(II) monometallic complex with an NAD⁺ model ligand (NAD⁺ = nicotinamide adenine dinucleotide), [(bpy)₂Ru(pbn)]²⁺ (pbn = 2-(2-pyridyl)benzo[b]-1,5-naphthyridine), undergoes two proton coupled electron transfers in the presence of an ED.^{72,73} In spite of their PEC abilities, the lack of RM in these systems renders them unable to catalyze the reduction of H₂O to H₂.

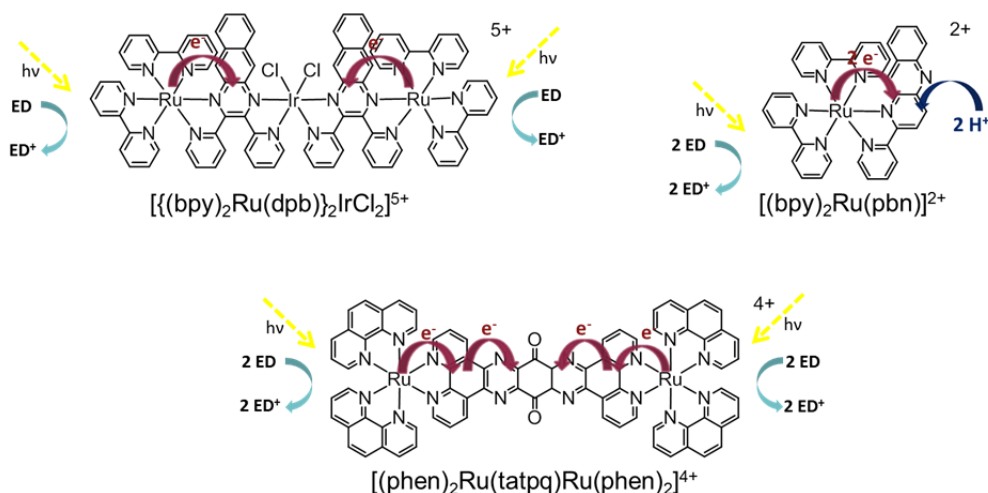


Figure 1.21: Structural representations of three photoinitiated electron collectors. ED = electron donor, bpy = 2,2'-bipyridine, dpb = 2,3-bis(2-pyridyl)benzoquinoxaline, pbn = 2-(2-pyridyl)benzo[b]-1,5-naphthyridine, phen = 1,10-phenanthroline, and tatpq = 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3'''-n]pentacene-10,21-quinone.

1.4.2.2. Supramolecular H₂O Reduction Photocatalysts

Recently, several reports of supramolecular photocatalysts for H₂O reduction which feature one or more [Ru(bpy)₃]²⁺-like LA and a RM such as Pt,⁷⁴⁻⁷⁸ Pd,⁷⁹⁻⁸¹ Co,^{82,83} Fe,⁸⁴ and Rh^{46,85-90} have emerged, and some notable examples are discussed herein (**Figure 1.22**). The first photoinitiated electron collector reported to act as an active photocatalyst in H₂O reduction, [{(bpy)₂Ru(dpp)}₂RhCl₂]⁵⁺,^{87,91} has recently undergone TL and halide modification to result in the more active complex [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺ with a quantum efficiency (Φ) of 0.073 and 610 TON (turnovers) in 20 h in the presence of *N,N*-dimethylaniline (DMA).⁴⁶ The impact of TL variation in this supramolecular architecture is surprising, as the use of Ph₂phen only slightly extends the excited state lifetime compared

to the TL = bpy analogue. The TL impact is likely a result of enhanced visible light absorption and increased steric bulk preventing $\text{Rh}^{\text{I}}\text{-Rh}^{\text{I}}$ dimer formation due to the Ph_2phen ligand compared to the smaller bpy ligand. The complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RhCl}_2(\text{Ph}_2\text{phen})]^{3+}$ was the first reported Ru,Rh bimetallic complex to function as a photocatalyst for H_2 production from H_2O , relying on a balance between steric and electronic factors to promote efficient catalysis.⁹⁰ A system with $\text{RM} = \text{Co}$ coupled to Ru LA produces H_2 from H_2O with $[(\text{bpy})_2\text{Ru}(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)]^{2+}$ ($\text{L-pyr} = (4\text{-pyridine})\text{oxazolo}[4,5\text{-}f]\text{phenanthroline}$, $\text{dmgBF}_2 = (\text{difluoroboryl})\text{dimethylglyoximate}$) affording 56 TON in 4 h when photolyzed in the presence of triethylamine (Et_3N) and $[\text{Et}_3\text{NH}]^+$.⁸² A bimetallic complex with a *cis*- PdCl_2 RM site, $[(^t\text{Bu}_2\text{bpy})_2\text{Ru}(\text{tpphz})\text{PdCl}_2]^{2+}$ ($^t\text{Bu}_2\text{bpy} = 4,4'\text{-di-}t\text{-butyl-2,2'}$ -bipyridine, $\text{tpphz} = \text{tetrapyrido}[3,2\text{-}a:2',3'\text{-}c:3'',2''\text{-}h:2''',3'''\text{-}j]\text{phenazine}$), was reported to produce H_2 with 56 TON in 30 h.⁹²

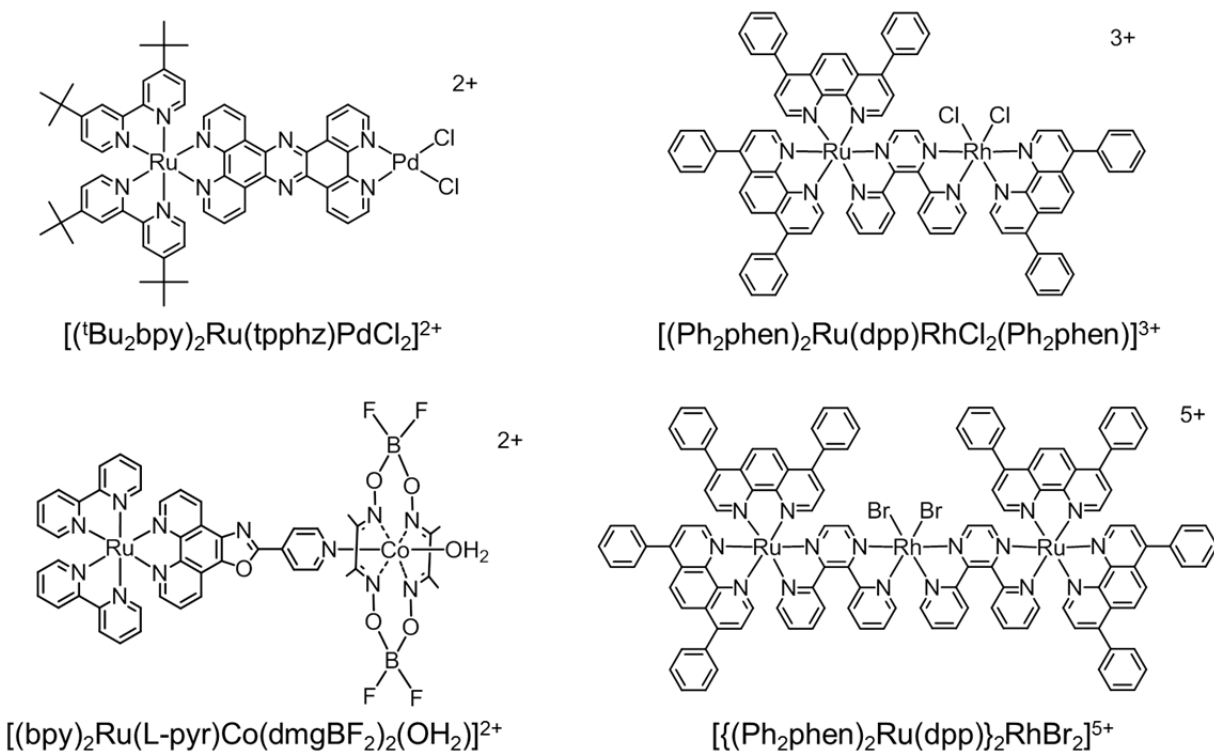


Figure 1.22: Structural representations of supramolecular complexes with Ru(II)-polyazine light absorbers which function as photocatalysts for the reduction of H_2O to H_2 . bpy = 2,2'-bipyridine, $^t\text{Bu}_2\text{bpy}$ = 4,4'-di-*tert*-butyl-2,2'-bipyridine, tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine, L-pyr = (4-pyridine)oxazolo[4,5-*f*]phenanthroline, dmgBF_2 = (difluoroboryl)dimethylglyoximate, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

Few Ru(II),Pt(II) H₂O reduction photocatalysts have been reported, and their functioning is not well understood. A series of Ru(II),Pt(II) bimetallic complexes and a Ru(II)₂Pt(II)₂ tetrametallic complex are depicted in **Figure 1.23**. The bimetallic complexes feature a [(bpy)₂Ru(phen)]²⁺-type LA linked to a *cis*-(Rbpy)Pt^{II}Cl₂ RM (where R = –COOH, –COOEt, or –CH₃) through an amidate bridge, [(bpy)₂Ru(phenNHCO(Rbpy))PtCl₂]²⁺.^{74,75} The first reported photocatalyst of this type, [(bpy)₂Ru(phenNHCO(COOHbpy))PtCl₂]²⁺, was reported to undergo 5 TON in 10 h in catalytic H₂ production from H₂O (Φ = 0.01).^{75,93,94} Population of the Ru(dπ)→phen(π*) CT excited state is followed by intramolecular electron transfer to populate a Ru(dπ)→COOHbpy(π*) ³CS (charge separated) excited state. This electron transfer toward the *cis*-Pt^{II}Cl₂ RM site is controlled by varying the R group to tune the bpy acceptor energy. The analogue with R = –COOEt exhibits a lower catalytic efficiency as a result of less efficient intramolecular electron transfer to the Rbpy group due to the slightly higher energy ³CS excited state. Replacing the R group with –CH₃ destabilizes the bpy acceptor orbital, placing the ³CS state higher in energy than the Ru(dπ)→phen(π*) ³CT state, making electron transfer thermodynamically unfavorable. This complex is not an active photocatalyst for H₂ production. A dimer of this architecture linked through the Rbpy group by an ethylene bridge was reported to double the photocatalytic efficiency.⁹⁵ The increased efficiency is suggested to be a result of providing two Pt(II) centers in close proximity to dimerize and undergo a proton-coupled electron transfer (PCET) to produce a Pt(II)-Pt(III)-hydride intermediate that can then undergo a second PCET to release H₂ and regenerate the two Pt(II) centers or undergo a bimolecular reaction with another Pt(II)-Pt(III)-hydride to release H₂ and regenerate the Pt(II) centers. The chemical integrity of Ru(II),Pt(II) and Ru(II),Pd(II) complexes upon photolysis has raised controversy as several reports demonstrate a colloidal Pt or Pd active catalyst.^{96,97} Detailed investigations are necessary to understand how each mixed-metal system functions.

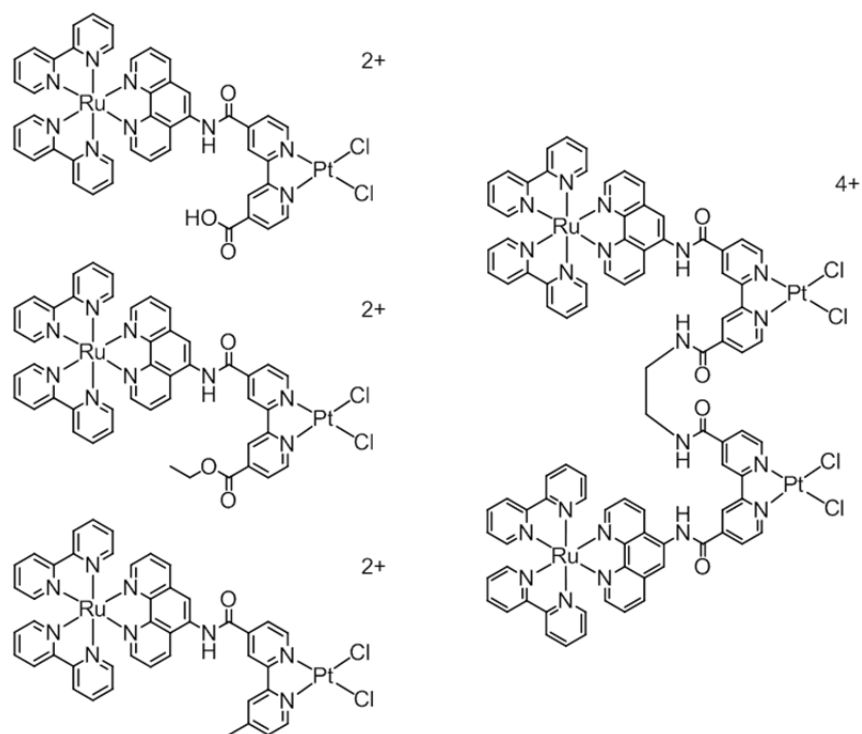


Figure 1.23: Structural representations of a series of Ru(II),Pt(II) supramolecular photocatalysts, $[(bpy)_2Ru(phenNHCO(Rbpy))PtCl_2]^{2+}$, where R = $-COOH$, $-COOEt$, or $-CH_3$ (left) and a dimer of the Ru(II),Pt(II) complex linked through the Rbpy group (right).

1.5. Project Description

The goal of this research is to use component and structural modification in mixed-ligand Ru(II),Pt(II) supramolecular complexes to understand through detailed analysis the complicated redox and photophysical properties and their functioning as single component H_2O reduction photocatalysts to produce H_2 fuel. Systematic component variation in the tetrametallic supramolecular architecture $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$, where TL = phen or Ph_2phen and $BL' = dpp$ or dpq , and comparison to the trimetallic precursors $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$ provides information into the effects of TL and BL' on the redox, spectroscopic, photophysical, and photochemical properties. Replacing one $(TL)_2Ru^{II}(dpp)$ LA unit with a bpy ligand to produce the Ru(II),Pt(II) trimetallic complexes of the motif $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL')PtCl_2]^{4+}$ ($BL' = dpp$ or dpq) results in complexes which possess analogous properties in comparison to the parent tetrametallic complexes, but loss of one MLCT light absorber results in fewer overlapping MLCT transitions in the visible region, providing a more suitable

supramolecular architecture for spectroscopic analysis. The tetrametallic and trimetallic complexes discussed in this dissertation are pictured below in **Figure 1.24**.

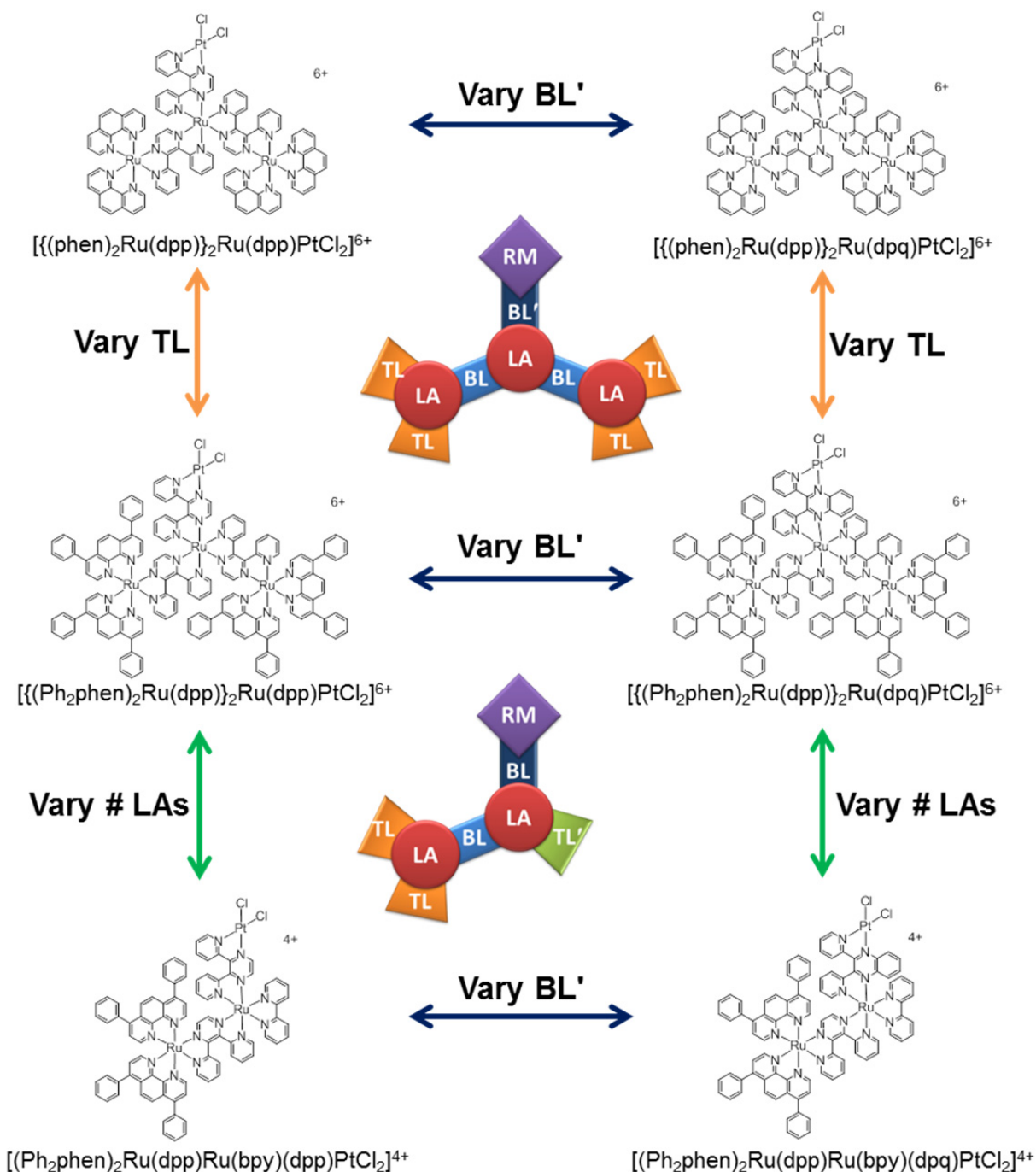


Figure 1.24: Component and structural variation in Ru(II),Pt(II) supramolecular complexes. TL/TL' = terminal ligand, LA = light absorber, BL/BL' = bridging ligand, RM = reactive metal, phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

2. Experimental

2.1. Materials

All materials were used as received unless otherwise stated. The precursor *cis*-dichlorobis(dimethylsulfoxide)platinum(II)⁹⁸ ($[\text{PtCl}_2(\text{DMSO})_2]$) and the ligand 2,3-bis(2-pyridyl)quinoxaline⁹⁹ (dpq) were synthesized by previously reported methods. Ruthenium(III) trichloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$), silver trifluoromethanesulfonate (AgSO_3CF_3), trifluoromethanesulfonic acid (HSO_3CF_3), 2,2'-bipyridine (bpy), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen), lithium chloride (LiCl), and tetra-*n*-butylammonium chloride (Bu_4NCl) were purchased from Alfa Aesar. *N,N*-dimethylaniline (DMA), 1,10-phenanthroline (phen), 2,3-bis(2-pyridyl)pyrazine (dpp), and Sephadex® LH-20 were purchased from Aldrich Chemical Company. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from Fluka. Ammonium hexafluorophosphate (NH_4PF_6) and tetrakis(dimethylsulfoxide)dichlororuthenium(II) ($[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$) were purchased from Strem Chemicals, Inc. Ethanol (EtOH) was obtained from Decon Labs. Spectral grade acetonitrile (CH_3CN) was purchased from Burdick and Jackson. Acetone, CH_3CN , toluene, dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), methanol (MeOH), *N,N*-dimethylformamide (DMF), ethylene glycol, and 80-200 mesh alumina were purchased from Fisher Scientific.

2.2. Synthesis

2.2.1. *cis,cis*- $[(\text{bpy})\text{RuCl}_2(\text{DMSO})_2]$

The starting material *cis,cis*- $[(\text{bpy})\text{RuCl}_2(\text{DMSO})_2]$ was synthesized following a previously reported procedure.¹⁰⁰ A 1:1 mixture of bpy (0.64 g, 4.0 mmol) and $[\text{RuCl}_2(\text{DMSO})_4]$ (2.00 g, 4.0 mmol) in 40 mL of a 9:1 EtOH/DMSO solution was heated at reflux for 1.5 h. The reaction mixture was cooled to RT and the yellow precipitate was collected by vacuum filtration. The solid was washed with 60 mL cold Et_2O and dried *in vacuo* (1.58 g, 3.3 mmol, yield = 80 %).

2.2.2. [(phen)₂RuCl₂]

The precursor [(phen)₂RuCl₂] was synthesized by modification of a previously reported procedure.¹⁰¹ The starting material RuCl₃•3H₂O (1.6 g, 6.2 mmol), the TL phen (2.0 g, 11 mmol), and excess LiCl (3.9 g, 92 mmol) were dissolved in 75 mL of DMF and heated at reflux for 8 h. The reaction mixture was cooled to RT, added to 100 mL acetone, and stored in the refrigerator overnight. The mixture was then added to an aqueous LiCl solution (2.0 g in 200 mL) and the dark purple precipitate was collected by vacuum filtration. The orange filtrate containing the impurity [Ru(phen)₃]Cl₂ was discarded. The purple/black solid was washed with H₂O to remove [Ru(phen)₃]Cl₂ until the filtrate was colorless (ca. 400 mL), then the solid was washed with 100 mL of Et₂O and dried under vacuum (1.4 g, 2.6 mmol, yield = 40 %).

2.2.3. [(Ph₂phen)₂RuCl₂]

The precursor [(Ph₂phen)₂RuCl₂] was synthesized by modification of a previously reported procedure.¹⁰² The starting material RuCl₃•3H₂O (0.87 g, 3.3 mmol), the TL Ph₂phen (2.0 g, 6.0 mmol), and excess LiCl (2.8 g, 67 mmol) were dissolved in 75 mL of DMF and heated at reflux for 8 h. The reaction mixture was cooled to RT, added to 100 mL acetone, and placed in the refrigerator overnight. The mixture was then added to an aqueous LiCl solution (2.0 g in 200 mL) and the dark purple precipitate was collected by vacuum filtration. The orange filtrate containing the impurity [Ru(Ph₂phen)₃]Cl₂ was discarded. The complex was purified by adsorption column chromatography (3.5 cm x 10 cm) with a deactivated 80-200 mesh alumina stationary phase and a 4:1 CH₂Cl₂/acetone mobile phase. The first light yellow band, free ligand, was discarded. A purple band containing the [(Ph₂phen)₂RuCl₂] product which followed was collected. The orange [Ru(Ph₂phen)₃]Cl₂ band remained near the top of the column. The solvent from the purple fraction was removed under vacuum, dissolved in minimal CH₂Cl₂ (10 mL), and added dropwise to 500 mL of stirring Et₂O. The resulting dark purple precipitate was collected by vacuum filtration, washed with 100 mL of Et₂O and dried under vacuum (1.1 g, 1.3 mmol, yield = 40 %).

2.2.4. $[(phen)_2Ru(dpp)](PF_6)_2$

The monometallic complex $[(phen)_2Ru(dpp)](PF_6)_2$ was synthesized by modification of a previously reported procedure.³² The precursor $[(phen)_2RuCl_2]$ (2.0 g, 3.7 mmol) was reacted with excess dpp (1.8 g, 7.5 mmol) in 2:1 EtOH/H₂O (90 mL) by heating at reflux for 3 h. The resulting orange reaction mixture was cooled to RT and added to an aqueous NH₄PF₆ solution (1.0 g in 50 mL) to metathesize the product from a Cl⁻ salt to a PF₆⁻ salt. The precipitate was collected by vacuum filtration and washed with 100 mL H₂O. The complex was purified by adsorption column chromatography (3.5 cm x 10 cm) with a deactivated 80-200 mesh alumina stationary phase and a 3:2 toluene/CH₃CN mobile phase. The first light orange band containing the dpp free ligand was discarded. The second orange band which contained the desired product, $[(phen)_2Ru(dpp)](PF_6)_2$, was collected and the solvent was removed under vacuum. The third band containing the purple colored $[(phen)_2Ru(dpp)Ru(phen)_2](PF_6)_4$ impurity was discarded. The orange product was dissolved in minimal CH₃CN (10 mL) and added dropwise to 300 mL of stirring Et₂O. The orange precipitate was collected by vacuum filtration, washed with 100 mL Et₂O and dried under vacuum (1.5 g, 1.5 mmol, yield = 40 %).

2.2.5. $[(Ph_2phen)_2Ru(dpp)](PF_6)_2$

The monometallic complex $[(Ph_2phen)_2Ru(dpp)](PF_6)_2$ was synthesized by modification of a previously reported method.²⁶ The precursor $[(Ph_2phen)_2RuCl_2]$ (1.0 g, 1.2 mmol) and excess dpp (0.43 g, 1.8 mmol) were added to 45 mL of 2:1 EtOH/H₂O and heated at reflux for 3 hours. The resulting orange reaction mixture was cooled to RT and added to an aqueous NH₄PF₆ solution (1.0 g in 50 mL) to metathesize the product from a Cl⁻ salt to a PF₆⁻ salt. The solid was collected by vacuum filtration and washed with 150 mL of H₂O. The complex was purified by adsorption column chromatography (3.5 cm x 10 cm) with a deactivated 80-200 mesh alumina stationary phase and a 3:2 toluene/CH₃CN mobile phase. The first light orange band containing the dpp free ligand was discarded. The second orange band which contained the desired product, $[(Ph_2phen)_2Ru(dpp)](PF_6)_2$, was collected and the solvent was

removed under vacuum. The third band containing the purple colored $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{Ph}_2\text{phen})_2](\text{PF}_6)_4$ impurity was discarded. The orange product was dissolved in minimal CH_3CN (10 mL) and added dropwise to 400 mL of stirring Et_2O . The orange precipitate was collected by vacuum filtration, and washed with 100 mL of Et_2O and dried under vacuum (0.75 g, 0.058 mmol, yield = 65 %).

2.2.6. $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$

The trimetallic complex $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ was synthesized by combining two equivalents of $[(\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (2.5 g, 2.5 mmol), one equivalent of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.26 g, 1.3 mmol), and excess LiCl (0.54 g, 13 mmol) in 50 mL of EtOH and heating at reflux for 24 h. The dark green reaction mixture was cooled to RT and added to aqueous NH_4PF_6 (0.50 g in 100 mL) to metathesize the complex from a Cl^- salt to a PF_6^- salt. The precipitate was collected by vacuum filtration and washed with 100 mL of H_2O . Purification was achieved using adsorption column chromatography (3.5 cm x 15 cm) with a deactivated 80-200 mesh alumina stationary phase and a 7:4 toluene/ CH_3CN mobile phase. The orange $[(\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ band eluted first and was discarded. The next band containing the green $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ product was collected and the solvent was removed under vacuum. The green product was dissolved in minimal CH_3CN (10 mL) and added dropwise to stirring Et_2O (400 mL). The precipitate was collected by vacuum filtration, washed with 90 mL of Et_2O and dried under vacuum (1.1 g, 0.51 mmol, yield = 40 %). (+)ESI-MS: $[\text{M}-3\text{PF}_6]^{3+}$, $m/z = 569.69$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-1**.

2.2.7. $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$

The trimetallic complex $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ was synthesized by combining two equivalents of the monometallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (2.0 g, 1.6 mmol), one equivalent of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.20 g, 0.79 mmol), and excess LiCl (0.50 g, 11 mmol) in 50 mL of EtOH and heating at reflux for 24 h. The dark green reaction mixture was cooled to RT and added to aqueous NH_4PF_6 (0.50 g

in 100 mL) to metathesize the complex from a Cl^- salt to a PF_6^- salt. The precipitate was collected by vacuum filtration and washed with 100 mL of H_2O . Purification was achieved using adsorption column chromatography (3.5 cm x 15 cm) with a deactivated 80-200 mesh alumina stationary phase and a 7:4 toluene/ CH_3CN mobile phase. The orange $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ band eluted first and was discarded. The next band containing the green $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ product was collected and the solvent was removed under vacuum. The green product was dissolved in minimal CH_3CN (10 mL) and added dropwise to stirring Et_2O (400 mL). The green precipitate was collected by vacuum filtration, rinsed with 100 mL of Et_2O and dried under vacuum (1.4 g, 0.51 mmol, yield = 65 %). (+)ESI-MS: $[\text{M}-2\text{PF}_6]^{2+}$, $m/z = 1231.14$, $[\text{M}-3\text{PF}_6]^{3+}$, $m/z = 772.44$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-2**.

2.2.8. $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$

The trimetallic complex $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ was synthesized by first combining $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (0.35 g, 0.16 mmol) with two equivalents of AgSO_3CF_3 (0.83 g, 0.32 mmol) in order to replace the Cl^- ligands with more labile SO_3CF_3^- ligands. The two reactants were dissolved in 30 mL of EtOH and heated at reflux for 2 h. The hot reaction mixture was then added dropwise to a hot, stirring solution of dpp ligand (0.30 g, 1.2 mmol) in ethylene glycol (20 mL) and the mixture was heated at reflux for 16 h. The mixture was cooled to RT and Bu_4NCl (0.088 g, 0.32 mmol) was added to precipitate Ag^+ as AgCl(s) . The reaction mixture was allowed to stir for 30 minutes followed by addition of 0.50 g of NH_4PF_6 to promote metathesis to a PF_6^- salt. The purple precipitate was collected by vacuum filtration and washed with 50 mL of H_2O . Purification of the crude product was achieved by successive syringe filtrations to remove insoluble impurities and metatheses to remove remaining Ag^+ as AgCl(s) . The solid was dissolved in minimal acetone (5 mL) and added dropwise to a saturated Bu_4NCl solution in 15 mL of acetone to produce $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})]\text{Cl}_6$ which formed as a precipitate and was collected by vacuum filtration. The chloride salt was dissolved in minimal H_2O (10 mL) and added dropwise to an aqueous NH_4PF_6 solution to precipitate the

$[\{(phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$ product. The product was collected by vacuum filtration and washed with 60 mL of H_2O . This process was repeated twice. The purple-red product was then dissolved in minimal CH_3CN (10 mL) and added dropwise through a syringe filter into 300 mL of Et_2O . The precipitate was collected by vacuum filtration, washed with 50 mL of Et_2O and dried under vacuum (0.28 g, 0.11 mmol, yield = 70 %). (+)ESI-MS: $[M-2PF_6]^{2+}$, $m/z = 1153.54$, $[M-3PF_6]^{3+}$, $m/z = 720.71$, $[M-4PF_6]^{4+}$, $m/z = 504.29$, $[M-5PF_6]^{5+}$, $m/z = 374.44$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-3**.

2.2.9. $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$

The trimetallic complex $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$ was synthesized by combining the trimetallic precursor $[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ (0.30 g, 0.11 mmol) with two equivalents of $AgSO_3CF_3$ (0.057 g, 0.22 mmol) to replace the Cl^- ligands with more labile $SO_3CF_3^-$ ligands. The reactants were dissolved in 30 mL $EtOH$ and heated at reflux for 2 h. The hot reaction mixture was added dropwise to a hot, stirring solution of dpp ligand (0.30 g, 1.2 mmol) in 20 mL of ethylene glycol and the reaction was heated at reflux for 16 h. The mixture was cooled to RT and Bu_4NCl (0.088 g) was added to precipitate Ag^+ as $AgCl(s)$. The reaction mixture was allowed to stir for 30 minutes followed by addition of 0.50 g of NH_4PF_6 to promote metathesis to a PF_6^- salt. The purple precipitate was collected by vacuum filtration and washed with 100 mL of H_2O . The crude product was purified by size exclusion chromatography with a Sephadex® LH-20 column (2.2 cm x 100 cm) and a 2:1 $EtOH/CH_3CN$ mobile phase. The crude product dissolved in $EtOH/CH_3CN$ was syringe filtered prior to chromatography to remove the insoluble $AgCl$. The large trimetallic complex which eluted first as a red-purple band was collected and the solvent was removed under vacuum. The smaller second band which contained the orange dpp ligand was discarded. The purple-red product was dissolved in minimal CH_3CN (5 mL) and added dropwise through a syringe filter into 300 mL of Et_2O . The resulting precipitate was collected by vacuum filtration, washed with 50 mL of Et_2O and dried under vacuum (0.28 g, 0.087 mmol, yield = 85

%). (+)ESI-MS: $[M-2PF_6]^{2+}$, $m/z = 1458.18$, $[M-3PF_6]^{3+}$, $m/z = 923.80$, $[M-4PF_6]^{4+}$, $m/z = 656.28$.

Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-4**.

2.2.10. $[\{(phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6$

The trimetallic complex $[\{(phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6$ was synthesized and purified following the same procedure as used for $[\{(phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$ (**Section 2.2.8**) by substituting dpq (0.33 g, 1.2 mmol) in the second step, yielding a dark purple precipitate (0.29 g, 0.11 mmol, yield = 70 %). (+)ESI-MS: $[M-PF_6]^+$, $m/z = 2503.09$, $[M-2PF_6]^{2+}$, $m/z = 1178.57$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-5**.

2.2.11. $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6$

The trimetallic complex $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6$ was synthesized and purified following the same procedure as used for $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$ (**Section 2.2.9**) by substituting dpq (0.30 g, 0.10 mmol) in the second step, yielding a dark purple-red precipitate (0.30 g, 0.082 mmol, yield = 75 %). (+)ESI-MS: $[M-2PF_6]^{2+}$, $m/z = 1483.19$, $[M-3PF_6]^{3+}$, $m/z = 940.47$, $[M-4PF_6]^{4+}$, $m/z = 669.11$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-6**.

2.2.12. $[\{(phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6$

The tetrametallic complex $[\{(phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6$ was synthesized by the reaction of the trimetallic complex $[\{(phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$ (0.16 g, 0.060 mmol) with excess *cis*- $[PtCl_2(DMSO)_2]$ (0.075 g, 0.18 mmol) in 25 mL of EtOH heated at reflux for 3 days. The reaction mixture was cooled to RT and excess NH_4PF_6 (0.25 g) was added to precipitate the complex as a PF_6^- salt. The purple precipitate was collected by vacuum filtration and washed with 100 mL of H_2O . The solid was then dissolved in minimal CH_3CN (5 mL) and added to 250 mL of Et_2O by syringe filtration to remove Pt^0 particles. The red-purple precipitate was collected by vacuum filtration, washed with 50 mL

of Et₂O, and dried under vacuum. This syringe filtration and precipitation process was repeated once (0.16 g, 0.056 mmol, yield = 95 %). (+)ESI-MS: [M–PF₆]⁺, *m/z* = 2718.08, [M–3PF₆]³⁺, *m/z* = 809.34, [M–4PF₆]⁴⁺, *m/z* = 570.76. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-7**.

2.2.13. [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆*

The tetrametallic complex [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ was synthesized and purified following the same procedure as used for [*{(phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (**Section 2.2.12**) by substituting [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (0.10 g, 0.031 mmol), yielding a dark purple-red precipitate (0.10 g, 0.030 mmol, yield = 95 %). (+)ESI-MS: [M–3PF₆]³⁺, *m/z* = 1011.96, [M–4PF₆]⁴⁺, *m/z* = 722.58. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-8**.***

2.2.14. [*{(phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆*

The tetrametallic complex [*{(phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ was synthesized and purified following the same procedure as used for [*{(phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (**Section 2.2.12**) by substituting [*{(phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ (0.12 g, 0.049 mmol), yielding a dark purple-red precipitate (0.11 g, 0.037 mmol, yield = 75 %). (+)ESI-MS: [M–2PF₆]²⁺, *m/z* = 1312.01. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-9**.***

2.2.15. [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆*

The tetrametallic complex [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ was synthesized and purified following the same procedure as used for [*{(phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (**Section 2.2.12**) by substituting [*{(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ (0.10 g, 0.031 mmol), yielding a dark purple-red precipitate (0.11 g, 0.030 mmol, yield = 95 %). (+)ESI-MS: [M+3CH₃CN–2PF₆]²⁺, *m/z* =***

1070.20, $[M+CH_3CN-3PF_6]^3+$, $m/z = 1041.92$, $[M-PtCl_2-3PF_6]^3+$, $m/z = 940.00$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-10**.

2.2.16. $[(Ph_2phen)_2Ru(dpp)RuCl_2(bpy)](PF_6)_2$

The bimetallic precursor $[(Ph_2phen)_2Ru(dpp)RuCl_2(bpy)](PF_6)_2$ was synthesized by dissolving $[(Ph_2phen)_2Ru(dpp)](PF_6)_2$ (0.30 g, 0.39 mmol) and excess *cis,cis*- $[(bpy)RuCl_2(DMSO)_2]$ (0.39 g, 0.80 mmol) in 40 mL EtOH and heating at reflux for 16 h. The reaction mixture was cooled to RT and 0.5 g of NH_4PF_6 was added to precipitate the product as a PF_6^- salt. The precipitate was collected by vacuum filtration and washed with 100 mL of H_2O . Purification was achieved by size exclusion chromatography using a Sephadex® LH-20 column (2.2 cm x 100 cm) and a 2:1 EtOH/ CH_3CN mobile phase. The green-brown desired product that eluted first was collected and the solvent was removed under vacuum. Unreacted $[(Ph_2phen)_2Ru(dpp)](PF_6)_2$ and $[(bpy)RuCl_2(DMSO)_2]$ eluted as an orange band after the desired product and this band was discarded. The product was dissolved in minimal CH_3CN (5 mL) and added dropwise into 300 mL of Et_2O by syringe filtration. The green-brown precipitate was collected by vacuum filtration, washed with 60 mL of Et_2O and dried under vacuum (0.29 g, 0.18 mmol, yield = 45 %). (+)ESI-MS: $[M-PF_6]^+$, $m/z = 1473.14$, $[M-2PF_6]^{2+}$, $m/z = 664.09$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-11**.

2.2.17. $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpp)](PF_6)_4$

The bimetallic complex $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpp)](PF_6)_4$ was synthesized by dissolving the precursor $[(Ph_2phen)_2Ru(dpp)RuCl_2(bpy)](PF_6)_2$ (0.30 g, 0.19 mmol) and two equivalents of $AgSO_3CF_3$ (0.97 g, 0.38 mmol) in 30 mL EtOH and heating at reflux for 2 h to replace Cl^- ligands with more labile $SO_3CF_3^-$ ligands. The hot reaction mixture was then added to a hot, stirring solution of dpp (0.3 g, 1.2 mmol) in 20 mL of ethylene glycol and the mixture was heated at reflux for 16 h. The reaction mixture was then cooled to RT and 0.075 g of Bu_4NCl was added and stirred with the mixture for 30 minutes to precipitate Ag^+ as $AgCl$. Excess NH_4PF_6 (0.5 g) was added to metathesize the complex to

form the PF_6^- salt. The precipitate was collected by vacuum filtration and washed with 50 mL of H_2O . Purification was achieved by size exclusion chromatography using a Sephadex® LH-20 column (2.2 cm x 100 cm) and a 2:1 $\text{EtOH}/\text{CH}_3\text{CN}$ mobile phase. The red-purple desired product that eluted first was collected and the solvent was removed under vacuum. Unreacted dpp eluted next as an orange band and was discarded. The product was dissolved in minimal CH_3CN (5 mL) and added dropwise to 300 mL of Et_2O by syringe filtration. The red precipitate was collected by vacuum filtration, washed with 60 mL of Et_2O , and dried under vacuum (0.23 g, 0.11 mmol, yield = 60 %). (+)ESI-MS: $[\text{M}-\text{PF}_6]^+$, $m/z = 1927.21$, $[\text{M}-2\text{PF}_6]^{2+}$, $m/z = 890.73$, $[\text{M}-3\text{PF}_6]^{3+}$, $m/z = 545.76$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-12**.

2.2.18. $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$

The bimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ was synthesized and purified following the same procedure as used for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (section 2.2.17.) by substituting dpq (0.33 g, 1.2 mmol) in the second step, yielding a dark purple-red color precipitate (0.21 g, 0.10 mmol, yield = 55 %). (+)ESI-MS: $[\text{M}-2\text{PF}_6]^{2+}$, $m/z = 890.73$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-13**.

2.2.19. $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$

The trimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ was synthesized by dissolving $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (0.10 g, 0.048 mmol) and excess *cis*- $[\text{PtCl}_2(\text{DMSO})_2]$ (0.10 g, 0.24 mmol) in 30 mL EtOH and heating at reflux for 4 h. The reaction mixture was cooled to RT and 0.5 g of NH_4PF_6 was added to precipitate the product as a PF_6^- salt. The precipitate was collected by vacuum filtration and washed with 60 mL of H_2O . The product was dissolved in minimal CH_3CN (5 mL) and added dropwise to 300 mL of Et_2O by syringe filtration to remove Pt^0 particles. The red precipitate was collected by vacuum filtration, washed with 50 mL of Et_2O and dried under vacuum (0.11 g, 0.046 mmol, yield = 95 %). (+)ESI-MS: $[\text{M}-\text{PF}_6]^+$, $m/z = 2193.11$, $[\text{M}-2\text{PF}_6]^{2+}$, $m/z = 1024.07$, $[\text{M}-3\text{PF}_6]^{3+}$,

$m/z = 634.07$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-14**.

2.2.20. $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpq)PtCl_2](PF_6)_4$

The trimetallic complex $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpq)PtCl_2](PF_6)_4$ was synthesized and purified using the same procedure as used for $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpp)PtCl_2](PF_6)_4$ (**Section 2.2.19**) by substituting $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpq)](PF_6)_4$ (0.10 g, 0.047 mmol), yielding a dark purple-red precipitate (0.11 g, 0.045 mmol, yield = 95 %). (+)ESI-MS: $[M-2PF_6]^{2+}$, $m/z = 1049.08$, $[M-3PF_6]^{3+}$, $m/z = 651.07$. Calculated and experimental mass spectra for the molecular ion peak are given in **Figure A-15**.

2.3. Instrumentation and Methods

2.3.1. Mass Spectrometry

Positive ion electrospray ionization mass spectrometry, (+)ESI-MS, experiments were performed in the Virginia Tech Chemistry Department Analytical Services laboratory by Mr. William Bebout using an Agilent Technologies 6220 Accurate-Mass time-of-flight (TOF) instrument with a dual ESI source. The samples were dissolved in HPLC grade CH_3CN and directly injected into the instrument source through a preloading capillary at 1.2 kV with a 0.4 mL/min flow rate. N_2 gas at a pressure of 60 psig was used as the inert nebulizing gas. The charging voltage was 2000 V, the fragmentor voltage was 125 V, and the skimmer voltage was 65 V. Isotopic distribution patterns were simulated using Sheffield Chempurter¹⁰³ and compared to the observed molecular ion peaks.

2.3.2. Electrochemistry

Electrochemical experiments were performed with an Epsilon potentiostat from Bioanalytical Systems, Inc. using a one compartment, three electrode cell with a glassy carbon working electrode, silver wire pseudo reference electrode, and a platinum wire auxiliary electrode (**Figure 2.1**). Ferrocene was

added to the sample as an internal standard ($\text{FeCp}_2^+/\text{FeCp}_2 = 0.46 \text{ V vs. Ag/AgCl}(3 \text{ M NaCl})$)¹⁰⁴ following electrochemical analysis. The working electrode was polished with 0.5 μm alumina paste prior to each experiment. The CH_3CN electrolyte solution containing 0.1 M Bu_4NPF_6 was deoxygenated by bubbling with Ar for 10 minutes and a background scan was performed to ensure the absence of electrochemically active impurities. Cyclic voltammetry (CV) studies were performed at a scan rate of 0.1 V/s. Osteryoung square wave voltammetry (SWV) studies were performed with pulse frequency (τ) = 15 Hz, pulse time (t_p) = 30 ms, fixed pulse potential magnitude (ΔE_p) = 25 mV, and potential step (ΔE_s) = 4 mV. The CV triangular waveform and the SWV pulsed staircase waveform are depicted in **Figure 2.2**.^{24,105} CV gives information about reversibility of redox couples, while SWV gives a higher signal-to-noise ratio.

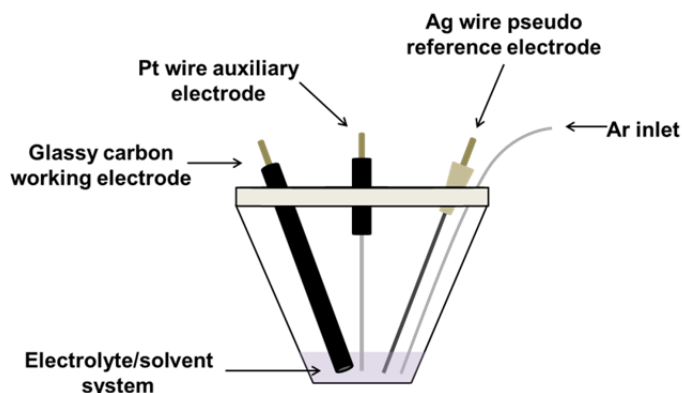


Figure 2.1: Diagram of the one-compartment, three electrode cell using a glassy carbon working electrode, Pt wire auxiliary electrode, and an Ag wire pseudo reference electrode. Argon was bubbled through the electrolyte/solvent system.

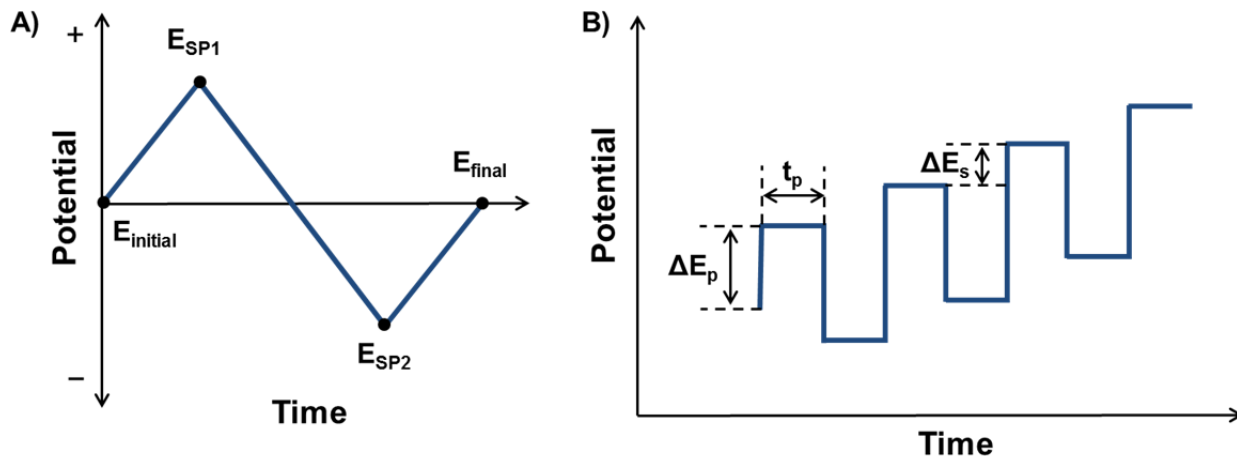


Figure 2.2: A) Triangular waveform for cyclic voltammetric analysis, where E_{initial} = initial potential, E_{SP1} = first switching potential, E_{SP2} = second switching potential, E_{final} = final potential. B) Pulsed staircase waveform for Osteryoung square wave voltammetric analysis, where ΔE_p = fixed pulse potential magnitude, t_p = pulse time, τ = pulse frequency, ΔE_s = potential step.

2.3.3. Electronic Absorption Spectroscopy

Electronic absorption spectra were measured using an Agilent 8453 diode array UV-Vis spectrophotometer with 1 nm resolution and a spectral range of 190 to 1100 nm. Samples were dissolved in RT spectral grade CH_3CN and measured in a 1 cm or 0.2 cm quartz cuvette (Starna Cells, Inc.; Atascadero, CA, USA). Extinction coefficient experiments were performed in triplicate with each solution prepared gravimetrically.

2.3.4. Spectroelectrochemistry

Spectroelectrochemical experiments were performed using an Agilent 8453 diode array UV-Vis spectrophotometer and an Epsilon potentiostat from Bioanalytical Systems, Inc. A two-compartment H-cell¹⁰⁶ (**Figure 2.3**) was used to separate the platinum mesh working electrode and Ag/AgCl (3 M $\text{NaCl}_{(\text{aq})}$) reference electrode from the carbon cloth auxiliary electrode. The working electrode, reference electrode, an Ar inlet to deoxygenate the solution, an electrolyte solution containing 0.1 M Bu_4NPF_6 in RT spectral grade CH_3CN , and the analyte were contained in the 1 cm quartz cuvette working

compartment. A constant potential was applied while continuously bubbling with Ar and spectra were periodically recorded.

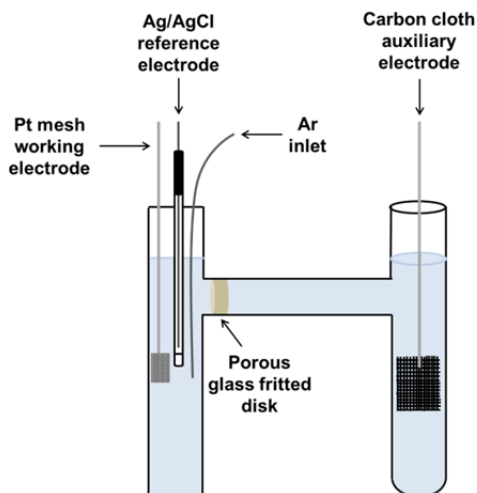


Figure 2.3: Schematic of the locally-designed H-cell for spectroelectrochemical analysis. The left compartment contains a Pt mesh working electrode, Ag/AgCl reference electrode, Teflon tube for Ar bubbling, the analyte, and the electrolyte/solvent system. The right compartment contains the carbon cloth auxiliary electrode and the electrolyte/solvent system. The two compartments are separated by a porous glass fritted disk.

2.3.5. Steady-State Emission Spectroscopy

Steady-state emission was measured using a QuantaMaster Model QM-200-45E fluorimeter (**Figure 2.4A**) from Photon Technologies International, Inc. The excitation source was a 150 W Xe arc lamp that was cooled by water circulation. The arc lamp output profile is given in **Figure 2.5**, adapted from the manufacturer's website.¹⁰⁷ The emission was collected at a 90° angle with a thermoelectrically cooled Hamamatsu 1527 photomultiplier tube (PMT) in photon counting mode with a 0.25 nm resolution. The monochromator used Czerny-Turner style grating set to 1200 lines/mm and 750 nm blaze. The slit widths for the excitation and emission monochromators were adjusted to 1.5 mm, which corresponds to ± 6 nm. The sample was dissolved in RT spectra grade CH₃CN with an absorbance ca. 0.3 at the chosen excitation wavelength (λ^{exc}). The solutions were deoxygenated by bubbling with Ar for 10 minutes prior

to analysis. Recorded spectra were an average of three scans unless otherwise stated. The quantum yields of emission (Φ^{em}) were calculated with $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ as a standard using **Equation 2.1**,

$$\Phi_{sample}^{em} = \Phi_{standard}^{em} \times \frac{Area_{sample}}{Area_{standard}} \times \frac{Absorbance_{standard}}{Absorbance_{sample}} \quad (2.1)$$

where Φ_{sample}^{em} is the quantum yield of emission of the sample, $\Phi_{standard}^{em}$ is the quantum yield of emission of $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ ($\Phi^{em} = 0.0046$ in RT deoxygenated CH_3CN),³⁶ $Area_{sample}$ is the area under the curve of the sample's emission profile, $Area_{standard}$ is the area under the curve of the standard's emission profile, $Absorbance_{sample}$ is the measured absorbance of the sample at the excitation wavelength, and $Absorbance_{standard}$ is the measured absorbance of the standard at the excitation wavelength. 77 K emission spectra were measured by dissolving the sample in 4:1 EtOH/MeOH in an NMR tube and slowly immersing the sample in a finger dewar filled with liquid N_2 . All emission spectra were corrected for PMT response using the manufacturer supplied correction file, **Figure 2.4B**.

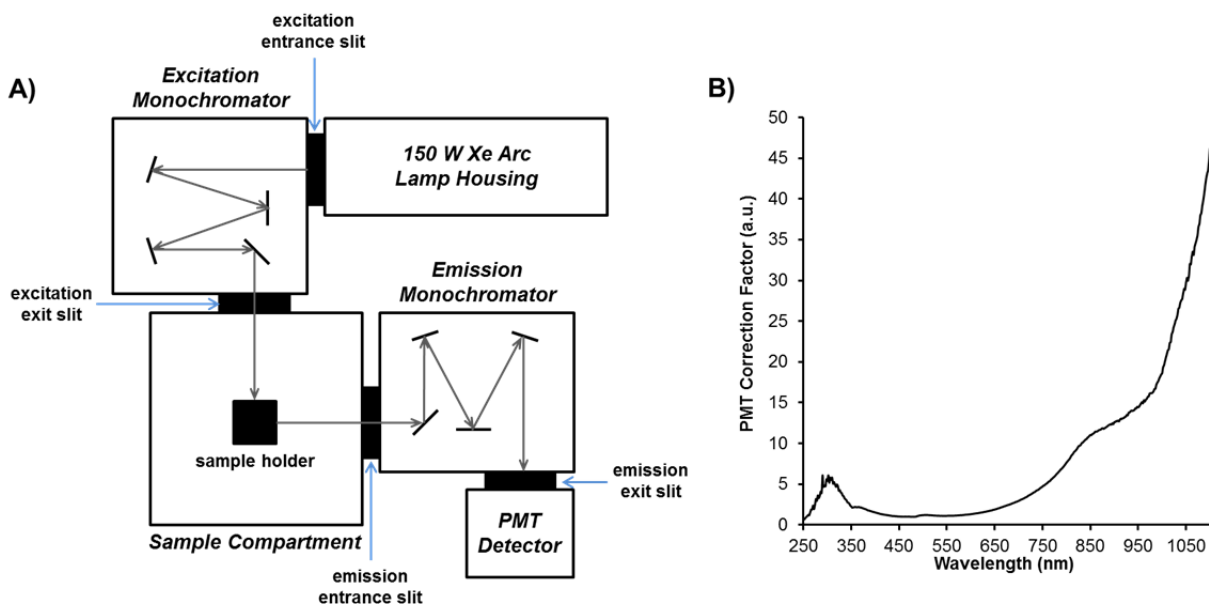


Figure 2.4: A) Schematic diagram of the experimental set-up for steady-state emission spectroscopy. B) Plot of the emission correction file for the Hamamatsu 1527 photomultiplier tube.

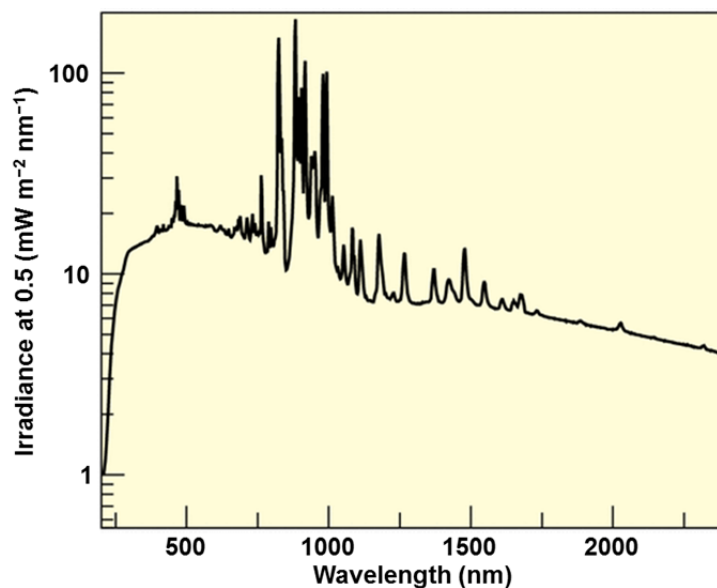


Figure 2.5: Output profile for the 150 W Xe arc lamp excitation source. Figure adapted from reference 107.

2.3.6. Time-Resolved Emission Spectroscopy

Time-resolved emission spectroscopy measurements were performed using a Photon Technologies International, Inc. PL-2300 N₂ laser with a PL-201 tunable dye laser (**Figure 2.6**). The dye used was Coumarin 540A (10 mM in EtOH). An emission monochromator was set to the maximum emission wavelength determined by steady-state emission measurements. A Hamamatsu R928 PMT operating in direct analog mode collected the time profile at a 90° angle relative to the excitation source. The signal was displayed on a LeCroy 9361 Dual 300 MHz oscilloscope (2.5 Gs/s). The data were applied to an exponential decay function, **Equation 2.2**,

$$I(t) = \sum_i \alpha_i e^{\frac{-t}{\tau_i}} \quad (2.2)$$

where $I(t)$ is the intensity of the signal at time t after the laser pulse, $\sum_i \alpha_i$ is the sum of the fractions that are contributed by each component to the overall observed decay, i is the component, and τ_i is the excited state lifetime of each component. The signals measured as potential (V) were graphed versus time, and a plot of $\ln(V)$ versus time yields a straight line with a slope that corresponds to τ^{-1} . The sample was

dissolved in RT spectra grade CH_3CN with an absorbance ca. 0.3 at the chosen excitation wavelength (λ^{exc}). The solutions were deoxygenated by bubbling with Ar for 10 minutes prior to analysis. The 77 K emission spectra were measured by dissolving the sample in 4:1 EtOH/MeOH in an NMR tube and slowly immersing the sample in a finger dewar filled with liquid N_2 .

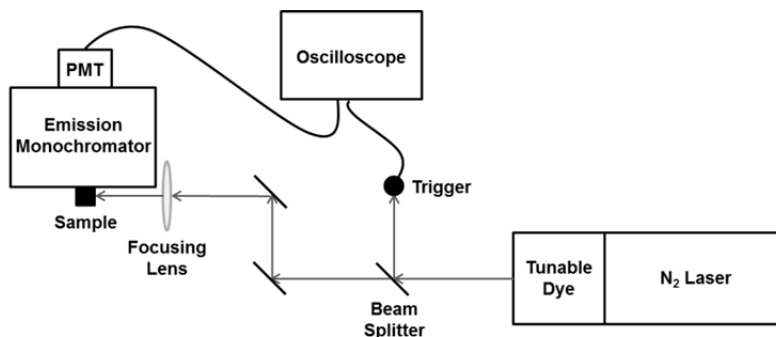


Figure 2.6: Schematic diagram of the experimental set-up for time-resolved emission spectroscopy.

2.3.7. Transient Absorption Spectroscopy

Nanosecond transient absorption spectroscopy studies were performed in the laboratory of Prof. Thomas J. Meyer at the University of North Carolina at Chapel Hill by Dr. M. Kyle Brennaman. The samples were dissolved in RT spectral grade CH_3CN in a 1 cm quartz cuvette and deoxygenated by bubbling with Ar for 30 minutes prior to analysis. Nanosecond laser pulses were generated by a Spectra-Physics Quant-Ray Lab-170 Nd:YAG laser combined with a VersaScan OPO (532 nm, 5-7 ns, operated at 1 Hz, 0.5 cm beam diameter, ~5 mJ/pulse) that was incorporated into a commercially available Edinburgh LP920 laser flash photolysis system. A 450 W Xe arc lamp produced white light probe pulses that passed through the sample then focused into the spectrometer (3 nm bandwidth), and detected by a Hamamatsu R928 photomultiplier tube. The full spectra (350-800 nm) were collected at various times after laser excitation using a gated CCD (Princeton Instruments, PIMAX-3) using 5 ns gatewidth and 3 nm bandwidth. Each spectrum was collected by averaging 200 repetitions for each pump/probe, probe only, and pump only shutter condition. A Tektronix TD S3032C digital phosphor oscilloscope interfaced

to a PC running the Edinburgh software package processed the detector outputs. Single wavelength kinetic data were the average of 50-150 laser shots and were fit using Origin software.

2.3.8. Photochemical Reduction

Electronic absorption spectroscopy was used to monitor spectral shifts as a result of photolysis of a solution containing the supramolecular complex and a sacrificial electron donor, DMA. A solution containing 20 μM complex and 2 mM DMA in a 1 cm quartz cuvette were photolyzed with a 470 nm LED light source and the spectra were measured after 0, 5, 10, 20, 30, 60, and 120 seconds of exposure to the light source. The samples were kept in the dark between photolysis and measurement of the spectra to minimize stray light interactions.

2.3.9. Excited State Reductive Quenching

The interaction between the excited state complex and the electron donor DMA was studied by monitoring the emission quenching by a Stern-Volmer analysis. Stock solutions of the complex and the DMA were prepared separately in CH_3CN . Solutions with a total volume of 2 mL were made in a 1 cm quartz cuvette with a constant complex concentration (30 μM) and varied DMA concentrations (0 - 24 mM). Measurements were made by injecting the DMA sample into the complex-containing cuvette in the dark to avoid undesired photochemical reactions. The steady-state emission spectra were measured and a Stern-Volmer plot of Φ_0/Φ vs. $[\text{DMA}]$ was constructed (Φ_0 = quantum yield of emission in the absence of DMA; Φ = quantum yield of emission in the presence of DMA).¹⁰⁸ The Stern-Volmer constant, K_{SV} , was determined by the slope of this plot, and the relationship is given in **Equation 2.3**.

$$\frac{\Phi_0}{\Phi} = 1 + K_{SV}[\text{DMA}] \quad (2.3)$$

The rate constant for quenching of the excited state, k_q , is calculated using **Equation 2.4**,

$$K_{SV} = k_q \tau_0 \quad (2.4)$$

where τ_0 is the excited state lifetime of the complex in the absence of quencher.

2.3.10. Photocatalytic H₂ Production

H₂ production experiments were performed using a locally designed LED array (**Figure 2.7**). The light sources were blue Luxeon® V Star LEDs with a spectral coverage of 470 ± 10 nm. The chemical actinometer K₃[Fe(C₂O₄)₃] was used to determine the light flux of the LEDs.¹⁰⁹ The calculated flux of $2.3 \pm 0.1 \times 10^{19}$ photons/min was the average of three experiments. HY-OPTIMA™ 700 in-line process H₂ sensors from H2scan (Valencia, CA) were used to quantify H₂ production in real time. Multiple sensors were used simultaneously by incorporating a USB-8COMi-RM data communication serial port. The sensors were calibrated periodically to ensure accurate H₂ readings by injecting known amounts of H₂, recording the % H₂ output, and generating a calibration curve.

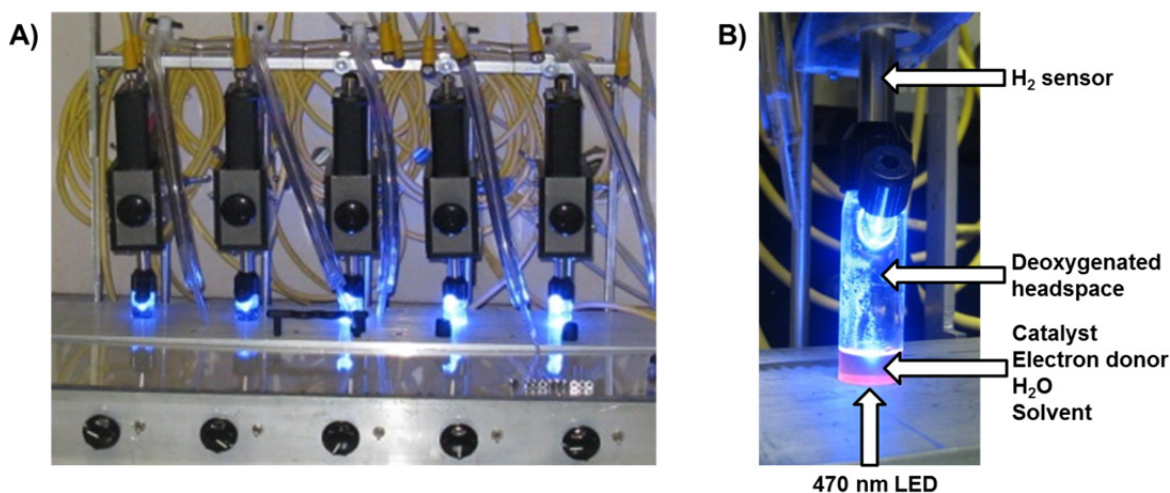


Figure 2.7: A) Picture of the locally designed and built LED array used for photocatalytic H₂ production experiments with 470 nm LEDs. B) Picture of one photocatalysis cell containing the catalyst, electron donor, H₂O and solvent in a deoxygenated environment. The LED irradiates the system from the bottom and H₂ is detected at the top of the air-tight cell.

Glass photolysis reaction cells were designed locally and manufactured by the Virginia Tech Chemistry Department Glassblowing Shop by Tom Wortalik. The two-neck reaction cell enables an air-tight connection of the H₂ sensor while providing an air-tight septum for deoxygenation and solution injection. The septum-capped cells were tightly attached to the H₂ sensor, and air was removed from the system with an Ar flow for 30 minutes. The sensors were powered on and a 5 % volume (ca. 1 mL) of H₂

was injected into each cell to prime the sensors. After 10 minutes of H₂ exposure, the cells were purged with Ar for 30 minutes to remove H₂. The metal complex stock solution in spectral grade CH₃CN, with a concentration determined by the absorbance and extinction coefficient at a given wavelength, and H₂O acidified to pH 2 with HSO₃CF₃ were injected into the reaction cells. The solution was deoxygenated by bubbling with Ar for 15 minutes. The sacrificial electron donor, DMA, was deoxygenated separately and injected into the cell immediately prior to photolysis. The LEDs were turned on to begin photolysis directly after injection of DMA. The cells were covered with aluminum foil to minimize interference of ambient light from the laboratory. The evolution of H₂ was monitored in real time using MOXA Pcomm Lite terminal emulator software. The % H₂ output was converted to moles of H₂, and the TON (turnover number) of the catalyst was calculated using **Equation 2.5**.

$$TON = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of catalyst}} \quad (2.5)$$

The quantum yield of H₂ production at time t was calculated using **Equation 2.6**.

$$\Phi_{H_2}(t) = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of incident photons}} \times 2 \quad (2.6)$$

The moles of incident photons were calculated using the light flux. The ratio of moles of H₂ produced and the moles of incident photons was multiplied by two due to the need for two photons to produce one H₂ molecule.

3. Results and Discussion

The goal of this research is to develop structurally diverse Ru(II),Pt(II) mixed-ligand supramolecular complexes with remote and thereby longer lived Ru→BL ³MLCT states and to study how their redox, spectroscopic, and photophysical properties imparted by component variation impact their photoinitiated electron collection and excited state dynamics with applications in solar energy conversion. This dissertation presents a collection of studies of unusual, photoactive multimetallic complexes with diverse supramolecular architecture allowing variation of coordinated ligands as well as the number of light absorbers. Structural diversity is important in supramolecular complexes as it provides control of energy and electron flow that leads to molecular machines with a specific function and reactivity. Only one Ru₃Pt complex, $[\{(bpy)_2Ru(dpp)\}_2Ru(dpp)PtCl_2]^{6+}$,¹¹⁰ and no Ru₂Pt complexes of this type were reported prior to this work.

3.1. Synthesis and Purification

The supramolecular complexes were synthesized according to a building block procedure in which smaller components were covalently coupled to construct larger systems composed of multiple units each having specific functions. The building block schemes for assembling the target tetrametallic $[\{(TL)_2Ru(BL)\}_2Ru(BL')PtCl_2]^{6+}$ and trimetallic $[(TL)_2Ru(BL)Ru(TL')(BL')PtCl_2]^{4+}$ architectures are pictured in **Figures 3.1** and **3.2**, respectively. This building block method allows systematic variation of TL, LA, BL, and structure as well as purification and analysis of reaction intermediates. Synthetic control, purification, and characterization at each step are essential to understand the properties of such complex molecules. The monometallic precursors were synthesized by first coupling two polyazine TLs to a Ru center to form the $[(TL)_2RuCl_2]$ synthon. $[(TL)_2RuCl_2]$ were purified and then reacted with excess BL to produce the monometallic $[(TL)_2Ru(BL)]^{2+}$ complexes. Synthetic schemes for the monometallic precursors $[(Ph_2phen)_2RuCl_2]$, $[(Ph_2phen)_2Ru(dpp)]^{2+}$, and $[(bpy)RuCl_2(DMSO)_2]$ are depicted in **Figure 3.3**. The *cis*-dichloride Ru-centered trimetallic complexes $[\{(TL)_2Ru(BL)\}_2RuCl_2]^{4+}$ were synthesized by coupling two $[(TL)_2Ru(BL)]^{2+}$ complexes through a Ru LA center via reaction with

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of EtOH as a reducing agent. The chloride ligands were then replaced with BL' to provide the trimetallic complexes $[\{(\text{TL})_2\text{Ru}(\text{BL})\}_2\text{Ru}(\text{BL}')]\text{PtCl}_2^{6+}$ which contain an open site on BL' for coordination of a RM center to produce the target tetrametallic complex $[\{(\text{TL})_2\text{Ru}(\text{BL})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$. The synthetic scheme for production of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ is provided in **Figure 3.4**. Assembly of the trimetallic architecture, $[(\text{TL})_2\text{Ru}(\text{BL})\text{Ru}(\text{TL}')(\text{BL}')\text{PtCl}_2]^{4+}$, is more complicated due to the tendency of Ru halides to react with NN diimine ligands to produce *cis*- $[\text{Ru}(\text{NN})_2\text{X}_2]$ motifs.¹⁰¹ The Ru_2Pt trimetallics first require synthesis of a Ru(II) monometallic complex with one coordinated TL, *cis,cis*- $[(\text{TL}')\text{RuCl}_2(\text{DMSO})_2]$. These complexes are then coupled to the monometallic species $[(\text{TL})_2\text{Ru}(\text{BL})]^{2+}$ to give the *cis*-dichloride Ru-containing bimetallic complex $[(\text{TL})_2\text{Ru}(\text{BL})\text{RuCl}_2(\text{TL}')]\text{PtCl}_2^{2+}$. BL' was then added to the $[(\text{TL})_2\text{Ru}(\text{BL})\text{RuCl}_2(\text{TL}')]\text{PtCl}_2^{2+}$ complex to replace the two chloride ligands to give $[(\text{TL})_2\text{Ru}(\text{BL})\text{Ru}(\text{TL}')(\text{BL}')]\text{PtCl}_2^{4+}$. The RM was then coupled to the bimetallic complex through the open coordination site on BL' to produce the target complex $[(\text{TL})_2\text{Ru}(\text{BL})\text{Ru}(\text{TL}')(\text{BL}')\text{PtCl}_2]^{4+}$. The synthetic scheme for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ is given in **Figure 3.5**.

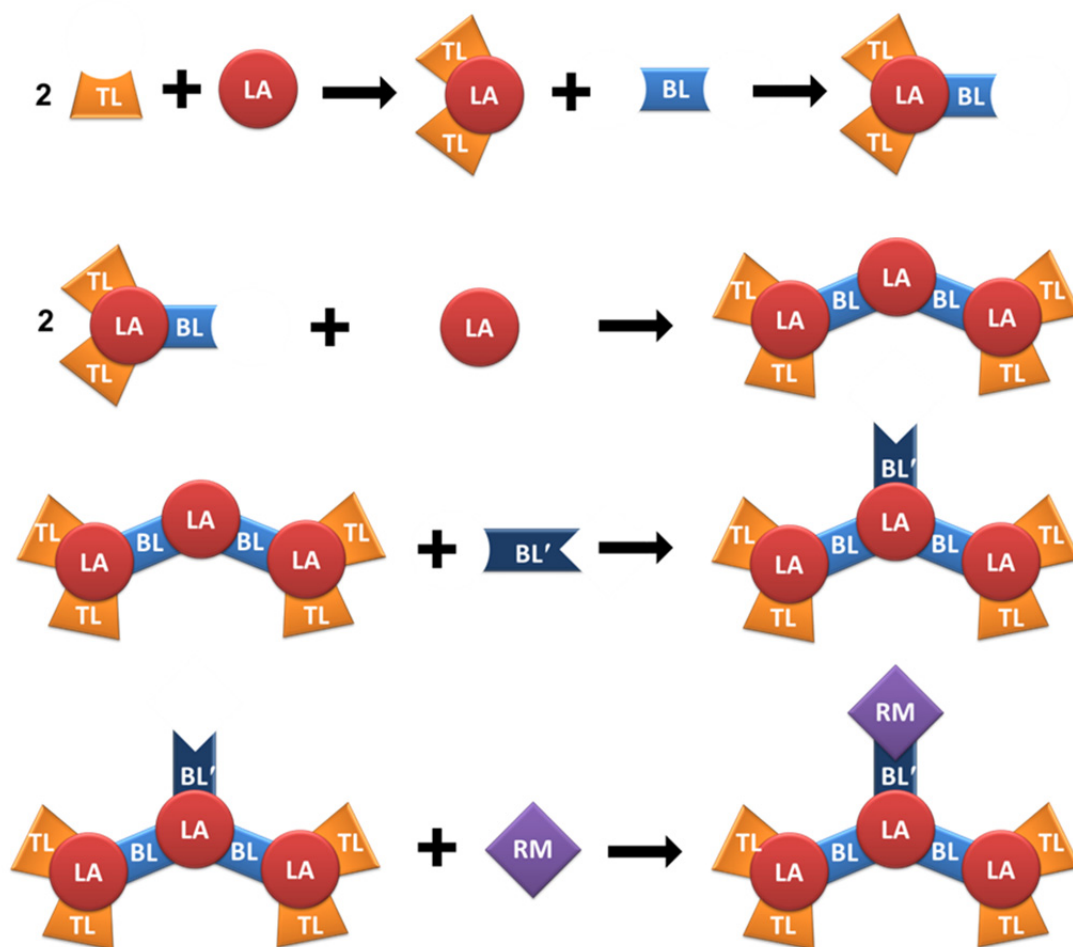


Figure 3.1: Generalized building block scheme for the synthesis of $[\{(\text{TL})_2\text{Ru}(\text{BL})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes. TL = terminal ligand, LA = light absorber metal center, BL/BL' = bridging ligand, RM = reactive metal.

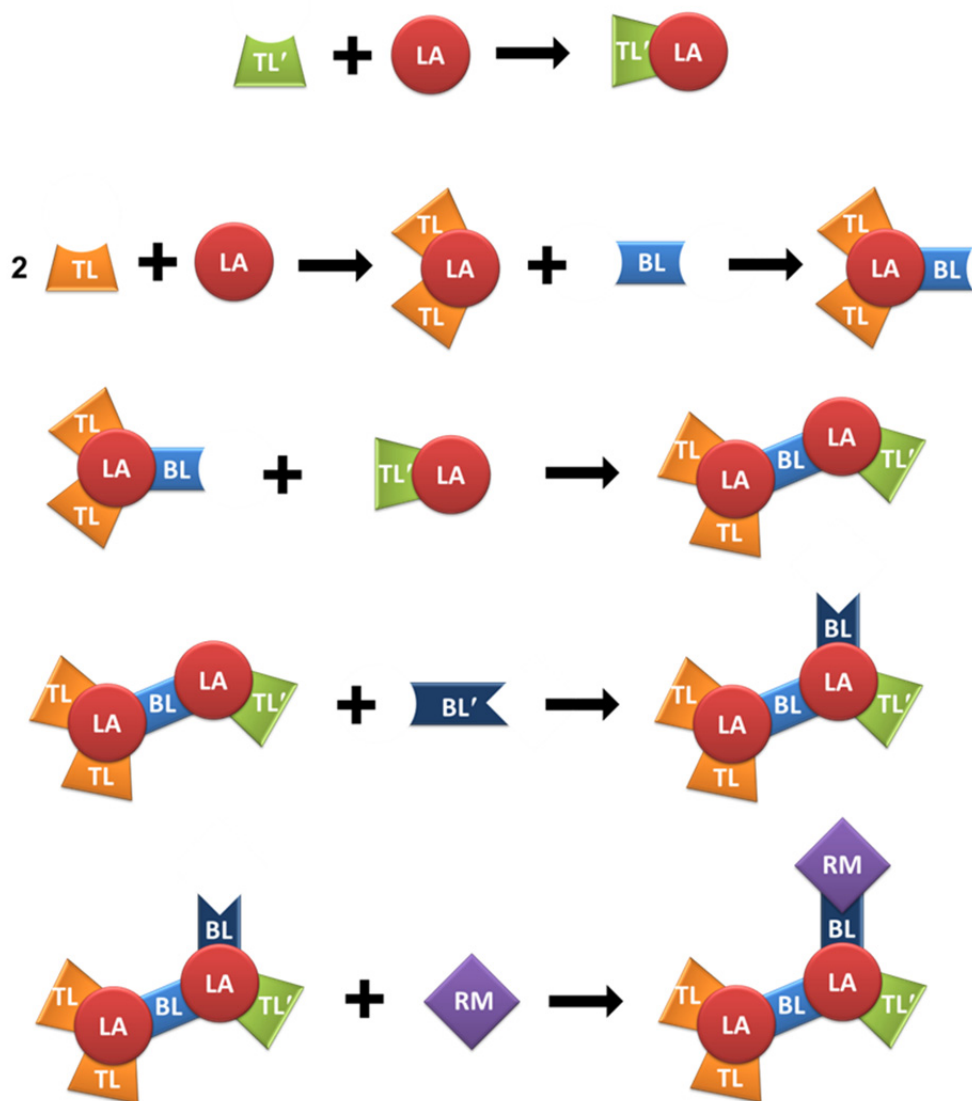


Figure 3.2: Generalized building block scheme for the synthesis of $[(\text{TL})_2\text{Ru}(\text{BL})\text{Ru}(\text{TL}')(\text{BL}')\text{PtCl}_2]^{4+}$ complexes. TL/TL' = terminal ligand, LA = light absorber metal center, BL/BL' = bridging ligand, RM = reactive metal.

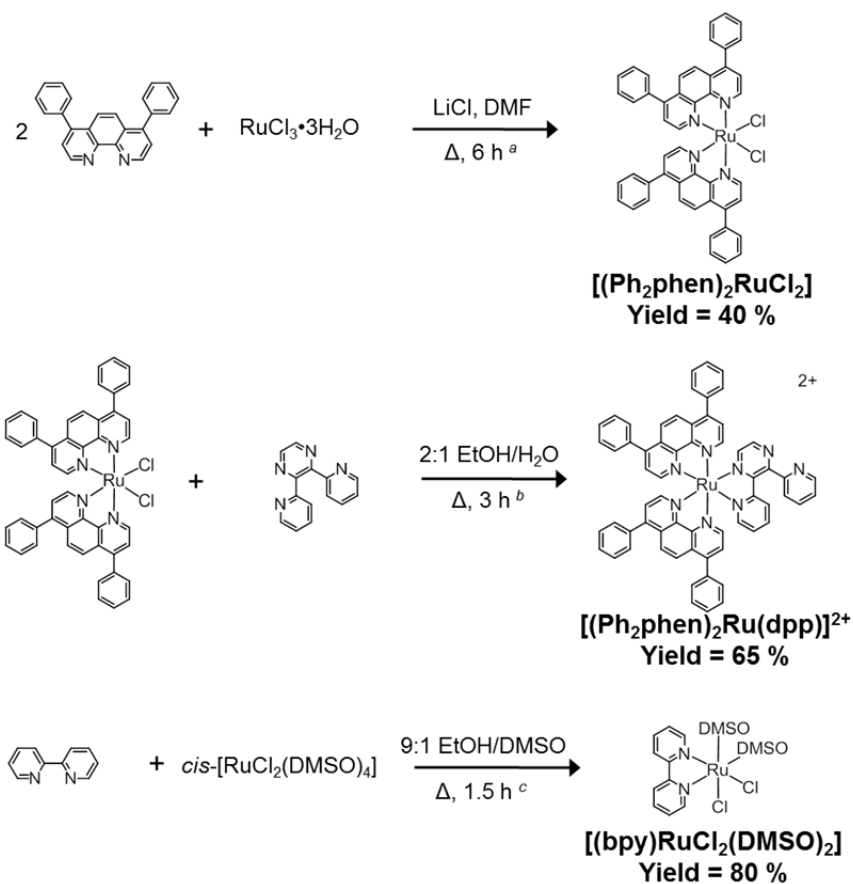


Figure 3.3: Synthetic schemes for the monometallic precursors $[(\text{Ph}_2\text{phen})_2\text{RuCl}_2]$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$, and *cis,cis*- $[(\text{bpy})\text{RuCl}_2(\text{DMSO})_2]$ which are generally applicable to all TLs in this study. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine. ^a From reference 102. ^b From reference 26. ^c From reference 100.

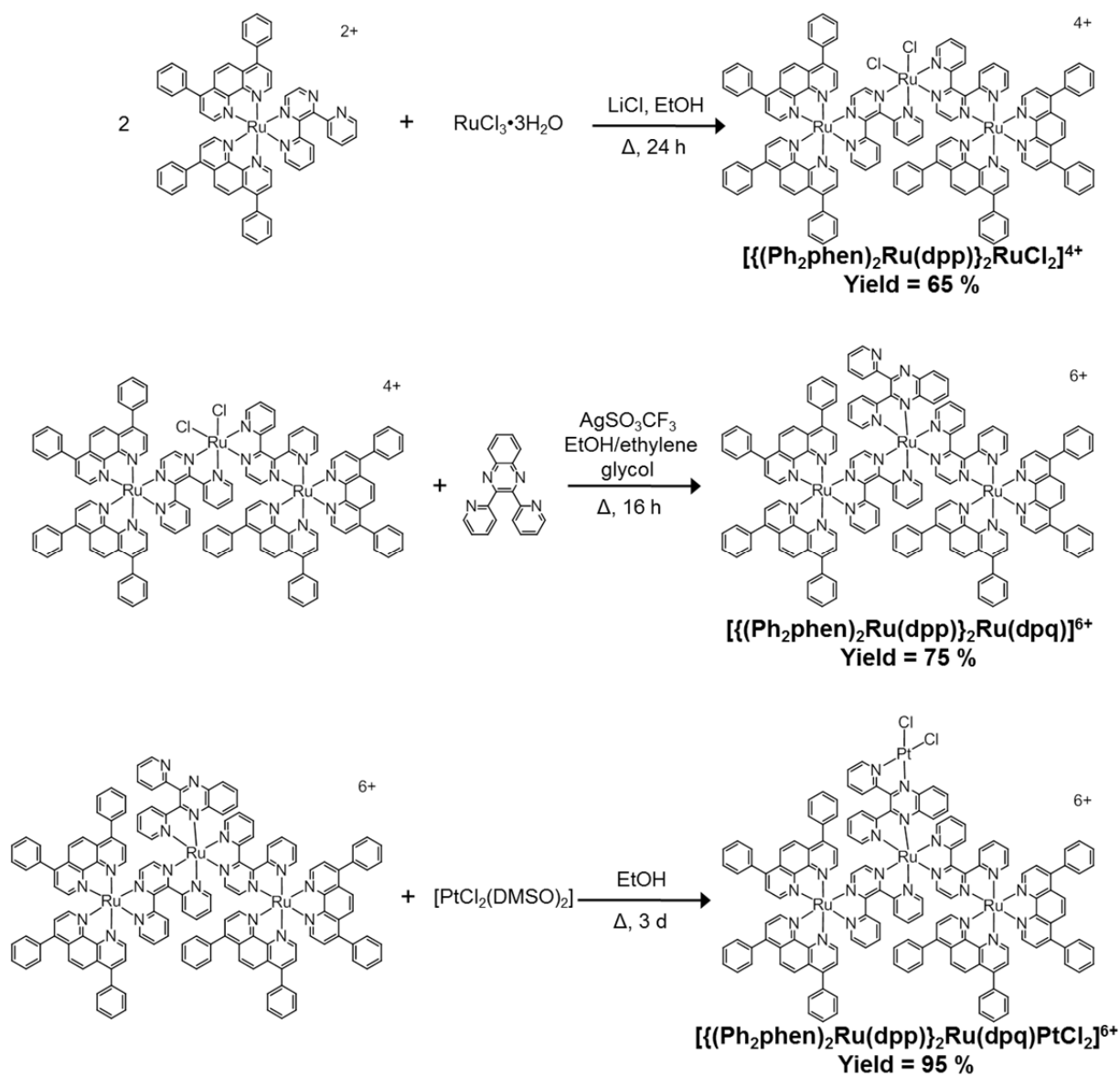


Figure 3.4: Synthetic scheme the tetrametallic complex $[\{ (\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}) \}_2 \text{Ru}(\text{dpq}) \text{PtCl}_2]^{6+}$. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

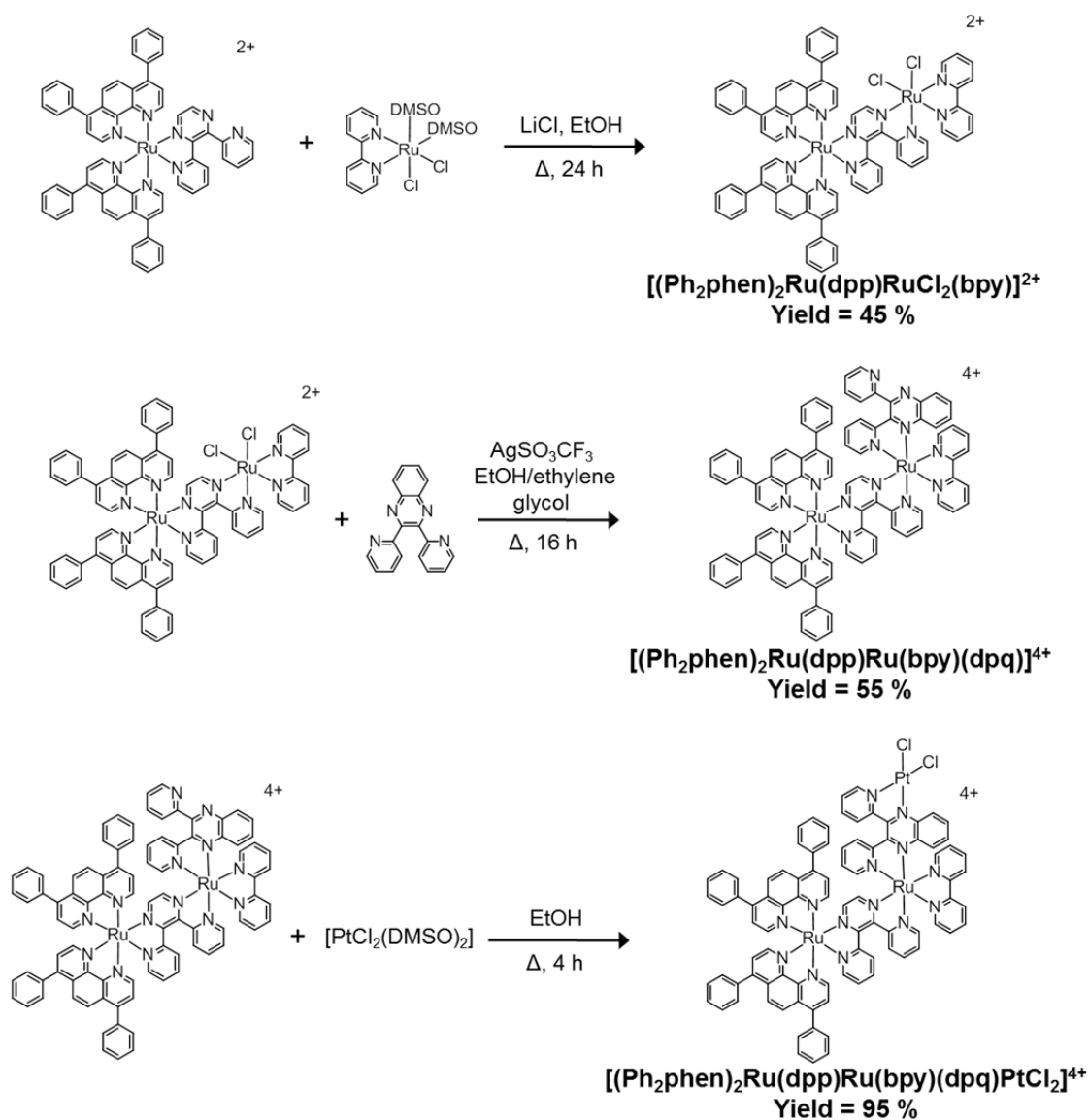


Figure 3.5: Synthetic scheme the trimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The building block methodology enables purification and analysis at each step of the synthetic scheme. ^1H NMR is not useful in characterization of the larger supramolecular complexes due to the large number of aromatic protons and the mixture of isomers formed throughout the synthesis (discussed below in **Section 3.2.1**). A combination of techniques, such as ESI-MS, square wave voltammetry, electronic absorption spectroscopy, and emission spectroscopy, as well as sub-unit variation, provides evidence that the products are consistent with proposed structures and of purity with respect to

electroactive and photoactive by-products. Products of repeated syntheses are compared to assure purity. The precursors, desired products, and common impurities have characteristic redox and spectroscopic properties, enabling detection of predicted impurities through electrochemical and spectroscopic analyses. For example, a common impurity in the $[(TL)_2RuCl_2]$ synthesis is the tris-homoleptic $[Ru(TL)_3]^{2+}$ complex. $[Ru(TL)_3]Cl_2$ is strongly emissive ($\Phi^{em} = 0.02-0.37$, **Section 1.2.3**) while no emission is detected for the analogous $[(TL)_2RuCl_2]$ complexes, so the amount of $[Ru(TL)_3]Cl_2$ in the $[(TL)_2RuCl_2]$ sample can be detected by monitoring the relative emission intensity compared to $[Ru(TL)_3]^{2+}$ samples. This spectroscopic analysis was also used to detect $[(TL)_2Ru(dpp)]^{2+}$ impurity in the non-emissive $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$ samples. The low detection limit of ca. 10^{-8} M makes this technique quite useful in detection of highly emissive species. In the synthesis of $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$, a common impurity is unreacted $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$. Emission spectroscopy is not a suitable means of detection for this impurity as it is non-emissive; however, major differences in the electrochemistry and electronic absorption spectroscopy exist between the desired product and the *cis*-dichloride trimetallic complex. Specifically, the anodic electrochemistry of $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$ exhibits only one couple ca. 1.6 V vs. Ag/AgCl, while the anodic electrochemistry of $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$ exhibits two couples around 1.6 V and 0.8 V. The presence of a small redox couple ca. 0.8 V in a $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$ sample suggests that the precursor is present and further purification is required. Square wave voltammetric analysis is useful as it has a detection limit of 10^{-7} M.¹⁰⁵ Additionally, the $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$ precursor displays a characteristic absorption band at 625 nm ($\epsilon = 34,000 \text{ M}^{-1}\text{cm}^{-1}$) in stark contrast to the lowest energy absorption band of $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$ at 540-550 nm ($\epsilon = 34,000-42,000 \text{ M}^{-1}\text{cm}^{-1}$). Absorption at an energy lower than this characteristic band is indicative of $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$ precursor impurity. Careful analysis of potential impurities in the desired complexes allows for a combination of electrochemical and spectroscopic methods in determining the composition and purity of products.

3.2. $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ Tetrametallic Complexes and Trimetallic Precursors

The Ru(II),Pt(II) tetrametallic supramolecular complexes were designed to couple an efficiently absorbing polyazine-bridged triruthenium LA to a *cis*-PtCl₂ RM center to produce a single component photocatalyst for H₂O reduction and to study excited state properties of structurally diverse photoactive molecules to understand impact of sub-unit variation on properties. As H₂O reduction to produce H₂ should occur by a multielectron process, the tetrametallic supramolecular architecture $[\{(\text{TL})_2\text{Ru}(\text{BL})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ was designed to have three polyazine bridging ligands (BL/BL') which are able to collect electrons on their π^* orbitals. Metal-to-ligand charge transfer (MLCT) transitions are exploited to move the electron through the molecule, and the selection of appropriate BL and BL' is important in directing electron flow toward the RM to enable photocatalytic reduction of the substrate. The BL' directly coordinated to the RM must have lower-lying acceptor orbitals compared to BL bridged between the terminal and central Ru centers to enable this directional electron flow. The terminal Ru→dpp ³MLCT state is designed to be the lowest lying ³MLCT state providing longer lived ³MLCT excited states than those directly coupled to the RM. Finally, the TL plays an important role in fine-tuning the light absorbing properties of the terminal Ru-based LAs, and the size of the TLs may provide sterics that dictate the isomers formed in this molecular architecture. **Figure 3.6** displays the four tetrametallic supramolecular complexes discussed herein of the form $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ with TL = phen or Ph₂phen and BL' = dpp or dpq. Analysis of the impacts of TL and BL' on the redox, spectroscopic, and photophysical properties of this motif provides important information about the variation of properties by sub-unit modification to provide a clear understanding of the impact of supramolecular assembly on sub-unit property perturbation. This understanding of perturbations of sub-unit properties in supramolecular assemblies and of the structure-property relationship is needed to allow optimization of properties and functions in many forums.

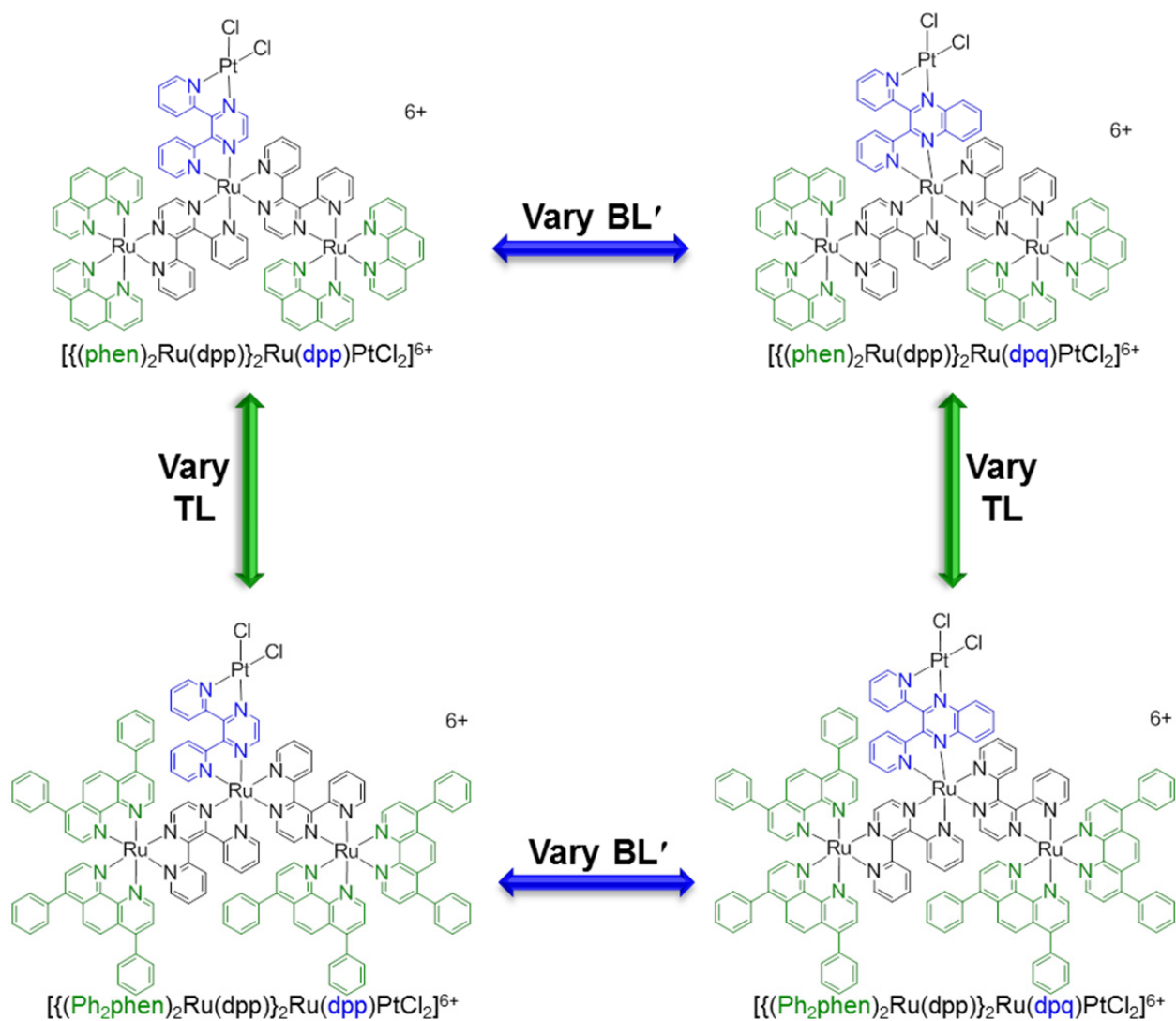


Figure 3.6: Illustration of systematic variation of TL and BL' in the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ supramolecular architecture. TL = phen or Ph_2phen . BL' = dpp or dpq. phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.2.1. Discussion of Isomers

Characterization of the tetrametallic complexes is complicated by the number of possible isomers in each sample. Each chiral pseudooctahedral Ru(II) center can be either the Λ or Δ optical isomer, and the AB chelating nature of dpp and dpq provides a mixture of geometric isomers. To calculate the number of possible isomers in $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ as an example, the central

(dpp)₂Ru^{II}(dpq) unit should first be considered. The chelating sites are labeled pz (pyrazine) and py (pyridine) for dpp and qn (quinoxaline) and py' (pyridine) for dpq. The central (dpp)₂Ru^{II}(dpq) unit has four possible geometric isomers (**Figure 3.7**): the two dpp pyrazines (pz) are *trans* to each other, the two dpp pyridines (py) are *trans* to each other, and two isomers with one py and one pz *trans* to each other. The two dpp ligands are considered equivalent as they are each coordinated to a Ru^{II}(phen)₂ unit. Because this Ru center can be either Δ or Λ , the (dpp)₂Ru(dpq) unit has eight possible isomers (four geometric isomers times two optical isomers each). The eight isomers of the (dpp)₂Ru(dpq) unit are depicted in **Figure 3.7**. Introducing the two terminal (phen)₂Ru^{II} units adds four combinations of optical isomers ($\Lambda\Lambda$, $\Delta\Delta$, $\Lambda\Delta$, and $\Delta\Lambda$) and no geometric isomers due to the symmetric nature of phen. Multiplying the eight isomers due to the central unit by the four combinations of optical isomers from the terminal units gives 32 possible isomers. Coordination of *cis*-PtCl₂ does not contribute to the isomer count, so [$\{(TL)_2Ru(dpp)\}_2Ru(BL')]$ ⁶⁺ and [$\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]$ ⁶⁺ have the same number of isomers. In the literature, the redox and photophysical properties of stereochemically defined samples of [Ru{(tpphz)Ru(phen)₂}₃]⁸⁺ were found to be indistinguishable between different stereoisomers.¹¹¹ While it is suggested that geometric isomerization will also have little impact on the properties of Ru(II)-polyazine complexes,^{39,56,112} the complexes discussed in this dissertation may in fact be influenced by isomerization, as varied distances between the remote LA donor and the BL' acceptor could impact Pt binding, steric effects on reactivity, charge separation distance, and orbital overlap. **Figure 3.8** depicts three dimensional models of two isomers of [$\{(phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2]$ ⁶⁺ and [$\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2]$ ⁶⁺ to highlight the steric bulk resulting from Ph₂phen vs. phen and the impact of structure conformation on the steric bulk around the Pt RM.

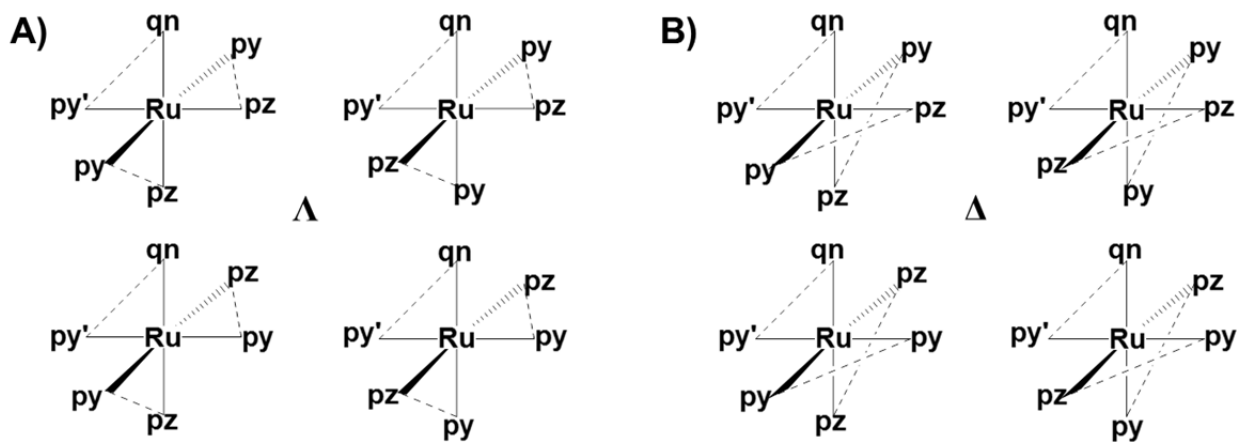


Figure 3.7: Depiction of the A) lambda (Λ) and B) delta (Δ) isomers of the central $(\text{dpp})_2\text{Ru}^{\text{II}}(\text{dpq})$ unit. qn = quinoxaline, py = pyridine, pz = pyrazine.

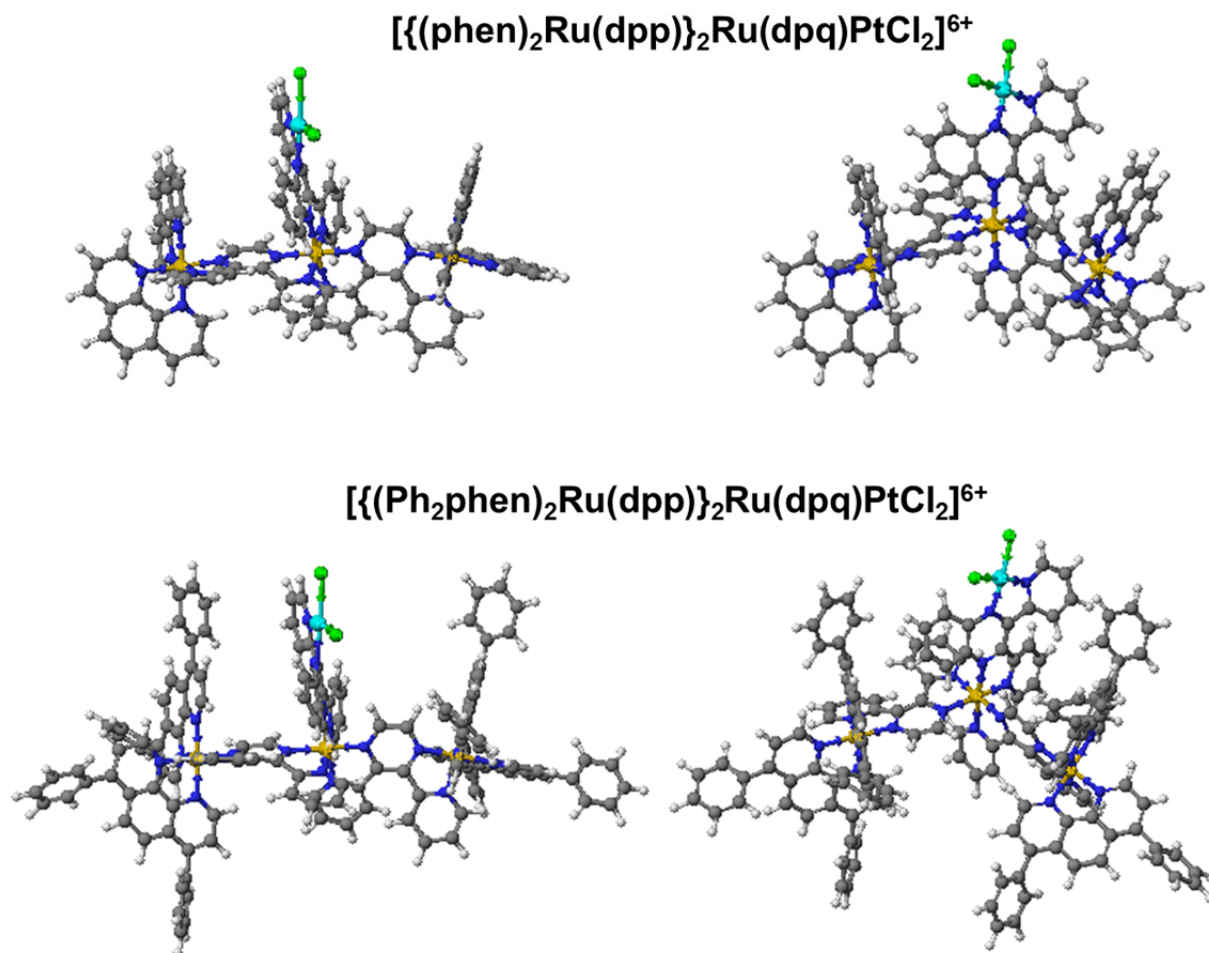


Figure 3.8: Three dimensional models of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ highlighting the difference in sterics among different isomers and by TL variation. Structures generated and energy minimized using Scigress 7.7.1 molecular modeling software using the MM3 method. Gold = Ru, light blue = Pt, green = Cl, blue = N, gray = C, white = H, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.2.2. Redox Properties

Electrochemical analysis gives information about the redox properties of supramolecular complexes. Ru(II)-polyazine complexes exhibit rich electrochemistry with metal-based oxidations and ligand-based reductions. Scanning anodically, $\text{Ru}^{\text{II/III}}$ oxidations are observed at potentials influenced by factors such as the σ -donating or π -accepting nature of the coordinated ligand set, electronic coupling of a metal center through a coordinated BL, the overall charge of the complex, and solvent identity.²⁴ Scanning cathodically, $\mu\text{-BL}^{0/-}$ couples are typically observed prior to -1 V vs. Ag/AgCl, at which point

BL⁻²⁻, TL^{0/-}, and TL⁻²⁻ couples are observed and often overlap, resulting in broad couples that cannot be easily identified, so the discussion of ligand-based reductions will be limited to potentials positive of ca. -1 V vs. Ag/AgCl. Due to the presence of Ru centers in more than one type of coordination environment, “terminal Ru” refers to the metal center in the (TL)₂Ru^{II}(μ-dpp) subunit and “central Ru” refers to the metal center in the (μ-dpp)₂Ru^{II}Cl₂ or (μ-dpp)₂Ru^{II}(BL') subunit in the [{(TL)₂Ru(dpp)}₂RuCl₂]⁴⁺, [{(TL)₂Ru(dpp)}₂Ru(BL')]⁶⁺, and [{(TL)₂Ru(dpp)}₂Ru(BL')PtCl₂]⁶⁺ complexes.¹¹³ The electrochemical data for each of the discussed complexes are compiled in **Tables 3.1** and **A-1**.

3.2.2.1. [{(TL)₂Ru(dpp)}₂RuCl₂](PF₆)₄ (TL = phen or Ph₂phen)

The electrochemistry of the *cis*-dichloride trimetallic complexes [{(phen)₂Ru(dpp)}₂RuCl₂](PF₆)₄ and [{(Ph₂phen)₂Ru(dpp)}₂RuCl₂](PF₆)₄ exhibits separate, distinct Ru-based couples and two dpp based couples between 2.0 V and -1.0 V vs. Ag/AgCl. A comparison of the cyclic voltammogram and the square wave voltammogram of [{(Ph₂phen)₂Ru(dpp)}₂RuCl₂]⁴⁺ is presented in **Figure 3.9** to highlight the correlation between the two electrochemical methods. Cyclic voltammetry gives information about reversibility of redox processes but lower signal-to-noise ratios. Square wave voltammetry gives better signal-to-noise ratios but no information about reversibility. Both techniques provide E_{redox} and relative currents for the number of electrons transferred in a redox process. The square wave voltammograms of [{(TL)₂Ru(dpp)}₂RuCl₂]⁴⁺ (TL = phen or Ph₂phen) are pictured in **Figure 3.10** for comparison of TL variation impact and the redox potentials are given in **Table 3.1**. Cyclic voltammograms are provided in **Figure A-16**. For [{(phen)₂Ru(dpp)}₂RuCl₂]⁴⁺, scanning anodically reveals the central Ru^{II/III} couple occurs first at 0.79 V vs. Ag/AgCl, followed by a couple observed at 1.56 V, assigned as two overlapping, one electron oxidations of the terminal Ru centers. The ΔE_p of ca. 90 mV indicates that this large couple is a result of two overlapping, one electron waves rather than a two electron oxidation. The terminal Ru^{II/III} couples occur at a more positive potential compared to the central Ru oxidation because the σ-donating Cl⁻ ligands coordinated to central Ru destabilize the dπ orbitals resulting in a metal center that is easier to oxidize than the terminal Ru coordinated to three π-accepting ligands. Scanning cathodically

gives two sequential couples at -0.70 V and -0.84 V, assigned as reduction of each of the μ -dpp ligands. Although these ligands are in equivalent coordination environments, they reduce at different potentials because they are electronically coupled through the central Ru. This is unlike the two terminal Ru oxidations which are shown at the same potential because they are electronically isolated due to separation by the $(\text{dpp})\text{Ru}^{\text{II}}\text{Cl}_2(\text{dpp})$ unit. The related compound $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$ exhibits the same behavior with the two central $\text{Ru}^{\text{II/III}}$ couples overlapping at 1.62 V vs. Ag/AgCl and the two μ -dpp $^{0/-}$ couples occurring separately at -0.67 V and -0.83 V.⁵³ The Ph_2phen analogue, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, has very similar redox properties, as the Ph_2phen TL has only a minor impact on the reduction potentials of the Ru centers and the dpp ligands in this motif. The central $\text{Ru}^{\text{II/III}}$ oxidation occurs at 0.86 V vs. Ag/AgCl followed by the two terminal $\text{Ru}^{\text{II/III}}$ oxidations at 1.59 V, and the two dpp $^{0/-}$ reductions occur at -0.68 V and -0.81 V. The electrochemistry of this motif suggests a central Ru-based HOMO and a μ -dpp-based LUMO, and the lowest-lying excited state is expected to be terminal $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ CT in nature.

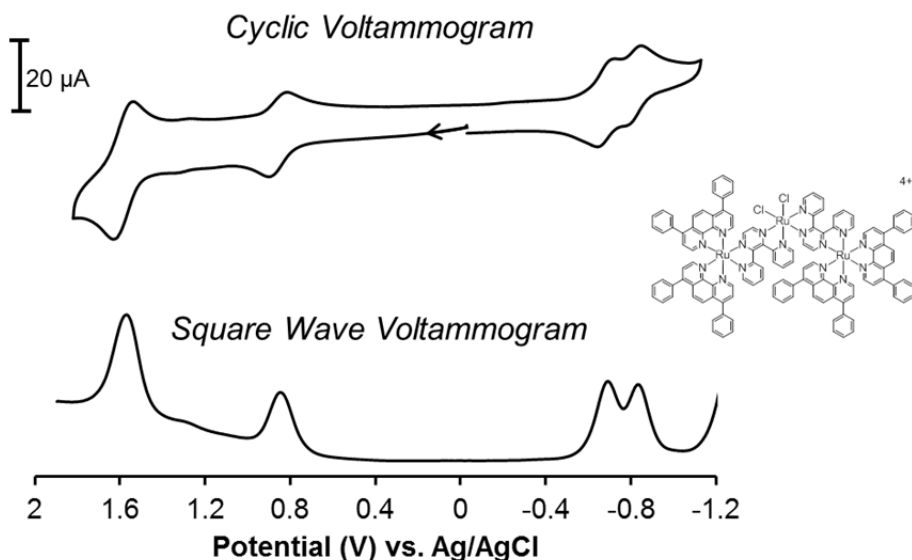


Figure 3.9: Stacked cyclic voltammogram (top) and square wave voltammogram (bottom) for $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$ measured in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FcCp}_2^{0/+} = 0.46$ V vs. Ag/AgCl). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

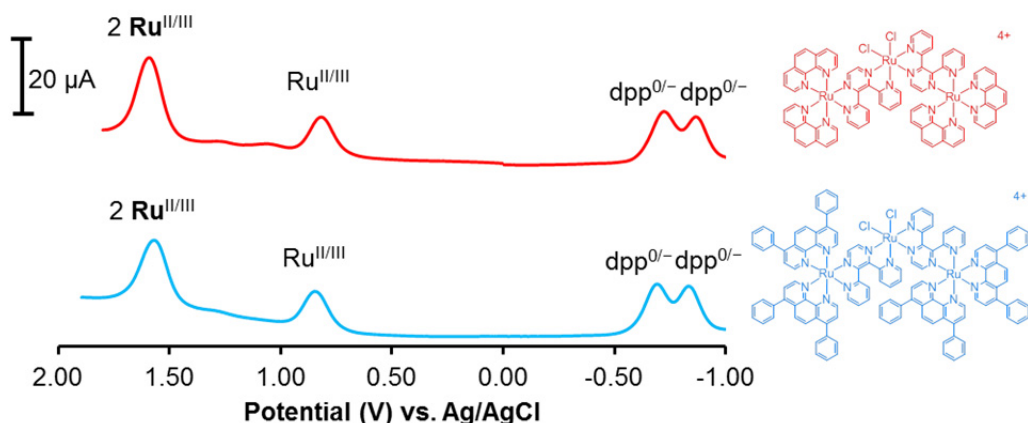


Figure 3.10: Square wave voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—) and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FcP}^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline. **Ru** indicates terminal Ru.

3.2.2.2. $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ (TL = phen or Ph_2phen ; BL' = dpp or dpq)

Substituting the Cl^- ligands with BL' in the *cis*-dichloride trimetallic complexes $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ to produce $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ has a significant impact on the electrochemistry of the supramolecular architecture. The electrochemical data for the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ complexes (TL = phen or Ph_2phen ; BL' = dpp or dpq) are given in **Table 3.1**, the square wave voltammograms are given in **Figure 3.11**, and cyclic voltammograms are provided in **Figure A-17**. The most significant impact of BL' substitution for the two chlorides is that the central $\text{Ru}^{\text{II/III}}$ oxidation that occurred at 0.79 V vs. Ag/AgCl for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ shifts outside the electrochemical window ($E_{1/2} > 2.0$ V in CH_3CN) for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ (BL' = dpp or dpq), a result of replacing σ -donating Cl^- ligands with a π -accepting polyazine ligand, stabilizing the $\text{Ru}(\text{d}\pi)$ orbitals. $\text{Ru}^{\text{II}}(\mu\text{-BL})_3$ motifs provide $\text{Ru}^{\text{II/III}}$ couples at high potential reported as 2.3 V vs. Ag/AgCl for $[\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{Ru}\{(\text{dpp})\text{Ru}(\text{bpy})_2\}_2]^{12+}$ measured in liquid SO_2 .¹¹⁴ The terminal Ru orbitals in the $(\text{TL})_2\text{Ru}^{\text{II}}(\mu\text{-dpp})$ subunits are destabilized compared to the central Ru orbitals in the $(\text{dpp})_2\text{Ru}^{\text{II}}(\text{BL}')$ subunit because polyazine BLs such as dpp and dpq are more electron withdrawing than

polyazine TLs such as phen and Ph₂phen, and BLs between two metal centers (μ -BL) are more electron withdrawing than a BL with an open coordination site. The oxidation potentials of the terminal Ru centers, 1.61 V (BL' = dpp) and 1.56 V (BL' = dpq), are relatively unaffected by coordination of BL' to central Ru. Three couples are observed when scanning cathodically at -0.45 V, -0.59 V, and -1.00 V for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ and -0.42 V, -0.59 V, and -0.80 V for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$. In each case, the first two reductions correspond to the two μ -dpp^{0/-} couples, which occur at a less negative potential compared to the μ -dpp couples in $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ as a result of an electronically coupled π -accepting BL' coordinated to central Ru rather than σ -donating Cl⁻ and the increased overall positive charge of the complex. The third reduction in each case corresponds to BL', with dpp reducing at a more negative potential compared to dpq, as dpp π^* orbitals are destabilized compared to dpq. Bis-bidentate ligands like dpp and dpq are more easily reduced when coordinated to two electropositive metal centers than when only coordinated to one.³² The $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ analogues exhibit similar redox properties, with the terminal Ru oxidation shifted to slightly less positive potentials due to the electron donating nature of Ph₂phen (1.55 V for BL' = dpp or dpq). The μ -dpp and BL' reduction potentials are relatively unaffected by identity of TL. The electrochemistry of this motif suggests a terminal Ru($d\pi$)-based HOMO and a μ -dpp-based LUMO, and the lowest-lying excited states are expected to be at similar energies for the four complexes in this series as the HOMO and LUMO are only slightly impacted by TL and BL' identity.

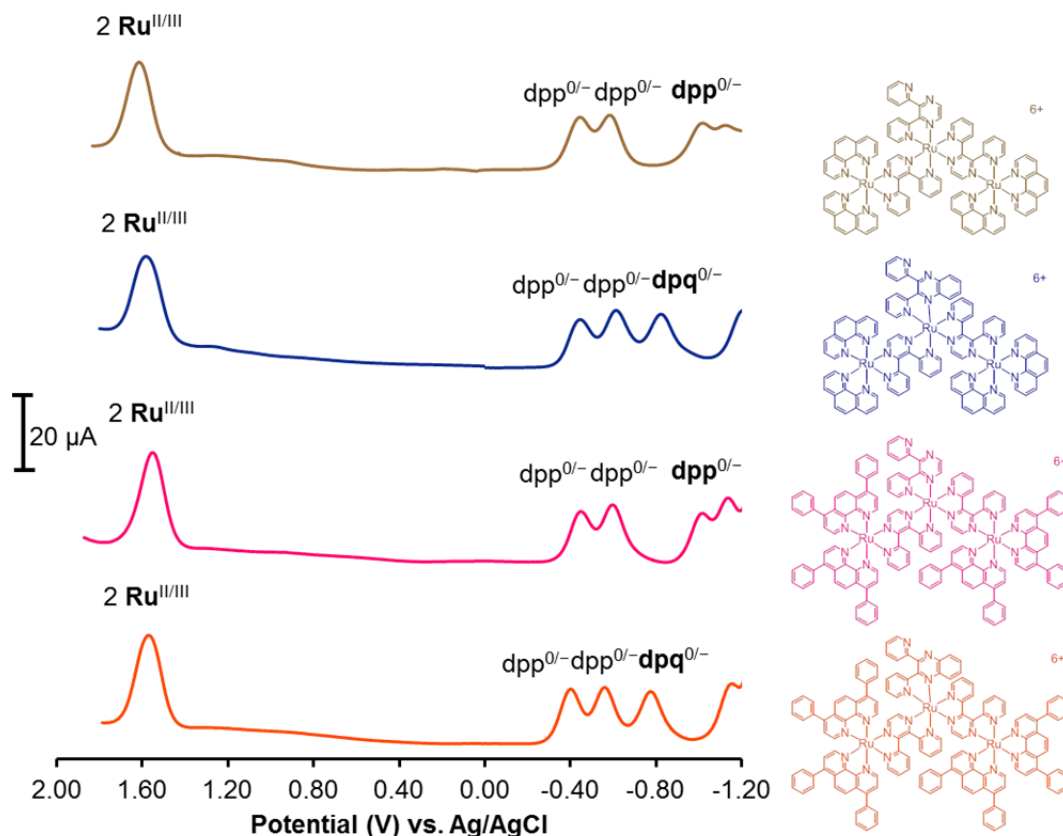


Figure 3.11: Square wave voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s using a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FcCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline. **Ru** indicates terminal Ru and **dpp/dpq** indicates dpp/dpq coordinated only to central Ru.

3.2.2.3. $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ (TL = phen or Ph_2phen , BL' = dpp or dpq)

Coordination of a *cis*- PtCl_2 unit to the trimetallic $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ complexes has a major impact on the cathodic electrochemistry of the supramolecular motif (**Figure 3.12** and **Table 3.1**). Cyclic voltammograms are provided in **Figure A-18**. In the case of the TL = phen complexes, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$, while the terminal Ru orbitals experience little effect from remote *cis*- PtCl_2 coordination and the $E_{1/2}$ remains at a similar potential to the trimetallic complexes (1.63 V for BL' = dpp and 1.58 V for BL' = dpq), the BL' reduction shifts to more positive potential and reduces prior to the μ -dpp ligands. The μ -BL' reduction potentials are sensitive to the nature of the

ligand, with BL' = dpp reduced at -0.32 V and BL' = dpq reduced at -0.05 V vs. Ag/AgCl, similar to the trend observed for the $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ analogues. A polyazine ligand that bridges Ru and Pt is stabilized compared to the same ligand that bridges two Ru centers as evidenced by the first $\text{dpq}^{0/-}$ couple at -0.07 V vs. Ag/AgCl for $[\text{Ru}\{(\text{dpq})\text{PtCl}_2\}_3]^{2+}$ compared to the first $\text{dpq}^{0/-}$ couple at -0.27 V for $[\text{Ru}\{(\text{dpq})\text{Ru}(\text{bpy})_2\}_3]^{8+}$.⁴⁹ The two μ -dpp ligands are reduced at -0.51 V and -0.63 V (when BL' = dpp) and at -0.42 V and -0.59 V (when BL' = dpq). The orbital inversion which occurs upon *cis*-PtCl₂ coordination in $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ to produce $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ is important in this molecular architecture providing a BL' based LUMO as well as a HOMO and LUMO that are now spatially separated to provide a lowest-lying terminal Ru($d\pi$)→remote BL'(π^*) charge separated (CS) excited state. The same trend is also observed when TL = Ph₂phen. Electrochemical analysis of the effects of TL and BL' component variation on this supramolecular architecture shows that the TL serves to fine tune the energy of the terminal Ru-based HOMO while the BL' greatly impacts the energy of the LUMO and subsequently the low-lying CS excited state.

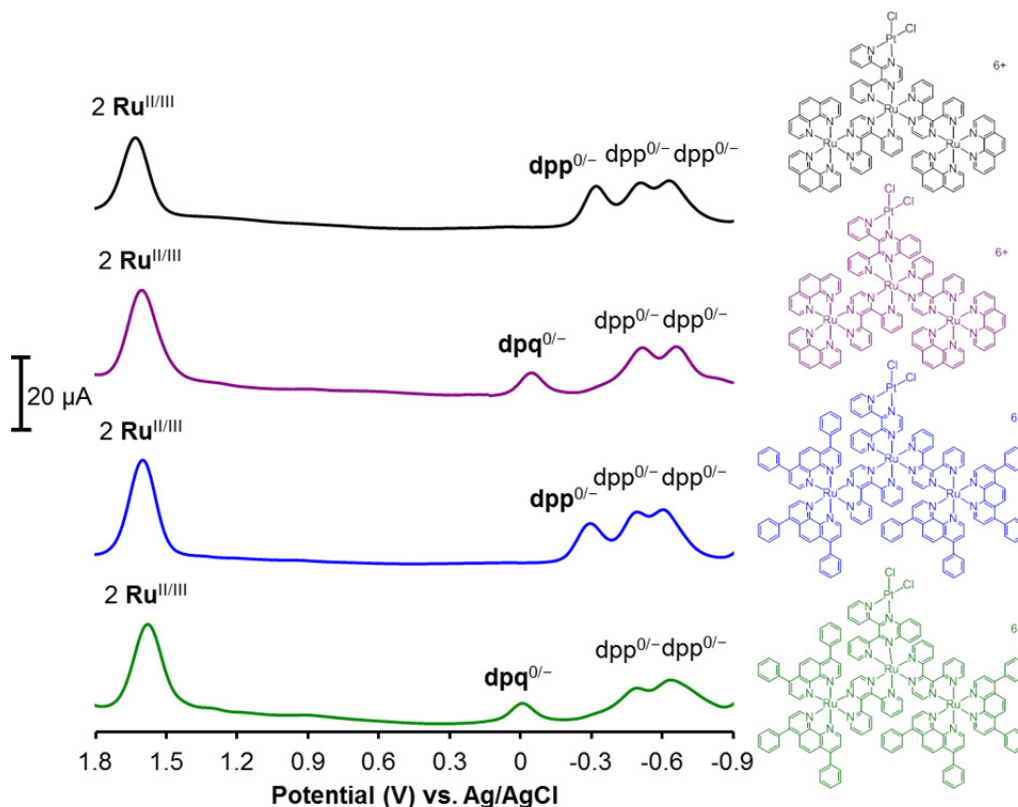


Figure 3.12: Square wave voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline. **Ru** indicates terminal Ru and **dpp/dpq** indicates dpp/dpq between central Ru and Pt.

Figure 3.13 shows the changes in redox properties that result from assembly of the supramolecular architecture using $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ and its precursors as an example, and **Figure 3.14** shows an orbital energy diagram for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})]^{6+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})]^{6+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ to highlight the changes in orbital energetics upon building the supramolecular architecture. It is important to note that building up the architecture from $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ to $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ to $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ has a negligible effect on the potential of the terminal $\text{Ru}^{\text{II/III}}$

oxidation as there is little electronic communication between the terminal Ru and the 2Cl^- , dpq, or $(\mu\text{-dpq})\text{Pt}^{\text{II}}\text{Cl}_2$ units coordinated to the remote site on the central Ru. Coordination of dpq to the central Ru to afford $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ results in orbital inversion of the HOMO, moving the HOMO from the central Ru to the terminal Ru. Coordination of *cis*- PtCl_2 to dpq to form the target tetrametallic complex $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ results in orbital inversion, providing a dpq-localized LUMO in $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ rather than a dpp-localized LUMO in $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})]^{6+}$. The complicated electrochemistry resulting from the presence of multiple metal centers and bridging ligands is more easily understood through analysis of each step of the synthetic scheme and the variation of each ligand to allow ease of assignment. This analysis provides important information into the redox properties and orbital energetics that is useful in understanding the complex photophysical properties of this motif.

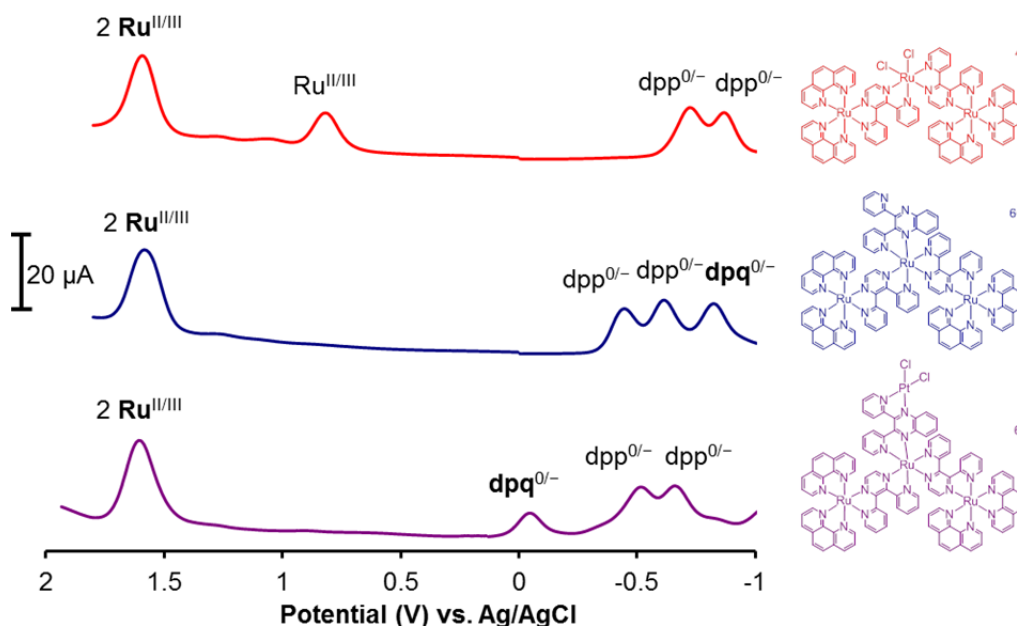


Figure 3.13: Square wave voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. **Ru** indicates terminal Ru.

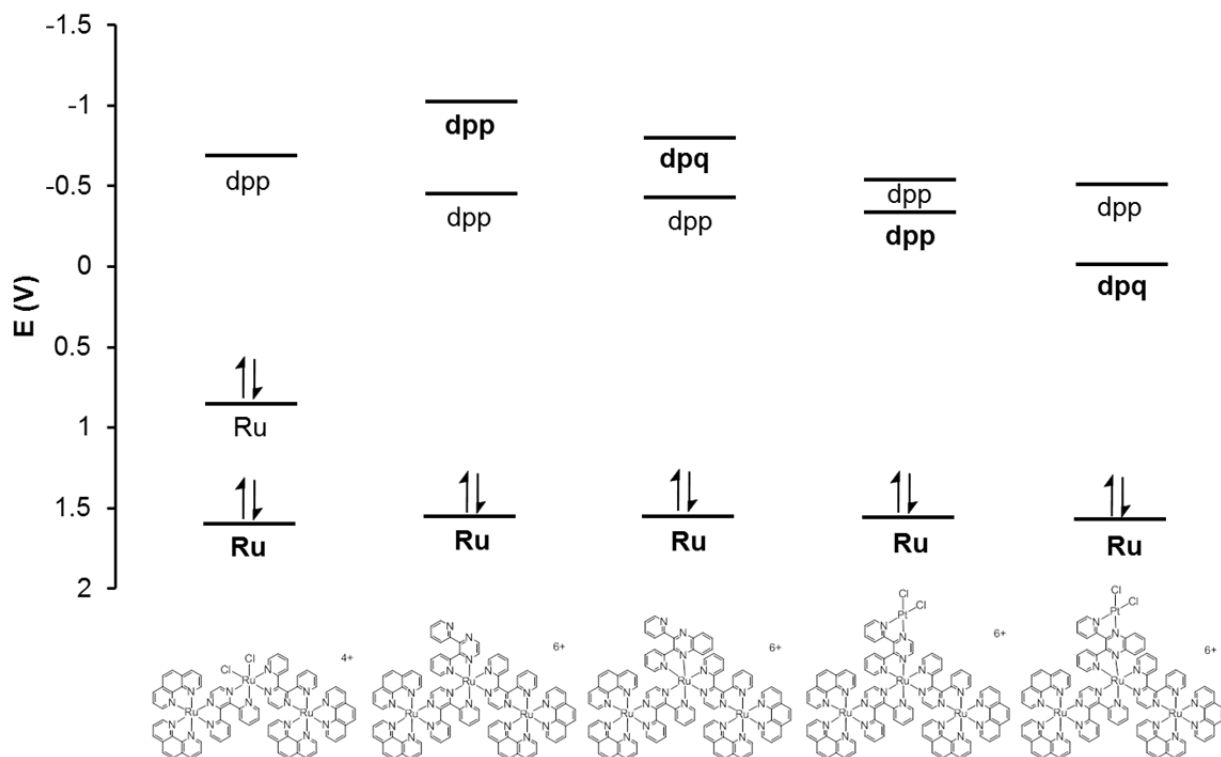


Figure 3.14: Orbital energy diagram of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})]^{6+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})]^{6+}$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$. phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Table 3.1: Electrochemical Data for the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, and $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ Complexes ^a

Complex	E _{1/2} (V vs. Ag/AgCl)				
	Oxidation (assignment) ^b		Reduction (assignment) ^c		
[{(Ph ₂ phen) ₂ Ru (dpp)} ₂ RuCl ₂](PF ₆) ₄	0.86 (Ru ^{II/III})	1.59 (2 Ru^{II/III})	−0.68 (dpp ^{0/−})	−0.81 (dpp ^{0/−})	
[{(phen) ₂ Ru (dpp)} ₂ RuCl ₂](PF ₆) ₄ ^d	0.79 (Ru ^{II/III})	1.56 (2 Ru^{II/III})	−0.70 (dpp ^{0/−})	−0.84 (dpp ^{0/−})	
[{(Ph ₂ phen) ₂ Ru (dpp)} ₂ Ru(dpp)](PF ₆) ₆	1.55 (2 Ru^{II/III})		−0.45 (dpp ^{0/−})	−0.60 (dpp ^{0/−})	−1.02 (dpp^{0/−})
[{(Ph ₂ phen) ₂ Ru (dpp)} ₂ Ru(dpq)](PF ₆) ₆	1.55 (2 Ru^{II/III})		−0.42 (dpp ^{0/−})	−0.58 (dpp ^{0/−})	−0.79 (dpq^{0/−})
[{(phen) ₂ Ru (dpp)} ₂ Ru(dpp)](PF ₆) ₆ ^e	1.61 (2 Ru^{II/III})		−0.45 (dpp ^{0/−})	−0.59 (dpp ^{0/−})	−1.00 (dpp^{0/−})
[{(phen) ₂ Ru (dpp)} ₂ Ru(dpq)](PF ₆) ₆ ^d	1.56 (2 Ru^{II/III})		−0.42 (dpp ^{0/−})	−0.59 (dpp ^{0/−})	−0.80 (dpq^{0/−})
[{(Ph ₂ phen) ₂ Ru (dpp)} ₂ Ru(dpp)PtCl ₂](PF ₆) ₆	1.56 (2 Ru^{II/III})		−0.33 (dpp^{0/−})	−0.53 (dpp ^{0/−})	−0.64 (dpp ^{0/−})
[{(Ph ₂ phen) ₂ Ru (dpp)} ₂ Ru(dpq)PtCl ₂](PF ₆) ₆	1.57 (2 Ru^{II/III})		−0.02 (dpq^{0/−})	−0.50 (dpp ^{0/−})	−0.65 (dpp ^{0/−})
[{(phen) ₂ Ru (dpp)} ₂ Ru(dpp)PtCl ₂](PF ₆) ₆ ^e	1.63 (2 Ru^{II/III})		−0.32 (dpp^{0/−})	−0.51 (dpp ^{0/−})	−0.63 (dpp ^{0/−})
[{(phen) ₂ Ru (dpp)} ₂ Ru(dpq)PtCl ₂](PF ₆) ₆ ^d	1.58 (2 Ru^{II/III})		−0.05 (dpq^{0/−})	−0.42 (dpp ^{0/−})	−0.59 (dpp ^{0/−})

^a Measurements recorded in deoxygenated CH₃CN at RT with 0.1 M Bu₄NPF₆ electrolyte. phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. ^b Bold indicates terminal Ru. ^c Bold indicates BL'. ^d From reference 78. ^e From reference 113.

3.2.3. Electronic Absorption Spectroscopy

The study of electronic absorption spectroscopy of the Ru(II),Pt(II) supramolecular complexes and Ru(II) trimetallic precursors provides insight into the light absorbing capabilities. Light absorption is characteristic of each structure and important in solar-to-chemical energy conversion schemes. Typical of Ru(II)-polyazine complexes, IL $\pi \rightarrow \pi^*$ transitions dominate the UV region and Ru($d\pi$) $\rightarrow$ ligand(π^*) CT transitions dominate the visible region. Electronic absorption spectra of these supramolecular complexes are complicated by the absorption of several IL and MLCT transitions due to the complexes possessing four TLs, two or three BL/BL's, and three Ru(II) centers (**Figure 3.15**). The electronic absorption spectroscopy data for the major transitions of the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, and $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes are presented in **Table 3.2**. All the polymetallic complexes are efficient light absorbers with $\epsilon \approx 140,000$ -210,000 $\text{M}^{-1}\text{cm}^{-1}$ in the UV and $\epsilon \approx 40,000 \text{ M}^{-1}\text{cm}^{-1}$ throughout the visible region extending into the low energy visible due to the reduced Ru($d\pi$) to BL(π^*) energy gap with bridging dpp and dpq ligands.

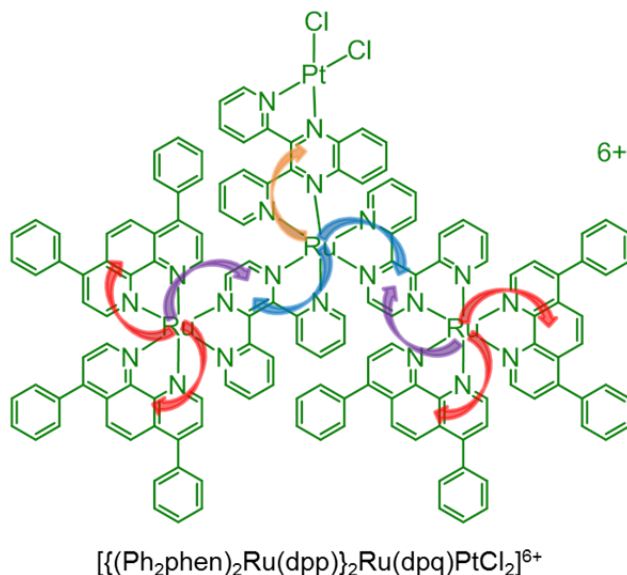


Figure 3.15: Illustration of the possible MLCT transitions in the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ tetrametallic complex. Arrows indicate an MLCT transition. MLCT = metal-to-ligand charge transfer, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The *cis*-dichloride trimetallic complexes $[\{(TL)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ are efficient UV and visible light absorbers. The electronic absorption spectra of $[\{(phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ are pictured in **Figure 3.16**. The only structural difference between the two complexes is TL selection, resulting in the same energy and extinction coefficient for the lowest energy $Ru(d\pi) \rightarrow \mu\text{-}dpp(\pi^*)$ CT transitions ($\lambda_{max} = 625$ nm, $\epsilon = 34,000$ $M^{-1}cm^{-1}$) for both $[\{(phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ and $[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$. This is expected as the terminal $Ru(d\pi) \rightarrow \mu\text{-}dpp(\pi^*)$ CT and central $Ru(d\pi) \rightarrow dpp(\pi^*)$ CT transitions should not be significantly impacted by TL variation. The $\mu\text{-}dpp \pi \rightarrow \pi^*$ transition at ca. 320 nm is expected to be unaffected by TL selection; however, the extinction coefficient of this transition in $[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ at 315 nm ($91,000$ $M^{-1}cm^{-1}$) is much greater than that of $[\{(phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ at 330 nm ($54,000$ $M^{-1}cm^{-1}$), a result of the overlapping, strongly absorbing $Ph_2phen \pi \rightarrow \pi^*$ transitions centered at 276 nm ($\epsilon = 213,000$ $M^{-1}cm^{-1}$) compared to the $phen \pi \rightarrow \pi^*$ transitions at 262 nm ($\epsilon = 172,000$ $M^{-1}cm^{-1}$). The terminal $Ru(d\pi) \rightarrow TL(\pi^*)$ CT transition is centered at 430 nm ($\epsilon = 29,000$ $M^{-1}cm^{-1}$) when $TL = phen$ and is red-shifted to 442 nm and increased in intensity ($\epsilon = 45,000$ $M^{-1}cm^{-1}$) when $TL = Ph_2phen$, and the enhanced spectral coverage in this region is typical of $(Ph_2phen)_2Ru^{II}$ subunits.

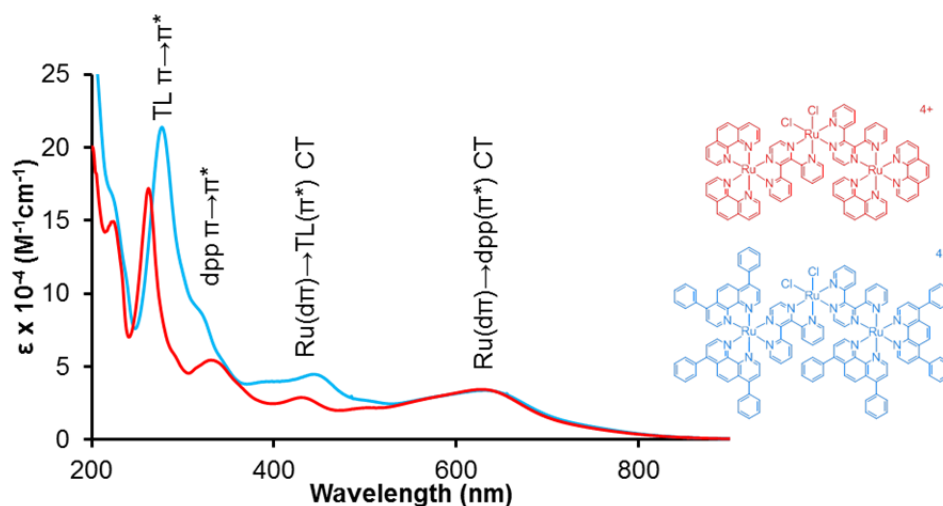


Figure 3.16: Electronic absorption spectra of $[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ (—) and $[\{(phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$ (—) measured in RT spectral grade CH_3CN in a 1 cm quartz cuvette. $phen = 1,10$ -phenanthroline, $dpp = 2,3$ -bis(2-pyridyl)pyrazine, $Ph_2phen = 4,7$ -diphenyl-1,10-phenanthroline.

Coordination of BL' to the *cis*-dichloride trimetallic complexes [$\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ to give the [$\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ motif, where TL = phen or Ph₂phen and BL' = dpp or dpq, has a significant impact on the lowest energy MLCT transition (**Figure 3.17**). The overlaid absorption spectra of [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ and [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ are pictured in **Figure 3.18** to highlight the spectroscopic shifts upon BL' coordination. Stabilizing the central Ru($d\pi$) orbitals by replacing the σ -donating Cl⁻ ligands with a π -accepting BL' results in a 75-85 nm blue shift of the lowest energy MLCT transition for [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ ($\lambda_{\text{max}} = 543 \text{ nm}$, $\epsilon = 34,000 \text{ M}^{-1}\text{cm}^{-1}$), [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ ($\lambda_{\text{max}} = 541 \text{ nm}$, $\epsilon = 38,000 \text{ M}^{-1}\text{cm}^{-1}$), [$\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ ($\lambda_{\text{max}} = 554 \text{ nm}$, $\epsilon = 42,000 \text{ M}^{-1}\text{cm}^{-1}$), and [$\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ ($\lambda_{\text{max}} = 550 \text{ nm}$, $\epsilon = 36,000 \text{ M}^{-1}\text{cm}^{-1}$). This broad, lowest energy absorption is dominated by overlapping terminal Ru→ μ -dpp CT, central Ru→ μ -dpp CT, and central Ru→BL' CT transitions. The absorptivity of the Ru→TL CT transition in each case remains similar to the *cis*-dichloride trimetallic analogues, as the subunit involved in this transition is remote from BL'. New BL' (dpp or dpq) $\pi \rightarrow \pi^*$ transitions are expected to be hidden under the overlapping μ -dpp $\pi \rightarrow \pi^*$ transitions ca. 350 nm (**Figure 3.17**). The TL $\pi \rightarrow \pi^*$ transitions occur at 262 nm (TL = phen) and 276 nm (TL = Ph₂phen), and the extinction coefficient for this transition in each complex is influenced by the overlapping dpp and BL' $\pi \rightarrow \pi^*$ transitions.

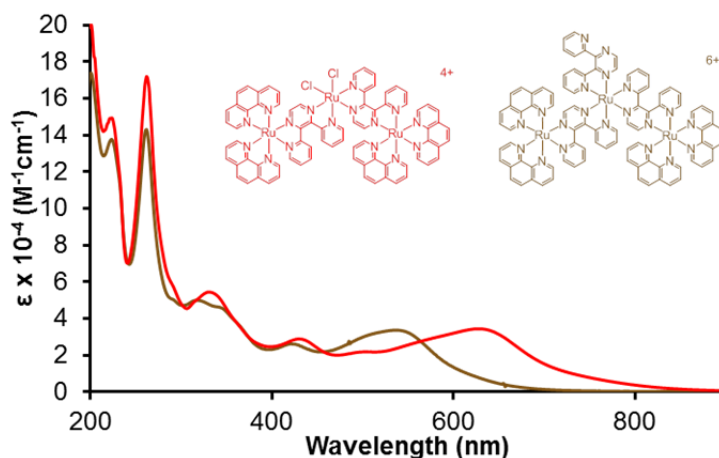


Figure 3.17: Electronic absorption spectra of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—) and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—) measured in RT spectral grade CH_3CN in a 1 cm quartz cuvette. phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

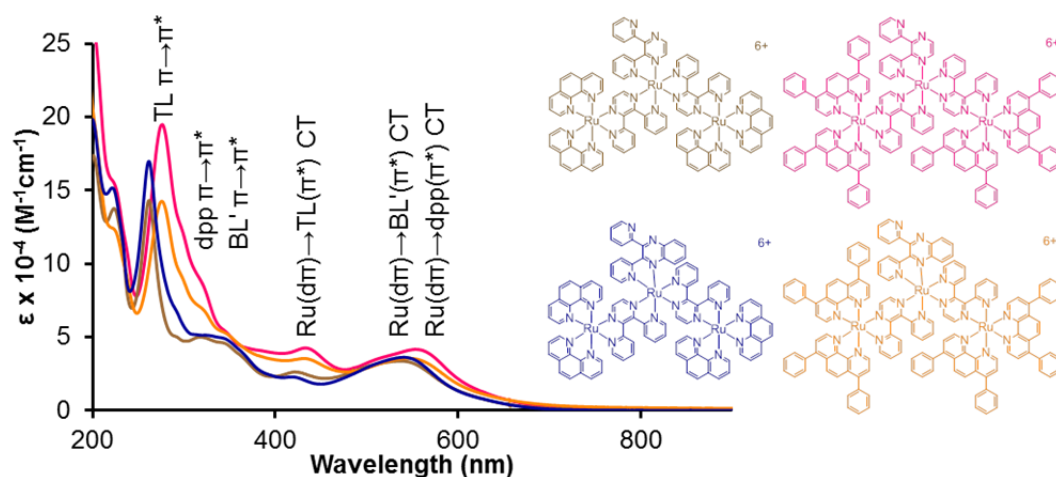


Figure 3.18: Electronic absorption spectra of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—) measured in RT spectral grade CH_3CN in a 1 cm quartz cuvette. phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline.

Addition of *cis*- PtCl_2 RM into the trimetallic LA motif $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_4$ to provide the target tetrametallic complexes, $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$, maintains the rich light absorbing properties of the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ complexes. The overlaid electronic absorption spectra of the four $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes (TL = phen or Ph_2phen , BL' = dpp or dpq) are shown in **Figure 3.19**. Only minor spectroscopic changes are expected upon

platination of $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ to produce $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$. These observed minor changes are a reflection of the majority of the transitions being unchanged by the $\text{BL}'(\pi^*)$ stabilization that occurs upon platination. Expected changes upon platination are a red shift of the $\text{BL}' \pi \rightarrow \pi^*$ and the central $\text{Ru} \rightarrow \text{BL}'$ MLCT transitions. The TL and dpp $\pi \rightarrow \pi^*$ transitions and the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{TL}(\pi^*)$ CT transition are not significantly impacted by stabilization of the $\text{BL}'(\pi^*)$ orbitals as BL' is not involved in these transitions. The transitions contributing to the broad absorption band between 450 nm and 650 nm are largely unaffected by the *cis*- PtCl_2 coordination. When terminal $\text{Ru} \rightarrow \mu\text{-dpp}$ CT and central $\text{Ru} \rightarrow \mu\text{-dpp}$ CT transitions remain at the same energy and the central $\text{Ru} \rightarrow \text{BL}'$ CT transition is red shifted, a subtle low energy tail is observed due to this shifted underlying transition. **Figure 3.20** depicts this red shifted MLCT transition in the overlaid absorption spectra of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (**Figure 3.20A**). The change in absorption upon platination is more clearly shown in **Figure 3.20B** which plots $\Delta\text{Absorbance}$ vs. wavelength, where $\Delta\text{Absorbance}$ is the absorbance of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ minus the absorbance of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ using concentration matched samples. This plot more clearly highlights the red-shift in the MLCT transition and the ligand $\pi \rightarrow \pi^*$ transitions (increase in absorbance centered at 620 nm and 390 nm, respectively) as a result of BL' stabilization.

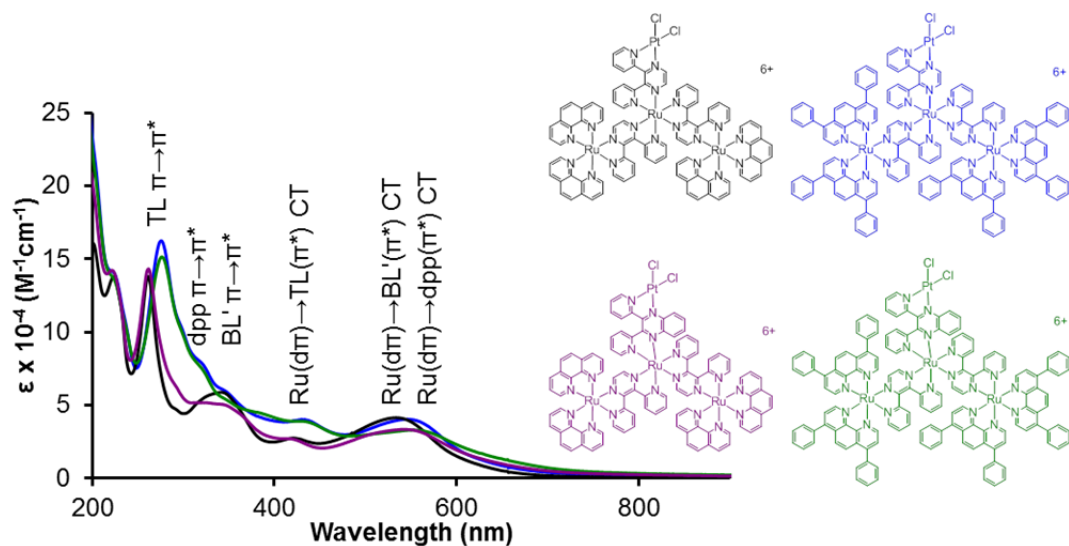


Figure 3.19: Electronic absorption spectra of $[\{(\text{phen})_2\text{Ru(dpp)}\}_2\text{Ru(dpp)PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru(dpp)}\}_2\text{Ru(dpq)PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}\}_2\text{Ru(dpp)PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}\}_2\text{Ru(dpq)PtCl}_2](\text{PF}_6)_6$ (—) measured in RT spectral grade CH₃CN in a 1 cm quartz cuvette. phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline.

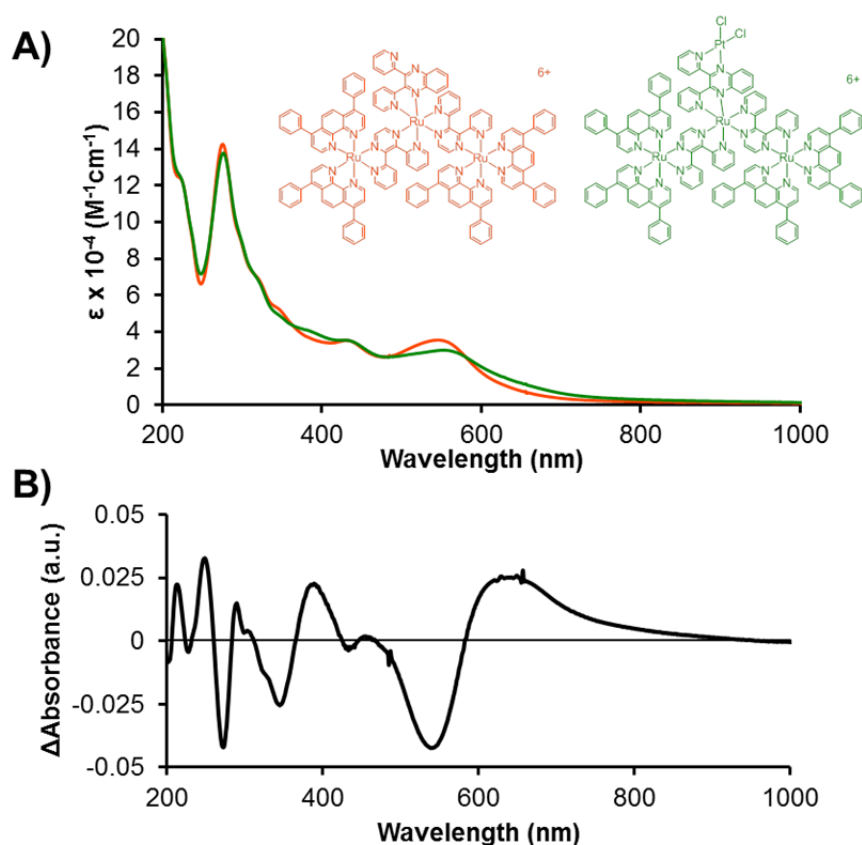


Figure 3.20: A) Electronic absorption spectra of $[\{ (\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{dpq})] (\text{PF}_6)_6$ (—) and $[\{ (\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{dpq})\text{PtCl}_2] (\text{PF}_6)_6$ (—) measured in RT spectral grade CH_3CN in a 1 cm quartz cuvette. B) Plot of $\Delta\text{Absorbance}$ vs. Wavelength, where $\Delta\text{Absorbance}$ is the change in electronic absorption upon platination of $[\{ (\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{dpq})] (\text{PF}_6)_6$ to produce $[\{ (\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{dpq})\text{PtCl}_2] (\text{PF}_6)_6$. Samples were concentration matched. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

While the rich light absorbing properties of the trimetallic $[\{ (\text{TL})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{BL}')] (\text{PF}_6)_6$ and tetrametallic $[\{ (\text{TL})_2\text{Ru}(\text{dpp}) \}_2\text{Ru}(\text{BL}')\text{PtCl}_2] (\text{PF}_6)_6$ complexes in the UV and visible regions are suitable for solar energy harnessing schemes, the presence of many overlapping, dominant transitions causes spectroscopic analysis techniques such as transient absorption spectroscopy to be quite difficult to understand the excited state dynamics. Altering one CT transition results in only a small spectroscopic shift. A simplified molecular architecture that features similar orbital energetics yet fewer metal centers and ligands participating in MLCT absorption is beneficial for such techniques (**Section 3.3**).

Table 3.2: Electronic Absorption Spectroscopic Data for the $[\{(TL)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$, $[\{(TL)_2Ru(dpp)\}_2Ru(BL')](PF_6)_6$, and $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2](PF_6)_6$ Complexes ^a

Complex	λ_{max}^{abs} (nm)	$\epsilon \times 10^{-4}$ (M ⁻¹ cm ⁻¹)	Assignment
$[\{(Ph_2phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4$	276	21.3	Ph ₂ phen $\pi \rightarrow \pi^*$
	315 (sh)	9.1	dpp $\pi \rightarrow \pi^*$
	442	4.5	Ru(d π) $\rightarrow$ Ph ₂ phen(π^*) CT
	625	3.4	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(phen)_2Ru(dpp)\}_2RuCl_2](PF_6)_4^b$	262	17.2	phen $\pi \rightarrow \pi^*$
	330	5.4	dpp $\pi \rightarrow \pi^*$
	430	2.9	Ru(d π) $\rightarrow$ phen(π^*) CT
	625	3.4	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6$	276	19.5	Ph ₂ phen $\pi \rightarrow \pi^*$
	340 (sh)	5.7	dpp $\pi \rightarrow \pi^*$
	432	4.2	Ru(d π) $\rightarrow$ Ph ₂ phen(π^*) CT
	554	4.2	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6$	276	14.4	Ph ₂ phen $\pi \rightarrow \pi^*$
	340 (sh)	5.5	dpp $\pi \rightarrow \pi^*$, dpq $\pi \rightarrow \pi^*$
	430	3.6	Ru(d π) $\rightarrow$ Ph ₂ phen(π^*) CT
	550	3.6	Ru(d π) $\rightarrow$ dpp(π^*) CT, Ru(d π) $\rightarrow$ dpq(π^*) CT
$[\{(phen)_2Ru(dpp)\}_2Ru(dpp)](PF_6)_6^c$	262	16.6	phen $\pi \rightarrow \pi^*$
	340	4.2	dpp $\pi \rightarrow \pi^*$
	421	2.8	Ru(d π) $\rightarrow$ phen(π^*) CT
	543	3.4	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(phen)_2Ru(dpp)\}_2Ru(dpq)](PF_6)_6^b$	262	15.9	phen $\pi \rightarrow \pi^*$
	350 (sh)	4.8	dpp $\pi \rightarrow \pi^*$, dpq $\pi \rightarrow \pi^*$
	415	2.6	Ru(d π) $\rightarrow$ phen(π^*) CT
	541	3.8	Ru(d π) $\rightarrow$ dpp(π^*) CT, Ru(d π) $\rightarrow$ dpq(π^*) CT
$[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6$	276	17.0	Ph ₂ phen $\pi \rightarrow \pi^*$
	326 (sh)	7.7	dpp $\pi \rightarrow \pi^*$
	432	4.2	Ru(d π) $\rightarrow$ Ph ₂ phen(π^*) CT
	550	4.2	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2](PF_6)_6$	276	13.9	Ph ₂ phen $\pi \rightarrow \pi^*$
	340 (sh)	5.2	dpp $\pi \rightarrow \pi^*$, dpq $\pi \rightarrow \pi^*$
	430	3.6	Ru(d π) $\rightarrow$ Ph ₂ phen(π^*) CT
	550	3.1	Ru(d π) $\rightarrow$ dpp(π^*) CT, Ru(d π) $\rightarrow$ dpq(π^*) CT
$[\{(phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6^c$	262	15.5	phen $\pi \rightarrow \pi^*$
	330 (sh)	5.6	dpp $\pi \rightarrow \pi^*$
	421	2.9	Ru(d π) $\rightarrow$ phen(π^*) CT
	543	4.2	Ru(d π) $\rightarrow$ dpp(π^*) CT
$[\{(phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2](PF_6)_6^b$	262	15.0	phen $\pi \rightarrow \pi^*$
	350 (sh)	4.8	dpp $\pi \rightarrow \pi^*$, dpq $\pi \rightarrow \pi^*$
	415	3.2	Ru(d π) $\rightarrow$ phen(π^*) CT
	541	3.8	Ru(d π) $\rightarrow$ dpp(π^*) CT, Ru(d π) $\rightarrow$ dpq(π^*) CT

^a Measurements recorded in deoxygenated CH₃CN at RT. phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

^b From reference 78. ^c From reference 113.

Different building blocks in the supramolecular architecture significantly impact electrochemical analysis and electronic absorption spectroscopy. As previously discussed, electrochemical analysis demonstrated that the choice of BL' has a large impact on the energy of the LUMO, while TL variation only serves to fine tune the terminal Ru HOMO. Conversely, BL' variation has little impact on the overall light absorbing properties between analogous complexes because shifting the energy of one transition (central Ru $\rightarrow$ BL' CT) is masked by the strongly absorbing central and terminal Ru $\rightarrow$ dpp CT

transitions. However, TL variation greatly enhances the light absorption and results in fewer spectral gaps when TL = Ph₂phen vs. phen. The combination of electrochemical and spectroscopic analysis with component variation gives considerable insight into the properties of structurally diverse supramolecular systems.

3.2.4. Excited State Dynamics

The excited state processes of the tetrametallic complexes are complicated by the number of energetically close excited states and complex photophysics. The emissive nature of the terminal Ru(dπ)→dpp(π*) ³MLCT excited state enables the use of steady-state and time-resolved emission spectroscopy as a probe into the excited state dynamics. **Table 3.3** summarizes the excited state properties of the [{(TL)₂Ru(dpp)}₂Ru(BL')](PF₆)₆ trimetallic and [{(TL)₂Ru(dpp)}₂Ru(BL')PtCl₂](PF₆)₆ tetrametallic complexes (TL = phen or Ph₂phen, BL' = dpp or dpq) at RT in CH₃CN and at 77 K in a 4:1 EtOH/MeOH rigid matrix. Emission was not observed for the [{(TL)₂Ru(dpp)}₂RuCl₂](PF₆)₄ complexes, as the destabilized central Ru(dπ) orbitals provides a lowest-lying central Ru→μ-dpp CT excited state expected to occur around 900 nm with low Φ^{em} based on the analogous [{(bpy)₂Ru(dpp)}₂RuCl₂](PF₆)₄,⁵³ and the PMT used is not sensitive enough in this region. Excitation of Ru(II)-polyazine complexes to populate a ¹MLCT excited state typically leads to intersystem crossing to populate a ³MLCT state with near unit efficiency, and this process can be followed by intra- and intermolecular electron transfer. Electrochemical analysis predicts the same terminal Ru(dπ)→dpp(π*) ³MLCT emissive state in the trimetallics and tetrametallics and a lowest-lying charge separated (CS) excited state in the tetrametallic architecture. Unexpectedly, this is complicated by non-unity population of the emissive state, a property that is very uncommon in Ru(II)-polyazine complexes.^{17,28,47} The trimetallic complexes, while able to populate many energetically close excited states, exhibit less complicated photophysics as they obey Kasha's rule by populating the lowest-lying, emissive terminal Ru(dπ)→μ-dpp(π*) ³MLCT excited state with unit efficiency from higher-lying states. The HOMO and LUMO are not spatially separated in the trimetallic complexes as they are in the tetrametallic complexes, indicating that charge separation does

not occur upon photoexcitation. To understand the intramolecular electron transfer processes that result in charge separation in the tetrametallics from either of the optically accessible terminal $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3CT or central $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-BL}'(\pi^*)$ ^3CT states, the trimetallic analogues were used as photophysical models as the terminal $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ $^3\text{MLCT}$ emissive state is similar in nature and energy to that of the analogous tetrametallic complexes.

Table 3.3: Steady-State and Time-Resolved Emission Spectroscopy Data for the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ and $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ Complexes ^a

Complex	RT						77 K	
	λ^{em} (nm)	Φ^{em} $\times 10^3$ ^b	τ (μs) ^c	$k_r \times 10^{-3}$ (s^{-1}) ^d	$k_{nr} \times 10^{-6}$ (s^{-1}) ^d	$k_{et} \times 10^{-6}$ (s^{-1})	λ^{em} (nm)	τ (μs) ^c
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$	764	1.0	0.11	9.3	8.9	--	705	2.0
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$	764	1.1	0.11	9.7	8.9	--	715	2.0
$[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ ^e	760	1.0	0.11	9.2	9.1	--	705	2.1
$[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ ^f	752	1.0	0.11	9.2	9.1	--	715	2.0
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$	766	0.71	0.077	9.3	8.9	4.1	715	2.0
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$	760	0.37	0.075	9.7	8.9	4.4	715	2.0
$[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ ^e	756	0.71	0.083	9.2	9.1	3.0	705	2.1
$[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ ^f	752	0.32	0.080	9.2	9.1	3.4	715	2.0

^a RT measurements were performed on CH_3CN solutions deoxygenated with Ar and excited at 540 nm. 77 K measurements were performed in a 4:1 EtOH/MeOH glass. Values corrected for PMT response. phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, k_r = rate constant for radiative decay, k_{nr} = rate constant for non-radiative decay, k_{et} = rate constant for intramolecular electron transfer. ^b Error associated with quantum yield measurements is $\pm 5\%$. ^c Error associated with lifetime measurements is $\pm 5\%$. ^d Values for the tetrametallic complexes are assumed to be the same as the values for the corresponding trimetallic complexes. ^e From reference 113. ^f From reference 78.

The photophysical properties of the trimetallic models are quite similar, regardless of TL or BL' identity. Each $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ complex emits at a similar energy between 752 and 764 nm from a lowest-lying terminal $\text{Ru}(\text{d}\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3CT excited state. The emission spectra of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ in RT CH_3CN are shown in **Figure 3.21**. The nature of the emissive excited state, terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$, is consistent with electrochemical analysis. The trimetallic models exhibit an emission quantum yield (Φ^{em}) of 1.0-1.1

$\times 10^{-3}$ and an excited state lifetime (τ) of 110 ns. This analysis suggests that the identity of TL and BL' has no significant impact on the excited state dynamics of this motif as these sub-units do not participate in the lowest-lying $^3\text{MLCT}$ emissive state. Terminal $\text{Ru} \rightarrow \text{TL}$ and central $\text{Ru} \rightarrow \text{BL}'$ CT excited states are higher in energy than the emissive state due to the destabilized ligand acceptor orbitals compared to μ -dpp, and these higher lying states deactivate to the lowest-lying emissive state with unit efficiency. A comparison of the RT and 77 K emission profiles of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ is given in **Figure 3.22**. At 77 K in a 4:1 EtOH/MeOH rigid matrix, the emission band narrows in comparison to the RT emission band and blue shifts to 710 nm while exhibiting vibronic structure which is characteristic of a $^3\text{MLCT}$ excited state.^{115,116} The relative RT emission spectra of the complexes with TL = Ph_2phen are provided in **Figure A-19**, and the 77 K emission profiles are provided in **Figure A-20**.

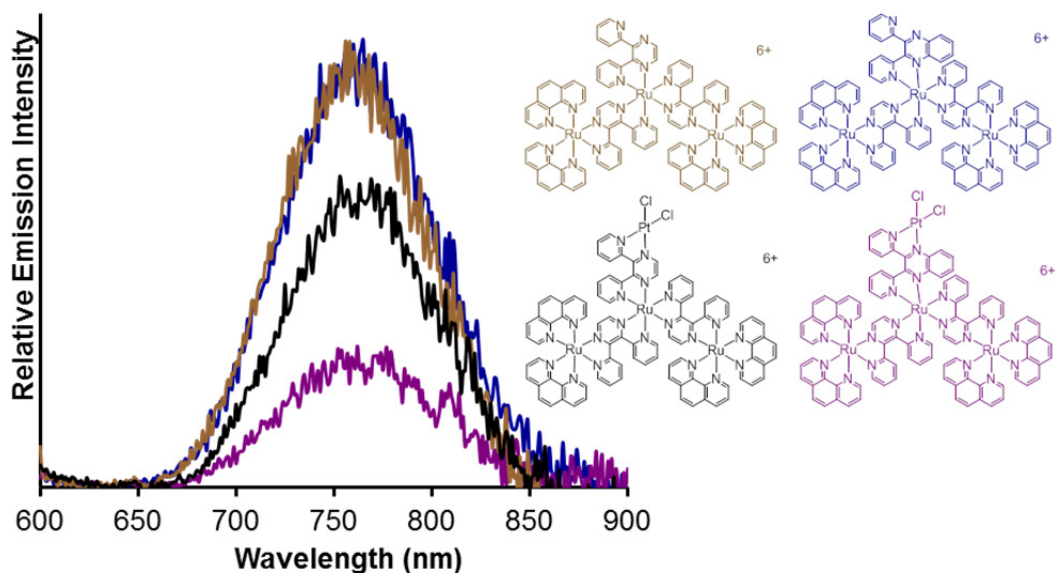


Figure 3.21: Emission spectra of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) measured in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Samples were absorbance matched at 540 nm ($\text{Abs} = 0.2$). Spectra were corrected for PMT response. phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

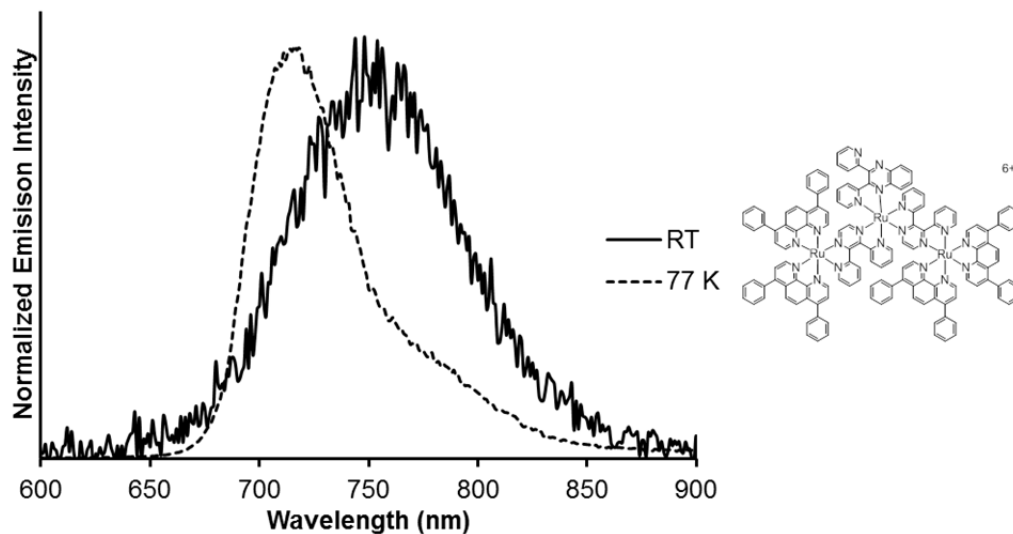


Figure 3.22: Normalized RT (solid line) and 77 K (dashed line) steady-state emission profiles of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$. RT samples were measured in spectral grade CH_3CN and 77 K samples were measured in a 4:1 EtOH/MeOH glass. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The selection of BL' in the tetrametallic $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes greatly impacts the excited state dynamics, while TL has a much smaller impact. The tetrametallic complexes emit at energies nearly identical to the trimetallic models (752-766 nm), as the nature of the emissive state is also terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$. In contrast to the trimetallic models, the lifetime of this $^3\text{MLCT}$ excited state is shortened to 75-83 ns (decrease of about 30 % relative to trimetallic models) and the emission quantum yield is quenched to a degree greatly influenced by the BL' identity. The relative emission spectra of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ are shown in **Figure 3.21** overlaid with their trimetallic model analogues, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (absorbance matched to allow direct comparison), to highlight the degree of emission quenching in the tetrametallic complexes compared to the models. The emission is quenched by 30 % ($\Phi^{\text{em}} = 7.1 \times 10^{-4}$) when $\text{BL}' = \text{dpp}$ and by 68 % ($\Phi^{\text{em}} = 3.2 \times 10^{-4}$) when $\text{BL}' = \text{dpq}$. TL has little impact on Φ^{em} , with the emission of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ quenched by 32 % ($\Phi^{\text{em}} = 7.4 \times 10^{-4}$) and

$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ quenched by 66 % ($\Phi^{\text{em}} = 3.7 \times 10^{-4}$) relative to the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ models. This suggests that there is minimal contribution from TL orbitals in the $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ excited states and little influence on excited state dynamics. An important aspect of this molecular architecture is that emission arises from the part of the molecule that is remote from BL' and Pt, and the identity of BL' , despite its distance from that part of the molecule, has major impacts on the emission quantum yield. The unusual discrepancy in the impact on Φ^{em} and τ suggests that another excited state is competitively populated by different degrees, strongly influenced by the energy of the BL' acceptor orbitals. This is a violation of Kasha's rule which states that emission occurs only from the lowest-lying excited state that is populated with unit efficiency³⁵ and is unusual for polymetallic polyazine-bridged complexes.^{20,39,56,60,112} The excited state lifetime remains the same at 77 K upon platination of the trimetallic to produce the tetrametallic complexes (**Table 3.3**) and the emission profiles are nearly identical, indicative of the same terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ state being the emissive state. Intramolecular electron transfer is impeded in low temperature rigid media so identical emission at 77 K and varied Φ^{em} and τ at RT is evidence of intramolecular electron transfer at RT.

Simplified state diagrams, **Figure 3.23**, explain the unusual photophysical properties of the tetrametallic complexes in comparison to the trimetallic models. The state diagrams shown are greatly simplified to highlight just the excited states that participate in emission and closely lying states important in the non-unity population of the emissive $^3\text{MLCT}$ state which are impacted by *cis*- PtCl_2 coordination, terminal $\text{Ru} \rightarrow \text{dpp}$ MLCT and central $\text{Ru} \rightarrow \text{BL}'$ MLCT excited states. Other charge transfer excited states such as central $\text{Ru} \rightarrow \text{dpp}$ CT and terminal $\text{Ru} \rightarrow \text{TL}$ CT can also be populated upon visible light excitation, but they are omitted from the state diagrams as their energies, and subsequent impact on population of the emissive state, are not expected to change upon *cis*- PtCl_2 coordination. In the simplified case of $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, visible light excitation results in population of a terminal $\text{Ru} \rightarrow \text{dpp}$ $^1\text{MLCT}$ or a central $\text{Ru} \rightarrow \text{BL}'$ $^1\text{MLCT}$ excited state which then undergo intersystem crossing (k_{isc}) with $\Phi = 1$ to populate the respective $^3\text{MLCT}$ excited states, typical of $\text{Ru}(\text{II})$ -polyazine complexes. The higher-

lying central $\text{Ru} \rightarrow \text{BL}'$ $^3\text{MLCT}$ excited state undergoes internal conversion (k_{ic}) to populate the lowest-lying terminal $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ excited state with $\Phi = 1$, in agreement with Kasha's rule. This is verified in the excitation spectra presented in **Figure 3.24** and discussed below. This lowest-lying excited state finally undergoes radiative (k_r) or non-radiative (k_{nr}) decay to relax back to the ^1GS . Coordination of *cis*- PtCl_2 to provide the tetrametallic complex $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ lowers the energy of the central $\text{Ru} \rightarrow \text{BL}'$ MLCT excited state, yet the energy of the terminal $\text{Ru} \rightarrow \text{dpp}$ MLCT states are unaffected. Stabilization of the BL' acceptor orbitals enables competitive population of a terminal $\text{Ru} \rightarrow \text{BL}'$ ^3CS (charge separated) state through intramolecular electron transfer from the terminal $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ state (k_{et}) as well as some direct population thought to occur from the central $\text{Ru} \rightarrow \text{BL}'$ $^3\text{MLCT}$ excited state, an unusual property of $\text{Ru}(\text{II})$ -polyazine complexes.

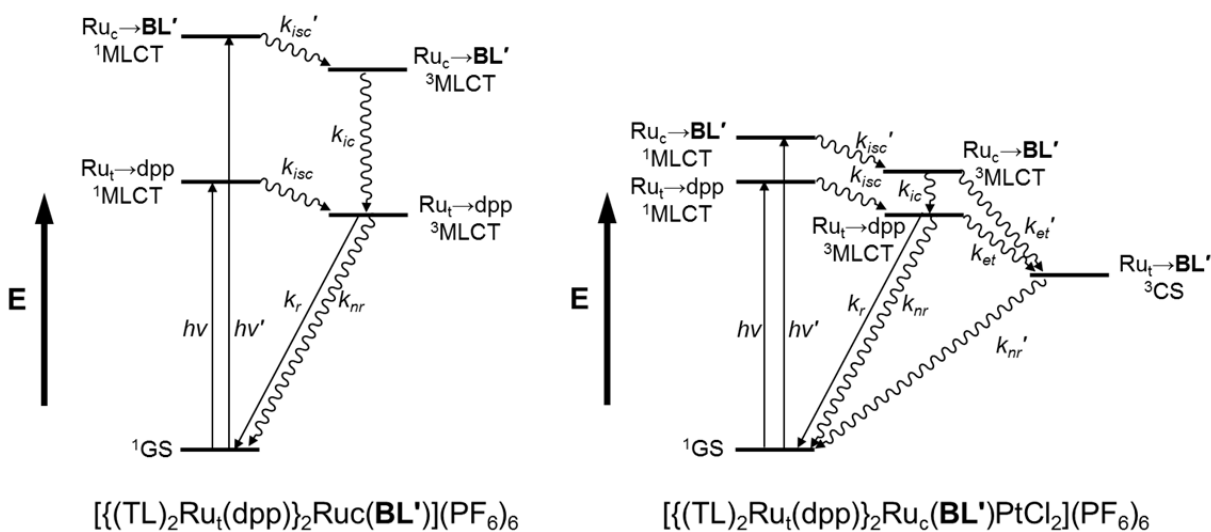


Figure 3.23: Simplified state diagrams for the trimetallic models $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ and the tetrametallic complexes $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ (TL = phen or Ph_2phen , $\text{BL}' = \text{dpp}$ or dpq). E = energy, ^1GS = singlet ground state, $^1\text{MLCT}$ = singlet metal-to-ligand charge transfer state, $^3\text{MLCT}$ = triplet metal-to-ligand charge transfer state, ^3CS = triplet charge separated state, k_{isc} = rate constant for intersystem crossing, k_{ic} = rate constant for internal conversion, k_r = rate constant for radiative decay, k_{nr} = rate constant for non-radiative decay, k_{et} = rate constant for intramolecular electron transfer. Ru_t indicates the metal center in the $(\text{TL})_2\text{Ru}^{\text{II}}(\text{dpp})$ unit, and Ru_c indicates the metal center in the $(\text{dpp})_2\text{Ru}^{\text{II}}(\text{BL}')$ unit. $\text{Ph}_2\text{phen} = 4,7$ -diphenyl-1,10-phenanthroline, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The intramolecular electron transfer to populate a charge separated state was studied through comparison of the tetrametallic complexes to the trimetallic models. These complexes are particularly valid models as they possess the same Ru→μ-dpp ³MLCT emissive state with the dpp coordinated to two Ru centers as the title tetrametallic complex, the excited states are similar in energy and band shape, and the TLs bound to Ru are the same. In addition, the model and the tetrametallics possess the same emission profile and lifetime at 77 K where electron transfer is impeded. The excited state lifetimes of the tetrametallic complexes and models were used to determine the rate constant for intramolecular electron transfer from the terminal Ru→dpp ³MLCT state (k_{et}) following **Equations 3.1** and **3.2**,

$$\tau_{model} = \frac{1}{k_r + k_{nr}} \quad (3.1)$$

$$\tau_{tetrametallic} = \frac{1}{k_r + k_{nr} + k_{et}} \quad (3.2)$$

where τ_{model} is the lifetime of the trimetallic model, $\tau_{tetrametallic}$ is the lifetime of the analogous tetrametallic complex, k_r is the rate constant for radiative decay (calculated by dividing the trimetallic Φ^{em} by the trimetallic τ), and k_{nr} is the rate constant for non-radiative decay. An assumption is made that the k_r and k_{nr} values for one tetrametallic complex are the same as those calculated for the analogous trimetallic model to enable calculation of k_{et} ; the values for these rate constants are given in **Table 3.3**. [$\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ and [$\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ have larger k_{et} values than their BL' = dpp analogues, indicating more efficient population of the ³CS excited state from the lowest-lying emissive ³MLCT state when BL' = dpq. This enhanced efficiency is expected due to the ca. 0.3 V increased driving force for intramolecular electron transfer in the complexes with a dpq acceptor relative to dpp.

The quantum yields of emission can also be related to the rate constants for the processes deactivating the emissive state with the trimetallic as a model. This relationship, **Equations 3.3** and **3.4**, was used to determine the efficiency of population of the emissive excited state,

$$\Phi_{3MLCT}^{em(model)} = \Phi_{3MLCT}^{pop(model)} \left(\frac{k_r}{k_r + k_{nr}} \right) \quad (3.3)$$

$$\Phi_{3MLCT}^{em(tetrametallic)} = \Phi_{3MLCT}^{pop(tetrametallic)} \left(\frac{k_r}{k_r + k_{nr} + k_{et}} \right) \quad (3.4)$$

where $\Phi_{3MLCT}^{em(model)}$ is the quantum yield of emission of the trimetallic model, $\Phi_{3MLCT}^{pop(model)}$ is the quantum yield of population of the emissive state in the trimetallic model, $\Phi_{3MLCT}^{em(tetrametallic)}$ is the quantum yield of emission of the analogous tetrametallic complex, $\Phi_{3MLCT}^{pop(tetrametallic)}$ is the quantum yield of population of the emissive state in the tetrametallic complex. In **Equation 3.3**, $\Phi_{3MLCT}^{pop(model)}$ is assumed to be unity, typical of Ru(II)-polyazine complexes. Uncommon in this type of complex, the value of $\Phi_{3MLCT}^{pop(tetrametallic)}$ in **Equation 3.4** is not unity due to population of the ^3CS state from a higher lying excited state, central Ru→BL' ^3MLCT . Using the values of k_r , k_{nr} , and k_{et} from **Equation 3.2**, Φ^{pop} of the emissive state was calculated for each of the tetrametallic complexes. The BL' = dpp complexes populate the emissive excited state with $\Phi = 0.93$ and 0.99 for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$, respectively, similar to typical Ru complexes, suggesting minimal indirect population of the non-emissive ^3CS state from higher lying ^3MLCT states. In stark contrast, the BL' = dpq complexes populate the emissive state with $\Phi = 0.44$ and 0.51 for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$, respectively, suggesting indirect population of the ^3CS state which is an uncommon property imparted by this tetrametallic motif. This suggests the population of the emissive state (and subsequent population of the ^3CS state) exhibits excitation wavelength dependence even though these complexes have a variety of MLCT states that are very close in energy.

Emission excitation spectroscopy was used to analyze the excitation wavelength dependence of the trimetallic and tetrametallic emission. **Figure 3.24** illustrates that the excitation spectra with $\lambda^{em} = 760$ nm follow the electronic absorption profile for the trimetallic complexes $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ and the tetrametallic complex $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$, in agreement with unity population of the emissive state for the trimetallic complexes and near unity population in the tetrametallic complex. The overlaid

electronic absorption and emission excitation spectra for $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ are not in agreement as observed in the other complexes. This observation is in agreement with non-unity population of the emissive terminal $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ state and more efficient population of the non-emissive ^3CS state when $\text{BL}' = \text{dpq}$. Low energy excitation, $\lambda^{\text{exc}} > 550$ nm, affords less efficient population of the emissive state and more efficient charge separation.

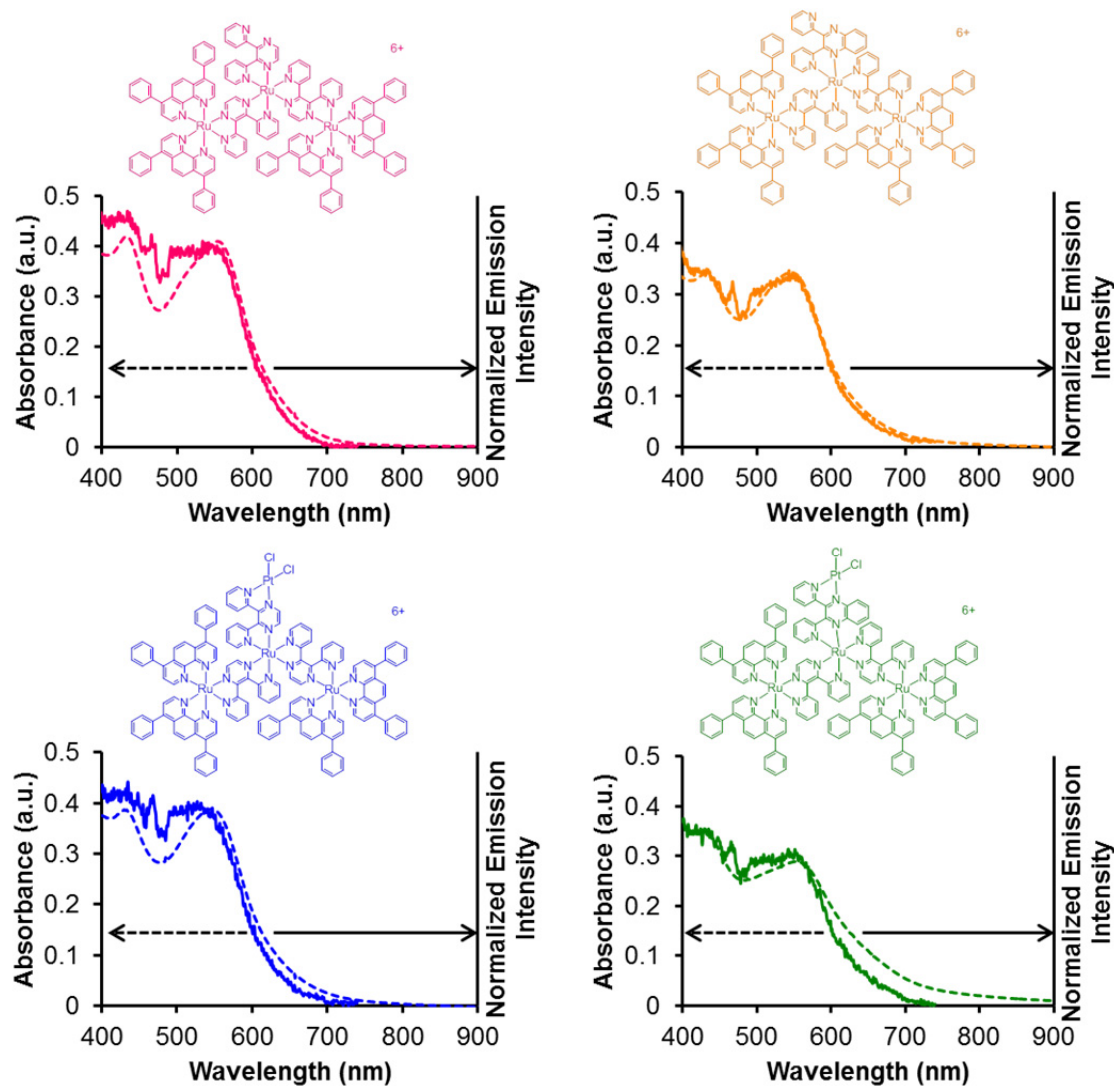


Figure 3.24: Overlaid electronic absorption spectra (dashed lines) and excitation spectra (solid lines) of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) measured in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Emission was monitored at 760 nm. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.2.5. Photochemistry

The ability of the supramolecular complexes to undergo photoinitiated electron collection (PEC) is important for applications in the arena of photocatalytic water reduction. Despite long term interest in PEC, few functional approaches exist. These systems are different in that the collected electrons reside on a set of bridging ligands bound to the central Ru in the (BL)Ru^{II}(BL') sub-unit. Analysis of the photophysical processes of the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ and $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes provides information into how excitation with visible light can move electrons to ligand(π^*) orbitals in Ru(II)-polyazine complexes. This knowledge was applied to studies involving interactions between the MLCT excited state complexes with a sacrificial electron donor (ED) to understand photoinitiated electron collection (PEC) in this supramolecular architecture and photocatalysis when a substrate such as water is included in the system containing the metal complex and ED.

3.2.5.1. Photochemical Reduction

Electronic absorption spectroscopy of the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes was studied in the presence of a sacrificial electron donor (ED), *N,N*-dimethylaniline (DMA). Occupation of a BL(π^*) orbital results in shifts of the transitions which involve the newly reduced BL. A solution of the tetrametallic complex with an excess of DMA in RT CH₃CN was photolyzed with a 470 nm LED and electronic absorption spectra were recorded over time. The spectral shifts resulting from 470 nm photolysis of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ with DMA are pictured in **Figure 3.25A**. The absorption spectra at $\lambda < 350$ are obscured due to strong absorption of DMA. As photolysis with an excess of ED is expected to localize electrons on the dpp and dpq ligands, the Ru($d\pi$) $\rightarrow$ dpp(π^*) and Ru($d\pi$) $\rightarrow$ dpq(π^*) ¹CT transitions are shifted, resulting in a loss of absorption in the broad band centered at 550 nm. The broad absorption between 350 nm and 425 nm in the original spectrum corresponding to dpp $\pi\rightarrow\pi^*$ and dpq $\pi\rightarrow\pi^*$ transitions also shifts, resulting in a loss of absorption in this region. The terminal Ru($d\pi$) $\rightarrow$ Ph₂phen(π^*) ¹CT transition centered at 430 nm is slightly red shifted due to increased

electron density on the dpp ligand directly coordinated to terminal Ru which destabilizes the $d\pi$ orbitals and results in a lower energy transition. The spectral changes observed from photochemical reduction agree with those observed by electrochemical reduction of the complex (**Figure 3.25B**) to produce the complex with two reduced dpp ligands and a reduced dpq ligand, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp}^-)\}_2\text{Ru}(\text{dpq}^-)\text{PtCl}_2]^{3+}$. The correlation of spectroelectrochemistry and photolysis in the presence of the DMA ED demonstrates that $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes undergo PEC to collect three electrons on the central $(\text{dpp})_2\text{Ru}^{\text{II}}(\text{BL}')$ sub-unit. Electrons on one diimine ligand are available to transfer to other ligands within a ps timescale¹¹⁷ making them available to a substrate when interacting with the Pt RM. Similar spectral shifts upon photochemical reduction with DMA are also observed in the three other tetrametallic complexes, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$, $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$, and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$. The spectral shifts observed upon photochemical and electrochemical reduction are consistent with photoinitiated electron collection leading to reduction of the dpp and dpq bridging ligands.

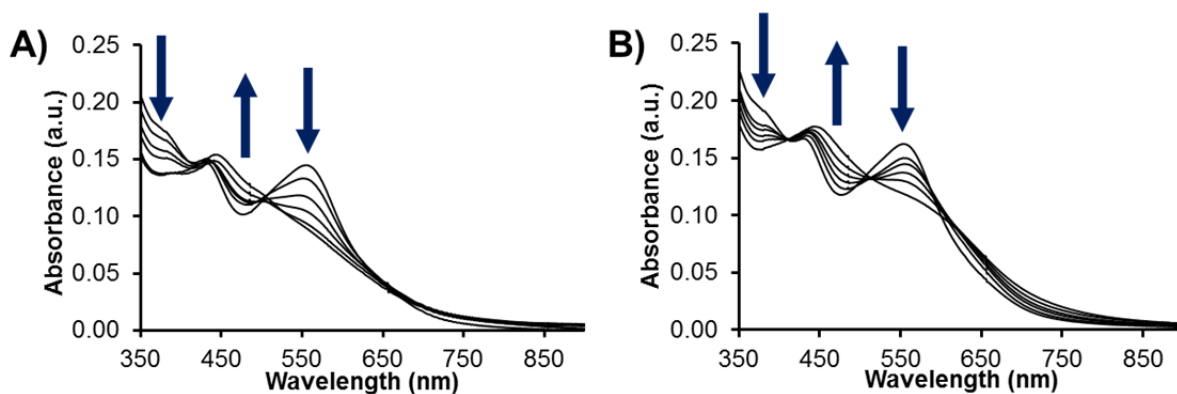


Figure 3.25: Electronic absorption spectra of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ in spectral grade CH_3CN in a 1 cm cuvette following A) photochemical reduction in the presence of DMA with 470 ± 10 nm LED light source and B) electrochemical reduction with an applied potential of -0.80 V vs. Ag/AgCl . Initial spectrum is the sample and DMA prior to photolysis and the final spectrum corresponds to photolysis for 120 s. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, DMA = *N,N*-dimethylaniline.

3.2.5.2. Excited State Quenching

An electron donor that efficiently quenches the excited state of the $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2](PF_6)_6$ complexes by transferring an electron and forming a reduced species is necessary for photocatalytic water reduction schemes. The emissive nature of the excited state complex provides a probe into this excited state electron transfer quenching process, as photochemical reduction is expected to occur by DMA donating an electron to fill the hole on terminal Ru in the terminal $Ru(d\pi) \rightarrow dpp(\pi^*)$ ^3MLCT state through intermolecular electron transfer. A Stern-Volmer analysis¹⁰⁸ of the emissive ^3MLCT excited state quenching was performed by monitoring emission of samples with increasing concentrations of DMA and a fixed concentration of $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2](PF_6)_6$ (TL = phen or Ph₂phen, BL' = dpp or dpq). **Figure 3.26A** illustrates that as [DMA] increases, the quantum yield of emission of $[\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2](PF_6)_6$ decreases, a result of either intermolecular electron transfer from DMA to the $(Ph_2phen)_2Ru^{III}(BL^-)$ unit in the excited state providing DMA^{*+} and a $(Ph_2phen)_2Ru^{II}(dpp^-)$ unit (**Equation 3.5**) or bimolecular deactivation (**Equation 3.6**); radiative decay back to the ground state is prohibited in both cases (MC = metal complex).



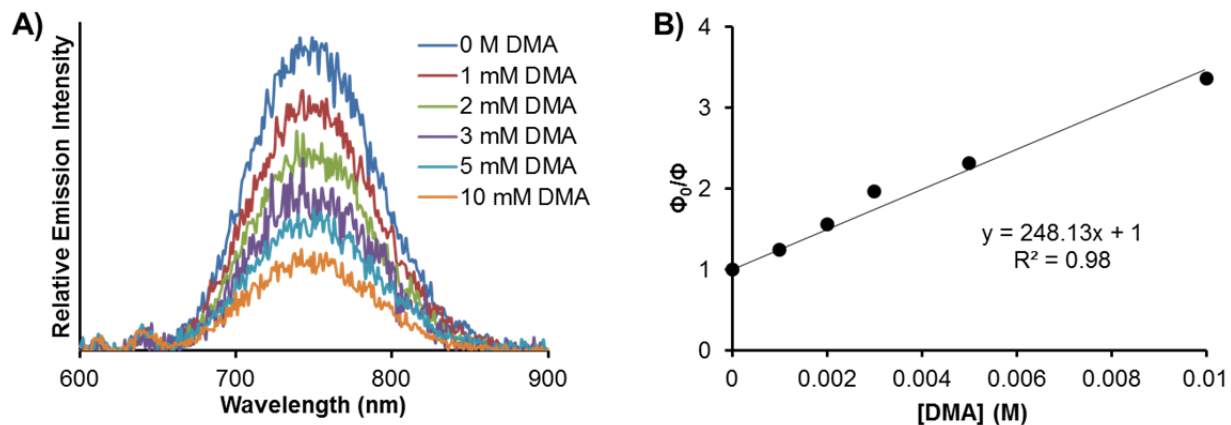


Figure 3.26: Emission quenching of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ illustrating A) the overlaid emission spectra in spectral grade CH_3CN in a 1 cm quartz cuvette with increasing concentrations of DMA from 0 M to 0.01 M and B) the Stern-Volmer plot showing the linear relationship between emission quenching and DMA concentration. DMA = *N,N*-dimethylaniline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

A linear relationship between the ratio of Φ^{em} in the absence of DMA to Φ^{em} with added DMA (Φ_0/Φ) and $[\text{DMA}]$, described in **Equation 3.7** is observed in the Stern-Volmer plot in **Figure 3.25B**.

$$\frac{\Phi_0}{\Phi} = 1 + K_{SV}[\text{DMA}] \quad (3.7)$$

The slope of the line corresponds to K_{SV} , and the rate constant for bimolecular quenching of the excited state by DMA was determined to be on the order of $10^9 \text{ M}^{-1}\text{s}^{-1}$ for each of the four tetrametallic complexes using **Equation 3.8**,

$$K_{SV} = k_q\tau_0 \quad (3.8)$$

indicating that the interaction between DMA and the excited state complex is very efficient, approaching the diffusion controlled limit of $10^{10} \text{ M}^{-1}\text{s}^{-1}$.¹⁰⁸ **Table 3.4** provides the Stern-Volmer emission quenching data for $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ (TL = phen or Ph_2phen , BL' = dpp or dpq). Additional Stern-Volmer quenching data for the tetrametallic complexes are provided in **Figures A-21 – A-24**. Two trends are observed in the k_q values for the tetrametallic complexes corresponding to the effects of TL and BL' variation. Excited state quenching occurs with a larger rate constant for the TL = phen complexes in comparison to the TL = Ph_2phen analogues, attributed to the structural differences in phen and Ph_2phen .

The planar aromatic phen ligand can allow π – π stacking with small, aromatic species such as DMA to afford more efficient interactions between the electron donor and the excited state complex, while the phenyl rings in Ph₂phen are not coplanar with the phen portion of the ligand which may prevent π – π stacking with DMA close to the Ru center. A trend is also observed with BL' variation, with the dpq complexes more efficiently quenched than the dpp analogues. Bimolecular deactivation of the ³MLCT excited state competes with deactivation of this state through intramolecular electron transfer (k_{et}) to populate the ³CS state. The larger k_{et} values for the complexes with BL' = dpq vs. dpp from enhanced stabilization of the ³CS is expected to result in a smaller k_q value for the BL' = dpq complexes. Despite the effects of TL and BL' variation in this supramolecular motif, each of the four tetrametallic complexes undergo efficient bimolecular excited state quenching in the presence of DMA and photoreduction of the complex is expected to be rapid in H₂O reduction photocatalysis experiments.

Table 3.4: Stern-Volmer Analysis for Bimolecular Quenching of the ³MLCT Excited State of [$\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2](PF_6)_6$ (TL = phen or Ph₂phen, BL' = dpp or dpq) with DMA. ^a

Complex	K _{SV} (M ⁻¹) ^b	τ_0 (ns)	$k_q \times 10^{-9}$ (M ⁻¹ s ⁻¹)
[$\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6$]	300	77	3.9
[$\{(Ph_2phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2](PF_6)_6$]	248	75	3.3
[$\{(phen)_2Ru(dpp)\}_2Ru(dpp)PtCl_2](PF_6)_6$]	445	83	5.4
[$\{(phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2](PF_6)_6$]	370	80	4.6

^a Measured in the dark in spectral grade deoxygenated CH₃CN. Deoxygenated DMA was added to the complex in the cuvette just prior to measurement. Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, DMA = *N,N*-dimethylaniline. ^b Stern-Volmer constant from slope of Stern-Volmer linear plot.

3.2.5.3. Photocatalytic H₂ Production from H₂O

The ability of the [$\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2](PF_6)_6$ supramolecules to undergo photoinitiated electron collection on the dpp and BL' π^* orbitals motivated the study of the complexes as photocatalysts for H₂O reduction to produce H₂. Each of the four tetrametallic complexes catalytically produces H₂ when photolyzed with 470 nm light in the presence of DMA electron donor and H₂O

substrate in a system that contains 50 μM tetrametallic complex, 1.5 M DMA, 0.62 M H_2O , 110 μM $[\text{DMAH}^+][\text{SO}_3\text{CF}_3^-]$ and CH_3CN solvent. Despite long term interest, few motifs are known that can absorb light, collect electrons and catalyze H_2O reduction to H_2 with a single molecule. A plot comparing the $\mu\text{mol H}_2$ and TON (turnover number) vs. time for $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ (TL = phen or Ph_2phen , BL' = dpp or dpq) is given in **Figure 3.27**, and the data for a photolysis time of 10 h is given in **Table 3.5**. Experiments in which just one component was excluded, such as tetrametallic complex, H_2O , DMA, and light, produced little to no detectable H_2 , demonstrating that all components play necessary roles in the complicated photocatalytic process.

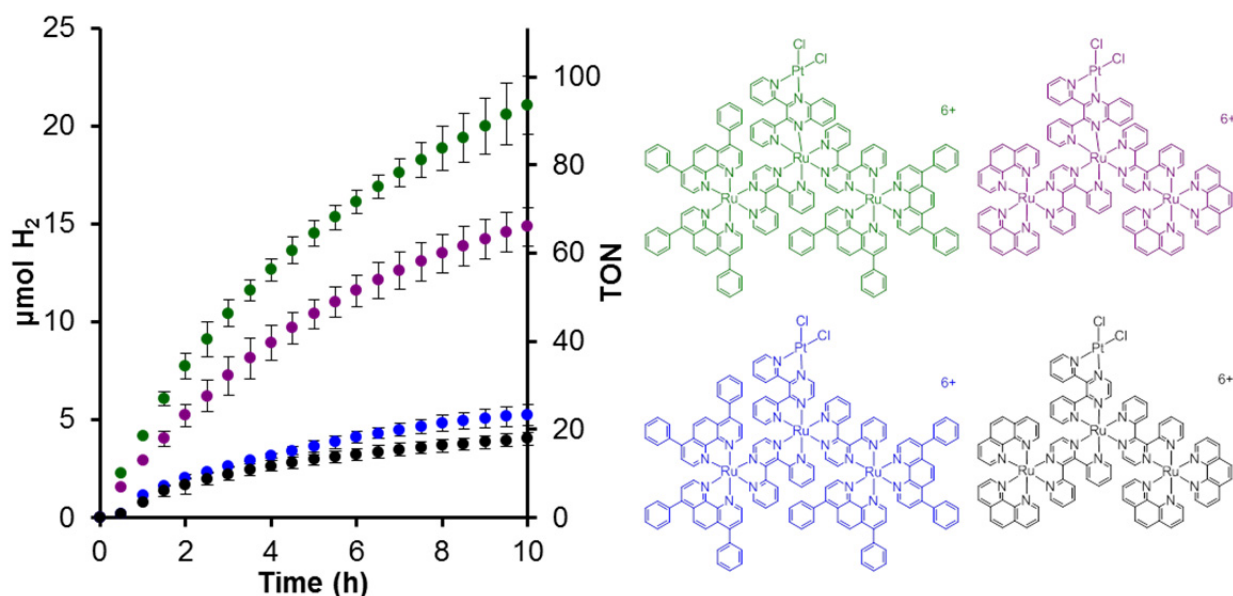


Figure 3.27: Photocatalytic hydrogen production profiles with $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (●), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (●), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (●), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (●). Photolysis systems contained 50 μM tetrametallic complex, 0.62 M H_2O , 1.5 M DMA, and 110 μM $[\text{DMAH}^+][\text{CF}_3\text{SO}_3^-]$ in deoxygenated CH_3CN and irradiated at 470 nm. TON = mol H_2 /mol catalyst, phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, DMA = *N,N*-dimethylaniline. Each set of data is the average of three experiments. Error bars correspond to one standard deviation.

Table 3.5: Photocatalytic H₂ Production Data for Ru(II),Pt(II) Tetrametallic Complexes ^a

Complex	μmol H ₂ at 10 h	TON at 10 h ^b
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpp)PtCl ₂](PF ₆) ₆	5 ± 1	23 ± 2
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpq)PtCl ₂](PF ₆) ₆	21 ± 1	94 ± 6
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpp)PtCl ₂](PF ₆) ₆	4 ± 1	18 ± 1
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpq)PtCl ₂](PF ₆) ₆	15 ± 1	66 ± 4
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpp)](PF ₆) ₆ + <i>cis</i> -[PtCl ₂ (DMSO) ₂]	< 3 ^c	--
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpq)](PF ₆) ₆ + <i>cis</i> -[PtCl ₂ (DMSO) ₂]	< 3 ^c	--
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpp)](PF ₆) ₆ + <i>cis</i> -[PtCl ₂ (DMSO) ₂]	< 3 ^c	--
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpq)](PF ₆) ₆ + <i>cis</i> -[PtCl ₂ (DMSO) ₂]	< 3 ^c	--

^a Results correspond to 10 h photolysis time with 470 nm LED light source (light flux = 2.36 × 10¹⁹ photons/min). Photolysis solutions contained 50 μM tetrametallic complex (or 50 μM trimetallic complex and 50 μM *cis*-[PtCl₂(DMSO)₂]), 0.62 M H₂O, 1.5 M DMA, 110 μM [DMAH⁺][CF₃SO₃⁻] in deoxygenated CH₃CN. ^b TON = mol H₂/mol catalyst. ^c No H₂ detected. H₂ sensors have a detection limit of 0.5 % H₂ (ca. 3 μmol).

Choice of BL' is important in photocatalysis of H₂O reduction to H₂ in this supramolecular motif, as the [{(TL)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ complexes produce substantially more H₂ in 10 h than their [{(TL)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ analogues. For example, 21 μmol H₂ (94 TON) and 5 μmol H₂ (23 TON) were produced when the photocatalysts utilized were [{(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ and [{(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆, respectively. The enhanced driving force for intramolecular electron transfer to populate a ³CS excited state, localizing reducing equivalents in close proximity to the Pt reactive metal center (RM), is consistent with the increased activity of the BL' = dpq complexes. The terminal Ru(dπ)→dpp(π*) ³MLCT excited state is populated with near unit efficiency when BL' = dpp, resulting in less efficient movement of electrons toward the RM. These large differences in photocatalysis by BL' = dpq vs. dpp imply that the terminal Ru(dπ)→BL'(π*) ³CS state is important in photocatalysis in these systems, making the discovery of indirect population of this ³CS state in BL' = dpq systems even more important.

The choice of TL in this motif has a smaller impact on the photocatalytic efficiency of these complexes. **Figure 3.27** shows that the [{(Ph₂phen)₂Ru(dpp)}₂Ru(BL')PtCl₂](PF₆)₆ complexes are more

efficient photocatalysts than their $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ counterparts, with 21 $\mu\text{mol H}_2$ (94 TON) and 15 $\mu\text{mol H}_2$ (66 TON) produced with $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$, respectively, and the same trend was observed for the $\text{BL}' = \text{dpp}$ complexes. The enhanced absorptivity of the complex at 470 nm due to the Ph_2phen TL likely plays a role in this trend. The increased sterics resulting from the bulky phenyl groups in the Ph_2phen TLs favoring formation of more active stereoisomers may also be operative. Additionally, as the phen complexes undergo more efficient quenching of the excited state by DMA compared to the Ph_2phen complexes, the π - π stacking of DMA with the phen ligands may result in slower cage escape and enhance back electron transfer to the DMA^{*+} and decrease photocatalytic efficiency in the phen vs. Ph_2phen systems.

The integrity of the supramolecular architecture in Ru(II),Pt(II) and Ru(II),Pd(II) polyazine-bridged photocatalysts, whether the active catalyst is the supramolecular complex or a heterogeneous system of the LA and the newly formed Pt^0 colloid, is a controversial subject.^{96,118} Studies of photodecomposition to generate Pd^0 colloid as the active photocatalyst were performed with a new Ru,Pd complex $[(\text{bpy})_2\text{Ru}(\text{Me}_2\text{bpy-DMB-Me}_2\text{bpy})\text{PdCl}_2]^{2+}$ ($\text{Me}_2\text{bpy} = 4,4'$ -dimethyl-2,2'-bipyridine; $\text{DMB} =$ dimethoxybenzene) in a 2:1 $\text{CH}_3\text{CN/TEA}$ mixture ($\text{TEA} =$ triethylamine, ED) that involved evaporation of the solvent to explore the surfaces of particles. While Pd^0 particles were observed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), this test leads to very high TEA concentrations as solvent is lost and conditions are changed, making it not definitive.¹¹⁸ Additionally, the use of Pt complexes as molecular catalysts, $[\text{Pt}(\text{dcbpy})_2\text{Cl}_2]$ and $[\text{Pt}(\text{ttpy})\text{Cl}]^+$ ($\text{dcbpy} = 4,4'$ -dicarboxyl-2,2'-bipyridine; $\text{ttpy} = 4$ -tolyl-2,2':6',2''-terpyridine), to demonstrate colloidal Pt^0 formation was studied under UV irradiation as well as solvent evaporation to study by TEM and XPS.⁹⁶ A counter-report using molecular Pt(II) catalysts such as *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ and $[(\text{tpy})\text{PtCl}]^+$ suggests that the catalytic activity is thermally driven process, and photodecomposition is not a likely pathway. XPS studies in which the solvent was not removed, rather the sample was freeze dried to keep solvent/ED

ratios constant, showed no evidence of Pt^0 formation and only the presence of Pt^{II} species.¹¹⁹ Further detailed studies on the active photocatalytic systems with molecular $\text{Pt}(\text{II})$ or $\text{Pd}(\text{II})$ H_2O reduction catalysts are needed in this area.

The mercury test, in which an excess of $\text{Hg}(\text{l})$ is added to the photocatalysis system, is a commonly used method to determine whether Pt^0 is the active catalyst, as $\text{Hg}(\text{l})$ acts as a colloidal metal sink and deactivates the catalyst through formation of an inactive alloy. This test can rule out colloids but not establish colloid formation as many metal complexes are known to adsorb on $\text{Hg}(\text{l})$ electrodes upon reduction. Addition of $\text{Hg}(\text{l})$ to a photocatalysis experiment using $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ resulted in a very minor impact on the amount of H_2 produced, suggesting that the complex does not decompose to the trimetallic $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ and a colloidal Pt active catalyst. The absence of impaired catalysis by $\text{Hg}(\text{l})$ addition rules out $\text{Pt}(\text{s})$ in this system. An additional control was performed in which the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ trimetallic analogue and an equimolar amount of *cis*- $[\text{PtCl}_2(\text{DMSO})_2]$ were used in place of the tetrametallic complex. This test probes the importance of supramolecular assembly. In addition, the trimetallic complex and *cis*- $[\text{PtCl}_2(\text{DMSO})_2]$ are expected to be the components present in the system if the Pt is decomplexed which can lead to *in situ* formation of nanoparticle $\text{Pt}(\text{s})$. No detectable hydrogen was produced in any of the four trimetallic and *cis*- $[\text{PtCl}_2(\text{DMSO})_2]$ systems, demonstrating that the supramolecular architecture is indeed critical for catalytic functioning and presenting perhaps the strongest evidence that Pt decomplexation is not operative in these systems. Further evidence that the supramolecular catalyst is active was observed in the electronic absorption spectroscopy of the trimetallic + *cis*- $[\text{PtCl}_2(\text{DMSO})_2]$ system after 10 h photolysis compared to that of the tetrametallic system after the same photolysis time as they are significantly different, demonstrating that the species in solution after photocatalysis are not the same (**Figure 3.28**). Finally, decomplexation of Pt to form the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ species should result in four trimetallic complexes which all possess lowest-lying terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ excited states with similar excited state properties,

lifetimes, and reactivities, so functioning as LAs in a heterogeneous system would be quite similar, regardless of BL' identity. Because the activity of the complexes varies greatly with BL', the possibility of the trimetallic LA and decomplexed Pt is not operative in this motif.

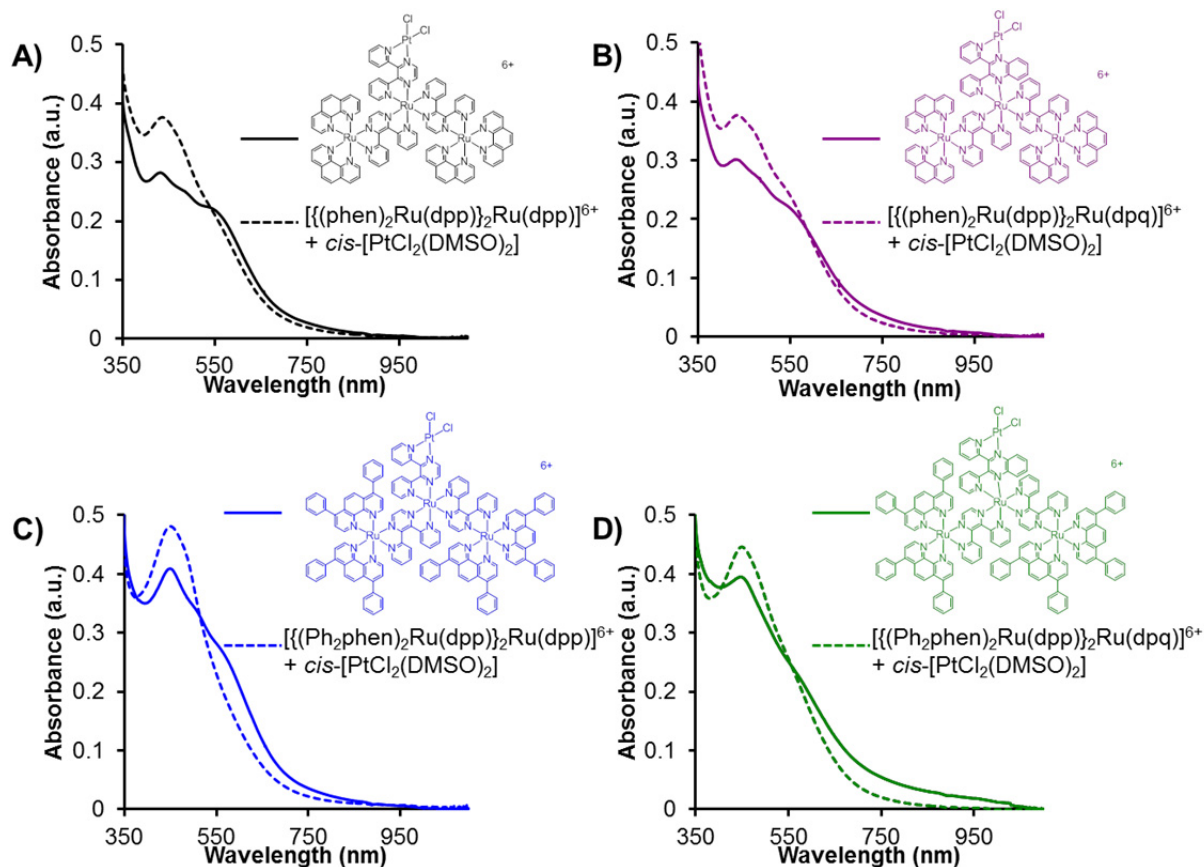


Figure 3.28: Electronic absorption spectroscopy after 10 hours of photolysis in CH₃CN in the presence of 1.5 M DMA, 0.62 M H₂O, 110 μM [DMAH⁺][CF₃SO₃⁻] and A) 50 μM [(phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (solid line) or 50 μM [(phen)₂Ru(dpp)}₂Ru(dpp)](PF₆)₆ and 50 μM *cis*-[PtCl₂(DMSO)₂] (dashed line), B) 50 μM [(phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ (solid line) or 50 μM [(phen)₂Ru(dpp)}₂Ru(dpq)](PF₆)₆ and 50 μM *cis*-[PtCl₂(DMSO)₂] (dashed line), C) 50 μM [(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)PtCl₂](PF₆)₆ (solid line) or 50 μM [(Ph₂phen)₂Ru(dpp)}₂Ru(dpp)](PF₆)₆ and 50 μM *cis*-[PtCl₂(DMSO)₂] (dashed line) and D) 50 μM [(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)PtCl₂](PF₆)₆ (solid line) or 50 μM [(Ph₂phen)₂Ru(dpp)}₂Ru(dpq)](PF₆)₆ and 50 μM *cis*-[PtCl₂(DMSO)₂] (dashed line). DMA = *N,N*-dimethylaniline, phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.3. [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂](PF₆)₄ Trimetallic Complexes and Bimetallic Precursors

A new Ru₂Pt trimetallic supramolecular architecture of the form [(TL)₂Ru(BL)Ru(TL')(BL')PtCl₂]⁴⁺ was designed as an analogue to the [(TL)₂Ru(BL)}₂Ru(BL')PtCl₂]⁶⁺

tetrametallic architecture to enable a more in depth spectroscopic analysis due to the replacement of one $(\text{TL})_2\text{Ru}^{\text{II}}(\text{BL})$ unit with a TL' (**Figure 3.29**). Removal of this unit simplifies the electronic absorption spectroscopy by exhibiting fewer IL and MLCT transitions attributed to the TL and BL $\pi \rightarrow \pi^*$ and $\text{Ru}(\text{d}\pi) \rightarrow \text{TL}(\pi^*)$ CT and $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}(\pi^*)$ CT transitions associated with one terminal LA (**Figure 3.30**). It also reduces the number of isomers but maintains the possibility of a lowest-lying ^3CS state and a terminal Ru remote from the Pt RM which is postulated to allow the long-lived terminal $\text{Ru} \rightarrow \text{dpp}$ $^3\text{MLCT}$ state which still populates the ^3CS state providing active photocatalysts. Fewer overlapping transitions in the visible region provide the possibility to unmask subtle shifts in the electronic absorption spectroscopy which aids in analysis by transient absorption spectroscopy. **Figure 3.31** illustrates the BL' variation discussed herein. While the trimetallic $[(\text{TL})_2\text{Ru}(\text{BL})\text{Ru}(\text{TL}')(\text{BL}')\text{PtCl}_2]^{4+}$ motif seems simpler and is designed to simplify some properties, it is synthetically much more challenging due to the tendency of Ru starting materials to react with diimine ligands to produce *cis*- $[\text{Ru}(\text{NN})_2\text{Cl}_2]$ motifs. Considerable synthetic development is needed to prepare this unknown molecular architecture.



Figure 3.29: Building block schemes of the tetrametallic (left) and trimetallic (right) supramolecular architectures. TL/TL' = terminal ligand, BL/BL' = bridging ligand, LA = light absorber, RM = reactive metal.

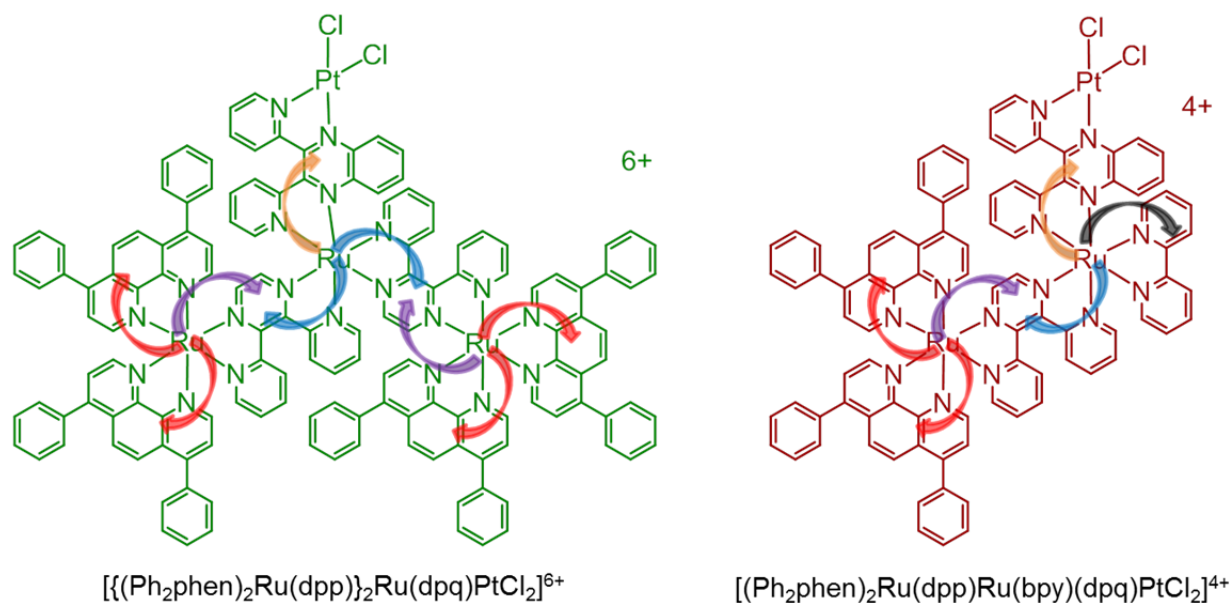


Figure 3.30: Illustration of the possible MLCT transitions in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ tetrametallic complex and the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ trimetallic complex. Arrows indicate an MLCT transition. MLCT = metal-to-ligand charge transfer, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

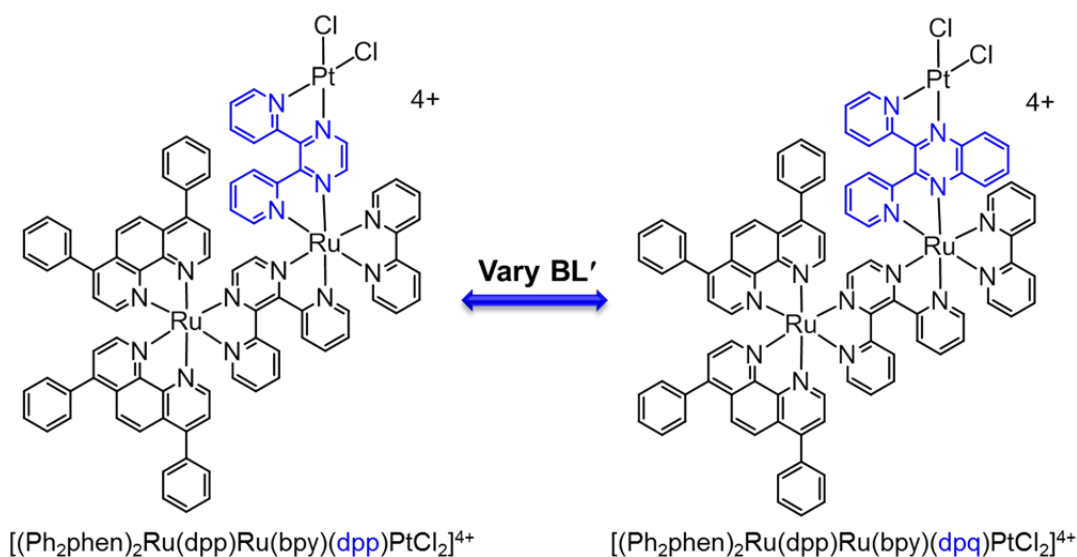


Figure 3.31: Illustration of systematic variation of BL' in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ supramolecular architecture ($\text{BL}' = \text{dpp}$ or dpq). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.3.1. Discussion of Isomers

Replacing one $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ unit with a bpy TL results in half the number of possible isomers for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ compared to the analogous $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes. Applying the same analysis from Section 3.2.1., the central $(\text{bpy})\text{Ru}^{\text{II}}(\text{dpp})(\text{dpq})$ has eight possible isomers (four geometric isomers x 2 optical isomers each), but this architecture only features one $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}$ unit, therefore the total number of isomers is calculated by multiplying eight isomers for the central unit by two optical isomers from the terminal unit which gives 16 isomers. **Figures 3.32** provides three dimensional models of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ to highlight the difference in steric bulk near the Pt RM imparted by the Ph_2phen TL in two different isomers.

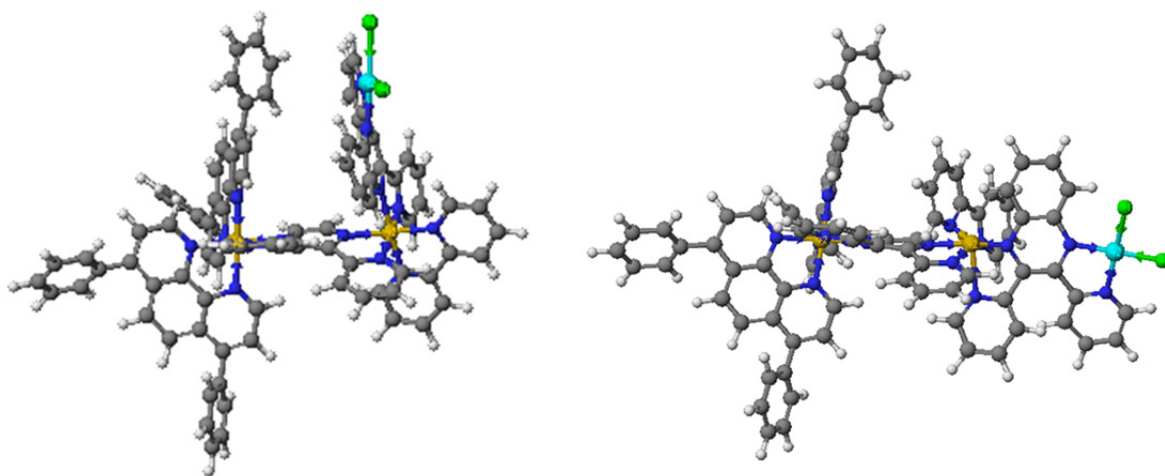


Figure 3.32: Three dimensional models of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ highlighting the difference in sterics among different isomers. Structures generated and energy minimized using Scigress 7.7.1 molecular modeling software with the MM3 method. Gold = Ru, light blue = Pt, green = Cl, blue = N, gray = C, white = H, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.3.2. Redox Properties

The electrochemistry of the new $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes ($\text{BL}' = \text{dpp}$ or dpq) and the bimetallic precursors $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ is consistent with orbital energetics analogous to the

$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ tetrametallic complexes and trimetallic precursors. Replacing one $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ unit with a bpy TL results in the loss of one terminal $\text{Ru}^{\text{II/III}}$ couple and one $\text{dpp}^{0/-}$ couple within the electrochemical window between 2.0 V and -1.0 V vs. Ag/AgCl. The square wave voltammograms for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ are given in **Figure 3.33** to highlight the changes in redox properties imparted by assembly of this supramolecular motif, and the electrochemical data are presented in **Table 3.6**. Cyclic voltammograms are provided in **Figure A-25**. The oxidative electrochemistry is similar to that of the tetrametallic complexes and their trimetallic precursors in both energy and nature of the redox couples. The square wave voltammogram of the *cis*-dichloride bimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$ shows two Ru-based oxidations at 0.66 V (central $\text{Ru}^{\text{II/III}}$) and 1.58 V (terminal $\text{Ru}^{\text{II/III}}$) vs. Ag/AgCl. The central $\text{Ru}^{\text{II/III}}$ couple is shifted 0.2 V less positive compared to the analogous central $\text{Ru}^{\text{II/III}}$ oxidation in $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, a direct result of coordination of a bpy TL in place of the more electron withdrawing $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ unit. The potential of the terminal $\text{Ru}^{\text{II/III}}$ couple is relatively unaffected by variation of the structural motif from $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ to $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$ as the coordination environment of the terminal Ru is quite similar in both cases. As observed in the analogous trimetallic complexes, coordination of BL' to the central Ru shifts the central $\text{Ru}^{\text{II/III}}$ couple outside of the electrochemical window, leaving terminal $\text{Ru}^{\text{II/III}}$ at 1.53 V (when BL' = dpp) and 1.54 V (when BL' = dpq) as the HOMO, and these potentials are consistent with the analogous couples in the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ electrochemistry. Coordination of *cis*-PtCl₂ has no significant impact on the remote terminal $\text{Ru}^{\text{II/III}}$ oxidation potential (1.54 V for BL' = dpp, 1.55 V for BL' = dpq).

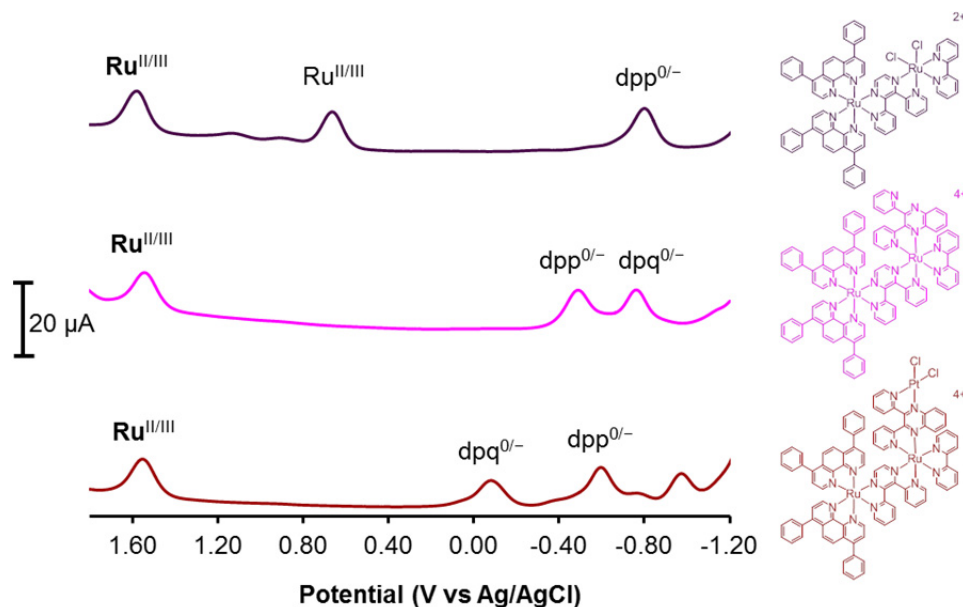


Figure 3.33: Osteryoung square wave voltammograms of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—), and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. **Ru** indicates terminal Ru.

Table 3.6: Electrochemical Data for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2(\text{PF}_6)_4$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{BL}')(\text{PF}_6)_6$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{BL}')\text{PtCl}_2(\text{PF}_6)_6$ Complexes ^a

Complex	$E_{1/2}$ (V vs. Ag/AgCl)		
	Oxidation (assignment) ^b		Reduction (assignment) ^c
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$	0.66 (Ru^{II/III})	1.58 (Ru^{II/III})	-0.80 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$	1.53 (Ru^{II/III})		-0.54 (dpp^{0/-}) -1.00 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$	1.54 (Ru^{II/III})		-0.49 (dpp^{0/-}) -0.77 (dpq^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$	1.54 (Ru^{II/III})		-0.39 (dpp^{0/-}) -0.60 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$	1.55 (Ru^{II/III})		-0.08 (dpq^{0/-}) -0.60 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2(\text{PF}_6)_4$	0.86 (Ru^{II/III})	1.59 (2 Ru^{II/III})	-0.68 (dpp^{0/-}) -0.81 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$	1.55 (2 Ru^{II/III})		-0.45 (dpp^{0/-}) -0.60 (dpp^{0/-}) -1.02 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$	1.55 (2 Ru^{II/III})		-0.42 (dpp^{0/-}) -0.58 (dpp^{0/-}) -0.79 (dpq^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{PtCl}_2(\text{PF}_6)_6$	1.56 (2 Ru^{II/III})		-0.33 (dpp^{0/-}) -0.53 (dpp^{0/-}) -0.64 (dpp^{0/-})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpq})\text{PtCl}_2(\text{PF}_6)_6$	1.57 (2 Ru^{II/III})		-0.02 (dpq^{0/-}) -0.50 (dpp^{0/-}) -0.65 (dpp^{0/-})

^a Measurements recorded in deoxygenated CH_3CN at RT with 0.1 M Bu_4NPF_6 electrolyte. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. ^b Bold indicates terminal Ru. ^c Bold indicates BL'.

The reductive electrochemistry of the new $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2]^{2+}$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')]^{4+}$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ complexes is also similar to the analogous $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')]^{6+}$, and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ complexes in both energy and nature of the redox couples. The major difference is observed in the presence of only one $\text{dpp}^{0/-}$ couple in the new, simpler motifs compared to two $\text{dpp}^{0/-}$ couples in the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ systems. The $\text{dpp}^{0/-}$ couple at -0.80 V vs. Ag/AgCl for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$ is shifted more negative compared to the first $\text{dpp}^{0/-}$ couple at -0.68 V for $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, consistent with the less electron withdrawing bpy TL coupled through the central Ru to the dpp BL in the bimetallic complex compared to the more electron withdrawing $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ unit coupled through the central Ru in the trimetallic complex. Coordination of a π -accepting BL' in place of the σ -donating chloride ligands to provide the bimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ results in a shift of the $\text{dpp}^{0/-}$ couple to -0.54 V (when BL' = dpp) and -0.49 V (when BL' = dpq), followed by the BL' reduction at -1.00 V (dpp) and -0.77 V (dpq) which are similar potentials as the same redox couples in the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ electrochemistry. The LUMO localization is shifted to the BL' ligand upon stabilization by *cis*-PtCl₂ coordination, and these couples occur at -0.39 V (dpp) and -0.08 V (dpq), followed by the dpp reduction at -0.60 V for both $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2]^{4+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$.

The localization of the HOMO and LUMO does not change when the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ tetrametallic architecture is modified to provide the analogous $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ trimetallic architecture. The square wave voltammograms of these tetrametallic and trimetallic complexes with varied BL', **Figure 3.34**, highlight the agreement in orbital energetics. The similar orbital energetics and predicted charge separated state with a terminal HOMO and remote BL' LUMO for the new supramolecular architecture suggest that these complexes are appropriate simplified analogues to the previously discussed tetrametallic complexes.

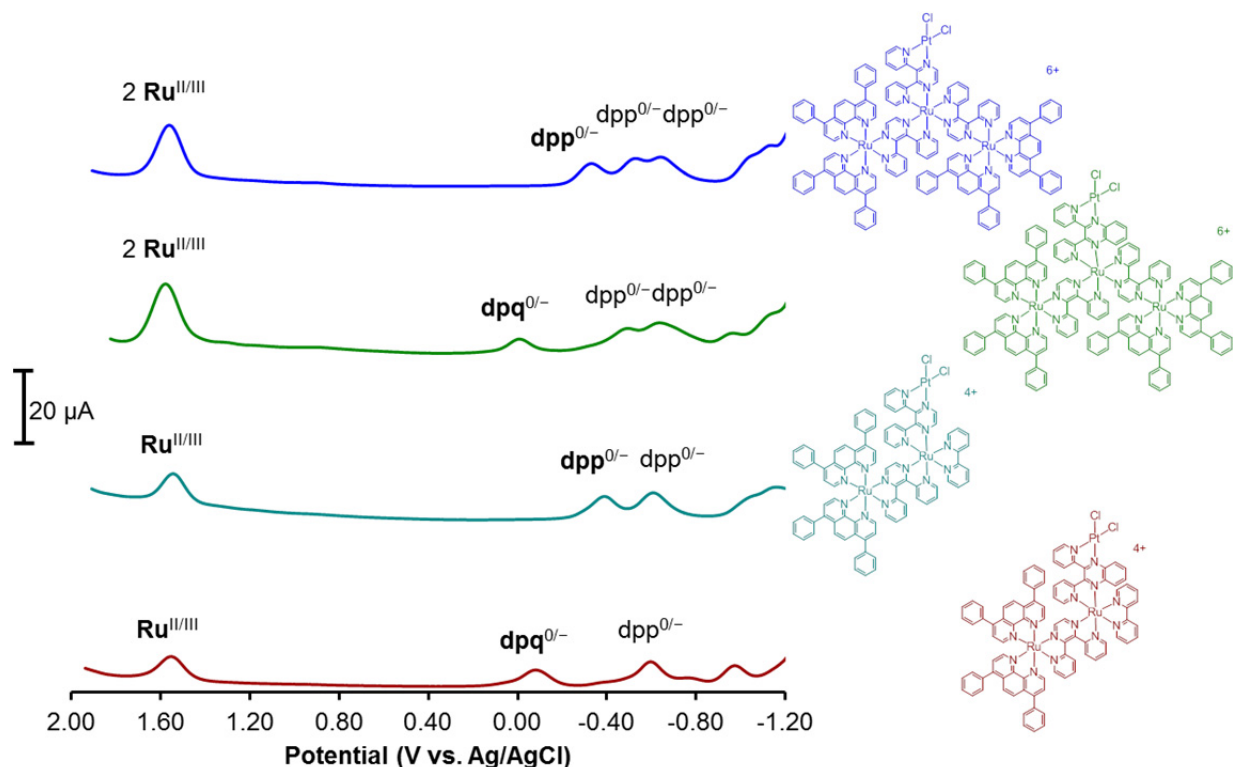


Figure 3.34: Osteryoung square wave voltammograms of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—), and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. **Ru** indicates terminal Ru, and **dpp/dpq** indicates dpp/dpq between central Ru and Pt.

3.3.3. Electronic Absorption Spectroscopy

The electronic absorption spectroscopy of the new $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ trimetallic supramolecules and the bimetallic precursors is less complicated due to fewer overlapping transitions in the UV and visible regions as the complexes possess one less $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ LA unit. **Table 3.7** provides the λ^{max} of the major transitions and the assignments for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes ($\text{BL}' = \text{dpp}$ or dpq) as well as the analogous

$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ for comparison. The electrochemistry predicts similar orbital energetics between the new trimetallic complexes and their $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ tetrametallic analogues, and the spectral profiles and transition energies in the electronic absorption spectroscopy are also similar. The UV region is dominated by IL $\pi \rightarrow \pi^*$ transitions and the visible region is dominated by $\text{Ru}(\text{d}\pi) \rightarrow \text{ligand}(\pi^*)$ CT transitions, where the Ph_2phen -based transitions occur at higher energy than analogous dpp- and dpq-based transitions. The main difference in the trimetallic complexes' electronic absorption spectroscopy compared to that of the analogous tetrametallic complexes is observed in the molar absorptivities as one less LA results in lower absorptivities of transitions in which Ph_2phen , dpp, and terminal Ru participate. The overlaid electronic absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ in RT CH_3CN are given in **Figure 3.35** to provide an example of this effect on absorption spectroscopy by structural variation.

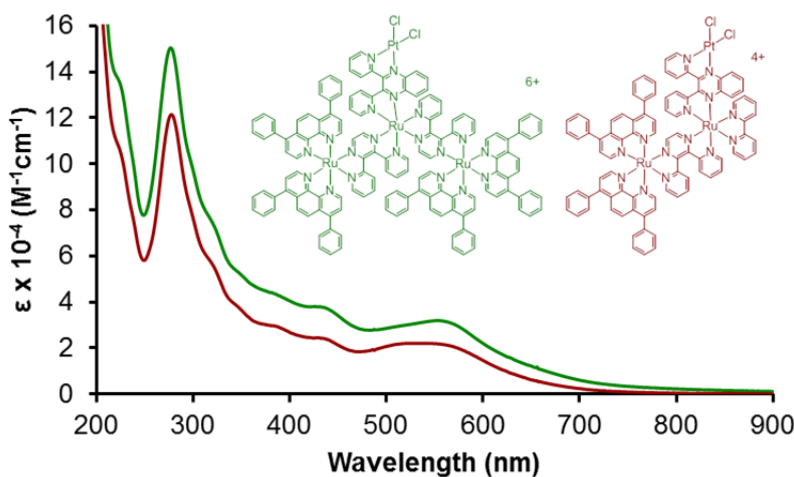


Figure 3.35: Overlaid electronic absorption spectra of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured in RT CH_3CN in a 1 cm quartz cuvette. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Table 3.7: Electronic Absorption Spectroscopic Data for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ Complexes ^a

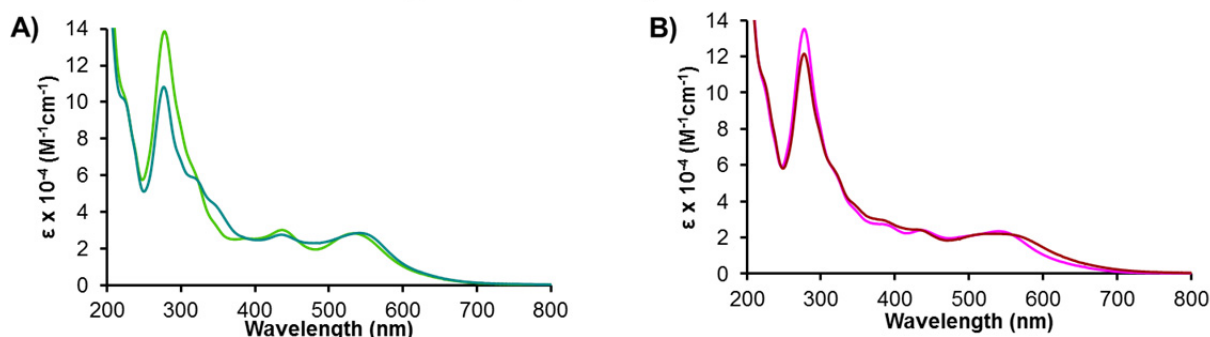
Complex	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	Assignment
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})](\text{PF}_6)_2$	278	11	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$, $\text{bpy } \pi \rightarrow \pi^*$
	326 (sh)	3.7	$\text{dpp } \pi \rightarrow \pi^*$
	450	2.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT
	580	1.9	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$	278	14	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$, $\text{bpy } \pi \rightarrow \pi^*$
	322 (sh)	5.8	$\text{dpp } \pi \rightarrow \pi^*$
	436	3.0	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT
	535	2.8	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$	278	14	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$, $\text{bpy } \pi \rightarrow \pi^*$
	328 (sh)	4.8	$\text{dpp } \pi \rightarrow \pi^*$, $\text{dpq } \pi \rightarrow \pi^*$
	436	2.4	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT
	545	2.3	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$	277	11	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$, $\text{bpy } \pi \rightarrow \pi^*$
	323 (sh)	5.6	$\text{dpp } \pi \rightarrow \pi^*$
	434	2.8	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT
	542	2.9	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$	277	12	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$, $\text{bpy } \pi \rightarrow \pi^*$
	326 (sh)	5.1	$\text{dpp } \pi \rightarrow \pi^*$, $\text{dpq } \pi \rightarrow \pi^*$
	434	2.4	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ CT
	543	2.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$	276	21.3	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	315 (sh)	9.1	$\text{dpp } \pi \rightarrow \pi^*$
	442	4.5	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT
	625	3.4	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$	276	19.5	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	340 (sh)	5.7	$\text{dpp } \pi \rightarrow \pi^*$
	432	4.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT
	554	4.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$	276	14.4	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	340 (sh)	5.5	$\text{dpp } \pi \rightarrow \pi^*$, $\text{dpq } \pi \rightarrow \pi^*$
	430	3.6	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT
	550	3.6	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$	276	17.0	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	326 (sh)	7.7	$\text{dpp } \pi \rightarrow \pi^*$
	432	4.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT
	550	4.2	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$	276	13.9	$\text{Ph}_2\text{phen } \pi \rightarrow \pi^*$
	340 (sh)	5.2	$\text{dpp } \pi \rightarrow \pi^*$, $\text{dpq } \pi \rightarrow \pi^*$
	430	3.6	$\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT
	550	3.1	$\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT, $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT

^a Measurements recorded in spectral grade CH_3CN at RT in a 1 cm quartz cuvette. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The effects of component variation and *cis*- PtCl_2 coordination are more pronounced in the trimetallic complexes and their bimetallic precursors as a result of fewer overlapping transitions masking the transitions of interest in comparison to their tetrametallic and trimetallic counterparts. **Figure 3.36** highlights the effects of *cis*- PtCl_2 coordination to the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ bimetallic

complexes (A and B) and BL' variation in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ bimetallic and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ trimetallic complexes (C and D, respectively). Stabilization of the $\text{BL}'(\pi^*)$ orbitals in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ motif to form the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes results in a red shift of the $\text{BL}' \pi \rightarrow \pi^*$ transitions between 300 and 400 nm and the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ CT transitions between 450 and 700 nm, while BL' variation results in smaller extinction coefficients observed for $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT transitions compared to $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ CT transitions. These trends are discussed in detail below.

Effects of *cis*-PtCl₂ Coordination



Effects of BL' Variation

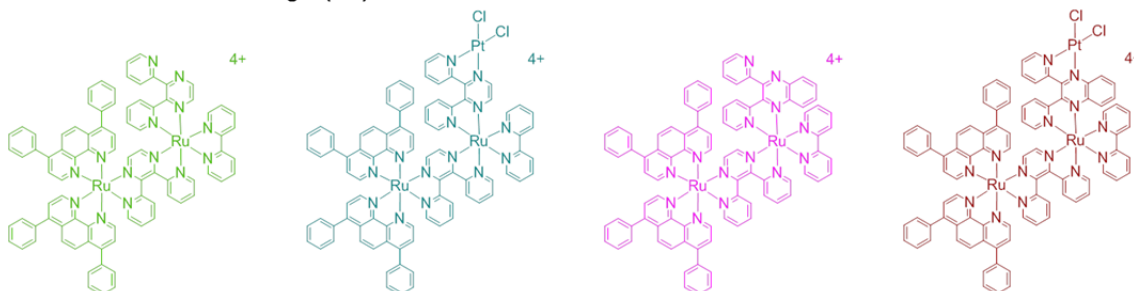
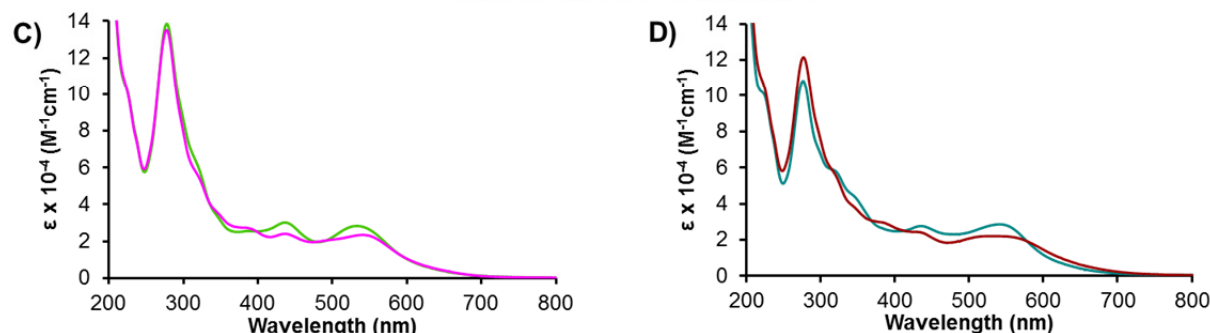


Figure 3.36: Overlaid electronic absorption spectra illustrating the effect of *cis*-PtCl₂ coordination with A) [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)](PF₆)₄ (—) and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)PtCl₂](PF₆)₄ (—), and B) [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)](PF₆)₄ (—) and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂](PF₆)₄ (—), and the effect of BL' variation with C) [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)](PF₆)₄ (—) and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)](PF₆)₄ (—) and D) [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)PtCl₂](PF₆)₄ (—) and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂](PF₆)₄ (—). The spectra were measured in RT CH₃CN in a 1 cm quartz cuvette. Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Electrochemical analysis suggests that the central Ru(dπ)→BL'(π*) MLCT transition is the highest in energy compared to the central Ru(dπ)→dpp(π*) CT and terminal Ru(dπ)→dpp(π*) MLCT transitions in the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')](PF₆)₄ motif, and the central Ru(dπ)→BL'(π*) MLCT transition is expected to be stabilized and occur at an energy lower than the central Ru(dπ)→dpp(π*)

MLCT transition and higher than the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT transition upon *cis*- PtCl_2 coordination. Overlaying the spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ suggests that the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ CT transition overlaps with the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ CT transition centered at 436 nm, as *cis*- PtCl_2 coordination results in a decrease in absorptivity at 436 nm (30,000 to 28,000 $\text{M}^{-1}\text{cm}^{-1}$) and an increase in absorptivity at 480 nm (20,000 to 23,000 $\text{M}^{-1}\text{cm}^{-1}$). A slight shift is also observed on the lower energy side of the band centered at 540 nm, a result of the underlying central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ CT transition stabilization. Similar shifts are also observed in the $\text{BL}' = \text{dpq}$ complexes. The transition centered at 438 nm for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ bimetallic complex is less defined from the lower energy transition centered at 545 nm as the $\text{BL}'(\pi^*)$ orbitals are stabilized when $\text{BL}' = \text{dpq}$ vs. dpp . Due to this lower energy central $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ CT transition, more enhanced tailing of the broad transition centered at 545 nm is observed at $\lambda > 550$ nm. A plot of the change in absorbance upon platination of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ to produce $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ ($\Delta\text{Absorbance}$) vs. wavelength is depicted in **Figure 3.37** to highlight the spectral shifts that occur when the $\text{BL}'(\pi^*)$ orbitals are stabilized. This analysis is important in understanding the subtle changes expected in the transient absorption spectroscopy of this supramolecular motif.

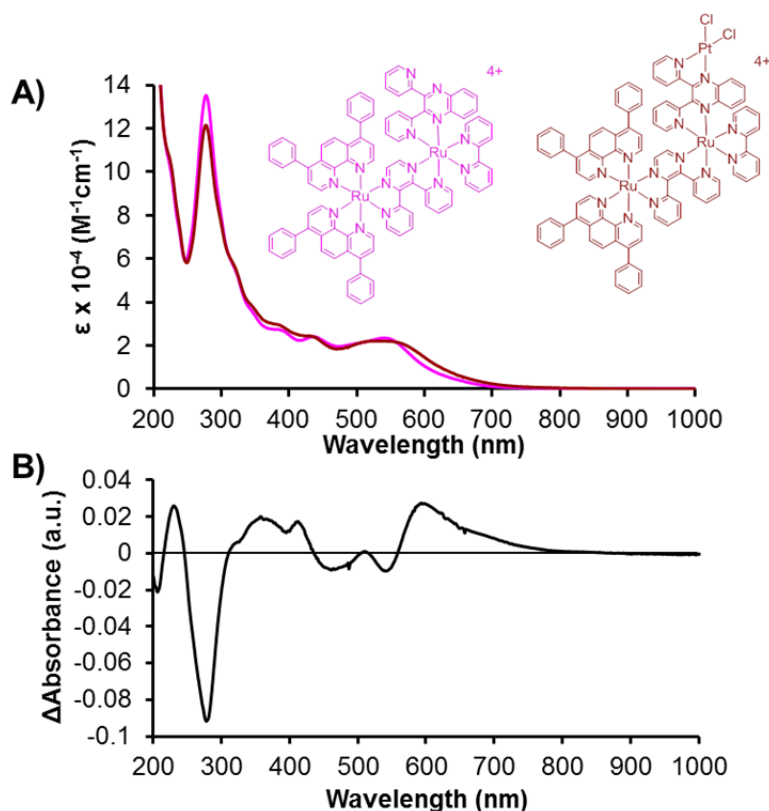


Figure 3.37: A) Electronic absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured in RT spectral grade CH_3CN in a 1 cm quartz cuvette. B) Plot of $\Delta\text{Absorbance}$ vs. Wavelength, where $\Delta\text{Absorbance}$ is the change in electronic absorption upon platination of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_6$ to produce $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$. Samples were concentration matched. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The overlaid absorption spectra in **Figure 3.36** showing the effects of BL' variation in the bimetallic architecture (C) and the trimetallic architecture (D) reveal that this component variation leads to losses in absorptivity when $\text{BL}' = \text{dpq}$ vs. dpp . The overlaid absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ reveal that a decrease in absorptivity is observed at 436 nm upon variation from dpp to dpq ($30,000 \text{ M}^{-1}\text{cm}^{-1}$ to $24,000 \text{ M}^{-1}\text{cm}^{-1}$) due to a shift of the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ CT transition to slightly lower energy as well as the commonly observed decreased extinction coefficient for dpq transitions compared to dpp transitions. The broad transition between 500 and 700 nm also displays similar impacts, as the extinction coefficient

is smaller with variation from dpp to dpq (28,000 M⁻¹cm⁻¹ at 535 nm for BL' = dpp to 23,000 M⁻¹cm⁻¹ at 545 nm for BL' = dpq). The near UV region (350-400 nm) also shows a subtle shift to lower energy attributed to the change in BL' $\pi \rightarrow \pi^*$ transition. Similar trends are observed in the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂](PF₆)₄ complexes with smaller extinction coefficients in the visible region observed when BL' = dpq. Utilization of BL' = dpq extends the absorption slightly into the red as a result of the stabilized central Ru(d π) $\rightarrow$ BL'(π^*) CT transition shifting the broad transition which is a sum of all the underlying MLCT transitions to lower energy. The presence of fewer overlapping MLCT transitions in the visible region, a benefit of the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂]⁴⁺ trimetallic architecture compared to the [{(Ph₂phen)₂Ru(dpp)}₂Ru(BL')PtCl₂]⁶⁺ tetrametallic architecture, more clearly provide information into the complex electronic absorption spectroscopy and suggests where certain transitions occur underneath strongly absorbing, overlapping MLCT transitions.

3.3.4. Excited State Dynamics

The new trimetallic supramolecular architecture maintains the unusual excited state dynamics of competitive population of a ³CS excited state through intramolecular electron transfer from the terminal Ru $\rightarrow$ dpp ³MLCT emissive state and a higher-lying ³MLCT excited state. The emissive nature of the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')](PF₆)₄ bimetallic and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂](PF₆)₄ trimetallic complexes provides a probe into the excited state dynamics. Transient absorption spectroscopy is a useful tool in further studying the excited state dynamics through non-emissive excited states in this supramolecular architecture, as important transitions are unmasked by the presence of fewer MLCT transitions.

3.3.4.1. Steady-State and Time-Resolved Emission Spectroscopy

The excited state processes of the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')](PF₆)₄ bimetallic and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂](PF₆)₄ trimetallic complexes are similar to the analogous [{(Ph₂phen)₂Ru(dpp)}₂Ru(BL')](PF₆)₆ trimetallic and [{(Ph₂phen)₂Ru(dpp)}₂Ru(BL')PtCl₂](PF₆)₆ tetrametallic analogues discussed in **Section 3.2.4**. The steady-state and time-resolved emission

spectroscopy data as well as rate constants for radiative (k_r) and non-radiative decay (k_{nr}) and intramolecular electron transfer (k_{et}) for the new bimetallic and trimetallic complexes are given below in **Table 3.8**, and the relative steady-state emission profiles for the four complexes are shown in **Figure 3.38**. The two bimetallic complexes $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ emit from a lowest-lying terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ excited state with nearly identical emission profiles, emission quantum yields ($\Phi^{\text{em}} = 1.5 \times 10^{-3}$), and excited state lifetimes of 120 ns. This trend was also observed in the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ trimetallic analogues. The remarkably similar while still unusual photophysics of the new Ru_2Pt trimetallics to the Ru_3Pt tetrametallics establishes these new Ru_2Pt complexes as effective models of the Ru_3Pt tetrametallics and the importance of excited state dynamics of these new types of structurally complex supramolecules.

Table 3.8: Steady-State and Time-Resolved Emission Spectroscopy Data for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$, and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ Complexes ^a

Complex	λ^{em} (nm)	Φ^{em} $\times 10^3$	τ (μs)	$k_r \times 10^{-4}$ (s^{-1}) ^b	$k_{nr} \times 10^{-6}$ (s^{-1}) ^b	$k_{et} \times 10^{-6}$ (s^{-1})
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$	762	1.5	0.12	1.2	8.3	--
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$	762	1.5	0.12	1.3	8.3	--
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$	765	1.1	0.09	1.2	8.3	2.8
$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$	761	0.52	0.10	1.3	8.3	1.7
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$	764	1.0	0.11	0.93	8.9	--
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$	764	1.7	0.11	0.97	8.9	--
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$	766	0.71	0.077	0.93	8.9	4.1
$[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$	760	0.37	0.075	0.97	8.9	4.4

^a RT measurements were performed on CH_3CN solutions deoxygenated with Ar and excited at 540 nm. Values corrected for PMT response. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline. ^b Values for the Ru_3Pt and Ru_2Pt complexes are assumed to be the same as the values for the corresponding Ru_3 or Ru_2 complexes.

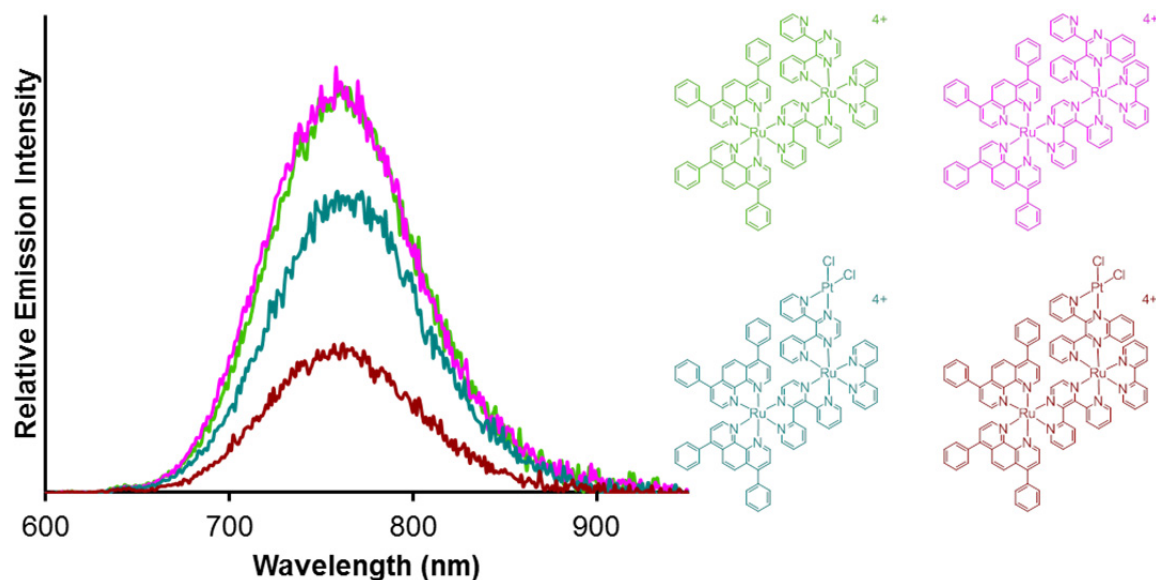


Figure 3.38: Emission spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—), and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Stabilization of the $\text{BL}'(\pi^*)$ orbitals through *cis*- PtCl_2 coordination results in photophysical processes analogous to those observed in the previously discussed $\{[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{BL}')\text{PtCl}_2\}(\text{PF}_6)_6$ tetrametallic complexes. Different degrees of quenched Φ^{em} compared to the analogous bimetallic complexes were observed for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ ($\Phi^{\text{em}} = 1.1 \times 10^{-3}$, 25 % quenching) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ ($\Phi^{\text{em}} = 5.2 \times 10^{-4}$, 65 % quenching), however the excited state lifetimes were shortened to a similar extent (100 ns and 110 ns, respectively). This discrepancy in quenched emission and shortened lifetimes between the bimetallic and trimetallic pairs with varied BL' is a result of differing degrees of population of a lowest-lying, non-emissive terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS excited state with contributions from the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT and central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CT excited states. The bimetallic complexes are suitable photophysical models to calculate the rate constant for intramolecular electron transfer to populate the ^3CS excited state as the emission energy between bimetallic and analogous trimetallic are similar (ca. 760 nm) and the emissive state arises from

the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ ^3CT excited state which is in a similar coordination environment. **Equations 3.1** and **3.2** were used to calculate the relevant rate constants given in **Table 3.8**. The simplified state diagrams in **Figure 3.23** are appropriate for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$, highlighting only the excited states that participate in emission (terminal $\text{Ru} \rightarrow \text{dpp}$) and that are impacted by *cis*- PtCl_2 coordination (central $\text{Ru} \rightarrow \text{BL}'$ and terminal $\text{Ru} \rightarrow \text{BL}'$). When $\text{BL}' = \text{dpq}$, enhanced population of the ^3CS state occurs compared to the dpp analogue due to the larger driving force for electron transfer, moving the electron from the $\text{dpp}(\pi^*)$ orbital (between terminal Ru and central Ru) to the $\text{BL}'(\pi^*)$ orbital. The k_{et} values for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ are calculated as $2.8 \times 10^6 \text{ s}^{-1}$ and $1.7 \times 10^6 \text{ s}^{-1}$, respectively. While this trend is inconsistent with the $\text{BL}' = \text{dpq}$ complex having enhanced ^3CS population, the higher-lying central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ $^3\text{MLCT}$ excited state also contributes to the population of the ^3CS state through a second intramolecular electron transfer process, k_{et}' . This process, in which reductive quenching of the hole on central Ru by the terminal Ru moves the oxidized site away from the reduced BL' , may have a more significant impact on the efficiency of charge separation than k_{et} . The inability to monitor the non-emissive higher-lying states and ^3CS state makes steady-state and time-resolved emission spectroscopy a limited technique in this motif, yet the information gained by probing the emissive excited state is valuable in setting the basis for transient absorption spectroscopy.

The photophysical properties of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes are remarkably similar to their $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ analogues (**Figure 3.39**). All of the complexes emit from a terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ excited state between 760 nm and 766 nm. The values of τ and Φ^{em} for the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes are slightly smaller than their analogous $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes as

a result of the enhanced non-radiative decay for the larger complexes as the increased size provides more vibrational modes. The k_{et} values of the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ complexes ($4.1\text{--}4.4 \times 10^6 \text{ s}^{-1}$) are about twice the magnitude of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes ($1.7\text{--}2.8 \times 10^6 \text{ s}^{-1}$). The rate of intramolecular electron transfer in a series of Ru(II)-Rh(III) polyazine complexes was reported to be inversely related to the Ru donor to Rh acceptor distance.¹²⁰ As the distance between the donor and acceptor increases, the orbital overlap decreases and electron transfer becomes less efficient. In the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ systems, the acceptor orbital is localized on the dpq ligand, and the donor orbital is attributed to the terminal Ru(II). As these supramolecular complexes can form a variety of geometric isomers, the donor-acceptor distance varies between individual molecules in a sample. **Figure 3.40** shows Scigress generated three dimensional models of these complexes in isomers with the smallest and largest donor-acceptor distances. For consistency, the distance in each molecule was measured from the terminal Ru center to the quinoxaline N coordinated to Pt. In $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$, the donor-acceptor can be at a distance as small as about 7.7 Å and as large as about 11.1 Å. Donor-acceptor analysis of the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ system is complicated due to the presence of two possible donor sites, therefore two distances are given for each isomer. In the isomer with the three Ru centers in a line, the donor acceptor distances are estimated to be approximately 7.9 Å and 9.0 Å, and the isomer that has the three Ru centers in a V-formation, the distances are estimated as approximately 7.3 Å and 11.6 Å. Because a sample of these supramolecular complexes is composed of a distribution of many isomers, the donor-acceptor distance likely impacts the electron transfer rate constant for each molecule and the calculated k_{et} values represent an average of the entire sample.

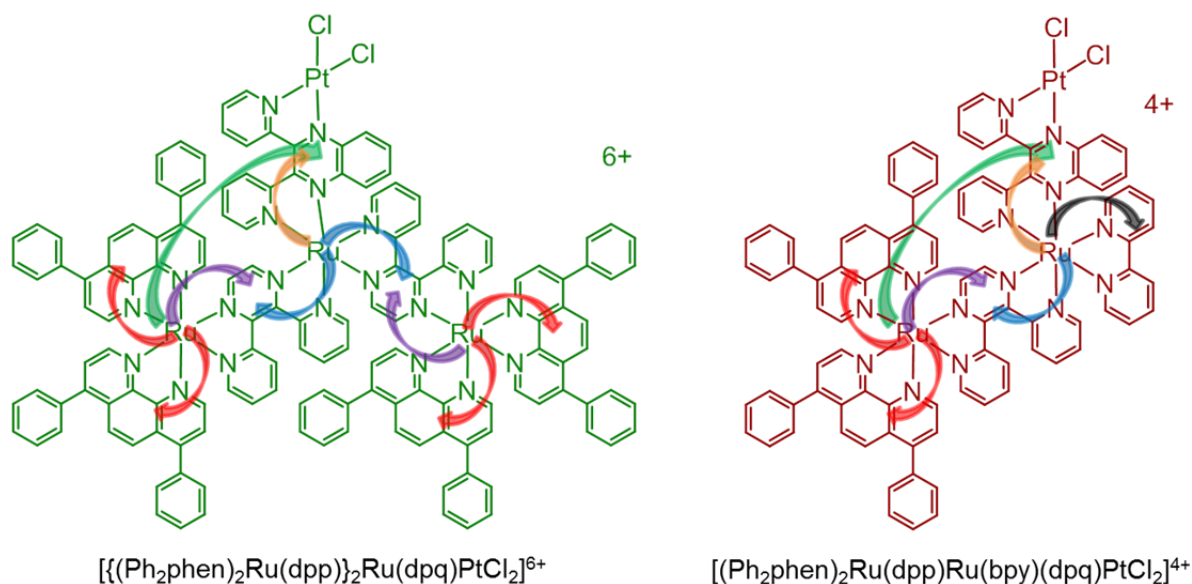


Figure 3.39: Illustration of the possible MLCT transitions which occur in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ trimetallic complex and the $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ tetrametallic complex. Arrows indicate an MLCT transition, and the green arrows represent the charge separated (CS) state. MLCT = metal-to-ligand charge transfer, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

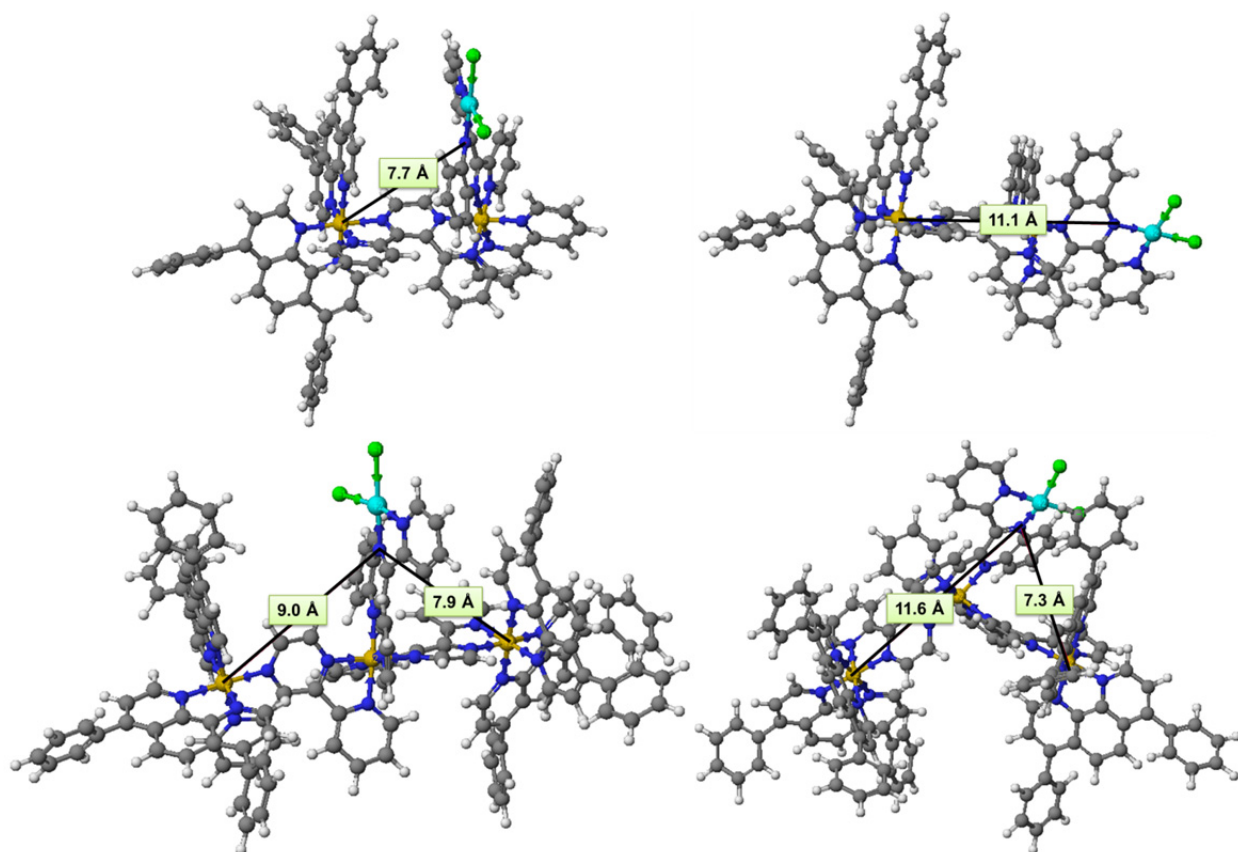


Figure 3.40: Three dimensional models of isomers of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ (top) and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ (bottom) highlighting the donor-acceptor distances in different geometric isomers. The terminal Ru atom was chosen for the donor and the quinoxaline N coordinated to Pt was chosen for the acceptor. Structures generated using Scigress 7.7.1 molecular modeling software with the MM3 method. Gold = Ru, light blue = Pt, green = Cl, blue = N, gray = C, white = H, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.3.4.2. Emission Excitation Spectroscopy

Similar to the previously discussed $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')](\text{PF}_6)_6$ trimetallic and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2](\text{PF}_6)_6$ tetrametallic complexes, the unusual excited state dynamics of the new supramolecular bimetallic and trimetallic complexes were analyzed by emission excitation spectroscopy. Removal of one $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ LA allows central Ru MLCT transitions to be more evident and provides larger spectroscopic differences. The excitation spectra (solid lines) and electronic absorption spectra (dashed lines) in RT spectral grade CH_3CN are shown in **Figure 3.41** for each of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes

(BL' = dpp or dpq). The excitation spectra follow the electronic absorption profiles for the two bimetallic complexes, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$, indicating that the emissive state is populated with unit efficiency regardless of excitation wavelength. This is expected based on orbital energetics that do not facilitate population of a charge separated state. The excitation spectrum of the trimetallic complex $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ also closely follows the electronic absorption spectrum, indicating that the ^3CS is populated with very low efficiency, consistent with the small degree of emission quenching compared to the bimetallic model. This result is consistent with agreement between the excitation and absorption spectra of the analogous $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ tetrametallic complex. A substantial difference between the absorption and excitation spectra is observed for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ complex. This observation is expected due to the enhanced population of the ^3CS excited state by photoexcitation. Excitation between 550 and 750 nm results in population of a non-emissive excited state that competes with emission from the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ emissive excited state. This clear discrepancy between the two spectra suggests that excitation wavelength has a major impact on the excited state processes in this supramolecular motif, and low energy excitation ($\lambda > 550$ nm) enhances charge separation.

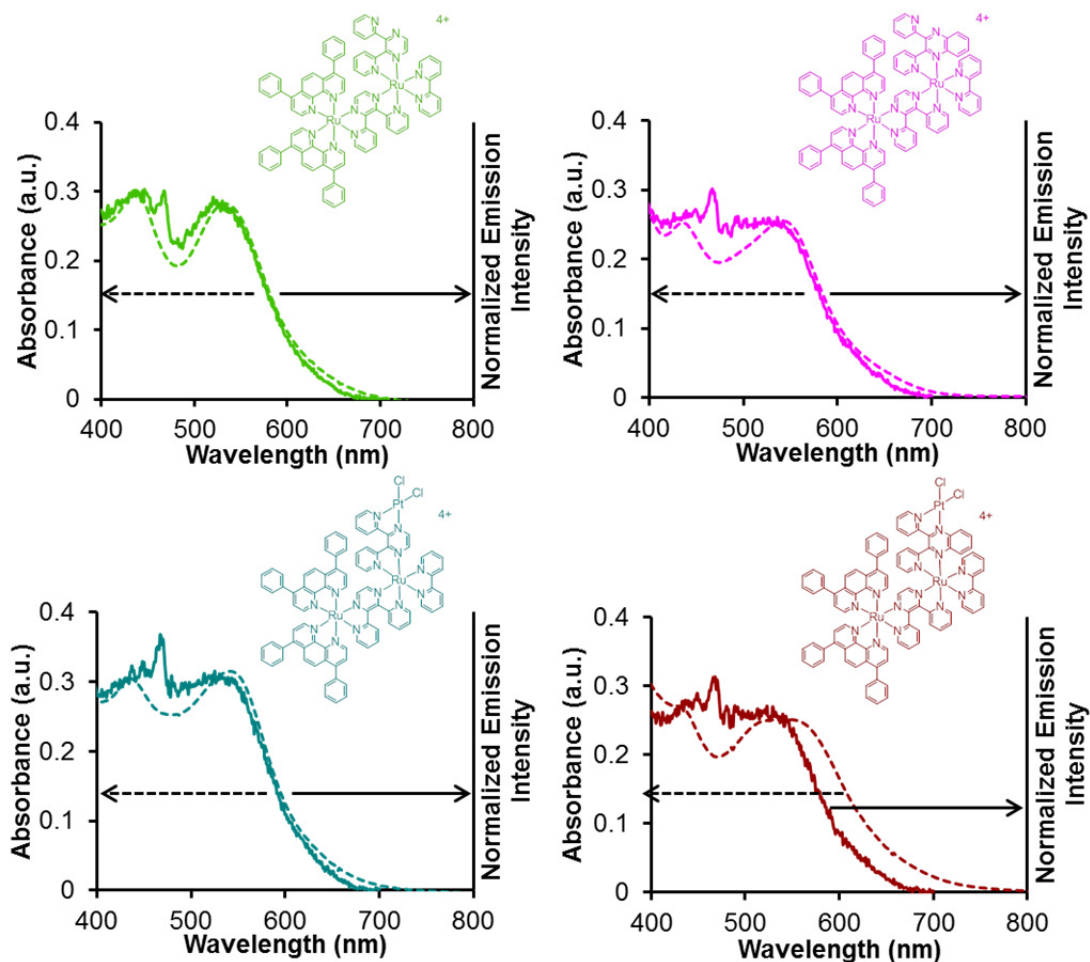


Figure 3.41: Overlaid electronic absorption spectra (dashed lines) and excitation spectra (solid lines) of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—), and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Emission was monitored at 760 nm. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

3.3.4.3. Transient Absorption Spectroscopy

Transient absorption (TA) spectroscopy provides a means to further analyze the excited state dynamics in this supramolecular motif by monitoring the electronic absorption spectroscopy of excited states. TA spectroscopy allows probing excited states that are not emissive as well as emissive states. No TA spectroscopy is reported for mixed-metal Ru,Pt systems with polyazine bridging ligands of this type. The unusual photophysics of the title Ru,Pt systems prompted a collaboration with Prof. Thomas Meyer

at the University of North Carolina at Chapel Hill and the U.S. Department of Energy (DOE) Center to probe the emissive and non-emissive excited states of these molecules in detail. The transient spectroscopy allows probing all excited states on the ns timescale including the non-emissive ^3CS excited state in the platinated systems. The TA spectra were measured 15-20 ns following excitation; on this timescale, the lowest energy excited states are expected to be populated as intersystem crossing or internal conversion and thermal equilibration of the excited state occurs given the sub-nanosecond timescale for these processes.³⁴ The TA spectra are presented as ΔOD vs. wavelength, where ΔOD is the difference between the absorptivity of the excited state species and the absorptivity of the ground state species. Ground state bleaching occurs when $\Delta\text{OD} < 0$, indicative of change in occupation of an orbital involved in the state populated by this transition. An excited state absorption occurs when $\Delta\text{OD} > 0$, which results from change in occupancy of an orbital that gives rise to a new transition. No change is observed in absorptivity between ground state and excited state when $\Delta\text{OD} = 0$. Analysis of the TA spectra provides electronic absorption spectrum of the excited state species. Analysis of decay kinetics at single probe wavelengths provides the lifetime of the transient species.

The TA spectroscopy of $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ has been well studied, and analysis of these systems provides insight into the electronic absorption spectroscopy of a $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT excited state, as this is the nature of the lowest energy excited state in each complex.⁴¹ The ground state electronic absorption spectroscopy in EtOH features a $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^1\text{MLCT}$ transition centered at 470 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and 525 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and a $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ $^1\text{MLCT}$ transition centered at 440 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and 425 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$. The electronic configurations of the ground state and lowest energy excited state for the monometallic and bimetallic complex (**Figure 3.42**) are useful in understanding the change in electronic absorption spectroscopy upon MLCT excitation. It should be noted that a change in occupancy of a molecular orbital changes the energy of that orbital, yet this situation is depicted in **Figure 3.42** to result in no energetic change for simplification. In each complex, the lowest lying MLCT excited state

features an oxidized Ru^{III} center and a reduced $\text{dpp}^{\cdot-}$, resulting in a bleached $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT transition at 450 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and at 540 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$. Bleaching of the $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ $^1\text{MLCT}$ absorption also occurs in the excited state for each complex. The TA spectrum of $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ exhibits a new absorption centered at 460 nm that is described as a $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT transition involving the other $\text{Ru}(\text{II})$ center and the second lowest π^* orbital on dpp. This transition is not present in the $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ MLCT excited state as the only Ru center is oxidized. Transient absorption bands are observed at 610-630 nm for both complexes as well as at 370 nm and 350 nm for $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{2+}$, respectively, as a result of $\text{dpp } \pi^* \rightarrow \pi^*$ absorption. These TA spectroscopic signatures of a $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT excited state are helpful in understanding more complex systems.

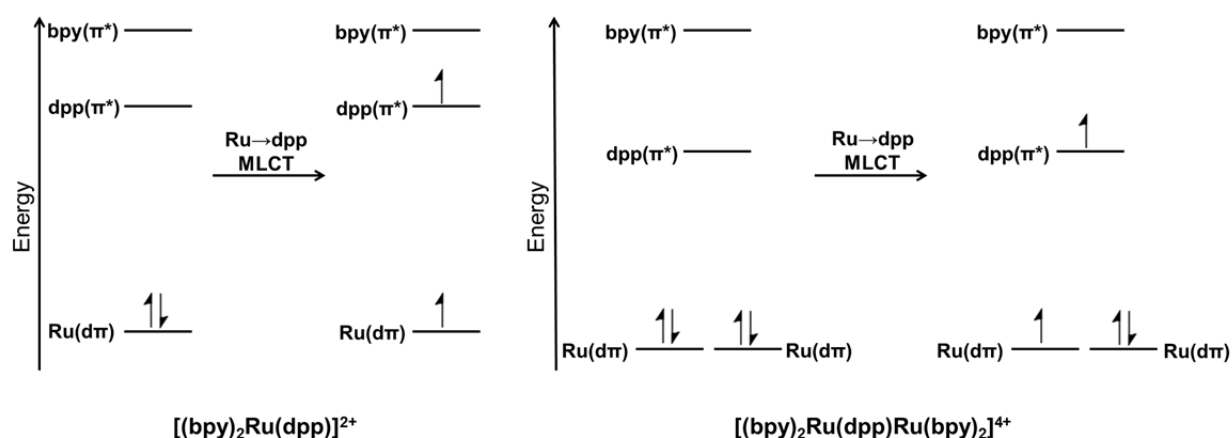


Figure 3.42: Molecular orbital diagrams depicting the electronic configuration of the ground state and lowest energy excited state in $[(\text{bpy})_2\text{Ru}(\text{dpp})]^{2+}$ (left) and $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ (right). bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.

Simplified molecular orbital diagrams of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')]^{4+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ ($\text{BL}' = \text{dpp}$ or dpq) that depict the change in electronic configuration upon excitation from the ground state to populate the lowest-lying excited state (**Figures 3.43 and 3.44**) are useful in forming a hypotheses regarding the resulting excited state absorption spectroscopy. In the bimetallic $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')]^{4+}$ complexes (**Figure 3.43**), the excited

state absorption should feature bleaching of the terminal Ru→dpp MLCT, terminal Ru→Ph₂phen MLCT, and central Ru→dpp MLCT transitions resulting from population of the lowest lying terminal Ru→dpp MLCT excited state. Additionally, dpp π*→π* absorption is also expected in these bimetallic complexes, similar to those observed in the previously discussed [(bpy)₂Ru(dpp)Ru(bpy)₂]⁴⁺ system. In the case of the [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')PtCl₂]⁴⁺ complexes, previously discussed electrochemical and excited state analysis suggests that the complex will populate both a terminal Ru→dpp MLCT (emissive) excited state and a terminal Ru→BL' CS excited state, and the degree of population of each state depends on the nature of BL'. The MO diagrams for these two states are pictured in **Figure 3.44**. In the ³CS excited state, bleaching of the terminal Ru→Ph₂phen MLCT, terminal Ru→dpp MLCT, and central Ru→BL' MLCT transitions is expected to occur, in addition to evolution of a BL' π*→π* absorption. In the MLCT excited state, bleaching of the terminal Ru→Ph₂phen MLCT, terminal Ru→dpp MLCT, and central Ru→dpp MLCT transitions is expected to occur, in addition to evolution of a dpp π*→π* absorption. When BL' = dpp, the excited sample is expected to be composed of primarily the terminal Ru→dpp ³MLCT excited state, and when BL' = dpq, the excited sample is expected to be composed of a mixture of the terminal Ru→dpp ³MLCT and terminal Ru→dpq ³CS excited states.

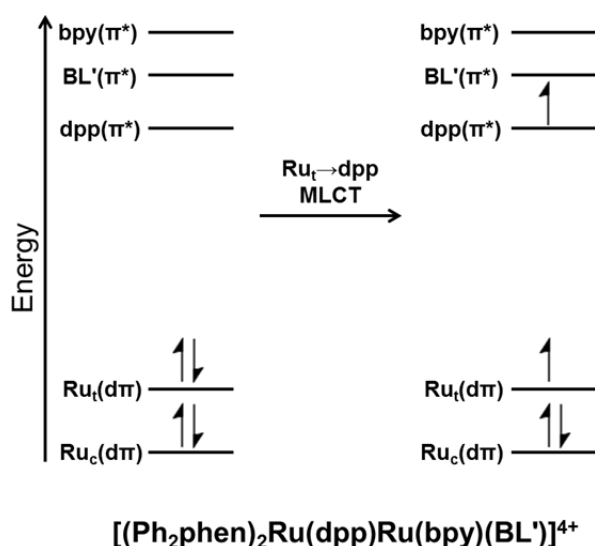


Figure 3.43: Molecular orbital diagrams depicting the electronic configuration of the ground state and lowest energy excited state in [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')]⁴⁺, where BL' = dpp or dpq. Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, bpy = 2,2'-bipyridine, MLCT = metal-to-ligand charge transfer.

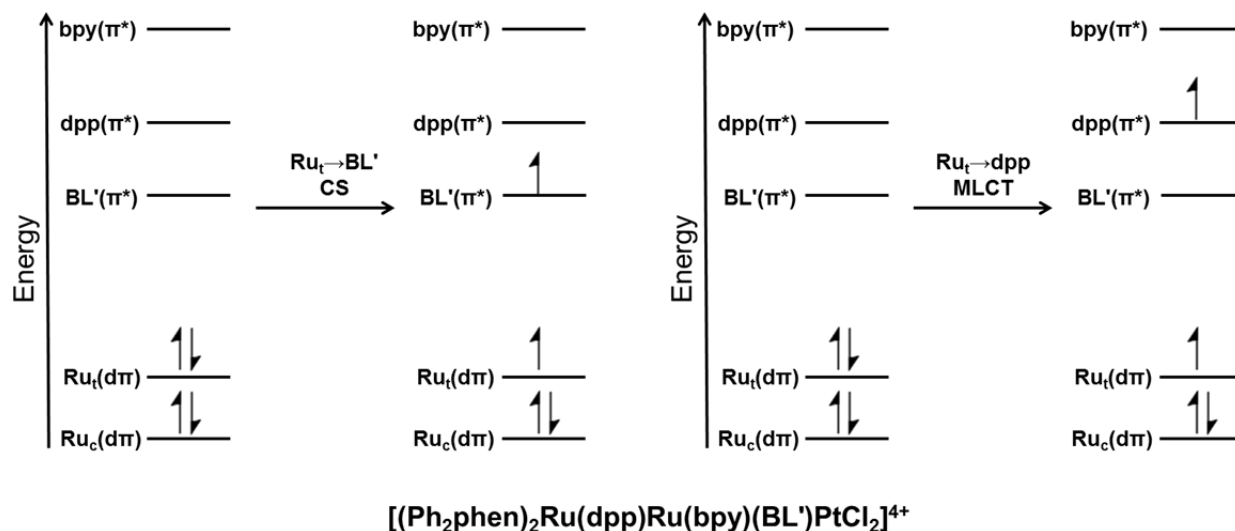


Figure 3.44: Molecular orbital diagrams depicting the electronic configuration of the ground state and the $\text{Ru}_t(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS excited state (left) or the $\text{Ru}_t(\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ excited state (right) in $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$, where $\text{BL}' = \text{dpp}$ or dpq . $\text{Ph}_2\text{phen} = 4,7$ -diphenyl-1,10-phenanthroline, $\text{dpp} = 2,3$ -bis(2-pyridyl)pyrazine, $\text{dpq} = 2,3$ -bis(2-pyridyl)quinoxaline, $\text{bpy} = 2,2'$ -bipyridine, $\text{MLCT} = \text{metal-to-ligand charge transfer}$, $\text{CS} = \text{charge separated}$.

The previously discussed emission and excitation spectroscopy studies of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ complexes provide important information to assist in analysis of the complexes by nanosecond TA spectroscopy. Excitation of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ with 532 nm light is expected to initially populate several $^1\text{MLCT}$ excited states, primarily terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^1\text{MLCT}$, central $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^1\text{MLCT}$, and central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'$ $^1\text{MLCT}$. The lowest energy excited state in both complexes is the emissive terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ state, in which the hole is formally localized on the terminal Ru and the electron is localized on the neighboring dpp ligand. The TA spectra for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ measured 20 ns following excitation are depicted in **Figure 3.45** along with their respective ground state electronic absorption spectra. **Figure 3.46** presents the overlaid TA spectra for these two bimetallic complexes to analyze the impact of BL' on the excited state absorption spectra. The ground state bleach at 430 nm in

each spectrum is attributed to the loss of the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ MLCT transition due to the oxidized terminal Ru in the excited state, shifting this transition out of this spectral region. A ground state bleach is observed at 535 nm and 545 nm for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$, respectively, which is a result of loss of the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT and central $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT transitions in the excited state complexes. The central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ MLCT and central $\text{Ru}(\text{d}\pi) \rightarrow \text{bpy}(\pi^*)$ MLCT absorptions are expected to remain relatively unchanged in the excited state. New excited state absorptions occur at 360 nm and 700 nm resulting from $\text{dpp } \pi^* \rightarrow \pi^*$ absorptions made possible by $\text{dpp}(\pi^*)$ occupation in the $\text{Ru} \rightarrow \text{dpp}$ MLCT excited state. The correlation of these two transitions in the two bimetallic complexes $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ confirms that the electron is localized on the same dpp ligand in each complex, providing a terminal $\text{Ru} \rightarrow \text{dpp } ^3\text{MLCT}$ lowest excited state which does not involve the BL' ligand.

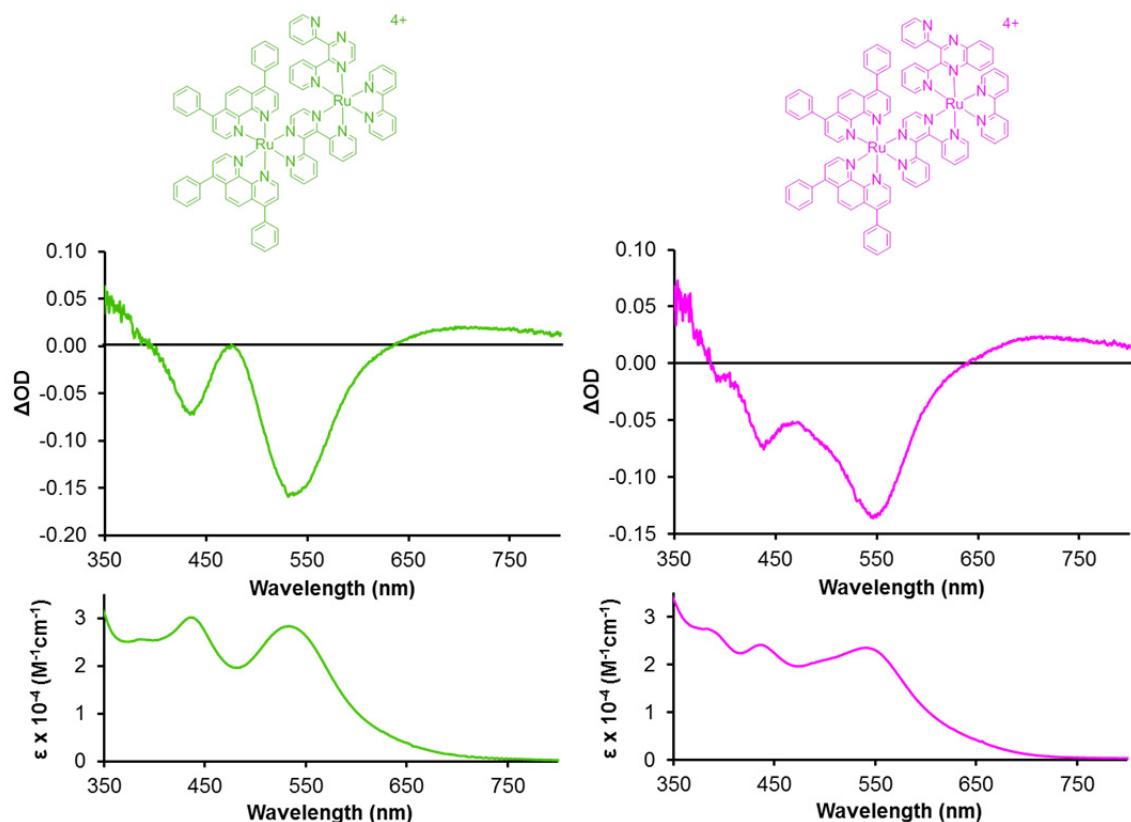


Figure 3.45: Transient absorption spectra (top) and electronic absorption spectra (bottom) of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—) in deoxygenated RT spectral grade CH_3CN . TA spectra were measured 20 ns following excitation at 532 nm. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline

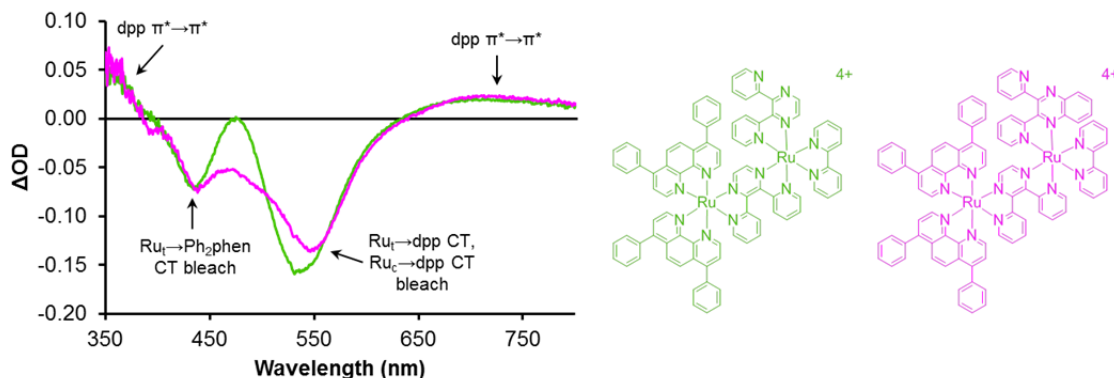


Figure 3.46: Transient absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—) measured 20 ns following excitation with 532 nm in deoxygenated RT spectral grade CH_3CN . Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The terminal Ru→dpp ³MLCT excited state lifetime was measured via TA spectroscopy in addition to emission spectroscopy (discussed in **Section 3.3.4.1**). Excited state lifetimes are measured by TA spectroscopy by measuring absorbance vs. time and fitting to an exponential decay using **Equations 3.9 and 3.10** for monoexponential and biexponential decays, respectively,

$$y = Ae^{-x/t} + y_0 \quad (3.9)$$

$$y = A_1e^{-x/t_1} + A_2e^{-x/t_2} + y_0 \quad (3.10)$$

where A is a pre-exponential factor and t is lifetime. The excited state decay occurs monoexponentially with a lifetime independent of excitation or probe wavelength for each [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL')](PF₆)₄ bimetallic complex, suggesting the population of one lowest energy excited state on the ns timescale, the terminal Ru→dpp ³MLCT state. The excited state lifetimes of [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)](PF₆)₄ and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)](PF₆)₄ measured by TA spectroscopy were 120 ns and 118 ns, respectively, and are in agreement with the 120 ns emission lifetime measured for each complex. The overlaid decay profiles of [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)](PF₆)₄ measured by the two techniques are shown in **Figure 3.47** to highlight the agreement in these measurements. The TA spectroscopy and emission data for the two bimetallic complexes that obey Kasha's rule are consistent with the proposed excited state dynamics with all excitation, regardless of wavelength, rapidly populating the lowest lying ³MLCT state with unit efficiency.

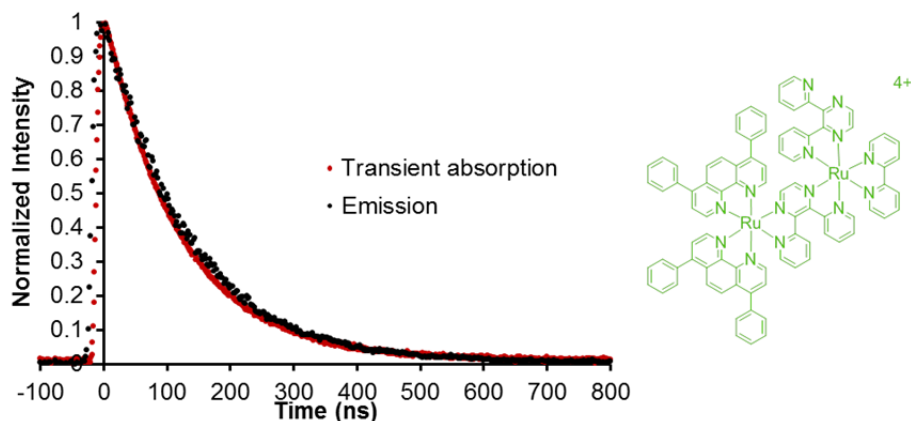


Figure 3.47: Overlaid excited state decay profiles of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ measured by transient absorption spectroscopy excited at 440 nm and probed at 540 nm (•) and time-resolved emission spectroscopy excited at 540 nm and probed at 760 nm (•). Both experiments were performed in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.

The TA spectroscopy of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ heterotrimetallic complexes ($\text{BL}' = \text{dpp}$ or dpq) exhibits a significant BL' variation effect as well as an excitation and probe wavelength effect on the TA spectra and the decay kinetics. A comparison of the TA spectra and ground state absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ are provided in **Figure 3.48**. Similar to the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ complexes, exciting at 532 nm initially populates several MLCT excited states, such as terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^1\text{MLCT}$, central $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^1\text{MLCT}$, and central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ $^1\text{MLCT}$ as these excited states are energetically close. The overlaid TA spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ are presented in **Figure 3.49** measured 20 ns following 532 nm excitation. The spectra of each complex exhibits a ground state bleach of the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{Ph}_2\text{phen}(\pi^*)$ MLCT transition centered at 430 nm and a larger ground state bleach centered at 550 nm attributed to loss of the $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}/\text{BL}'(\pi^*)$ MLCT transitions. The shape and intensity of this bleach at 550 nm is impacted by the identity of BL' . The excited state absorption observed at 350 nm and 700 nm results from dpp or BL' $\pi^* \rightarrow \pi^*$ absorption, as the electron is localized on dpp in the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ excited state or on BL' in the

terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS excited state. **Figure 3.50** depicts the impact of BL' stabilization via platination of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')](\text{PF}_6)_4$ to produce $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$. The slight red shift in the lowest energy bleach upon platination is consistent with stabilization of the central $\text{Ru} \rightarrow \text{BL}'$ $^3\text{MLCT}$ and population of the ^3CS excited state.

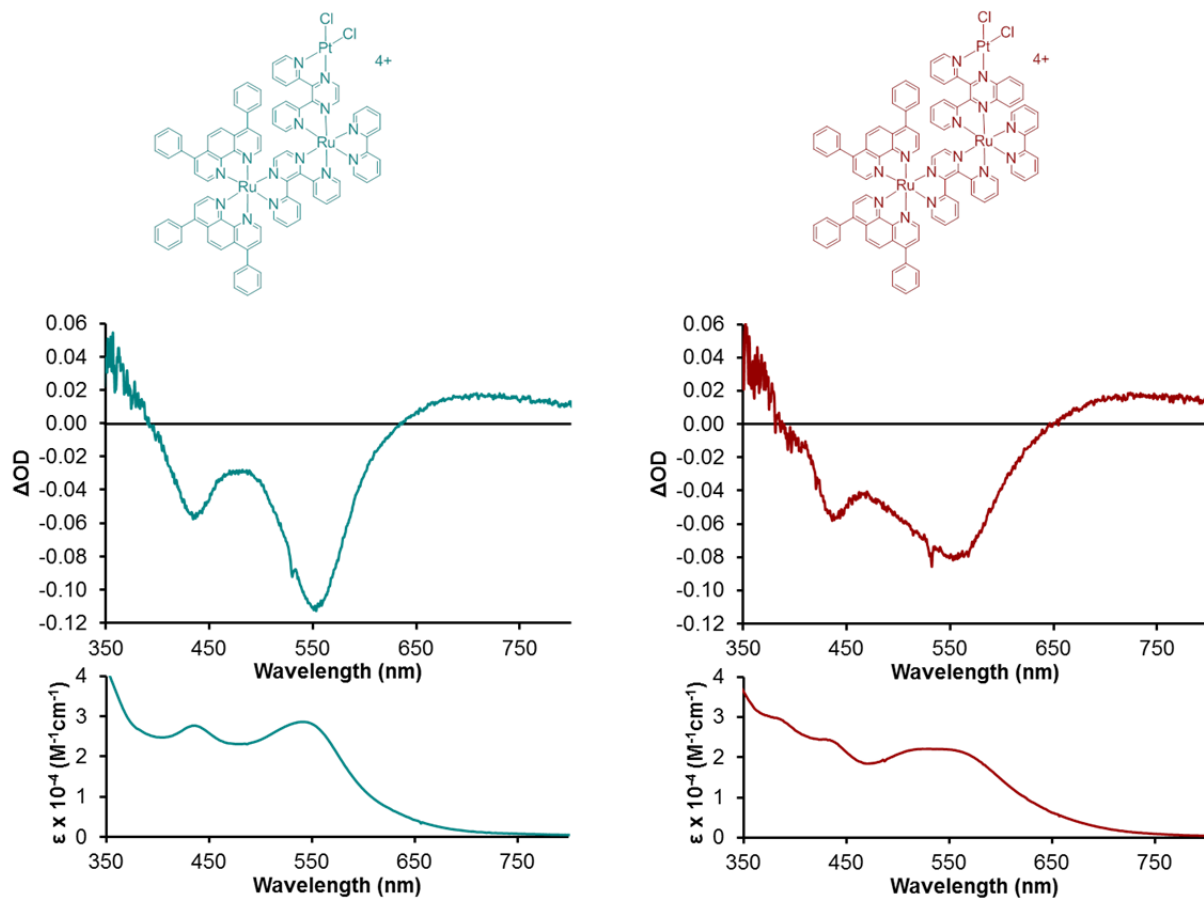


Figure 3.48: Transient absorption spectra (top) and electronic absorption spectra (bottom) of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) in deoxygenated RT spectral grade CH_3CN . TA spectra were measured 20 ns following excitation at 532 nm. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

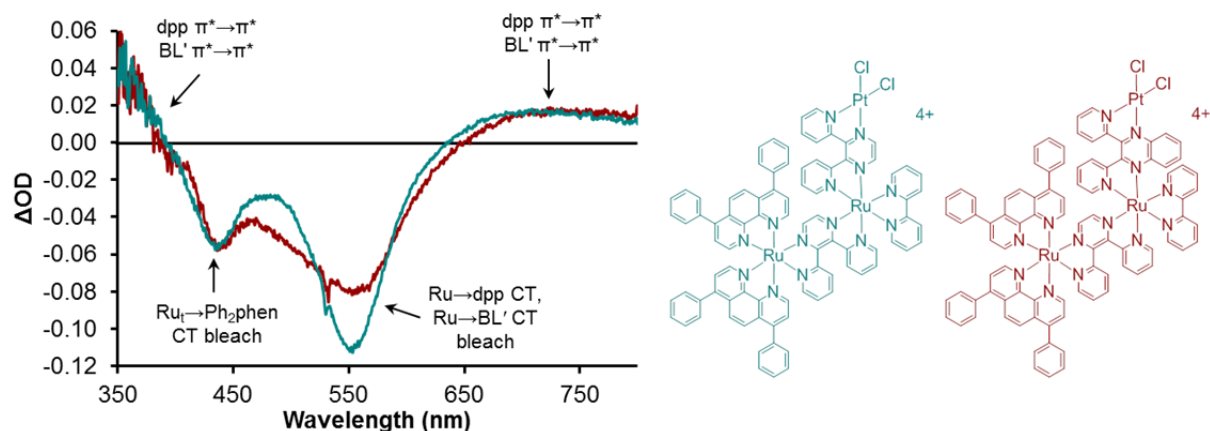


Figure 3.49: Transient absorption spectra of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured 20 ns following excitation with 532 nm in deoxygenated RT spectral grade CH_3CN . Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

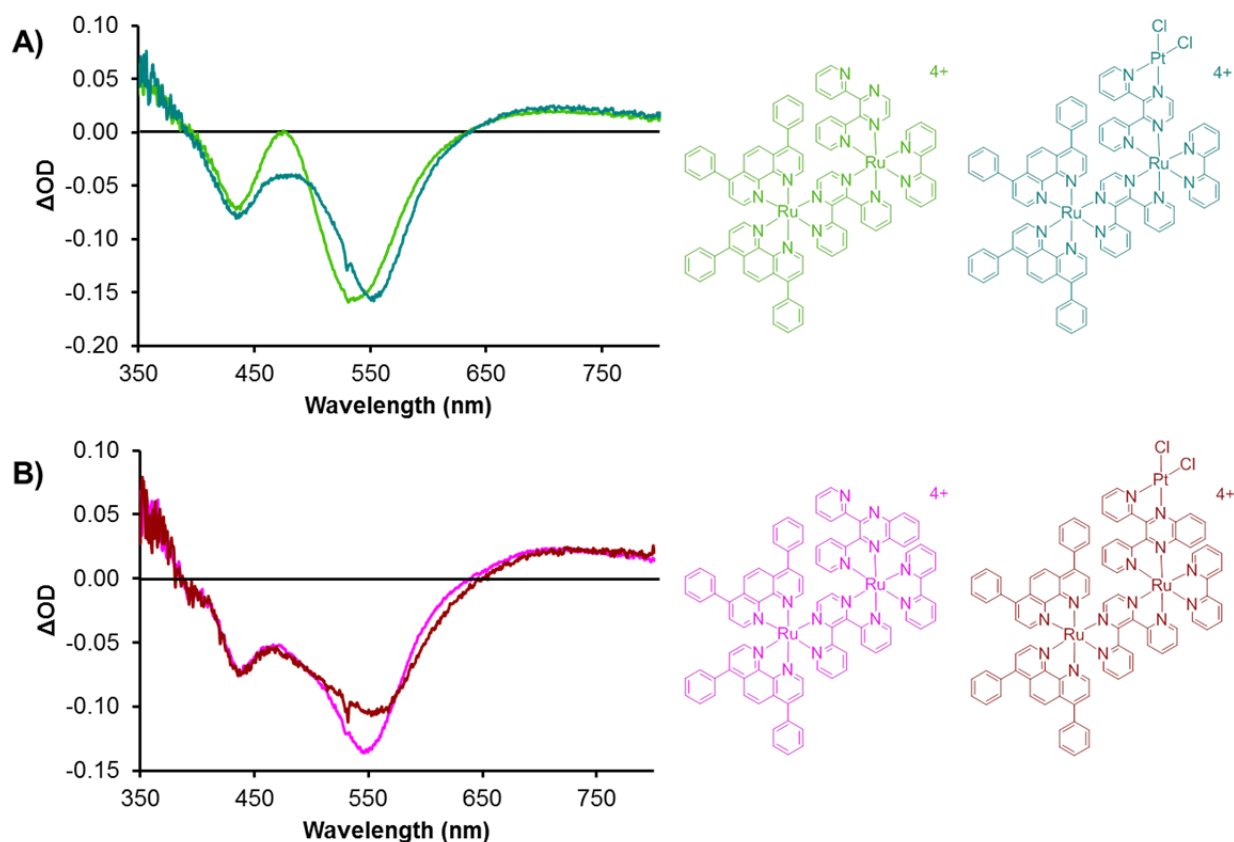


Figure 3.50: Normalized transient absorption spectra of A) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—) vs. $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—) and B) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—) vs. $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) measured 20 ns following excitation with 532 nm in deoxygenated RT spectral grade CH_3CN . Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Emission excitation spectroscopy predicts an excitation wavelength dependence on population of the emissive terminal Ru→dpp ³MLCT excited state and subsequently on the population of the ³CS excited state (state diagram for [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂]⁴⁺ in **Figure 3.23**). **Figure 3.51** depicts the normalized TA spectra of [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)PtCl₂](PF₆)₄ and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂](PF₆)₄ resulting from 425 nm, 532 nm, and 625 nm excitation. The spectral shifts are expected to be minor upon variation of excitation wavelength, and the time-resolve TA data provides more informative results. When BL' = dpp, no significant λ^{exc} dependence is observed in the TA spectra, consistent with the near unity population of the terminal Ru(dπ)→dpp(π*) ³CT excited state and a lower degree of population of the ³CS state. When BL' = dpq, the TA spectrum resulting from 625 nm excitation differs from the spectra resulting from λ^{exc} = 425 nm and 532 nm. This lower energy excitation, which is predicted to enhance population of the terminal Ru(dπ)→BL'(π*) ³CS state, produces a 10 nm red shift of the Ru(dπ)→dpp/BL'(π*) CT bleach compared to higher energy excitation. To understand these results, one must consider the expected TA spectrum in the case where the terminal Ru(dπ)→dpp(π*) CT state (referred to as the MLCT state) is populated with unit efficiency as well as where the terminal Ru(dπ)→BL'(π*) CS state (referred to as the CS state) is populated with unit efficiency. Population of the MLCT excited state would cause bleaching of the terminal Ru(dπ)→dpp(π*) MLCT and central Ru(dπ)→dpp(π*) MLCT transitions that contribute to the broad, lowest energy bleach and generation of dpp based π*→π* transitions. Population of the CS excited state would result in bleaching of the terminal Ru(dπ)→dpp(π*) MLCT and central Ru(dπ)→BL'(π*) MLCT transitions. As the central Ru(dπ)→BL'(π*) MLCT state is lower in energy than the central Ru(dπ)→dpp(π*) MLCT state, a sample which contains a significant portion of the excited state molecules in the CS state and the rest in the MLCT state should have less bleaching in the central Ru→dpp MLCT region and more in the central Ru→dpq CT region which now exhibits a slight red shift in the TA spectrum compared to a sample composed of primarily MLCT excited state molecules. This λ^{exc} dependence observed in the TA spectra of [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂](PF₆)₄ supports the notion that this complex violates Kasha's rule and that population of a CS state occurs for these systems.

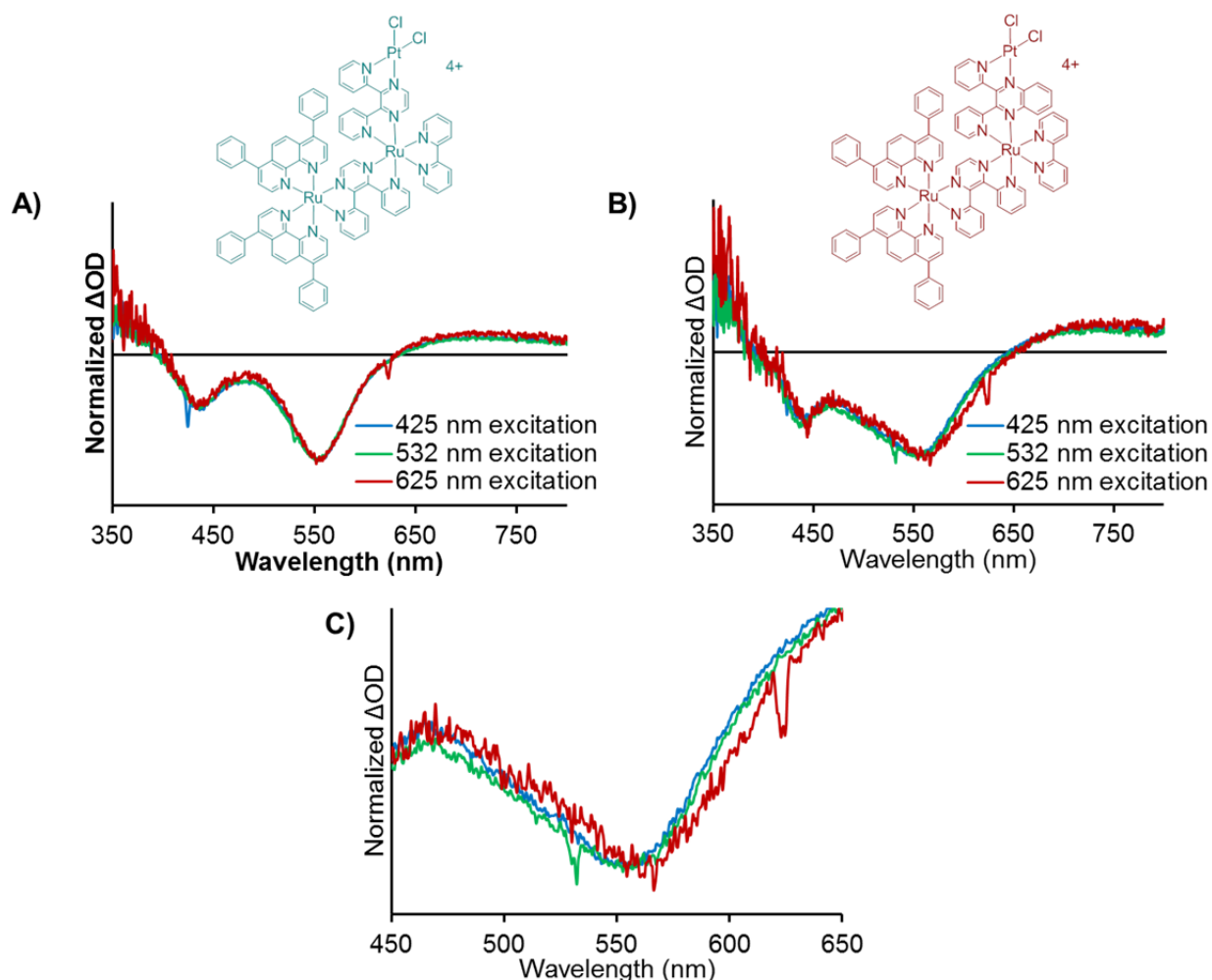


Figure 3.51: Transient absorption spectra of A) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ and B) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ measured 20 ns following excitation with 425 nm (—), 532 nm (—), and 625 nm (—) in deoxygenated RT spectral grade CH_3CN . Plot C is an expansion of the MLCT bleach in plot B to highlight the shift upon 625 nm excitation. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

Time dependence of the excited state spectroscopy via TA of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2](\text{PF}_6)_4$ complexes (where $\text{BL}' = \text{dpp}$ or dpq) provides substantial information regarding the interesting excited state dynamics of this supramolecular motif. In the case of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$, the ground state recovery of the bleach monitored at 550 nm occurs monoexponentially with a lifetime of 90 ns. This is in sound agreement with the emission

lifetime of 90 ns in **Section 3.3.4.1**. In the case of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$, however, the excited state decay measured by TA varies with excitation wavelength as well as probe wavelength and is never monoexponential. To highlight this, the $\ln(\text{intensity})$ vs. time plots and the residuals for a monoexponential fit for each of the trimetallic complexes are provided in **Figure 3.52**. This is consistent with two excited states with τ in the ns regime, $^3\text{MLCT}$ and ^3CS . The TA excited state decay curves for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ with $\lambda^{\text{exc}} = 440$ nm, 532 nm, and 625 nm and each probed at wavelengths around 430 nm, 550 nm, and 700 nm are shown in **Figure 3.53**. The data were fit to **Equation 3.8** with $t_1 = 120$ ns as this is the measured excited state lifetime for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ model. The emissive state of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$, terminal $\text{Ru} \rightarrow \text{dpp } ^3\text{MLCT}$, are isoenergetic and in the same coordination environment, so the bimetallic is a suitable model for the analogous platinated trimetallic. For each set of data, the value of t_2 was calculated and found to be 25 ± 4 ns, within experimental error of 25 ns. The short component is likely the ^3CS excited state, while the longer 120 ns component corresponds to the lifetime of the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*) ^3\text{CT}$ state. Values of A_1 and A_2 were calculated using **Equation 3.8** to fit the data with $t_1 = 120$ ns and $t_2 = 25$ ns. These pre-exponential factors, collected in **Table 3.9**, provide relative contributions from each of the excited states to the overall decay. Consistent with the emission excitation spectrum in **Figure 3.41**, the contribution in general from the ^3CS state (A_2) increases and the contribution from the $^3\text{MLCT}$ state (A_1) subsequently decreases as the excitation energy decreases. The values of A_1 range between 0.67-0.79 for 440 nm excitation, 0.55-0.74 for 532 nm excitation, and 0.42-0.54 for 625 nm excitation; conversely, the values of A_2 range between 0.21-0.33 for 440 nm excitation, 0.26-0.46 for 532 nm excitation, and 0.35-0.55 for 625 nm excitation. It should be noted that excitation of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ at 625 nm provides a substantially increased contribution of the CS state (and a subsequent decreased contribution from the MLCT state) with $\lambda^{\text{probe}} = 700\text{-}750$ nm ($A_2 = 0.23$ and 0.55 when $\lambda^{\text{exc}} = 440$ nm and 625 nm, respectively). As this excited state absorption feature is expected to be directly related to the localization of the electron on dpp or BL', it is expected to be

sensitive to excitation wavelength. This provides further evidence that low energy excitation drives intramolecular electron transfer to populate the ^3CS state with enhanced efficiency. This is an important result as previously no TA spectroscopy existed for these structurally diverse complexes, and no charge separation was observed in dpp-bridged Ru(II)-polyazine multimetallic complexes. The subtle shift in the TA spectrum upon excitation wavelength may be explained by ^3CS excited state species has a lifetime close to the delay time between the laser pulse and TA measurement which is 15 ns. Ultrafast transient absorption spectroscopy (on the ps timescale) may be useful in more clearly observing this short-lived excited state.

Table 3.9: Contribution of the $^3\text{MLCT}$ and ^3CS States to the Excited State Decay of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ Measured by Transient Absorption Spectroscopy with Varied Excitation and Probe Wavelengths.^a

$$y = A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + y_0$$

$$t_1 = 120 \text{ ns}, t_2 = 25 \text{ ns}^b$$

Excitation λ (nm)	Probe λ (nm)	A_1^c	A_2^c
440	430	0.67 ± 0.02	0.33 ± 0.02
440	550	0.79 ± 0.05	0.21 ± 0.05
440	700	0.79 ± 0.04	0.23 ± 0.04
532	440	0.55 ± 0.01	0.46 ± 0.01
532	550	0.72 ± 0.02	0.30 ± 0.02
532	700	0.74 ± 0.02	0.26 ± 0.02
625	440	0.54 ± 0.02	0.47 ± 0.02
625	560	0.67 ± 0.03	0.35 ± 0.03
625	750	0.42 ± 0.03	0.55 ± 0.03

^a Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine, dpq = 2,3-bis(2-pyridyl)quinoxaline. $^3\text{MLCT}$ excited state refers to the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ state and ^3CS excited state refers to the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpq}(\pi^*)$ ^3CS state. Samples were prepared in spectral grade CH_3CN and deoxygenated for 30 minutes prior to measurements. ^b Value for t_1 was chosen as 120 ns to correspond to the lifetime of the same state in the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ model. Value for t_2 was chosen from the average values of t_2 determined at each excitation/probe wavelength when fit to a biexponential curve with t_1 fixed at 120 ns. ^c A_1 and A_2 are pre-exponential factors and give relative contribution of each excited state to the overall lifetime.

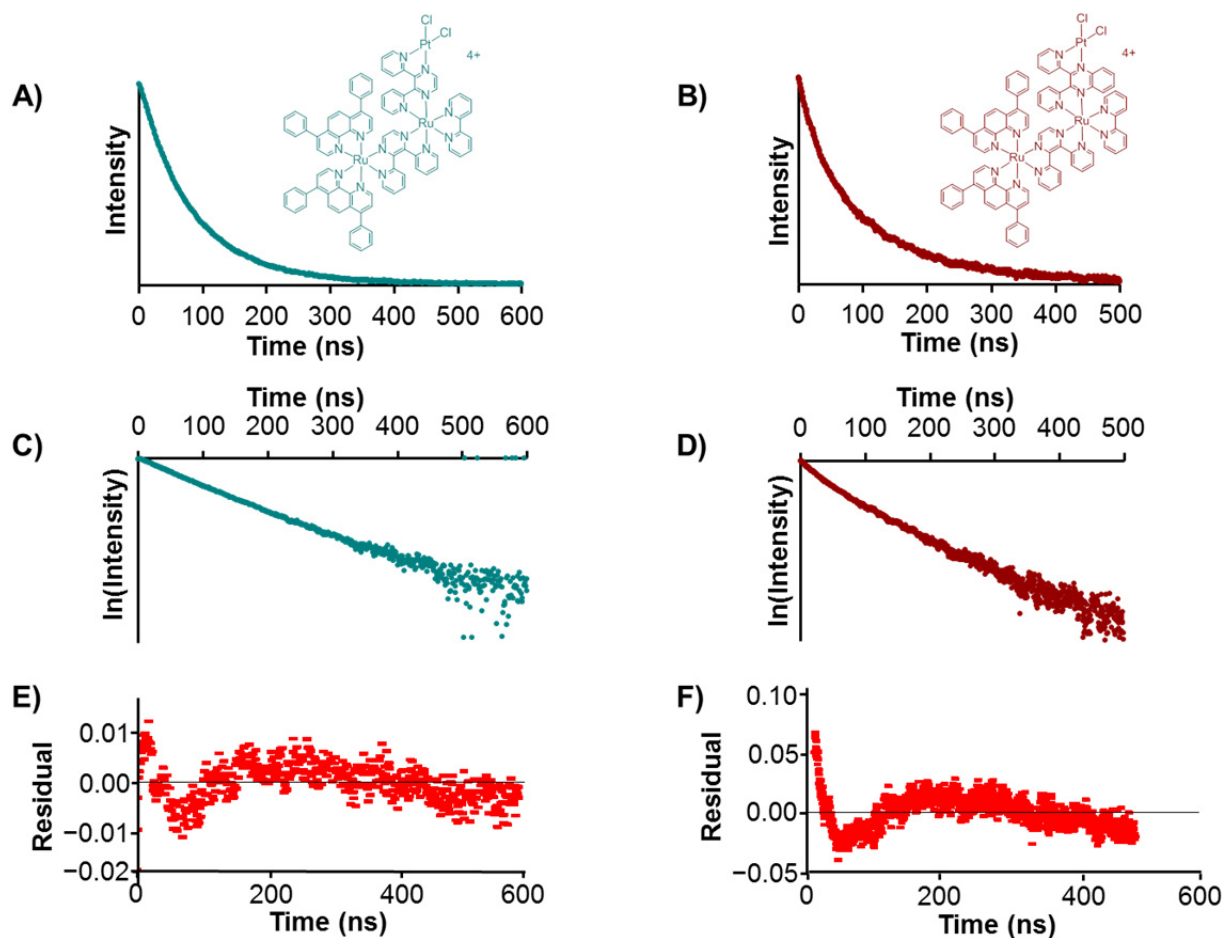


Figure 3.52: Excited state decay by transient absorption spectroscopy of A) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2]^{4+}$ and B) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$. Samples were prepared in deoxygenated RT spectral grade CH_3CN , excited at 532 nm, and probed at 550 nm. C and D display the corresponding $\ln(\text{intensity})$ vs. time plots, and E and D display the residuals for each data set for a monoexponential fit. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

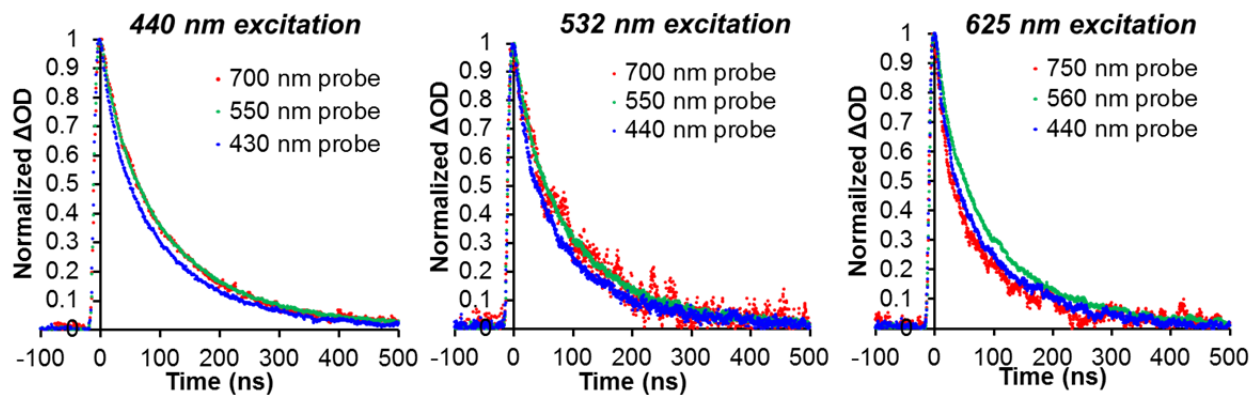


Figure 3.53: Overlaid excited state decay profiles for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ measured by time-resolved transient absorption spectroscopy excited at 440 nm (left), 532 nm (middle), and 625 nm (right), and probed at 430 or 440 nm ($\bullet$), 550 or 560 nm ($\bullet$) and 700 or 750 nm ($\bullet$). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, bpy = 2,2'-bipyridine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

4. Conclusions and Future Work

4.1. Conclusions

Two structurally diverse, mixed-metal Ru(II),Pt(II) supramolecular architectures were synthesized and their redox, spectroscopic, photophysical, photochemical, and photocatalytic properties were studied through systematic component variation. Design of the supramolecular motifs $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$ ($TL = phen \text{ or } Ph_2phen$; $BL' = dpp \text{ or } dpq$) and $[(TL)_2Ru(dpp)Ru(bpy)(BL')PtCl_2]^{4+}$ ($TL = Ph_2phen$; $BL' = dpp \text{ or } dpq$) were motivated by the first tetrametallic complex $[\{(bpy)_2Ru(dpp)\}_2Ru(dpp)PtCl_2]^{6+}$ which by virtue of moving the Pt away from the localization of the ^3MLCT state provides an excited state lifetime of ca. 100 ns. In addition, $[\{(bpy)_2Ru(dpp)\}_2Ru(dpp)PtCl_2]^{6+}$ photobinds and photocleaves DNA in the presence of light and O_2 . A detailed analysis of the important factors that influence the excited state dynamics and the photocatalytic activity such as TL and BL' identity and structure was needed to understand this complex motif. Many surprises were uncovered and a detailed understanding of sub-unit impact on photophysics and photochemistry was obtained.

The supramolecular complexes were prepared by a building block method which allows for purification and analysis following each step of the synthetic scheme. The tetrametallic complexes of the form $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$ were synthesized in five steps which include coupling two $[(TL)_2Ru(dpp)]^{2+}$ LAs to a central *cis*- $RuCl_2$ unit to provide the trimetallic precursor $[\{(TL)_2Ru(dpp)\}_2RuCl_2]^{4+}$ that contains two labile Cl^- ligands. These ligands are replaced by the bidentate BL' to provide the trimetallic LA $[\{(TL)_2Ru(dpp)\}_2Ru(BL')]^{6+}$ that possesses an open coordination site on BL' to enable RM coordination, resulting in the target tetrametallic $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$. Preparation of the trimetallic $[\{(TL)_2Ru(dpp)Ru(bpy)(BL')PtCl_2]^{4+}$ ($TL = Ph_2phen$; $BL' = dpp \text{ or } dpq$) is more synthetically challenging as α -diimine ligands produce *cis*- $[Ru(NN)_2Cl_2]$ when reacted with Ru halide materials. Preparation requires synthesis of *cis,cis*- $[(bpy)RuCl_2(DMSO)_2]$, and the overall synthetic scheme involved six steps. The two monometallic

complexes $[(\text{TL})_2\text{Ru}(\text{dpp})]^{2+}$ and *cis,cis*- $[(\text{bpy})\text{RuCl}_2(\text{DMSO})_2]$ were reacted to afford the structurally diverse bimetallic complex $[(\text{TL})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})]^{2+}$. The labile nature of the Cl^- ligands was exploited to coordinate BL' followed by the *cis*-PtCl₂ RM to produce the target trimetallic complex $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$. Due to the complexity of the molecular architecture, preparation of the desired Ru(II),Pt(II) tetrametallic and trimetallic complexes in high purity and reasonable yields requires considerable synthetic skill. The methods developed now allow control of each TL and BL in the entire motif as well as metal variation.

The building block method is critical, not only to the successful preparation of large mixed-ligand multimetallic complexes, but also to characterization and comprehension of the complicated orbital energetics, excited state dynamics, and photocatalytic activity of the supramolecules. The large number of potential isomers (32 and 16 for $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ and $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$, respectively) and the presence of only aromatic protons renders ¹H NMR a useless characterization method, so a combination of mass spectrometry, electrochemistry, electronic absorption spectroscopy, and emission spectroscopy must be utilized to confirm the identity of the proposed complexes. The changes observed with these methods can be controlled based on the nature of the building block added in each step and the properties of similar reported systems. Synthesis begins with TL and RuCl₃•3H₂O to produce $[(\text{TL})_2\text{RuCl}_2]$ and $[(\text{TL})_2\text{Ru}(\text{dpp})]^{2+}$ which contains only one metal and only two types of polyazine ligands, so the orbital energetics and resulting properties are less complicated to assess. Assembling the larger supramolecules results in a significant impact on one component of the complex, such as stabilization of the $\text{dpp}(\pi^*)$ orbital in $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$ upon coordination of the *cis*-Ru^{II}Cl₂(bpy) unit to produce $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{RuCl}_2(\text{bpy})]^{2+}$, which results in a $\text{dpp}^{0/-}$ couple shifted from -1.0 V to -0.80 V. Additionally, the HOMO is now localized on the central Ru ($E_{1/2} = 0.66$ V), providing a $\Delta E_{1/2}$ of 1.46 V. The lowest energy MLCT transition shifted from 460 nm to 580 nm, and the ³MLCT emission of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$ at 697 nm shifted to an energy too low to be detected. While $\Delta E_{1/2}$ (1.46 V) and E_{abs} (2.14 eV) are not equivalent, they are correlated because they

each involve the same frontier orbitals, and the difference is due to fact that $\Delta E_{1/2}$ does not account for vibrational reorganization parameters.¹²¹ Similar analyses were performed with the other synthetic steps, and trends were carefully predicted based on the metal and ligand sets.

The $[\{(TL)_2Ru(dpp)\}_2Ru(BL')PtCl_2]^{6+}$ tetrametallic complexes, which possess a HOMO localized on either of the terminal $Ru(d\pi)$ orbitals and a LUMO localized on the remote $BL'(\pi^*)$ orbitals, were designed to act as molecular photovoltaics to provide access to a lowest-lying charge separated state upon photoexcitation in which a potential gradient is produced on the molecular level. The tetrametallic complexes are robust light absorbers resulting from the many overlapping IL $\pi \rightarrow \pi^*$ and $Ru(d\pi) \rightarrow \text{ligand}(\pi^*)$ MLCT transitions in the UV and visible regions, respectively. Use of Ph_2phen vs. $phen$ provides enhanced absorptivity, while BL' does not greatly impact the absorptivity. The lowest energy optically accessible excited state is terminal $Ru(d\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ MLCT in nature, predicted by electrochemical analysis. The terminal $Ru(d\pi) \rightarrow BL'(\pi^*)$ CS state is lower in energy; however, the lack of orbital overlap prevents direct excitation into this excited state. Excitation with $\lambda = 540$ nm populates a variety of excited states, primarily the central $Ru(d\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1MLCT , central $Ru(d\pi) \rightarrow \mu\text{-}BL'(\pi^*)$ ^1MLCT , and terminal $Ru(d\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^1MLCT states.

While $Ru(II)$ -polyazine complexes typically deactivate to the emissive excited state with $\Phi = 1$, this supramolecular motif provides the competitively populated low-lying terminal $Ru(d\pi) \rightarrow BL'(\pi^*)$ ^3CS state which receives contributions from both the central $Ru(d\pi) \rightarrow \mu\text{-}BL'(\pi^*)$ ^3MLCT and terminal $Ru(d\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3MLCT states that are dictated by λ^{exc} , a very unusual occurrence. The degree of population of the ^3CS state is largely dependent on BL' identity; the lower energy $dpq(\pi^*)$ orbitals compared to those of dpp provide a larger driving force for ^3CS population, resulting in enhanced quenching of the terminal $Ru(d\pi) \rightarrow \mu\text{-dpp}(\pi^*)$ ^3MLCT emission compared to the trimetallic model complexes (66-68 % quenching when $BL' = dpq$ compared to 30-32 % quenching when $BL' = dpp$). The complexes are able to collect electrons on the dpp and $BL' \pi^*$ orbitals, and the enhanced charge separation which leads to a larger degree of electron localization adjacent to the Pt RM when $BL' = dpq$

provides a more active photocatalyst in H₂O reduction to produce H₂, with 15 μ mol and 4 μ mol H₂ produced in 10 h with $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, respectively. TL variation fine tunes the absorptivity of the complexes and enhances the photocatalytic activity (but to a lesser extent than BL' variation), with 21 μ mol and 5 μ mol H₂ produced in 10 h with $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2]^{6+}$ and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$, respectively.

The complicated spectroscopy of the $[\{(\text{TL})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{BL}')\text{PtCl}_2]^{6+}$ tetrametallic complexes due to the presence of two outer (TL)₂Ru^{II}(dpp) LAs providing a vast number of MLCT transitions makes spectroscopic analysis of these complexes quite difficult. To create a less complicated system with fewer strong MLCT transitions in the visible region, the supramolecular architecture was amended by replacing one (TL)₂Ru^{II}(dpp) LA with a simple bpy TL to provide the new trimetallic $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ analogues. These complexes maintain the spatially separated HOMO (terminal Ru) and LUMO (remote BL') as observed in the tetrametallic complexes. The presence of fewer ¹MLCT transitions in the visible region provides spectra that are similar to the tetrametallic analogues but with lower molar absorptivities, and they exhibit more pronounced spectroscopic changes upon shifting one particular transition of interest. This enabled analysis of the steady-state and time-resolved nanosecond transient absorption spectroscopy to gain further insight into the excited state dynamics by monitoring non-emissive excited states. The transient absorption spectroscopy of the bimetallic model complexes $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})]^{4+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})]^{4+}$ is consistent with a lowest-lying and emissive terminal Ru(d π) $\rightarrow$ μ -dpp(π^*) ³MLCT excited state that is populated with $\Phi = 1$ and exhibits an excited state lifetime consistent with time-resolved emission spectroscopy (ca. 120 ns for both complexes). Similar observations for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2]^{4+}$ suggest that the emissive state is populated with near unit efficiency and charge separation is not efficiently achieved by virtue of the small driving force for intramolecular electron transfer. Excitation and probe wavelength dependence is observed for the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ analogue, and the red-shift in the MLCT bleach centered around

560 nm is consistent with enhanced population of the low energy ^3CS state. The biexponential excited state decay consists of a long component (120 ns) and a short component (25 ns), likely due to GS recovery of the terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ $^3\text{MLCT}$ and terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ ^3CS states. Contribution of the ^3CS state to the biexponential excited state decay increases with decreasing excitation wavelength. This work is of great interest in gaining a deeper understanding of non-traditional Ru(II)-polyazine complexes.

In the scope of this dissertation, two synthetically challenging Ru(II),Pt(II) supramolecular architectures were studied through detailed comparisons to understand the impacts of TL and BL' on the excited state dynamics. The unusual excited state processes in which a low-lying ^3CS excited state is populated via two higher energy $^3\text{MLCT}$ excited states is important in the realm of Ru(II)-polyazine bridged supramolecular complexes. The ability to control the movement of electrons through a large molecule toward a RM by MLCT excitation is important in designing supramolecular devices that can photocatalytically deliver multiple electrons to H_2O to produce H_2 . The small impact of TL variation from phen to Ph_2phen on the photocatalytic activity is surprising considering the major impact Ph_2phen TLs have in providing a robust photocatalyst with Rh(III) RM, $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhX}_2]^{5+}$, compared to $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RhX}_2]^{5+}$ ($\text{X} = \text{Cl}^-$ or Br^-). This difference is likely due to the varied through bond and through space distance from TL to RM in the Pt and Rh complexes. Continued research in structurally diverse, mixed-metal complexes with Ru(II)-polyazine LAs is needed to realize the full potential of these supramolecular complexes as PMDs.

4.2. Future Work

4.2.1. Selective BL Deuteration for Excited State Analysis

Incorporating deuterated bridging ligands such as $\text{d}_{10}\text{-dpp}$ and $\text{d}_{12}\text{-dpq}$ into the $[(\text{TL})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ supramolecular complexes can be used to confirm the nature of the emissive excited state. While a terminal $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT excited state is predicted to be the lowest energy emissive state, the energy of the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ MLCT excited state may be

similar. The energy gap between the central Ru and BL' is ambiguous, as the central Ru^{II/III} oxidation occurs beyond the solvent window in square wave voltammetry. It is well known in Ru(II)-polyazine complexes that if the ligand involved in the emissive ³MLCT excited state is deuterated, a larger Φ^{em} and a longer τ are observed compared to the protiated species.¹²² The relative emission spectra and the normalized time-resolved emission profiles of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})]^{2+}$ and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{d}_{10}\text{-dpp})]^{2+}$ in RT CH₃CN are shown in **Figure 4.1** to highlight this effect in a complex with a Ru($d\pi$) $\rightarrow$ dpp(π^*) ³MLCT emissive state. Comparison of the steady-state and time-resolved emission spectroscopy of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{d}_{10}\text{-dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$, $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{d}_{12}\text{-dpq})\text{PtCl}_2]^{4+}$, and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ will provide the necessary information to confirm the excited state from which emission occurs. If emission arises from the terminal Ru($d\pi$) $\rightarrow$ dpp(π^*) ³MLCT state, the enhanced Φ^{em} and longer τ will be observed only for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{d}_{10}\text{-dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ and the remaining two complexes will exhibit the same Φ^{em} and τ . Conversely, if emission arises from the central Ru($d\pi$) $\rightarrow$ BL'(π^*) ³MLCT excited state, only an enhanced Φ^{em} and longer τ will be observed for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{d}_{12}\text{-dpq})\text{PtCl}_2]^{4+}$. Selective ligand deuteration may also be useful in time-resolved transient absorption spectroscopy to confirm the nature of transient excited states.

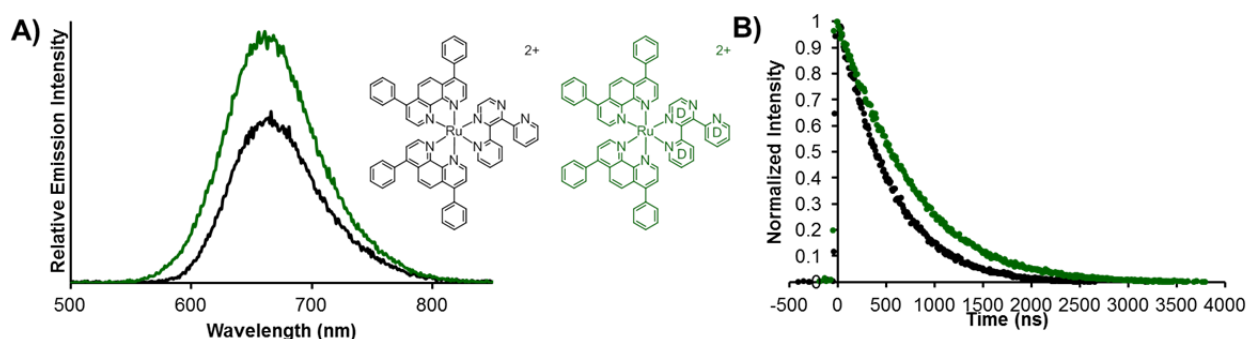


Figure 4.1: A) Steady-state emission spectra and B) time-resolved emission profiles of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2$ (—) and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{d}_{10}\text{-dpp})]^{2+}$ (—) in RT deoxygenated spectral grade CH₃CN. Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

4.2.2. Continued Analysis of Excited State Dynamics by Transient Absorption Spectroscopy

While significant strides were made in providing an analysis of the unusual excited state dynamics of the $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{BL}')\text{PtCl}_2]^{4+}$ complexes, a great deal of information can still be attained. First, TL substitution to phen or bpy may aid in TA analysis as the IL $\pi \rightarrow \pi^*$ and $\text{Ru}(\text{d}\pi) \rightarrow \text{TL}(\pi^*)$ MLCT transitions occur with lower molar absorptivity and this may provide TA spectra with more evident spectral shifts. It is important to follow the electron localization throughout the excited state dynamics to acquire a signature of a reduced dpp or BL'. Previous studies of the ns TA spectroscopy of $[\text{Ru}(\text{dpp})_3]^{2+}$ and $[\text{Ru}(\text{dpq})_3]^{2+}$, in which the excited electron in the lowest energy excited state is forced to be localized on dpp and dpq, respectively, highlight a ca. 20 nm red shift for the dpq $\pi^* \rightarrow \pi^*$ absorption (370 nm) compared to the dpp $\pi^* \rightarrow \pi^*$ absorption (350 nm).¹²³ A spectral map of the near-UV region between 300 and 400 nm can be measured with the PMT, as the CCD camera is not sensitive enough in this region. The dynamics of the dpp/dpq excited state absorption may provide a probe to monitor the movement of the excited electron. Ultrafast, sub-nanosecond TA spectroscopy can also be used to monitor the excited state dynamics of the higher energy, presumably short-lived central $\text{Ru}(\text{d}\pi) \rightarrow \text{dpp}(\pi^*)$ MLCT and central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ MLCT excited states. This can provide spectral shifts associated with nonradiative processes such as intramolecular electron transfer from the central $\text{Ru}(\text{d}\pi) \rightarrow \text{BL}'(\pi^*)$ MLCT state to the ^3CS state (k_{et}).

4.2.3. Ru(II),Pt(II) Supramolecular Complex Aggregation

The previously discussed decametallic complex $[\text{Ru}\{(\text{dpp})\text{Ru}[(\text{dpp})\text{Ru}(\text{bpy})_2]_2\}_3](\text{PF}_6)_{20}$ was reported to form aggregates in CH_3CN solution at concentrations as low as 10^{-6} M with a size of about 100 nm, and the ionic strength and solvent polarity influence aggregation.¹²⁴ This intermolecular interaction is caused by attraction between the hydrophobic aromatic ligands.¹²⁵ The ion-pairing between the positively charged supramolecule and the PF_6^- counterions to form a neutral ion-pair serves to decrease the electrostatic repulsion that may be expected between large positive charges. Analysis by light scattering and conductivity experiments indicate that these complexes can be considered as colloidal

systems rather than homogeneous solutions. While the trimetallic and tetrametallic complexes are smaller than the decametallic complexes, aggregation to form colloids in CH₃CN may still occur. Interpretation of the redox and excited state properties of these complexes by considering intermolecular interactions rather than viewing the sample as a composition of single, non-interacting molecules could lead to new perspectives about how the supramolecules act as photocatalysts in solution. The photocatalyst concentration (50 μM) in **Section 3.2.5.3** is on the same order of magnitude that causes decametallic aggregation. The hydrophobic nature of the Ph₂phen TLs and the hydrophilic *cis*-PtCl₂ unit of these complexes provide the possibility of aggregation in the form of micelles in a CH₃CN/H₂O solution. Light scattering and conductivity experiments can provide evidence whether this phenomenon occurs, and a detailed analysis of the effect of structure on aggregation may be achieved through a comparison of analogues such as [(TL)₂Ru(BL)PtCl₂]²⁺, [(TL)₂Ru(dpp)Ru(TL')(BL')PtCl₂]⁴⁺, and [{(TL)₂Ru(dpp)}₂Ru(BL')PtCl₂]⁶⁺, and the size and nature of the TL can be varied to observe impacts on ligand π-π interactions.

4.2.4. Photoinduced DNA Modification with [(TL)₂Ru(dpp)Ru(bpy)(BL')PtCl₂]⁴⁺

The new trimetallic supramolecular complexes of the design [(TL)₂Ru(dpp)Ru(bpy)(BL')PtCl₂]⁴⁺ are expected to behave as light activated DNA modification agents, as a plethora of Ru(II),Pt(II) bimetallic complexes and the previously mentioned [{(bpy)₂Ru(dpp)}₂Ru(dpp)PtCl₂]⁶⁺ are known to bind to and cleave DNA upon irradiation in the presence of O₂.^{50,110,126-128} These complexes should be useful in gaining a better understanding of the influence of TL on light-induced interactions with DNA, as they are intermediate in size between the [(TL)₂Ru(BL)PtCl₂]²⁺ bimetallic complexes and [{(TL)₂Ru(dpp)}₂Ru(BL')PtCl₂]⁶⁺ complexes (**Figure 4.2**). The trimetallic analogues provide a strongly absorbing Ru,Ru LA unit, however the architecture is attractive because the presence of only one terminal (TL)₂Ru^{II}(dpp) LA is expected to provide a more sterically accessible Pt bioactive site (BAS) for DNA binding compared to the tetrametallic complexes with two bulky terminal (TL)₂Ru^{II}(dpp) LAs. Additionally, this architecture may be an improvement on the avid binding and photocleavage agent

$[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$ as moving the bulky $(\text{Ph}_2\text{phen})_2\text{Ru}^{\text{II}}(\text{dpp})$ LA further from the Pt BAS affords a complex which maintains the rich LA and $^1\text{O}_2$ producing abilities of $\text{Ph}_2\text{phen-Ru(II)}$ complexes while providing a more sterically accessible BAS.

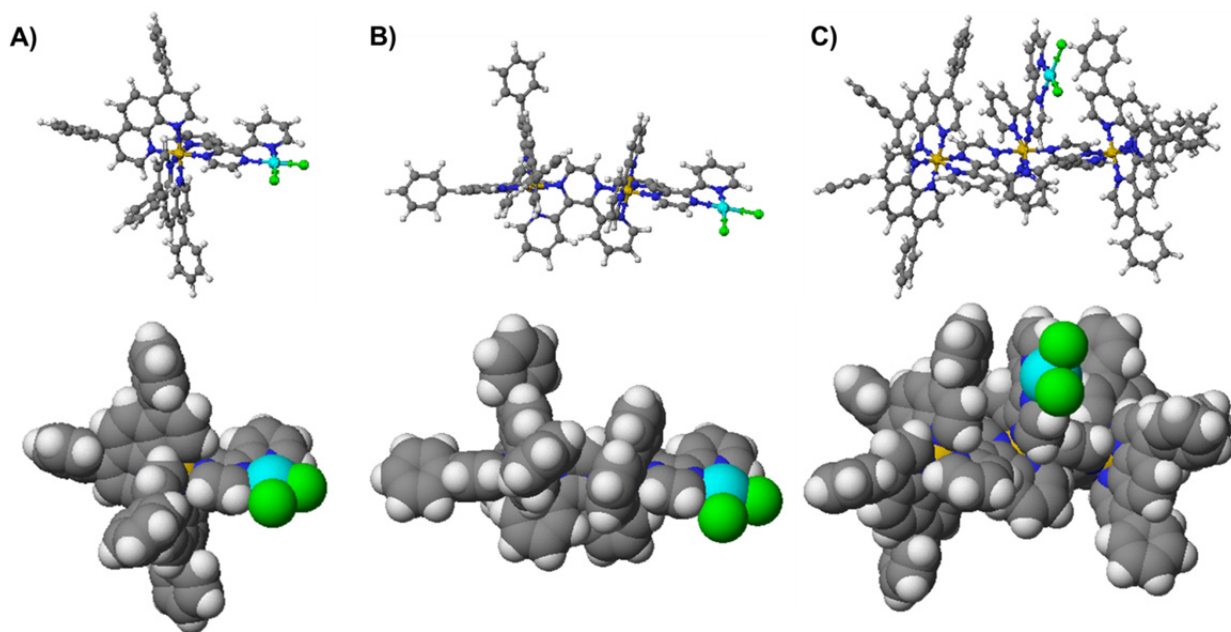


Figure 4.2: Three dimensional ball and stick and space filling models of A) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{2+}$, B) $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2]^{4+}$, and C) $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2]^{6+}$. Structures generated using Scigress 7.7.1 molecular modeling software. Gold = Ru, light blue = Pt, green = Cl, blue = N, gray = C, white = H, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine.

4.2.5. Dye-Sensitized Solar Cells with Ru_2Pt Complexes

The design of efficient p-type dye-sensitized solar cells (DSSCs) is important in the quest to efficiently harness solar energy and convert it into electricity.¹²⁹ Currently n-type DSSCs are well studied and more efficient than p-type DSSCs.¹³⁰⁻¹³² The efficiency of a solar cell is dependent on the photocurrent of both half cells being comparable. P-type DSSCs are constructed by anchoring a dye by carboxylate groups to NiO (often mesoporous). Upon excitation of the dye, NiO acts as an electron donor to enhance the charge separation distance. Systems that have acceptor orbitals spatially separated from the NiO donor are needed to impede fast back electron transfer. The $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ supramolecular complex is an attractive candidate for this as it

efficiently absorbs UV and visible light and populates a ^3CS excited state with the hole localized on the terminal Ru and the electron localized on the dpq ligand. Amending the complex to provide anchoring carboxylate groups on the phenyl rings of the Ph_2phen TLs would enable it to be immobilized on mesoporous NiO. The complexes immobilized on NiO can be studied by techniques such as transient absorption spectroscopy to monitor excited state evolution and hole injection and photoelectrochemical characterization to obtain incident photon-to-current efficiency. This project holds much promise as no systems are known which couple mixed-metal, mixed-ligand supramolecular complexes that undergo charge separation. This may provide a new pathway for photocatalytic H_2O reduction using these Ru_2Pt complexes and provide important knowledge in the field of DSSCs.

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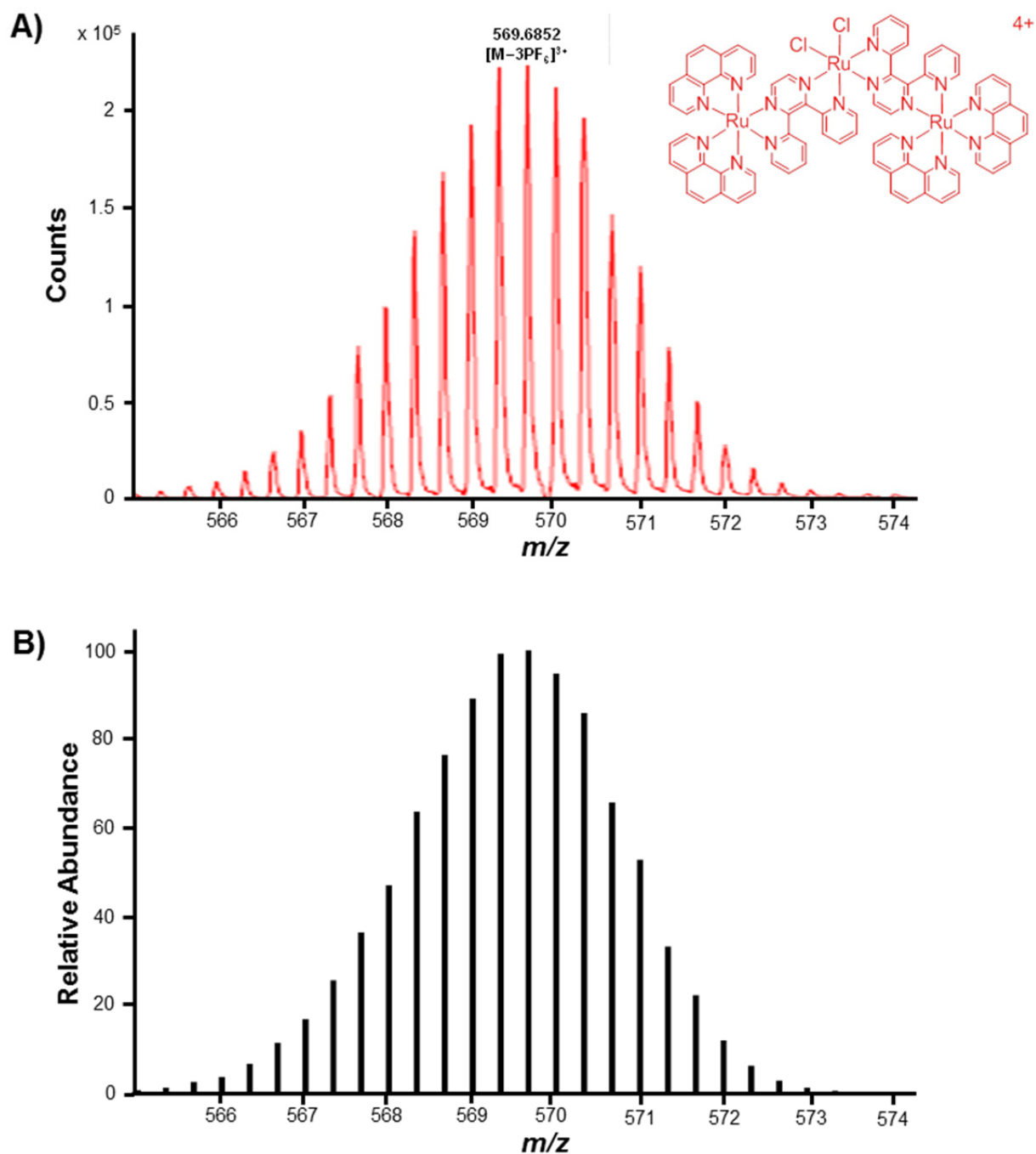


Figure A-1: ESI mass spectra for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2]^{4+}$ A) measured in CH_3CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to $[\text{M}-3\text{PF}_6]^{3+}$.

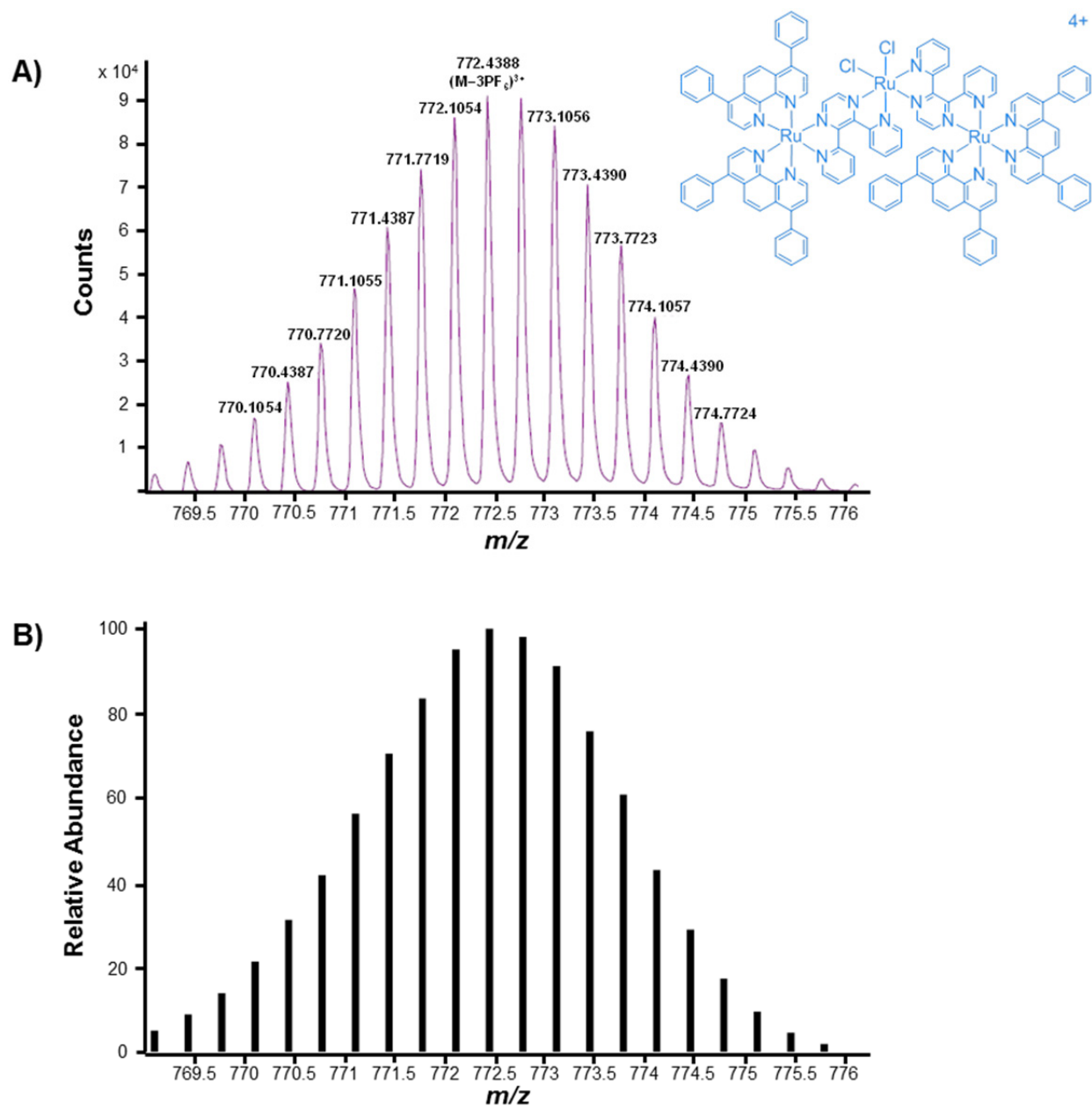


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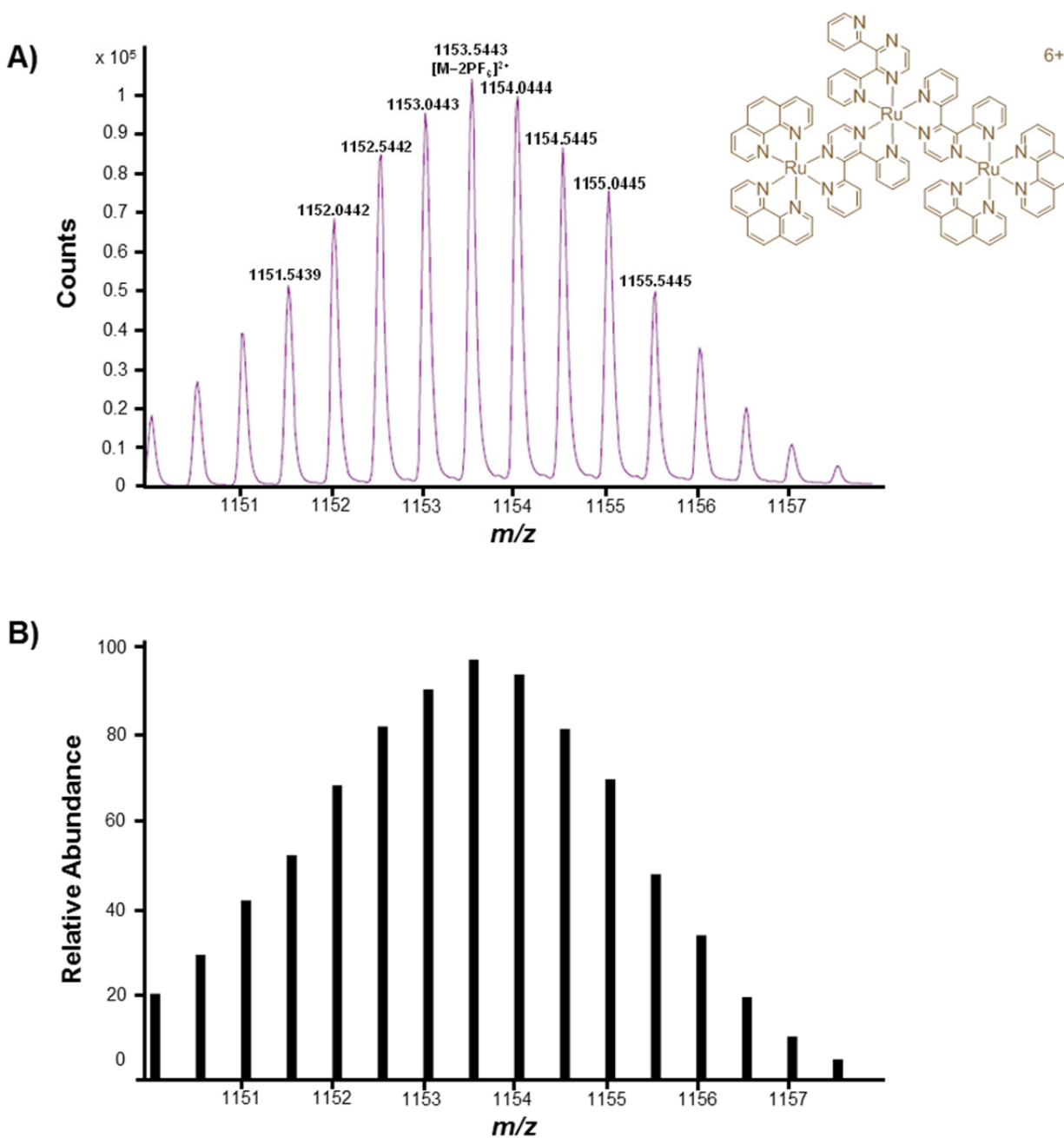


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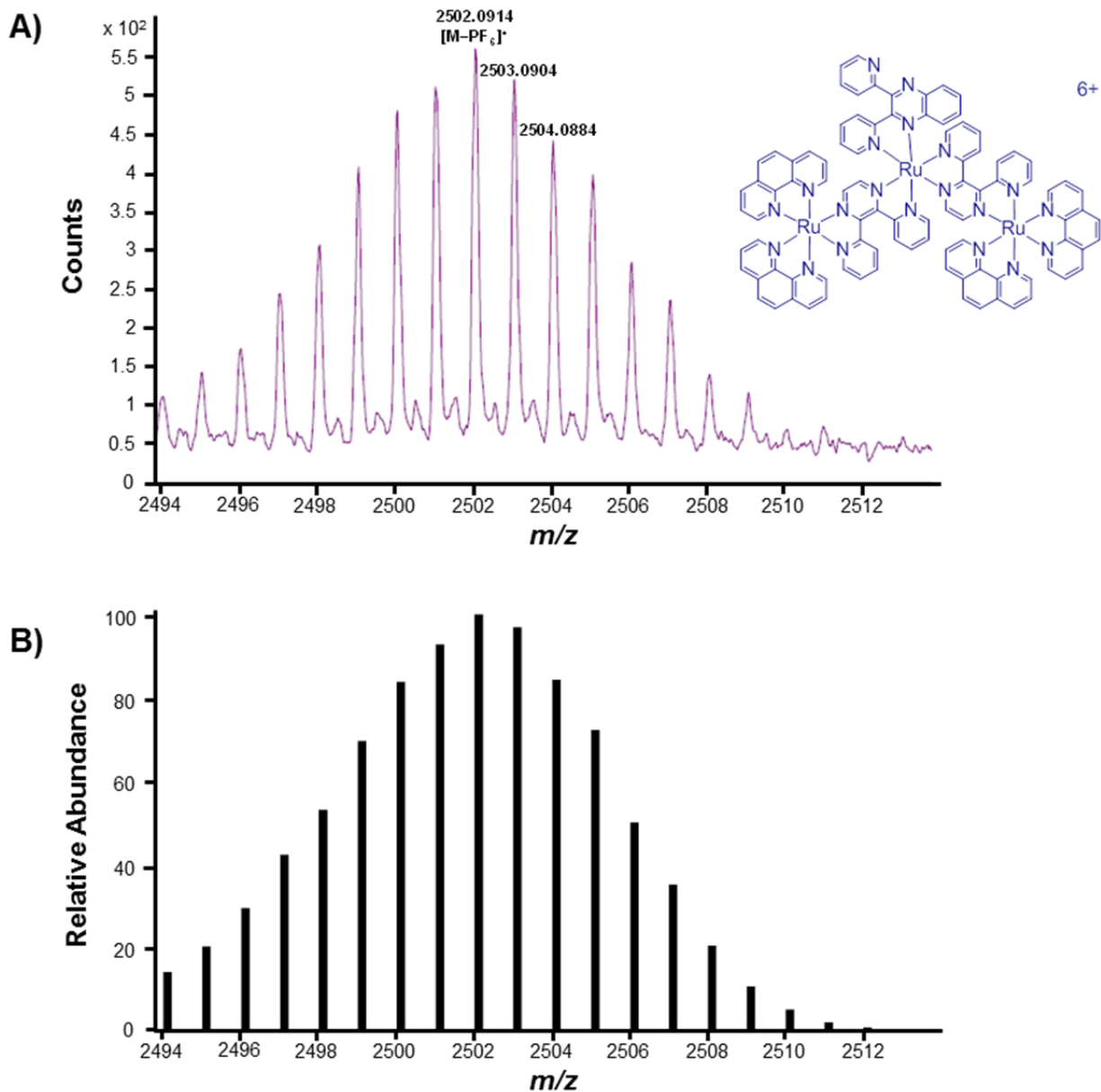


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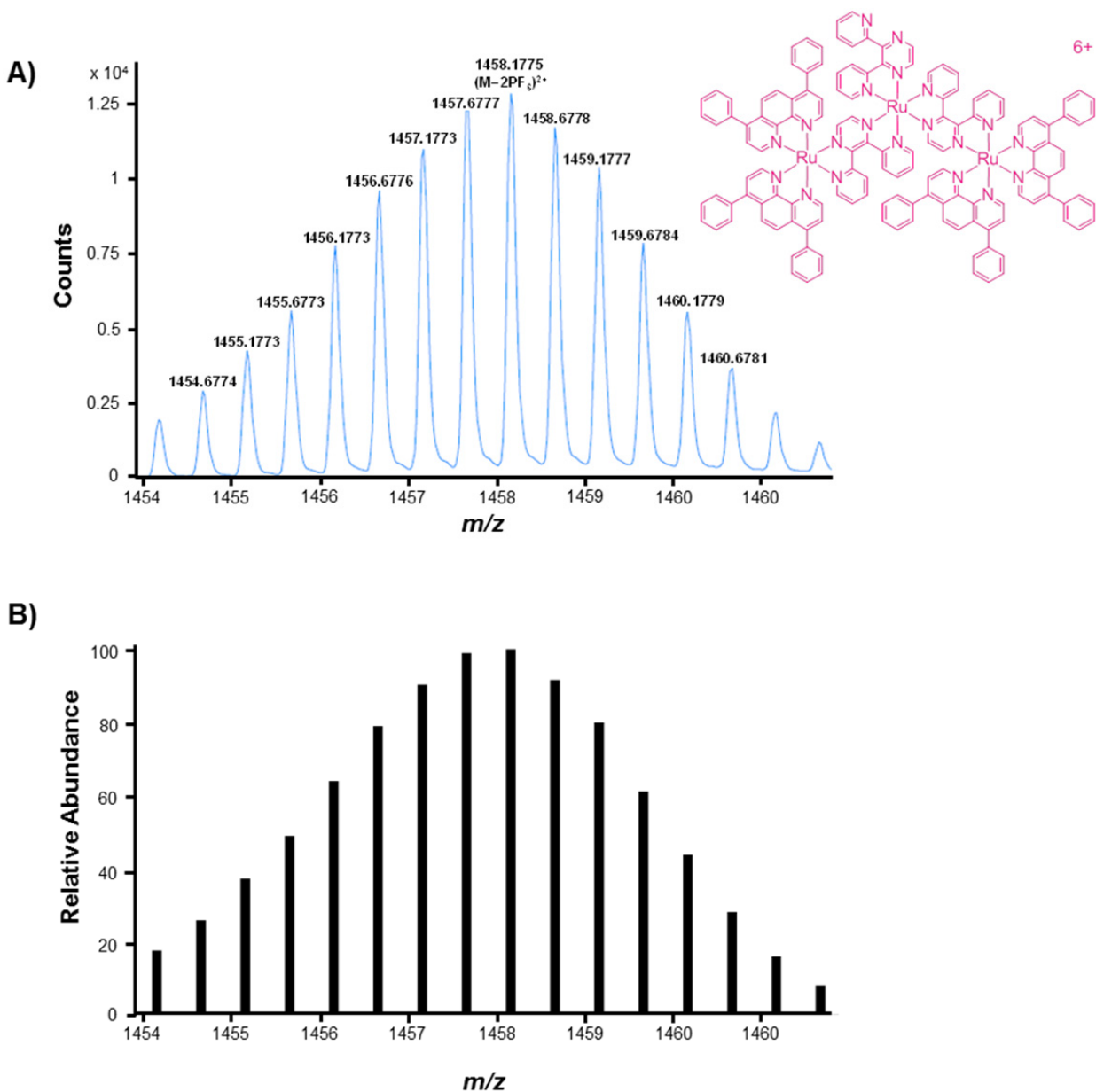


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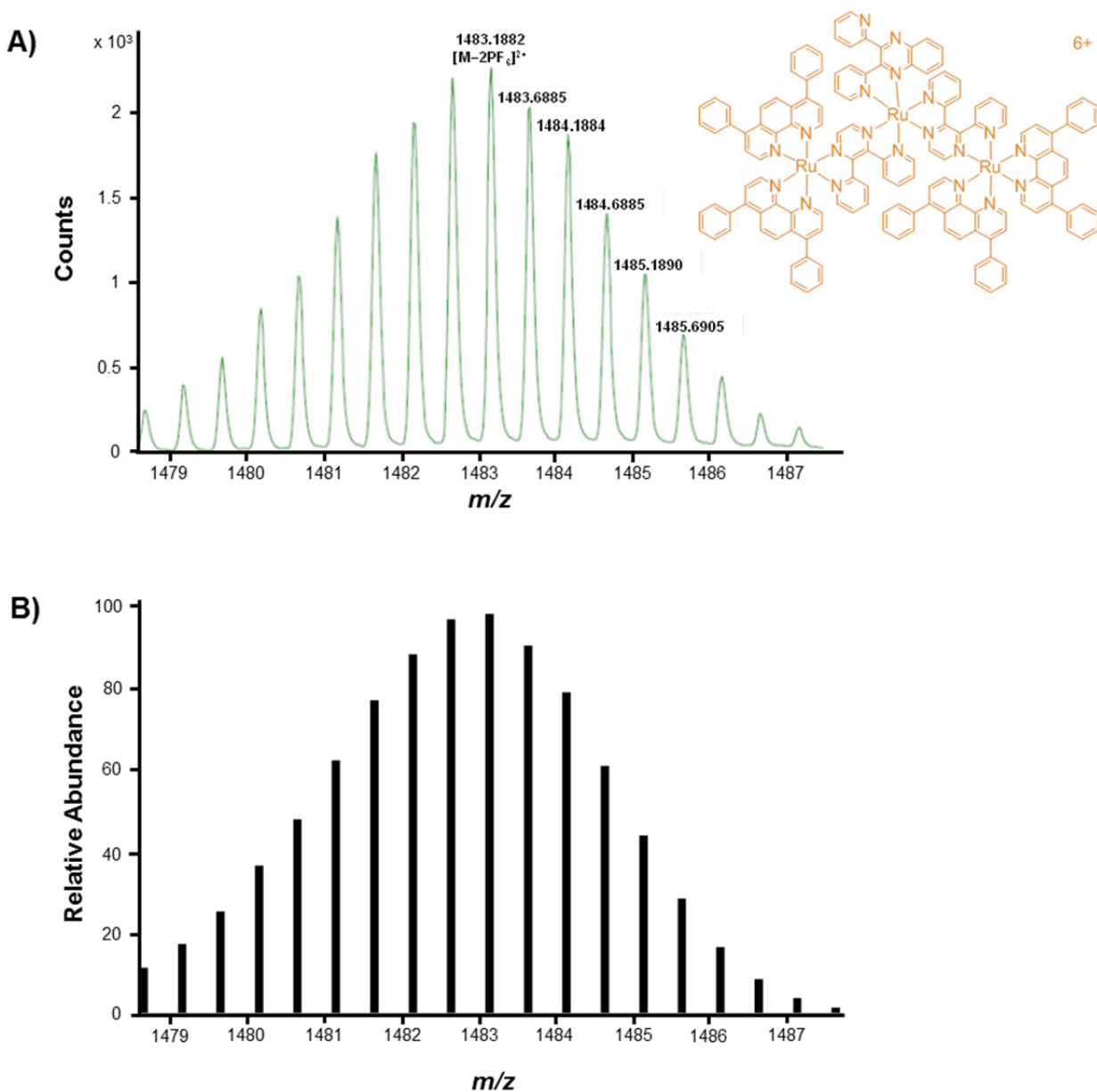


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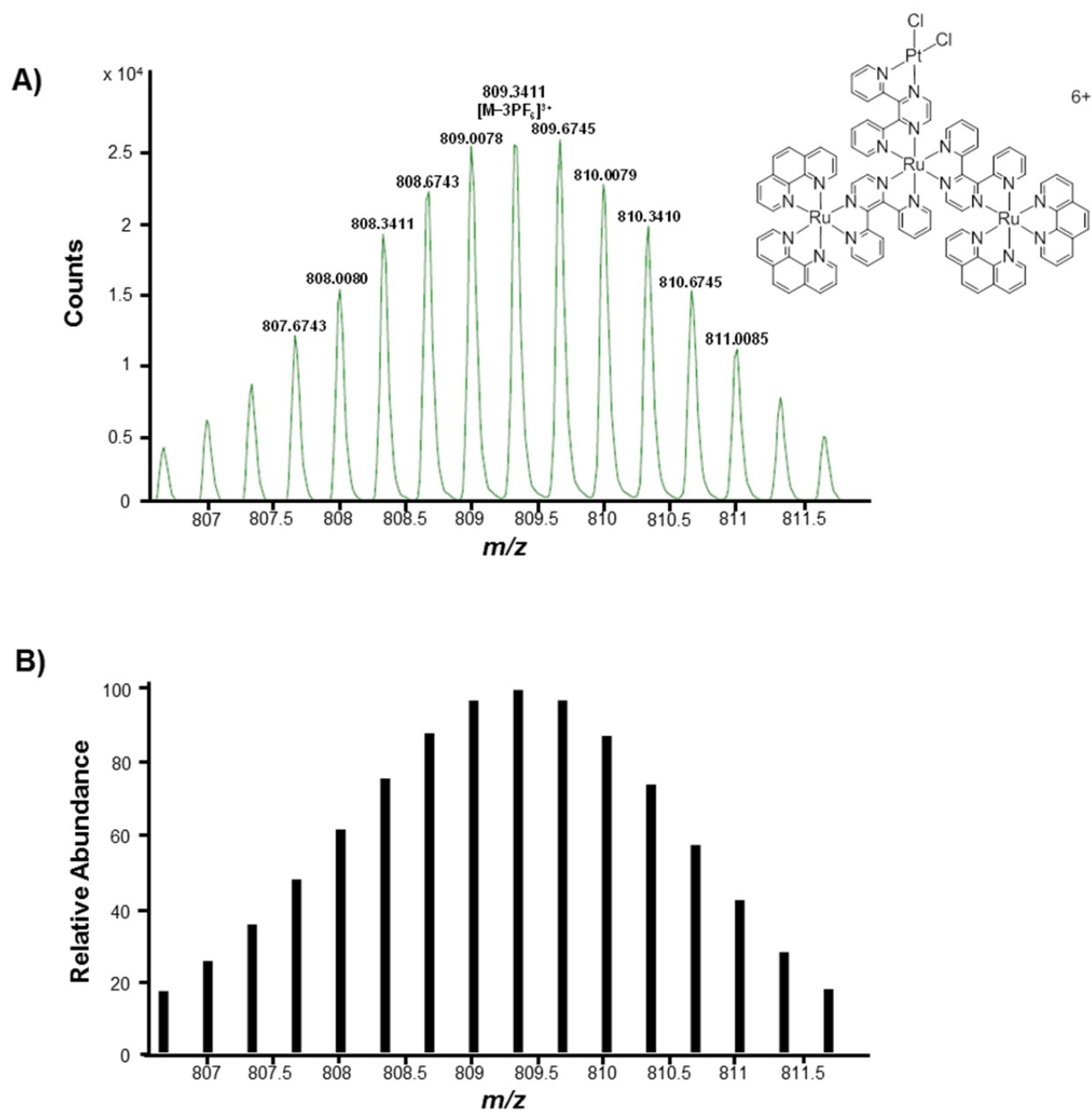


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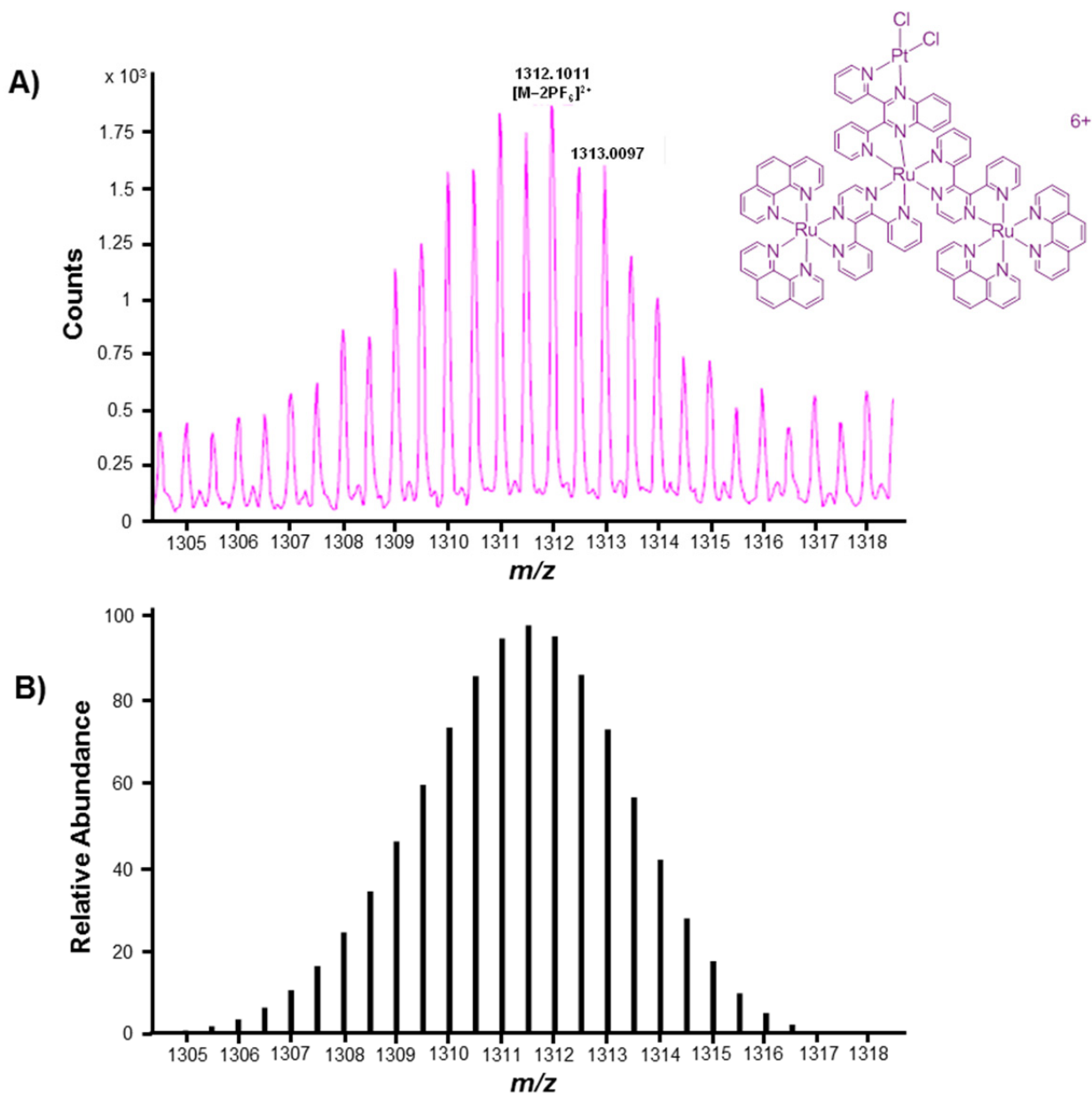


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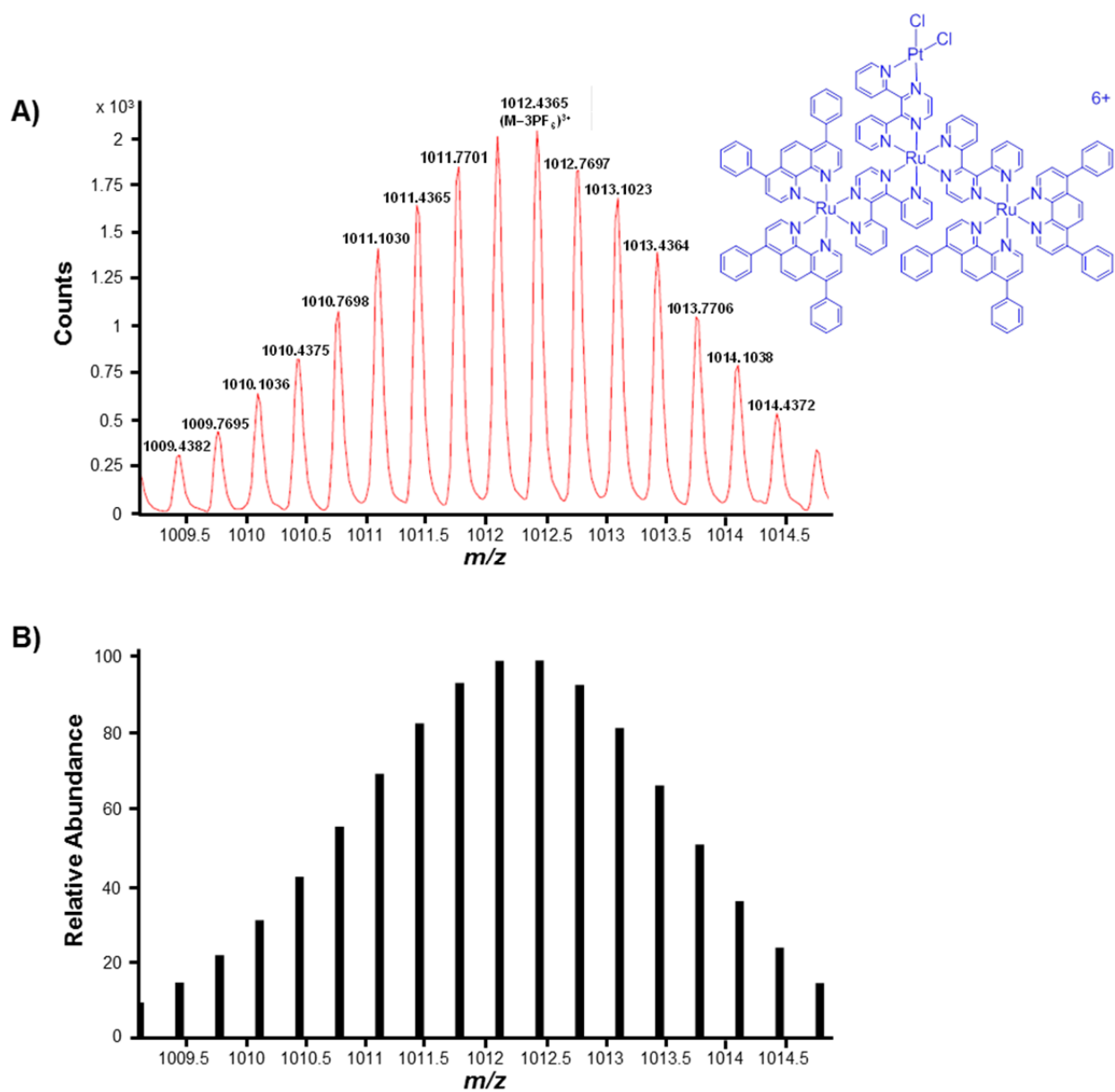


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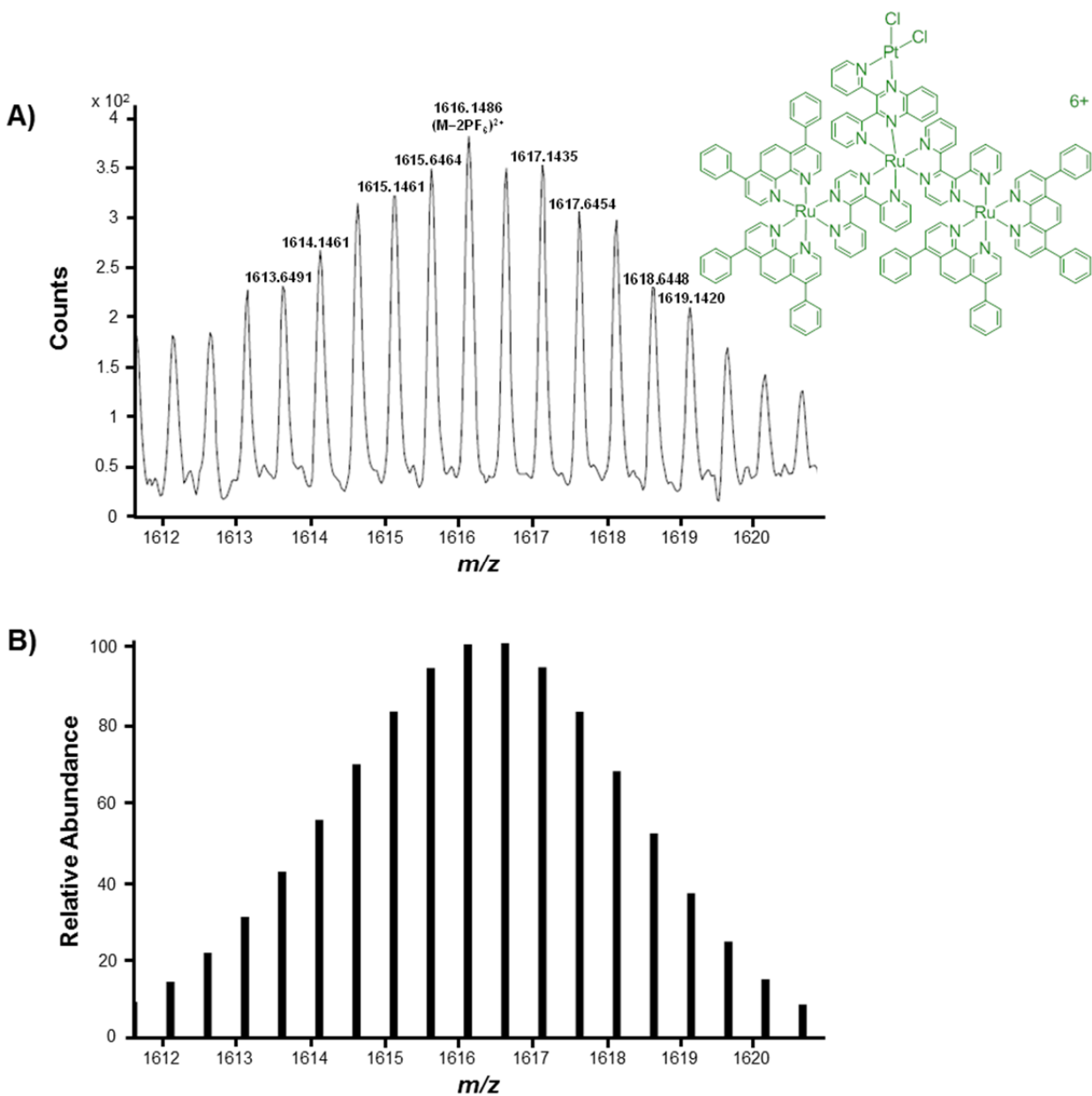


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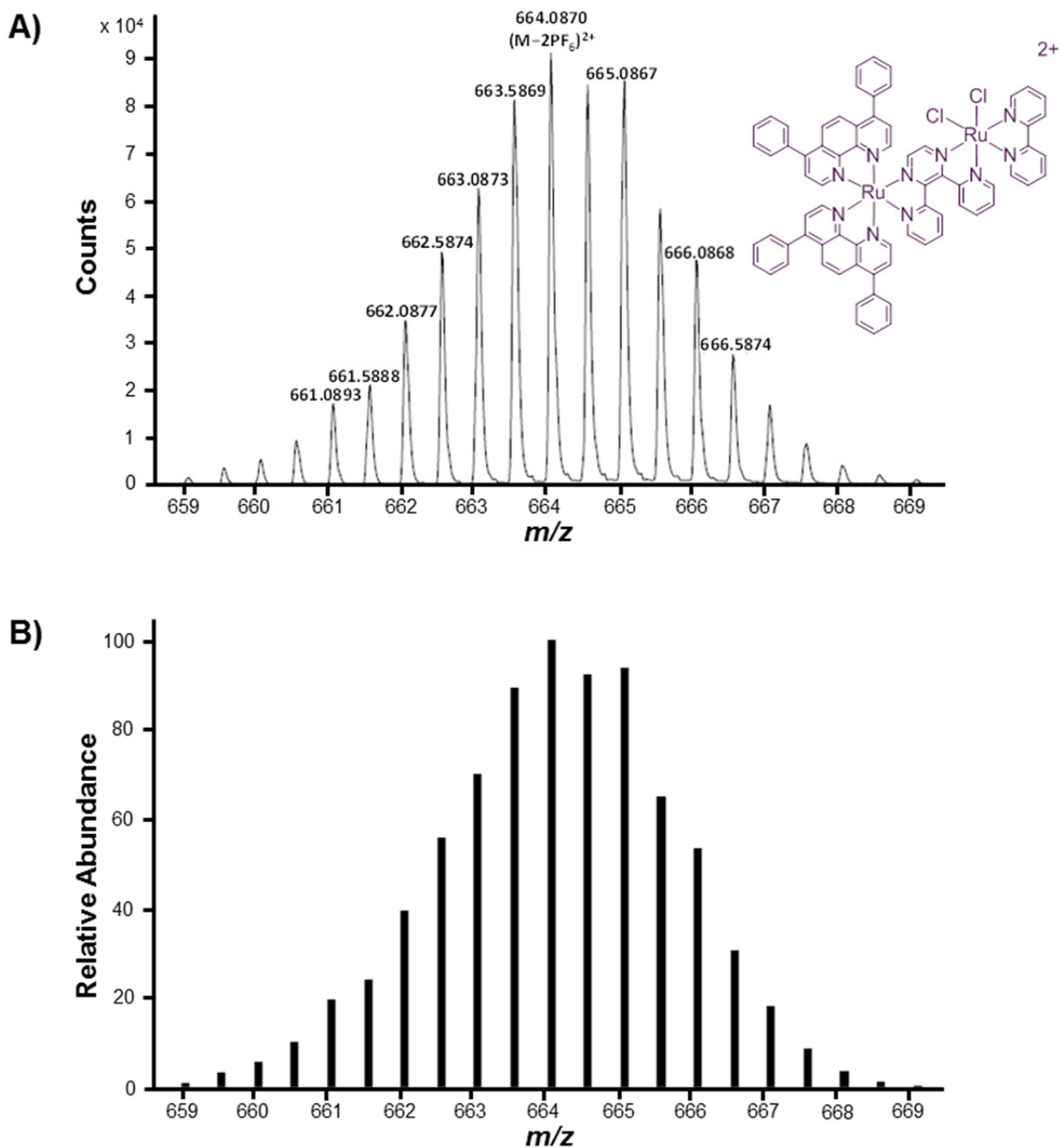


Figure A-11: ESI mass spectra for [(Ph₂phen)₂Ru(dpp)RuCl₂(bpy)]²⁺ A) measured in CH₃CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to [M-2PF₆]²⁺.

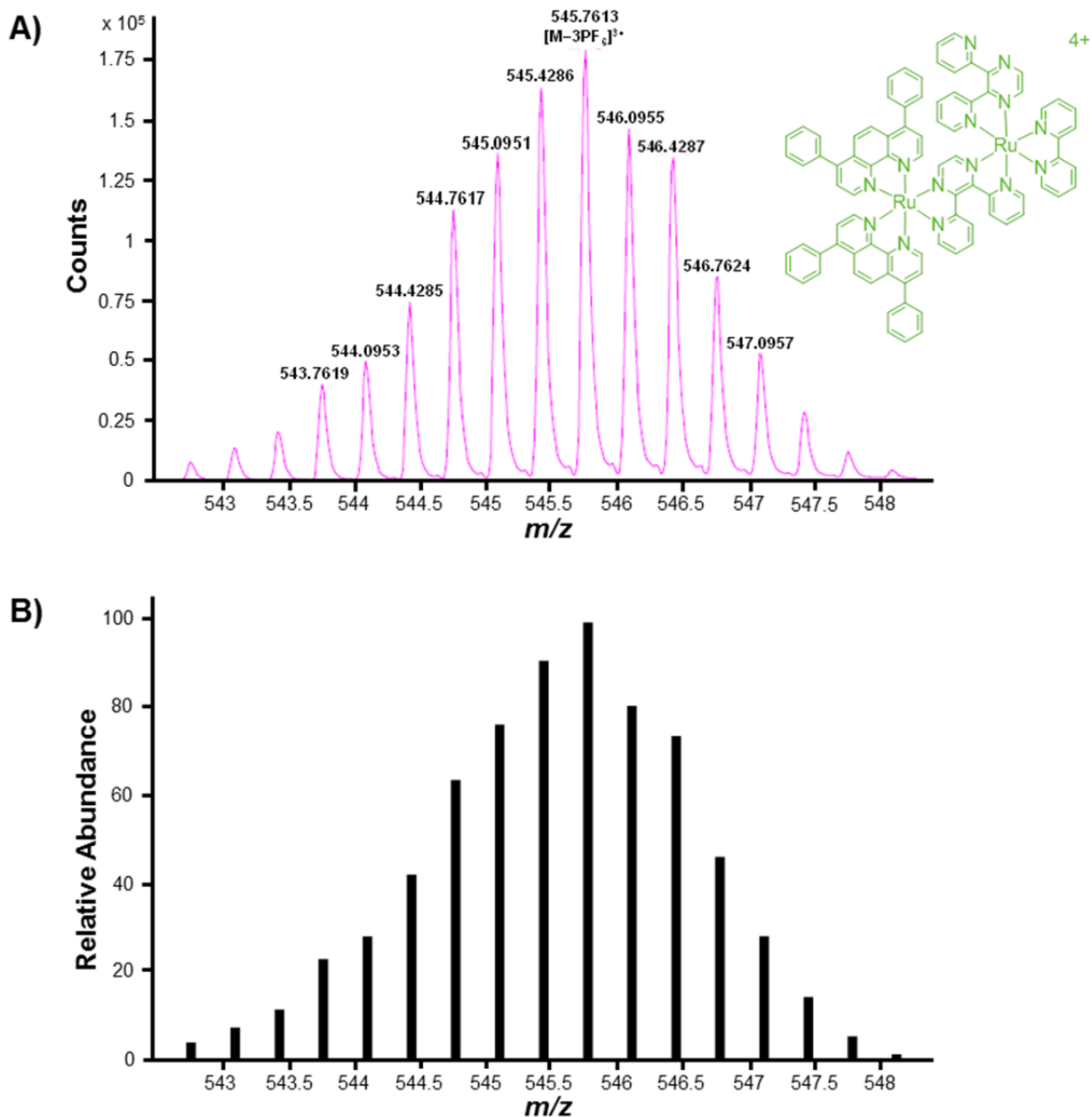


Figure A-12: ESI mass spectra for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})]^{4+}$ A) measured in CH_3CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to $[\text{M}-3\text{PF}_6]^{3+}$.

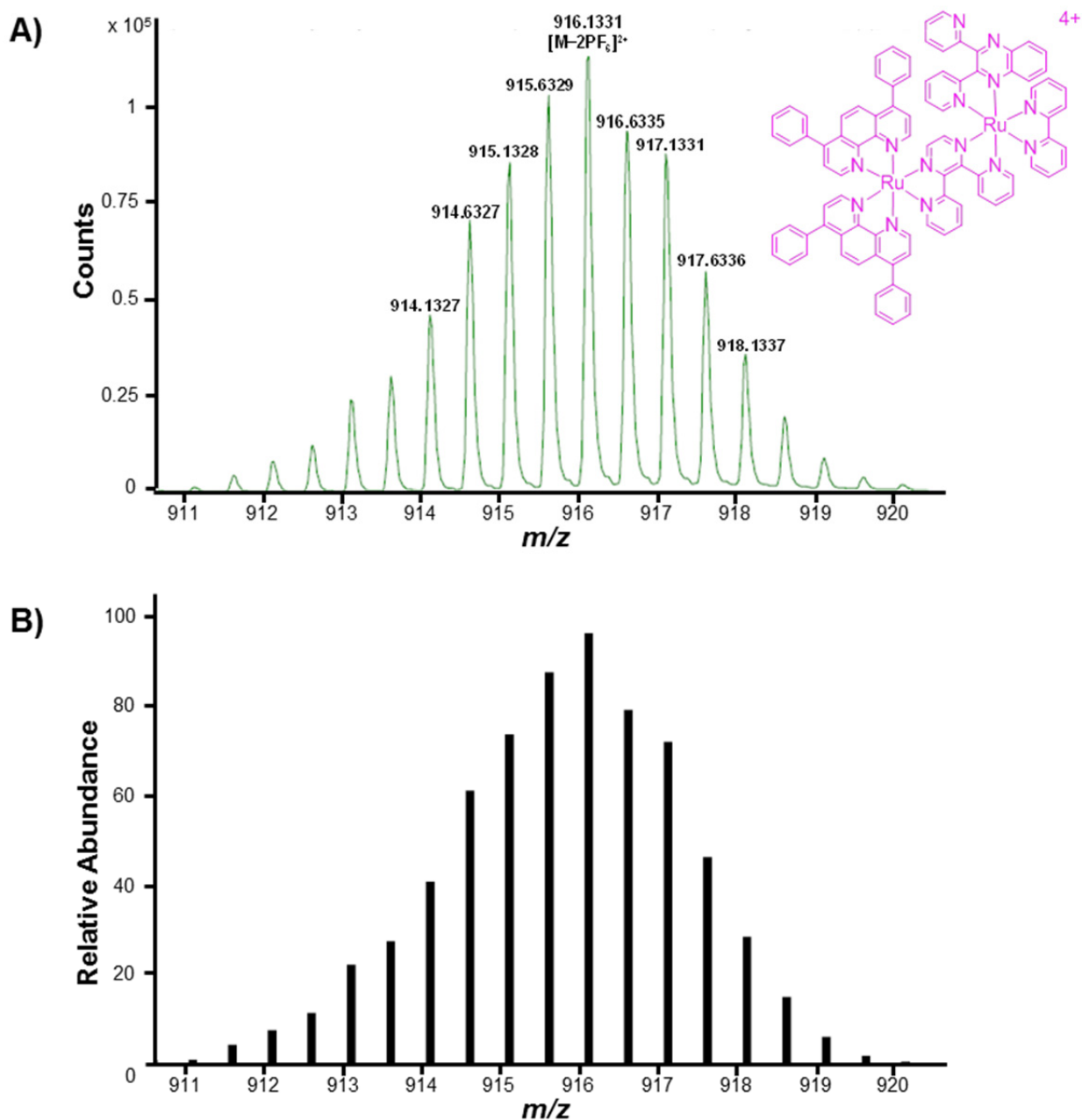


Figure A-13: ESI mass spectra for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})]^{4+}$ A) measured in CH_3CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to $[\text{M}-2\text{PF}_6]^{2+}$.

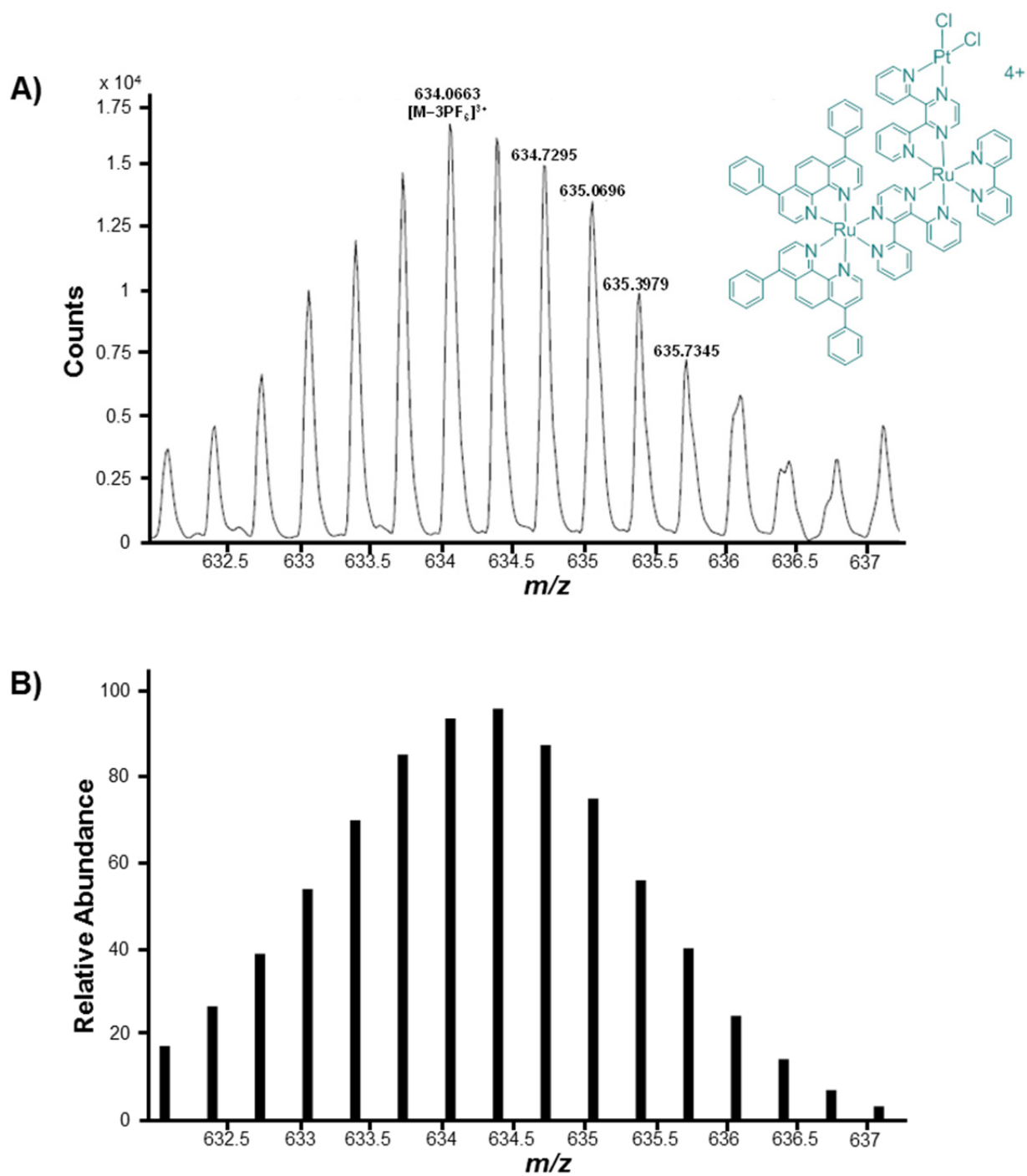


Figure A-14: ESI mass spectra for $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpp)PtCl_2]^{4+}$ A) measured in CH_3CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to $[M-3PF_6]^{3+}$.

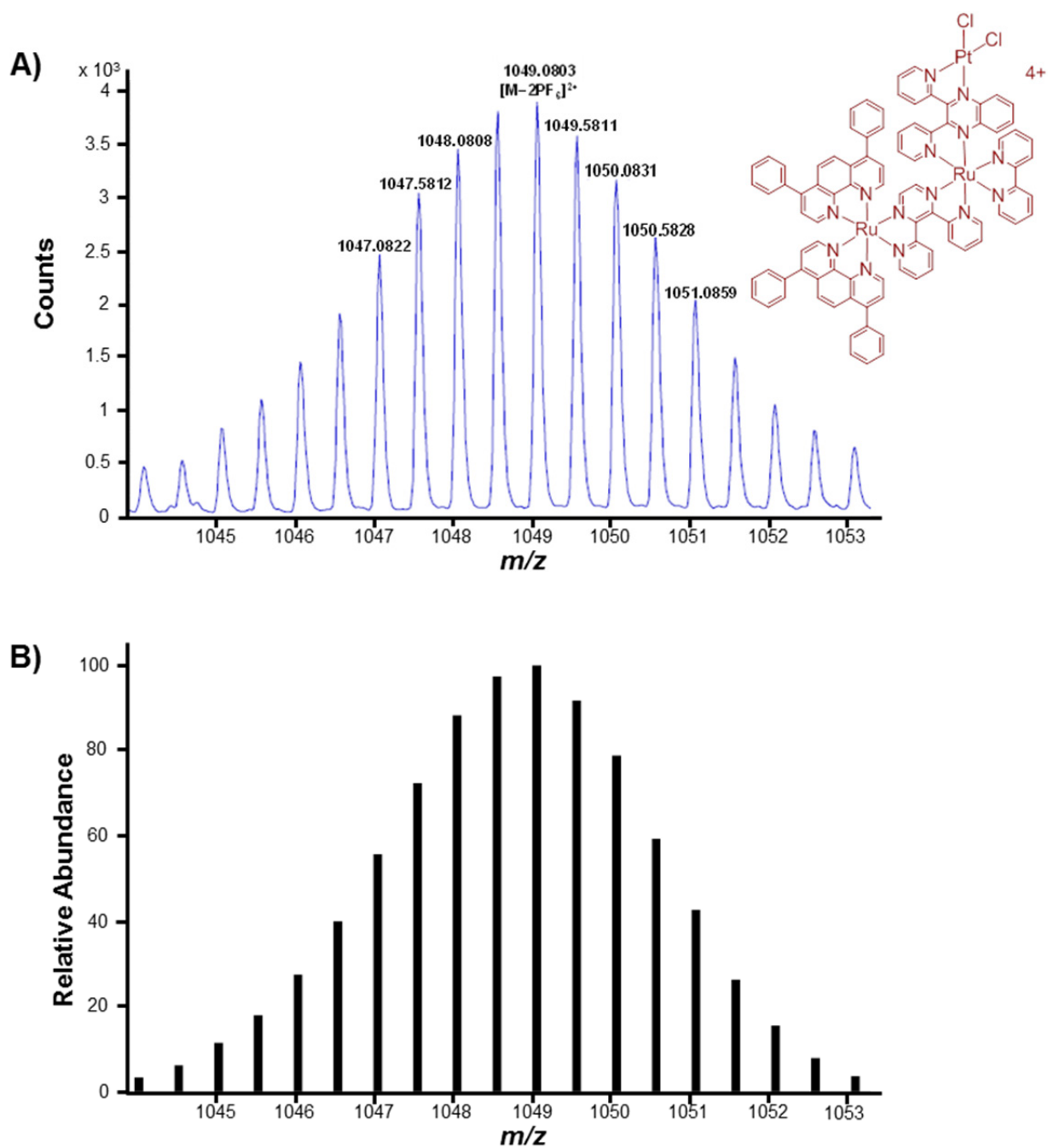


Figure A-15: ESI mass spectra for $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2]^{4+}$ A) measured in CH_3CN and B) calculated using Sheffield ChemPuter to obtain the corresponding isotopic distribution. The molecular ion peak corresponds to $[\text{M}-2\text{PF}_6]^{2+}$.

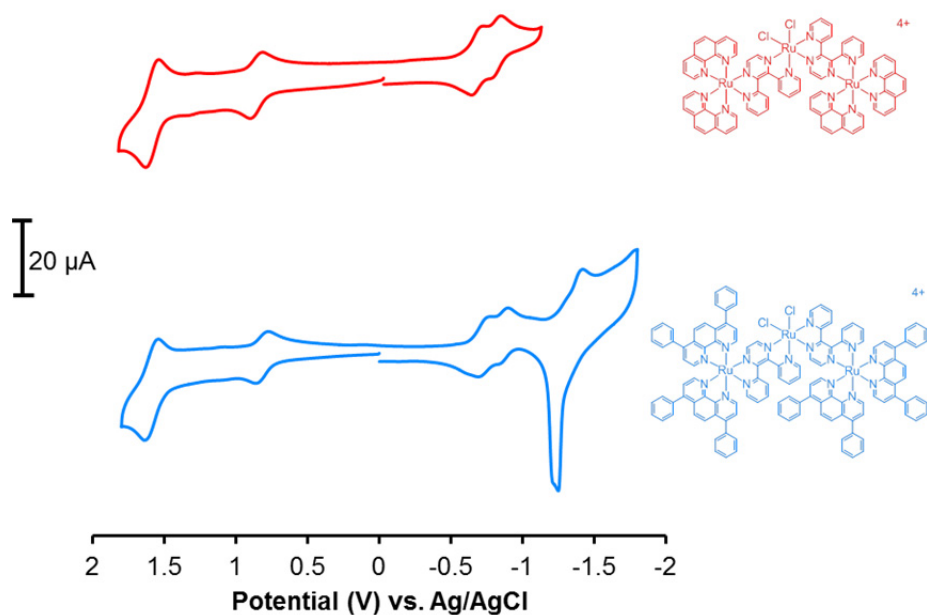


Figure A-16: Cyclic voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—) and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{RuCl}_2](\text{PF}_6)_4$ (—) in RT CH₃CN with 0.1 M Bu₄NPF₆ supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline.

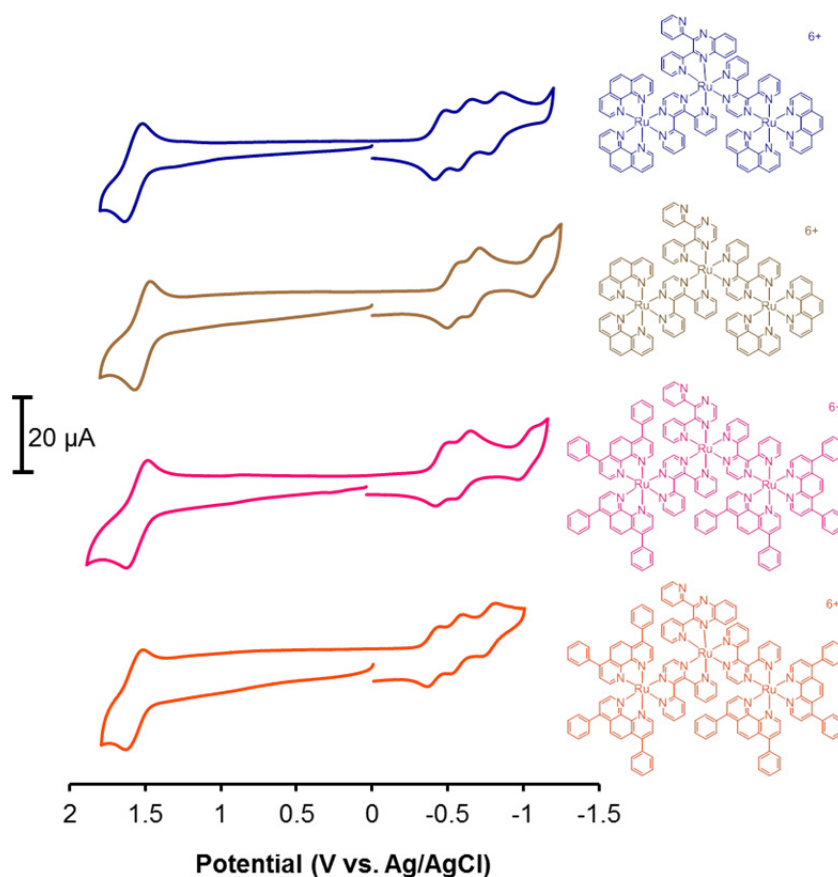


Figure A-17: Cyclic voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline.

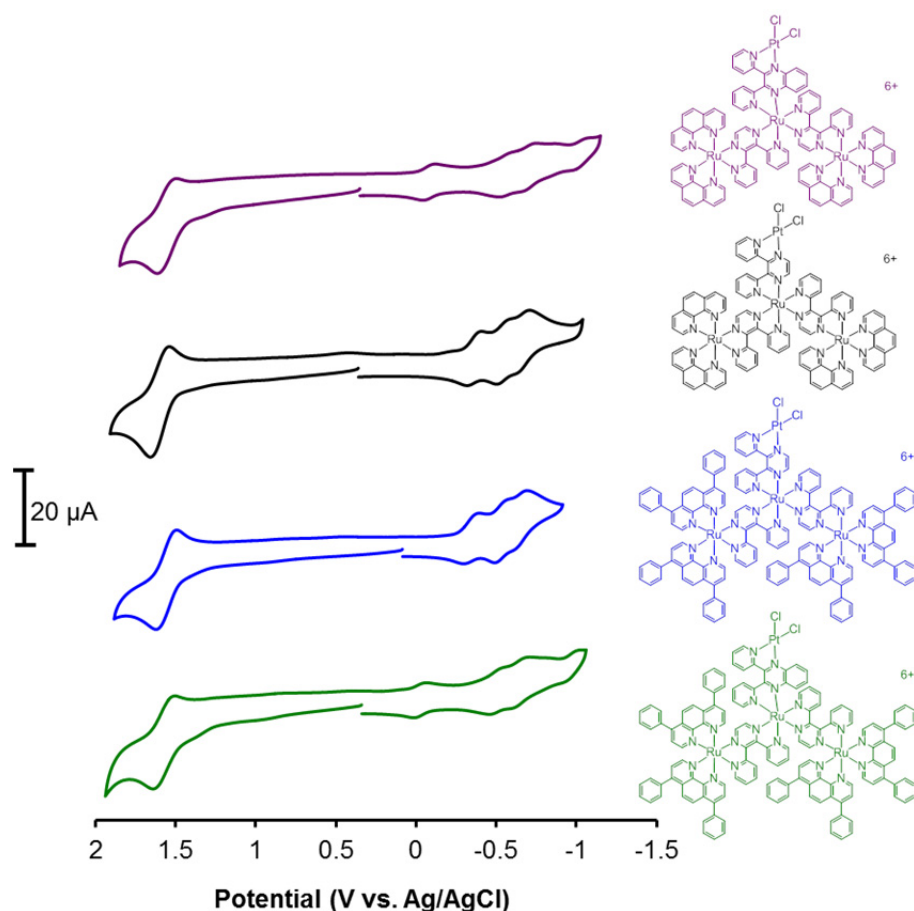


Figure A-18: Cyclic voltammograms of $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{phen})_2\text{Ru}(\text{dpq})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpq})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FeCp}_2^{+/0} = 0.46$ V vs. Ag/AgCl). phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline.

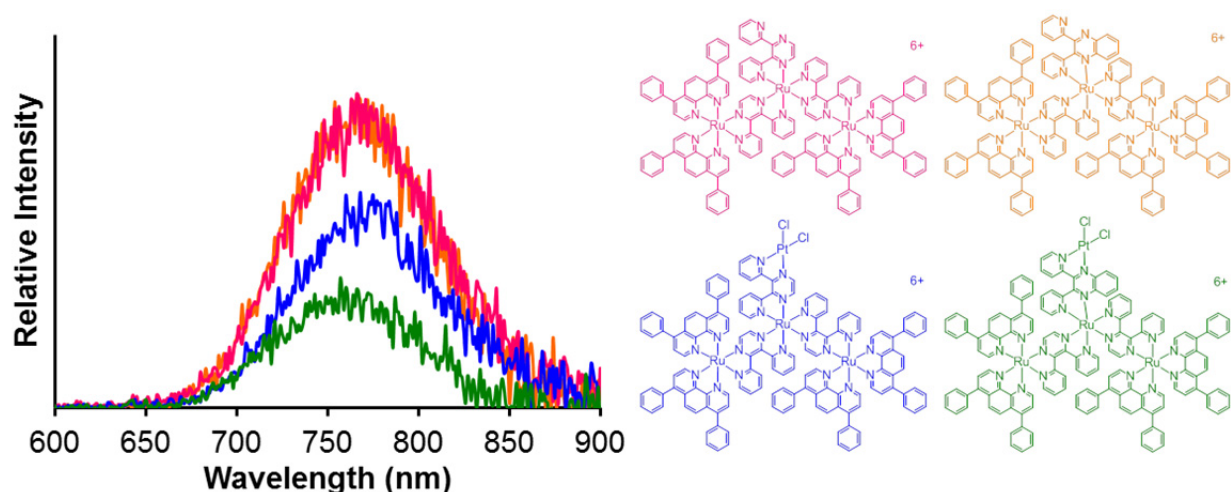


Figure A-19: Relative steady-state emission spectra of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) measured in deoxygenated RT spectral grade CH_3CN in a 1 cm quartz cuvette. Samples were absorbance matched at the excitation wavelength of 540 nm (Abs = 0.30). Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

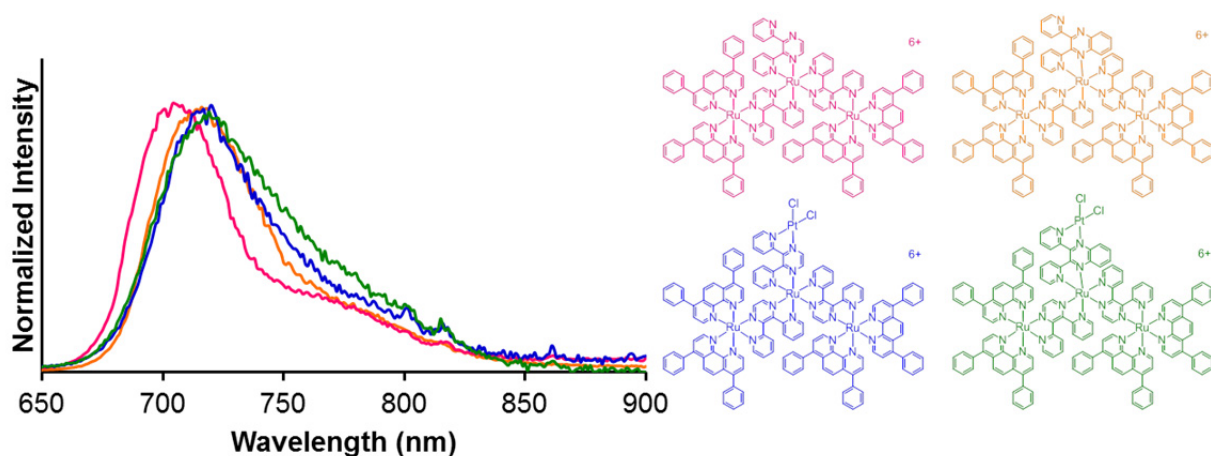


Figure A-20: Normalized emission spectra of $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})](\text{PF}_6)_6$ (—), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (—), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (—) measured at 77 K in a 4:1 EtOH/MeOH glass. Samples were excited at 540 nm. Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

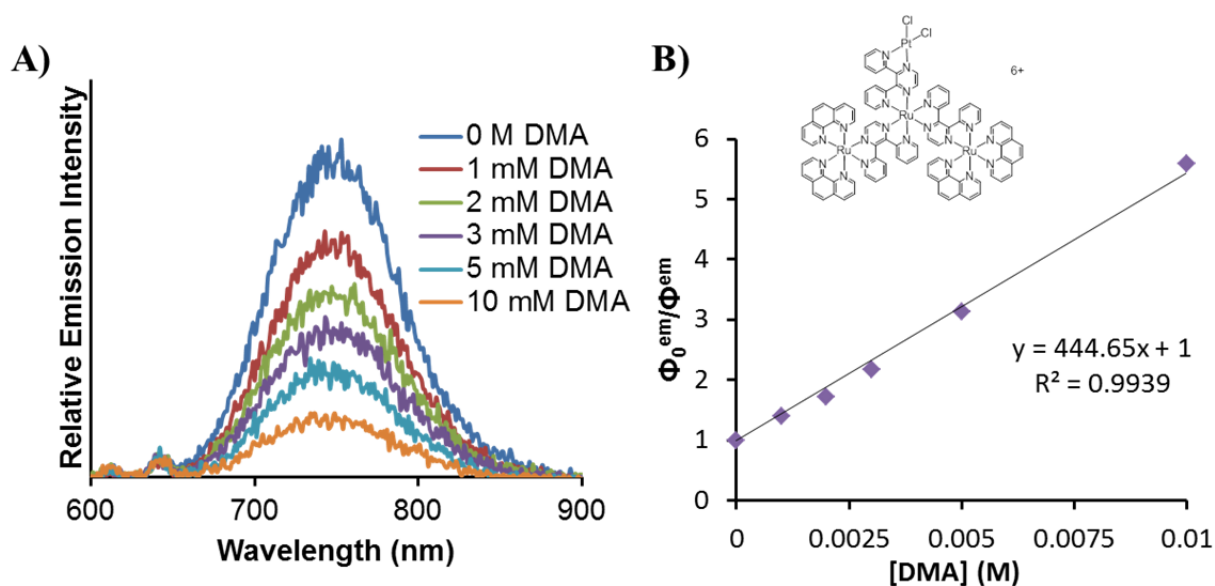


Figure A-21: Emission quenching of $[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpp})\text{PtCl}_2(\text{PF}_6)_6$ illustrating A) the overlaid emission spectra in spectral grade CH_3CN in a 1 cm quartz cuvette with increasing concentrations of DMA from 0 M to 0.01 M and B) the Stern-Volmer plot showing the linear relationship between emission quenching and DMA concentration. DMA = *N,N*-dimethylaniline, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

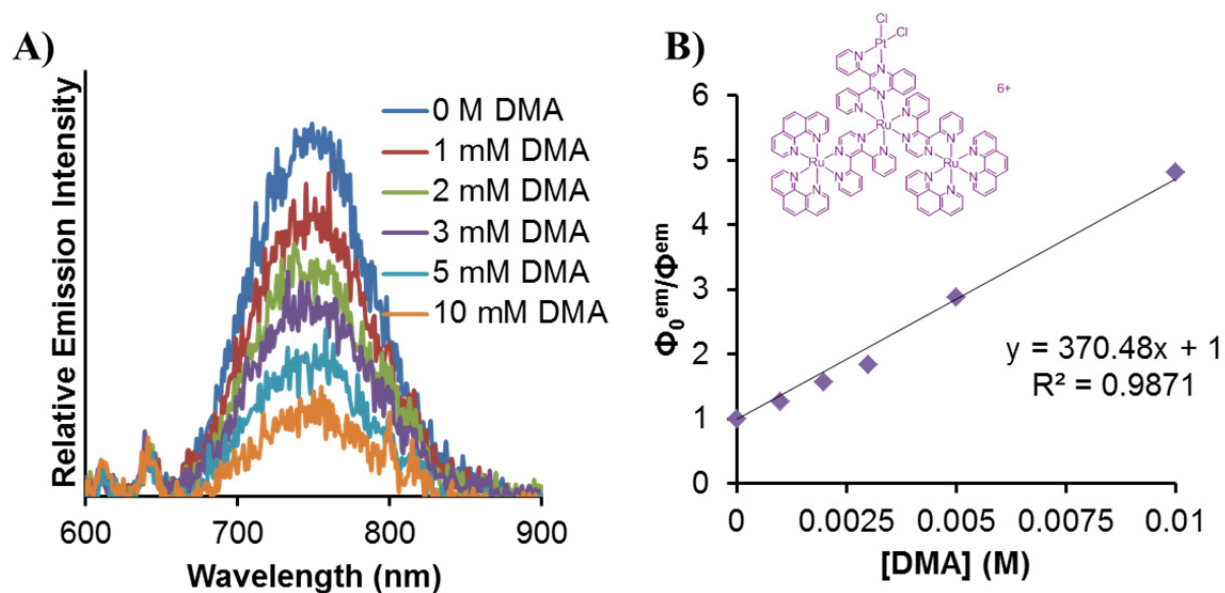


Figure A-22: Emission quenching of $[(\text{phen})_2\text{Ru}(\text{dpp})]_2\text{Ru}(\text{dpq})\text{PtCl}_2(\text{PF}_6)_6$ illustrating A) the overlaid emission spectra in spectral grade CH_3CN in a 1 cm quartz cuvette with increasing concentrations of DMA from 0 M to 0.01 M and B) the Stern-Volmer plot showing the linear relationship between emission quenching and DMA concentration. DMA = *N,N*-dimethylaniline, phen = 1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

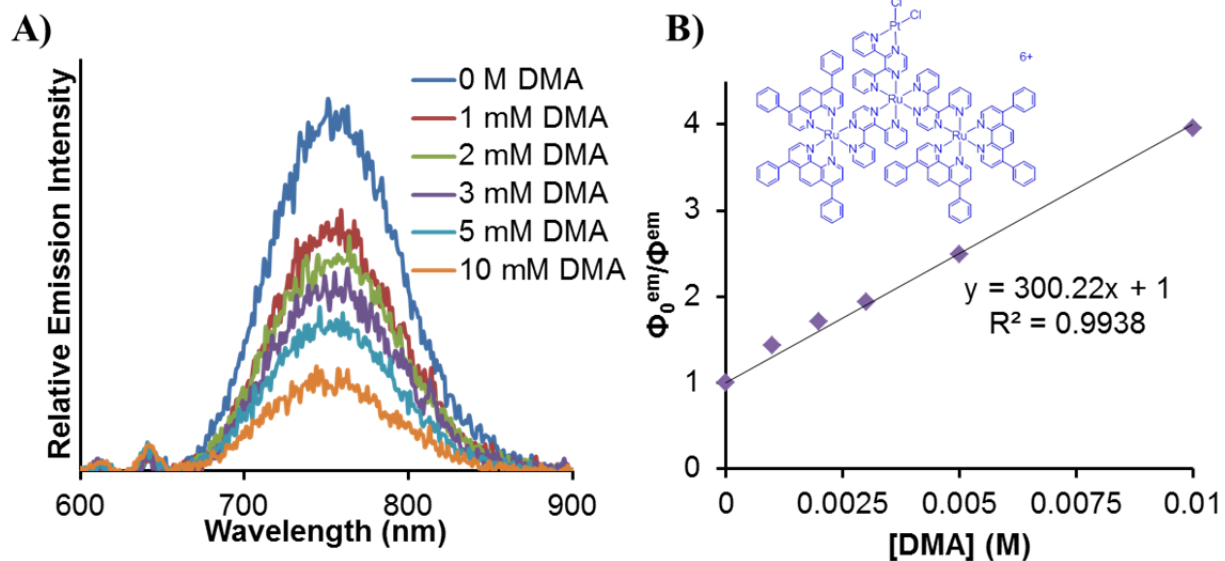


Figure A-23: Emission quenching of $[(Ph_2phen)_2Ru(dpp)]_2Ru(dpp)PtCl_2(PF_6)_6$ illustrating A) the overlaid emission spectra in spectral grade CH_3CN in a 1 cm quartz cuvette with increasing concentrations of DMA from 0 M to 0.01 M and B) the Stern-Volmer plot showing the linear relationship between emission quenching and DMA concentration. DMA = *N,N*-dimethylaniline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine.

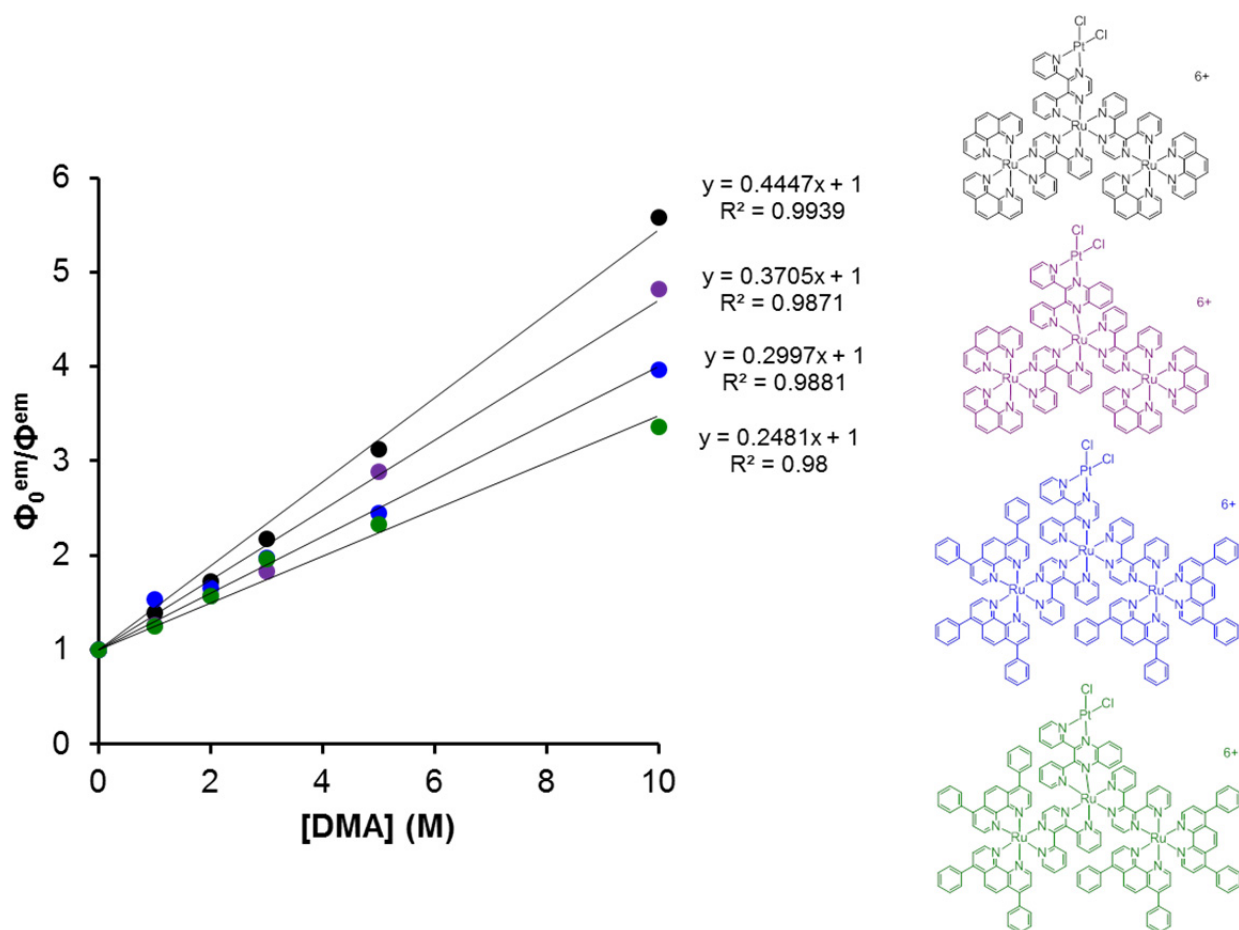


Figure A-24: Stern-Volmer plot showing the linear relationship between emission quenching and DMA concentration for $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (•), $[\{(\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (•), $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpp})\text{PtCl}_2](\text{PF}_6)_6$ (•), and $[\{(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\}_2\text{Ru}(\text{dpq})\text{PtCl}_2](\text{PF}_6)_6$ (•). DMA = *N,N*-dimethylaniline, phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

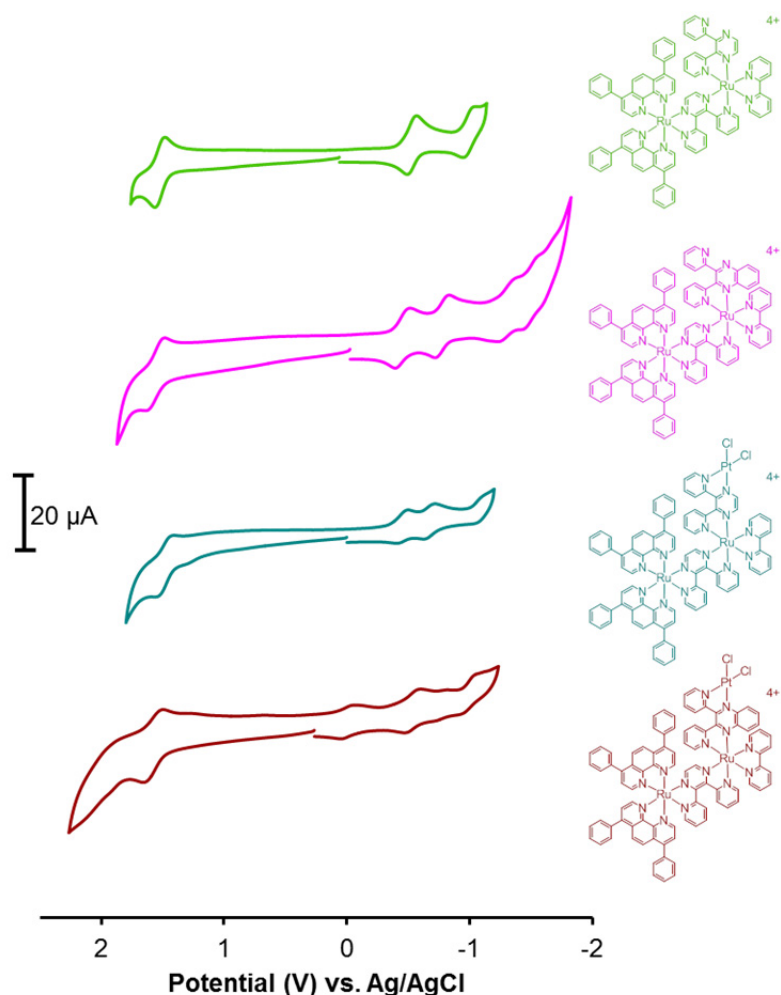


Figure A-25: Cyclic voltammograms of $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})](\text{PF}_6)_4$ (—), $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpp})\text{PtCl}_2](\text{PF}_6)_4$ (—), and $[(\text{Ph}_2\text{phen})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})(\text{dpq})\text{PtCl}_2](\text{PF}_6)_4$ (—) in RT CH_3CN with 0.1 M Bu_4NPF_6 supporting electrolyte under Ar. The scan rate was 0.1 V/s and the electrodes used were a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire pseudo-electrode (converted to Ag/AgCl using ferrocene as an internal standard; $\text{FcP}^{+/0}_2 = 0.46$ V vs. Ag/AgCl). bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline.

Table A-1: Electrochemical and Spectroscopic Data of Ru(II) Polyazine Complexes ^a

Complex ^b	E _{1/2} (V) ^c	Assignment	λ ^{abs} (nm) (ε, M ⁻¹ cm ⁻¹)	λ ^{em} (nm)	Φ ^{em}	τ (ns)
[Ru(bpy) ₃] ²⁺ ^d	1.30 -1.30 -1.49	Ru ^{II/III} bpy ^{0/-} bpy ^{0/-}	450 (15,000)	603 ^e	0.070 ^e	850 ^e
[Ru(phen) ₃] ²⁺ ^f	1.31 -1.31 -1.42	Ru ^{II/III} phen ^{0/-} phen ^{0/-}	443 (17,000)	585 ^e	0.020 ^e	400 ^e
[Ru(Ph ₂ phen) ₃] ²⁺ ^g	1.29 -1.27	Ru ^{II/III} Ph ₂ phen ^{0/-}	460 (30,000)	610 ^e	0.366 ^e	4680 ^e
[Ru(dpp) ₃] ²⁺ ^h	1.72 -0.91 -1.08	Ru ^{II/III} dpp ^{0/-} dpp ^{0/-}	455 (14,000)	636 ^e	ⁱ	270 ^e
[(bpy) ₂ Ru(dpp)] ²⁺ ^j	1.38 -1.01 -1.46	Ru ^{II/III} dpp ^{0/-} bpy ^{0/-}	430 (12,000)	680	0.012	380
[(bpy) ₂ Ru(dpq)] ²⁺ ^k	1.43 -0.74 -1.41	Ru ^{II/III} dpq ^{0/-} bpy ^{0/-}	517 (8,400)	760		< 20
[(bpy) ₂ Ru(dpb)] ²⁺ ^l	1.48 -0.62 -1.25	Ru ^{II/III} dpb ^{0/-} bpy ^{0/-}	550	--	--	--
[(phen) ₂ Ru(dpp)] ²⁺ ^m	1.39 -1.07 -1.35	Ru ^{II/III} dpp ^{0/-} phen ^{0/-}	435 (11,000)	654 ^e	0.027 ^e	252 ^e
[(Ph ₂ phen) ₂ Ru(dpp)] ²⁺ ⁿ	1.39 -1.04 -1.38	Ru ^{II/III} dpp ^{0/-} Ph ₂ phen ^{0/-}	444 (15,000)	697 ^e	0.036 ^e	1000 ^e
[{(bpy) ₂ Ru (dpp)} ₂ RuCl ₂] ⁴⁺ ^o	1.62 0.87 -0.67 -0.83	2 Ru ^{II/III} Ru ^{II/III} dpp ^{0/-} dpp ^{0/-}	625 (26,100)	904	--	< 10
[{(bpy) ₂ Ru (dpp)} ₂ Ru(bpy)] ⁶⁺ ^o	2.00 1.56 -0.47 -0.61	Ru ^{II/III} 2 Ru ^{II/III} dpp ^{0/-} dpp ^{0/-}	545 (23,500)	802	0.003	125
[Ru{(dpp) Ru (bpy) ₂ } ₃] ⁸⁺ ^p	1.55 -0.51 -0.69 -0.84	3 Ru ^{II/III} dpp ^{0/-} dpp ^{0/-} dpp ^{0/-}	422 (36,400)	772	0.001	89
[Ru{(dpp)Ru(phen) ₂ } ₃] ⁸⁺ ^p	1.48	3 Ru ^{II/III}	419 (35,700)	760		87
[Ru{(bpm)Ru(bpy) ₂ } ₃] ⁸⁺ ^q			613 (17,400)			< 10
[Os{(dpp)Ru[(dpp)PtCl ₂] ₂ } ₃] ⁸⁺ ^r			520 (67,100)	875		<10
[{[(bpy) ₂ Ru ₄ (dpp _o) ₂ Ru ₄ (dpp _i) ₂ Ru ₄ Cl ₂] ¹²⁺ ^s	1.61 0.91 -0.46 -0.57 -0.71	4 Ru ^{II/III} Ru _c ^{II/III} 2 dpp _o ^{0/-} 2 dpp _o ^{0/-} 2 dpp _i ^{0/-}	560 (50,900)	895	-	< 10 ^t
[Ru{(dpp)Ru[(dpp) Ru (bpy) ₂] ₂ } ₃] ²⁰⁺ ^u	1.48 -0.45	6 Ru ^{II/III} 9 dpp ^{0/-}	541 (125,000)	809	0.001	55

Complex ^b	E _{1/2} (V) ^c	Assignment	λ ^{abs} (nm) (ε, M ⁻¹ cm ⁻¹)	λ ^{em} (nm)	Φ ^{em}	τ (ns)
[Ru{(dpp)Ru(bpy)(dpp)Ru[(dpp)Ru(bpy) ₂] ₂] ₃ }] ^{26+ v}	1.55	6 Ru ^{II/III}	544 (133,000)	800	-	62
[Ru{(dpp)Ru[(dpp)Ru{(dpp)Ru(bpy) ₂] ₂] ₂] ₃ }] ^{144+ w}			542 (202,000)	786	0.0003	45
[{(bpy) ₂ Ru(dpp)} ₂ Ru(dpp)] ^{6+ x}	1.58	2 Ru ^{II/III}	542 (35,000)	747	0.00061	130
	-0.50	dpp ^{0/-}				
	-0.64	dpp ^{0/-}				
	-1.08	dpp ^{0/-}				
[{(bpy) ₂ Ru(dpp)} ₂ Ru(dpp)PtCl ₂] ^{6+ x}	1.58	2 Ru ^{II/III}	542 (35,000)	750	0.00032	100
	-0.40	dpp ^{0/-}				
	-0.60	dpp ^{0/-}				
	-0.71	dpp ^{0/-}				
[{(phen) ₂ Ru(dpp)} ₂ RuCl ₂] ^{4+ y}	1.56	2 Ru ^{II/III}	625 (34,000)			
	0.79	Ru ^{II/III}				
	-0.70	dpp ^{0/-}				
	-0.84	dpp ^{0/-}				
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ RuCl ₂] ⁴⁺	1.59	2 Ru ^{II/III}	625 (34,000)			
	0.86	Ru ^{II/III}				
	-0.68	dpp ^{0/-}				
	-0.81	dpp ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)RuCl ₂ (bpy)] ²⁺	1.58	Ru ^{II/III}	580 (19,000)			
	0.66	Ru ^{II/III}				
	-0.80	dpp ^{0/-}				
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpp)] ^{6+ z}	1.61	2 Ru ^{II/III}	543 (34,000)	760	0.00101	110
	-0.45	dpp ^{0/-}				
	-0.59	dpp ^{0/-}				
	-1.00	dpp ^{0/-}				
[{(phen) ₂ Ru(dpp)} ₂ Ru(dppq)] ^{6+ y}	1.56	2 Ru ^{II/III}	541 (38,000)	752	0.00101	110
	-0.42	dpp ^{0/-}				
	-0.59	dpp ^{0/-}				
	-0.80	dppq ^{0/-}				
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpp)] ⁶⁺	1.55	2 Ru ^{II/III}	554 (42,000)	764	0.00104	110
	-0.45	dpp ^{0/-}				
	-0.60	dpp ^{0/-}				
	-1.02	dpp ^{0/-}				
[{(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dppq)] ⁶⁺	1.55	2 Ru ^{II/III}	550 (36,000)	764	0.00109	110
	-0.42	dpp ^{0/-}				
	-0.58	dpp ^{0/-}				
	-0.79	dppq ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)Ru(bpy)(dpp)] ⁴⁺	1.53	Ru ^{II/III}	535 (28,000)	762	0.00146	120
	-0.54	dpp ^{0/-}				
	-1.00	dpp ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)Ru(bpy)(dppq)] ⁴⁺	1.54	Ru ^{II/III}	545 (23,000)	762	0.00150	120
	-0.49	dpp ^{0/-}				
	-0.77	dppq ^{0/-}				
[{(phen) ₂ Ru(dpp)} ₂ Ru(dpp)PtCl ₂] ^{6+ z}	1.63	2 Ru ^{II/III}	543 (42,000)	756	0.00071	83
	-0.32	dpp ^{0/-}				
	-0.51	dpp ^{0/-}				
	-0.63	dpp ^{0/-}				
[{(phen) ₂ Ru(dpp)} ₂ Ru(dppq)PtCl ₂] ^{6+ y}	1.58	2 Ru ^{II/III}	541 (38,000)	752	0.00032	80
	-0.05	dppq ^{0/-}				
	-0.42	dpp ^{0/-}				
	-0.59	dpp ^{0/-}				

Complex ^b	E _{1/2} (V) ^c	Assignment	λ ^{abs} (nm) (ε, M ⁻¹ cm ⁻¹)	λ ^{em} (nm)	Φ ^{em}	τ (ns)
[(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpp)PtCl ₂] ⁶⁺	1.56	2 Ru ^{II/III}	550 (42,000)	766	0.00071	77
	-0.33	dpp ^{0/-}				
	-0.53	dpp ^{0/-}				
	-0.64	dpp ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)} ₂ Ru(dpq)PtCl ₂] ⁶⁺	1.57	2 Ru ^{II/III}	550 (31,000)	760	0.00032	75
	-0.02	dpp ^{0/-}				
	-0.50	dpp ^{0/-}				
	-0.65	dpp ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)Ru(bpy)(dpp)PtCl ₂] ⁴⁺	1.54	Ru ^{II/III}	542 (29,000)	765	0.00110	90
	-0.39	dpp ^{0/-}				
	-0.60	dpp ^{0/-}				
	-0.60	dpp ^{0/-}				
[(Ph ₂ phen) ₂ Ru(dpp)Ru(bpy)(dpq)PtCl ₂] ⁴⁺	1.55	Ru ^{II/III}	543 (22,000)	761	0.00052	95
	-0.08	dpq ^{0/-}				
	-0.60	dpq ^{0/-}				
	-0.60	dpp ^{0/-}				

^a Measured in RT CH₃CN unless otherwise noted. ^b bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Ph₂phen = 4,7-diphenyl-1,10-phenanthroline, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, dpb = 2,3-bis(2-pyridyl)benzoquinoxaline, bpm = 2,2'-bipyrimidine. ^c Potentials vs. Ag/AgCl. ^d From references ^{32,42}. ^e Measured in RT H₂O. ^f From reference ²⁵. ^g From reference ³³. ^h From reference ⁴². ⁱ Value not reported. ^j From reference ³². ^k From reference ⁴⁵. ^l From reference ⁴⁴. ^m From reference ³². ⁿ From reference ²⁶. ^o From reference ⁵³. ^p From reference ⁴⁸. ^q From reference ⁵⁴. ^r From reference ⁶¹. ^s From reference ⁵⁵. ^t Approximately 1 ns based on transient absorption spectroscopy. ^u From references ^{56,57}. ^v From reference ⁵⁸. ^w From reference ^{59,60}. ^x From reference ¹¹⁰. ^y From reference ⁷⁸. ^z From reference ¹¹³.