OLIGOPEPTIDE DERIVATIZED [Ru(bpy)$_3$]$^{2+}$ COMPLEXES AS SCAFFOLDS FOR ARTIFICIAL PHOTOSYNTHETIC PROCESSES

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ABSTRACT

The design of supramolecular systems with controlled arrangement of chromophores, electron/energy donors and acceptors remains a challenge in artificial photosynthesis. Biological systems have been known to accomplish the intricacy presented simply by self-assembly. With this inspiration, biomimetic structures that utilize self-assembly to tether donors and acceptors together have been developed and studied. Using oligopeptides as the donor-acceptor bridging linkers and metal-ligand interactions as the only driving force for self-assembly, a variety of compounds with unique photophysical properties could be synthesized. Study of these compounds would provide useful information to fine tune the structures to create long-lived charge separated state and promote efficient solar energy conversion. This thesis describes the synthesis, characterization and application of a series of oligopeptide derivatized [Ru(bpy)$_3$]$^{2+}$ complexes for artificial photosynthesis. Factors affecting photophysical properties are investigated and the first example of using this motif to photocatalyze chemical reactions is thoroughly studied.

A series of [Ru(bpy)$_3$]$^{2+}$ compounds linked to 1-3 Pd$^{2+}$ by oligoaminoethylglycine(aeg) were synthesized for use in photocatalytically dimerizing α-methylstyrene. This is the first example using the aeg chain between a photosensitizer and a reaction center. The products had faster reaction rates and better selectivity than conjugated linkers described in the literature. Catalytic efficiency when linking [Ru(bpy)$_3$]$^{2+}$ with 1, 2 and 3 Pd$^{2+}$ centers was also compared and it was found the complex with three Pd centers had the lowest catalytic activity because of lower chemistry stability. The excited state quenching mechanism is likely to be an electron transfer process based on solvent study, variable temperature study and control experiments using added sacrificial electron donor.
A series of \([\text{Ru(bpy)}_3^{2+}]\) hairpin structures were designed to study impact of side chain change of different oligopeptide linkers (e.g. aminoethylglycine (gly), aminoethylvaline (val), aminoethylleucine (leu) and aminoethylphenylalanine (phe) ) on the emission photodynamics of \([\text{Ru(bpy)}_3]^{2+}\cdot[\text{M(bpy)}_2]^{2+}\) complexes (M = Cu, Pd or Zn). For the Ru-Cu and Ru-Pd complexes, the non-radiative decay rate decreases and the energy barrier for non-radiative decay process increases as the steric bulk of the side chain increases. However, no trend was observed for the Ru-Zn complexes. Solvent study showed all the Ru-Cu and Ru-Pd complexes have a negative trend of non-radiative decay rates vs. Pekar factor but no trend was observed for the Ru-Zn complexes, which indicates Ru-Cu and Ru-Pd have an electron transfer non-radiative decay mechanism and is different from the mechanism of Ru-Zn. The impact of side chain change on the non-radiative decay of Ru-Cu and Ru-Pd is probably due to bulky side chains restrict the necessary geometry change that accompanies the electron transfer.

To expand our study to hexacoordinate metal ions, we have developed a series of \([\text{Ru(bpy)}_3]^{2+}\) complexes with three pendant bpy ligands that can directly coordinate to a hexacoordinate metal ion such as Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) or Mn\(^{2+}\) to form \([\text{Ru(bpy)}_3]^{2+}\cdot[\text{M(bpy)}_3]^{2+}\). Spectrophotometric emission and absorption titrations confirmed a 1:1 metal binding stoichiometry and this was further supported by mass spectrometry and elemental analysis. The formation of \([\text{Ru(bpy)}_3]^{2+}\cdot[\text{M(bpy)}_3]^{2+}\) also caused quenching of the excited state emission of \([\text{Ru(bpy)}_3]^{2+}\) by \(\sim 50\% - 90\%\). Energy transfer mechanism is speculated to be the plausible explanation for this nonradiative quenching because of high energy barrier for electron transfer and spectrum overlap.

Finally, synthetic attempts towards multi-metallic, multi-functional mixed ligand complexes for redox cascade is described in the last chapter. Ru hairpin structures with 8-hydroxyquinoline as the pendant ligands were synthesized. Binding Cu\(^{2+}\) quenched the emission intensity of \([\text{Ru(bpy)}_3]^{2+}\) by electron transfer. Binding Zn\(^{2+}\) formed a two-chromophore complex,
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<td>A</td>
<td>adenine or ampere</td>
</tr>
<tr>
<td>abs</td>
<td>absorption</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile (CH$_3$CN)</td>
</tr>
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<td>aeg</td>
<td>N-(2-aminoethyl)glycine</td>
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</tr>
<tr>
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<td>static and optical dielectric constant</td>
</tr>
<tr>
<td>ds</td>
<td>double stranded</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>molar absorptivity</td>
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</table>
E<sub>0</sub>  formal potential
E<sub>a</sub>  activation energy
EDC  1-ethyl-3-(3-dimethylaminopropyl)carbodimide hydrochloride
ESI+  positive ion electrospray ionization mass spectrometry
Et<sub>2</sub>O  diethyl ether
EtOAc  ethylacetate
EtOH  ethanol
Fmoc  9-fluorenylmethoxycarbonyl
G  guanine
HBTU  O-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HMBC  heteronuclear multiple band coherence
HMQCP  heteronuclear multiple quantum correlation
HOBT  1-hydroxypyridone
HPLC  high performance liquid chromatography
hq/HQ  8-hydroxyquinoline
HR  high resolution
I  integrated emission
i  current
iDNA  inorganic DNA
K<sub>eq</sub>  equilibrium constant
K<sub>d</sub>  dissociation constant
k<sub>r</sub>  rate of radiative decay
k<sub>nr</sub>  rate of nonradiative decay
λ  wavelength
max  maxium
MeOH  methanol
min  minute
MLCT  metal-to-ligand charge transfer
MS  mass spectrometry
m/z  mass to charge ratio
NMR  nuclear magnetic resonance
OrBu  tert-butoxy
Φ  fluorescence quantum yield
ppm  parts per million
PNA  peptide nucleic acid
py  pyridine
RNA  ribonucleic acid
SCE  saturated calomel electrode
ss  single stand
T  temperature
T<sub>m</sub>  melting temperature
τ  lifetime
TBAP  tetrabutylammonium perchlorate
THF  tetrahydrofuran
TFA  trifluoroacetic acid (CF<sub>3</sub>COOH)
tpy  2,2′6′,2″-terpyridine
UV  ultraviolet
V  volt
vis  visible
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Chapter 1

Directed Self-Assembly of Inorganic Redox Complexes with Artificial Peptide Scaffolds

1.1 Introduction

Nature generally relies on self-assembly to create macromolecules that are essential for life. For example in the photosynthetic reaction center of purple bacteria (Figure 1-1), the redox cofactors such as the primary electron donor (P 865) and quinone electron acceptors (QA and QB) are tethered through non-covalent interactions and self-assembly. In photosynthetic organisms of this kind, chromophores absorb light, energy is transferred by a redox cascade to a series of electron acceptors and specialized reaction centers, and then the captured solar energy is converted into chemical energy using electron-transfer reactions.

Many supramolecular synthetic approaches have aimed to create artificial photosynthetic systems capable of shuttling excited state electrons along redox cascades that might ultimately be used for photocatalysis and solar fuel production. These include both organic and inorganic motifs, as well as fullerene, ruthenium, and porphyrin complexes. Most contain multiple chromophores and redox centers. The synthetic challenge is to find a facile way to construct large, expandable, robust, and versatile supramolecular structures with the desired functional ability for artificial photosynthesis.

Most non-covalent interactions that nature utilizes to assemble macromolecules include solvophobic forces, electrostatic interactions with permanent or induced dipoles, dispersive and charge-transfer interactions, and hydrogen bonds. In synthetic
supramolecular designing, hydrogen bonding, host – guest, and metal coordination are the most common interactions to control self-organization and to hold the supramolecular entities together. Supramolecular structures based on metal-ligand coordination emerged in the 1960s as a result of studies by Peterson and coworkers, who used organic crown ethers as the hosts. These were followed by more complex ensembles using cryptand and spherand hosts that were developed by Lehn and Cram. More recent examples include using metal-ligand coordination to self-assemble molecules to form biologically relevant enzyme mimics, catalysts, and molecular devices such as light harvesters, sensors, wires and rectifiers.

Metal-ligand coordination chemistry was first used to modify nucleic acid assemblies by Shionoya and coworkers in 1999 and has been extensively studied since then. In DNA and RNA, the nucleobases along the sugar phosphate backbone can be programmed in any sequence and length by choosing the desired nucleobases and desired number of repeating units. Amino acids are also of modular, repeating units that nature uses to build macromolecules essential to life. In this chapter, we focus on classic and most recent biomimetic structures that incorporate metal-nucleobase or metal-ligand coordination into natural nucleic acids and their analogues such as PNA or oligopeptides to direct the self-assembly of inorganic redox complexes.
Figure 1-1. Primary charge separation in the photosynthetic reaction center of purple bacteria. (Reprinted with permission from [1]. Copyright 2006 American Chemical Society.)
1.2 DNA with Metal-Ligand Pairs

Replacing natural nucleobases in DNA with metal-mediated base pairs could construct or induce ordered structures with greater thermal stability. Because of the unique optical, electrochemical, magnetic, and catalytic properties of the metal complexes, DNA duplexes with metallo-base pairs could potentially be used as artificial “DNAzymes”, DNA machines, as well as DNA nanomaterials such as wires and magnetic devices. In this motif, the Watson-Crick base pairs are replaced with a metal ion and complementary ligands with respect to the coordinative saturation of the metal center (Figure 1-2). For example, a tetracoordinate metal ion such as Cu²⁺, Ni²⁺, Pd²⁺, Pt²⁺ requires a bidentate-bidentate or tridentate-monodentate ligand pair. A hexacoordinate metal ion such as Co²⁺ or Fe²⁺ requires a tridentate-tridentate ligand pair as the complementary ligands.

The first “metallo-base pair” was reported by Shionoya and coworkers in 1999 using β-C-nucleoside with phenylenediamine as the ligand and Pd²⁺ as the metal center. The formation of the metal-base pair was confirmed with ¹H NMR titration by monitoring the proton resonance shift in the aromatic region to lower field as Pd²⁺ was added to the solution. When the concentration of Pd²⁺ reached half the concentration of β-C-nucleoside, the shift was complete, which indicated β-C-nucleoside and Pd²⁺ formed a stable 2:1 complex with a high binding constant. The formed product was also analyzed using mass spectrometry, which showed the molecular ion of the duplex.

Following that initial report, a number of additional examples have emerged in the past decade. Shionoya and coworkers also developed an artificial DNA with hydroxypyridone nucleobases as ligands. Adding octahedral Fe³⁺ ions to this DNA single strand
Figure 1-2. Artificial metal-mediated base pairing system (a computer-generated model) (Reprinted with permission from [48]. Copyright 2012 American Chemical Society.)
self-assembled into Fe-DNA triplex (Figure 1-3A). Three different artificial DNA single strands were synthesized, each with 2 - 4 hydroxypyridones on the backbone. Fe$^{III}$-mediated triple-strand formation was monitored by changes in the UV-Vis absorption at different concentrations of Fe$^{III}$, and it was found that the chelation reaction took 2 days at 85 °C to go to completion. Circular dichroism (CD) data indicated that the Fe$^{III}$ centers were asymmetric; the helicity of each triple-stranded DNA assembly induced a specific configuration of the octahedral Fe$^{III}$ center.

Müller and coworkers determined the first solution structure of a B-type oligonucleotide double helix that contained three consecutive Ag(I)-mediated base pairs with a series of NMR experiments including [$^1$H,$^1$H]-NOESY and [$^1$H,$^{15}$N]-HSQC (Figure 1-3B). The three metal ions were located along the helical axis and incorporation of the artificial metal-containing base pairs proceeded without major conformational distortions. Ag-Ag distances between consecutive metal-mediated base pairs was determined to be 3.92 Å and 3.97 Å for the lowest-energy structure. A feature of the structure is the potential for metal-metal interactions because of the flexibility of the duplex and close proximity of the metal ions.

Recently, Carell and coworkers determined the crystal structure of a DNA polymerase with a salen-type base pair and Cu$^{2+}$ as the metal center (Sal-Cu$^{2+}$(en)-Sal). The Cu(II)-mediated base pair was found to have a square-planer geometry and fit with the B-type duplex (Figure 1-4).
Figure 1-3. (A) Schematic representation of the formation of a linear Fe$^{III}$ array inside an artificial DNA triplex. (Reprinted with permission from [49]. Copyright 2009 Wiley and Sons) (B) (Left) Structure of the three consecutive metal-mediated base pairs in DNA. The natural adenine–thymine base pairs are colored in green, the imidazole nucleobases in gold, and the Ag$^+$ ions are shown as blue spheres. (Right) Top view on the three consecutive metal-mediated base pairs along the helix axis. (Reprinted with permission from [50]. Copyright 2010 Nature Publishing Group)
Figure 1-4. Sal–Sal mismatched base pairs and metal-mediated Sal–Cu$^{2+}$(en)–Sal base pairs inside a DNA polymerase, Bst Pol I (PDB 2XY5 and 2XY6). Native A–T base pairs are overlaid. (Reprinted from [51] Copyright 2011 Nature Publishing Group.)
1.3 PNA Duplexes with Metal-Ligand Pairs

Peptide nucleic acid (PNA) has been used to replace DNA to study metal ligand pairs in nucleic acid duplexes because of the ionic interaction of metal ions with the backbone phosphate in DNA. PNA uses an aminoethylglycine (aeg) peptide backbone which is charge neutral (Figure 1-5). The first example of a ligand-modified duplex PNA structure for coordination of a metal ion to form a metallobase crosslink was developed by Achim and coworkers. A bipyridine (bpy) derivative was inserted into two complementary PNA strands using standard solid phase peptide synthesis. Ni$^{2+}$, Pd$^{2+}$ or Pt$^{2+}$ formed well-known square-planar complexes [Ni(bpy)$_2$]$^{2+}$, [Pd(bpy)$_2$]$^{2+}$ or [Pd(bpy)$_2$]$^{2+}$, respectively, with bpy. Titration of these metal ions to the PNA single strand was expected to form PNA duplex linked by a metallobase pair. This was experimentally confirmed using UV-vis spectroscopic titrations and circular dichroism (CD). Of the metal ions, addition of only the Ni$^{2+}$ was found to increase the melting temperature, an indication of stabilization of the PNA duplex.

In a recent paper, Achim and coworkers reported an interesting study of coordination-driven inversion of handedness in ligand-modified PNA (Figure 1-6A). γ-(S)-methyl-aminoethylglycine was used as the backbone to induce a preference for a right-handed PNA duplex structure without metal binding. The chiral PNA monomer had a 2, 2':6', 2''-terpyridine (tpy) ligand instead of a nucleobase and PNA duplexes that contained one or two tpy ligands formed [Cu(tpy)$_2$]$^{2+}$ complexes in the presence of Cu$^{2+}$. When [Cu(tpy)$_2$]$^{2+}$ formed within one PNA duplex, the handedness of the duplex kept the same conformation (right-handed) because of the chiral center on the backbone. However, when the tpy ligands in [Cu(tpy)$_2$]$^{2+}$ were from two different PNA duplexes, the handedness switched from right- to
Figure 1-5. Cartoon Representation of a Metal-Containing, Ligand-Modified Nucleic Acid Duplex \( ^{54} \) (Reprinted with permission from [54]. Copyright 2011 American Chemical Society.)
Figure 1-6. (A) Switch of handedness of PNA duplex by coordination of Cu$^{2+}$ between two PNA duplexes. (Reprinted with permission from [53]. Copyright 2011 American Chemical Society.) (B) (Left) Coordination of Zn$^{2+}$ to bpy ligands in PNA duplex. (Right) Schematic representation of PNA molecules self-assemble on a gold surface in which the blue circle represents cysteine, the curl represents PNA, and the light brown circle represents ferrocene. The monolayer was analyzed using conductive probe atomic force microscopy. (Reprinted with permission from [55]. Copyright 2012 American Chemical Society.)
left-handed.

Charge transfer through ferrocene-modified PNA on gold electrodes with and without coordination of Zn\(^{2+}\) has also been studied by Waldeck and coworkers\(^{55}\) (Figure 1-6B). The C-terminus was modified with cysteine and the N-terminus contained ferrocene as the redox probe. The PNA monomer was also modified with bpy as the ligand for coordination of Zn\(^{2+}\). Characterization of the PNA in solution showed the stability of the duplexes was not affected significantly by the formation of [Zn(bpy)\(_2\)]\(^{2+}\). The charge transfer properties of self-assembled monolayers of these molecules were examined electrochemically (for ferrocene-terminated PNAs) and by conductive probe atomic force microscopy (for cysteine-terminated PNAs). Both electrochemical and single molecule studies showed that the bpy modification and Zn\(^{2+}\) binding did not significantly affect the charge transfer of the PNA duplexes.

Waldeck and coworkers also reported the first example of studying photoinduced charge transfer by connecting a [Ru(bpy)\(_3\)]\(^{2+}\) donor to a bis(8-hydroxyquinolinate)\(_2\) copper [Cu(HQ)\(_2\)] acceptor through a PNA bridge\(^{56}\) (Figure 1-7A). A PNA monomer that contained a [Ru(bpy)\(_3\)]\(^{2+}\) attached to the backbone was synthesized and introduced onto PNA oligomers at different positions, either terminal or central. When [Ru(bpy)\(_3\)]\(^{2+}\) was at the central position, an acetyl group was introduced to the complementary PNA strand at the same position. [Cu(HQ)\(_2\)] was created by coordination of Cu\(^{2+}\) to a pair of HQ ligands in the PNA duplex. The synthesized PNA duplexes sequences and their melting temperatures are shown in Table 1-1.

The HQ-modified PNA duplexes without Cu\(^{2+}\) showed a decrease of melting
temperature comparing to the unmodified duplex P indicating mismatch of the base pair caused decrease in stability. The formation of $[\text{Cu(HQ)}_2]$ increased the melting temperature because the increased stability as the $[\text{Cu(HQ)}_2]$ functions as an alternative base pair.
Table 1-1. Sequences and Melting Temperatures $T_m$ of the PNA Duplexes with and without Cu$^{2+}$ (Reprinted with permission from [56]. Copyright 2014 American Chemical Society.)

<table>
<thead>
<tr>
<th>Duplex</th>
<th>Sequence</th>
<th>$T_m$(°C)$^a$</th>
<th>no Cu$^{2+}$</th>
<th>with Cu$^{2+}$</th>
</tr>
</thead>
</table>
| P      | H-AGTGATCTAC-H  
         | H$_2$N-Lys-TCACAGATG-H | 67            | 67             |
| P-AG   | H-Ru$^{2+}$AGGATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TQCTAGATG-H | 56            | >75            |
| P-AA   | H-Ru$^{2+}$AGGATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TQCTAGATG-H | 56            | >75            |
| P-AG-IQ| H-Ru$^{2+}$AGGATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TQCTAGATG-H | 58            | 52             |
| P-AA-IQ| H-Ru$^{2+}$AGGATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TTACTAGATG-H | 58            | 56             |
| P-AGTGA| H-Ru$^{2+}$AGTGAQCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TCACAGATG-H | 47            | >75            |
| P-AT-P' | H-AGTGARu$^{2+}$ATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TCAATQAGATG-H | 48            | 70             |
| P-AG-P' | H-AGTGARu$^{2+}$ATCTAC-Lys-NH$_2$  
         | H$_2$N-Lys-TCAATQAGATG-H | 48            | 66             |

Ru = [Ru(bpy)$_3$]$^{2+}$, Q = 8-hydroxyquinoline and B = acetyl
Emission titration of the duplexes showed a decrease of the emission intensity of \([\text{Ru(bpy)}_3]^{2+}\) as the \(\text{Cu}^{2+}\) concentration increased, which the authors report was caused by electron transfer from \([\text{Ru(bpy)}_3]^{2+*}\) to Cu(HQ)_2. The lifetime of P-AG/Cu and P-AGTAG/Cu (Table 1-1) were 246 ns and 412 ns, respectively, and the major structural difference between these two duplexes was the donor-acceptor distance. The rate constant for electron transfer from \([\text{Ru(bpy)}_3]^{2+*}\) to Cu(HQ)_2 was 1.8 \(\mu\text{s}^{-1}\) for P-AG and 0.24 \(\mu\text{s}^{-1}\) for P-AGTCA. The decay parameter \(\beta\) was determined to be 0.4 Å\(^{-1}\), which is comparable to \(\beta\) values reported for hole transfers in DNA when the donor and acceptor are separated by 3-6 base pairs.\(^{57,58}\)

The P-AG and P-AG-P’ (Table 1-1) were designed to study the steric effects on the electron transfer of the PNA duplexes. For P-AG, \([\text{Ru(bpy)}_3]^{2+}\) was at the end of the duplex. For P-AG-P’, \([\text{Ru(bpy)}_3]^{2+}\) was in the middle, so it couldn’t access the top of the nucleobases stack. The excited state decay of \([\text{Ru(bpy)}_3]^{2+}\) in P-AG/Cu could be fit into a single exponential decay which had a life time of 265 ns. The excited state decay of \([\text{Ru(bpy)}_3]^{2+}\) in P-AG-P’/Cu could only be fit to a double exponential decay; these two components had lifetimes of 196 ns and 442 ns, respectively. The presence of two separate decay components was theorized to be caused by differences in the conformations available for the \([\text{Ru(bpy)}_3]^{2+}\).

Figure 1-7B shows the case of P-AG for which one of the three bpy ligands participates in a \(\pi-\pi\) stacking with a terminal base pair. This might restrict the flexibility of the \([\text{Ru(bpy)}_3]^{2+}\) and lead to the result that \([\text{Ru(bpy)}_3]^{2+*}\) complex in P-AG had one dominant conformation with respect to the Cu(HQ)\(_2\). The double exponential decay in P-AG-P’ suggested that the PNA existed at least as two distinct conformations that exchanged slower than the electron transfer process between \([\text{Ru(bpy)}_3]^{2+*}\) and Cu(HQ)_2 to create two distinct electron transfer
Figure 1-7. (A) Photoinduced electron transfer from \([\text{Ru(bpy)}_3]^{2+}\) donor to a \([\text{Cu(HQ)}_2]\) acceptor through a PNA bridge. (B) \(\pi-\pi\) interaction of one bpy (green) in \([\text{Ru(bpy)}_3]^{2+}\) with a terminal base pair (red) (Reprinted with permission from [56]. Copyright 2014 American Chemical Society.)
1.4 Electron Donor-Acceptor Systems with a Peptide Bridging Linker

In designing electron donor-acceptor systems, varying the donor-acceptor distance and changing the donor-acceptor ratio is helpful to tune the electronic properties, promote forward electron transfer, and prevent back electron transfer. Peptide coupling chemistry provides an easy way to systematically change the structural properties of the donor-acceptor systems and arrange different chromophores as well as redox centers in specific arrays. Several examples describing the classic system of \([\text{Ru(bpy)}_3]^{2+}\) linked to an organic donor phenothiazine (PTZ) and acceptor anthraquinone (ANQ) by an oligoproline backbone have been extensively reviewed.\(^{59-61}\) Changing the donor-acceptor distance and ratio were easily achieved by changing the number of monomers between donor(s) and acceptor(s) and the number of donor/acceptor substituted monomers introduced to the backbone by solid state peptide synthesis.

Fukuzumi and coworkers showed that organic photovoltaic cells using supramolecular complexes of porphyrin-functionalized \(\alpha\)-polypeptide with fullerene enhanced the photoelectrochemical performance. Broader photo response was accomplished by increasing the number of porphyrin units in this \(\alpha\)-polypeptide (Figure 1-8).\(^{62}\) Three porphyrin-functionalized \(\alpha\)-polypeptides were synthesized and contained 2, 4, or 8 porphyrin units. The highest power conversion efficiency of 1.3% and a maximum incident photon-to-photocurrent efficiency were achieved using the porphyrin octamer.
Figure 1-8. Porphyrin compounds used and the illustration of supramolecular assembly between porphyrin–peptide oligomers and fullerenes (Reprinted with permission from [60]. Copyright 2005 American Chemical Society.)
Guldi and coworkers developed an interesting bio-inspired nanohybrid in which a cyclopeptide bearing an electron-donor unit ([2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole, exTTF) (Figure 1-9A) was coupled by a β-sheet-like hydrogen-bond system to another cyclopeptide bearing a photoactive electron-acceptor unit (C$_{60}$) (Figure 1-9B). Three forms of cyclopeptidic heterodimers could form, in which the isomer shown in Figure 1-9C was more favorable because of van der Waals interactions between the C$_{60}$ and exTTF units. An observation of 50 mV shift of the exTTF/exTTF$^{2+}$ couple in cyclic voltammetry in the cyclopeptidic heterodimer comparing to the monomer indicated a weak intramolecular electronic interaction between the exTTF moiety and the fullerene-based peptide in the ground state. Electron transfer from exTTF to C$_{60}$ was confirmed by time-resolved transient absorption measurements. The fullerene moiety was photoexcited at 387 nm by 150-fs laser pulses. The fullerene singlet excited state decayed very quickly (i.e., 0.055 ns), and new transient absorption peaks at 680 and 1,040 nm (fingerprints of exTTF$^+$ and C60$^-$) confirmed the formation of the radical ion pair state, C60$^-$/exTTF$^+$. A very recent example developed by Sakai and coworkers used the strategy of peptide coupling reactions to increase the number of methyl viologen (MV) units in a [Ru(bpy)$_3$]$^{2+}$-MV donor-acceptor system linked by L-Asp-based peptide backbones (Figure 1-10). These three structures had 2 (RuMV$_2$), 4 (RuMV$_4$) or 6 (RuMV$_6$) MV units and are shown in Figure 1-10. All of these dyads underwent efficient intramolecular quenching and formed the charge-separated state Ru$_{III}$-MV$^+$. The forward electron transfer rate constants ($k_{ET}$) for the major components were calculated to be $k_{ET} = 1 - 8 \times 10^{10}$ s$^{-1}$, whereas the
backward electron transfer rate constants \( (k_{\text{BET}}) \) were determined to be \( 5 - 6 \times 10^7 \text{ s}^{-1} \). This is the first example of a \( \text{Ru(bpy)}_3^{2+}-\text{MV}^{2+} \) system in which three orders of magnitude of difference is achieved between the forward and backward electron transfer rate constants.
Figure 1-9: Cyclopeptide with (A) exTTF and (B) C_{60} moiety. (C) Computer-generated structure of heterodimer showing photo-induced electron transfer facilitated by the proximity of the donor and acceptor units (exTTF and C_{60}, respectively). (Reprinted with permission from [61]. Copyright 2007 National Academy of Sciences, U.S.A)
Figure 1-10. Structures of the peptide-based Ru(bpy)$_3^{2+}$-MV$^{2+}$ dyads, together with a model system (RuMe$_2$) prepared in this study. (Reprinted with permission from [62]. Copyright 2010 Royal Society of Chemistry.)
1.5 Metal-Linked Artificial Oligopeptides

In the above examples of DNA and PNA with metal-ligand pairs, the main driving force to form the DNA or PNA duplex was still the Watson-Crick base pairing. The metallobase pairs serve only to increase the stability of the duplex. By replacing the DNA backbone with a PNA backbone, the ionic interaction of metal ions with the backbone phosphates is avoided. However, in the scaffold of PNA, the electrochemical irreversibility of the nucleic acids still restricts the possibility of using PNA with metallobase pairs to build redox cascades for long range electron transfer. Our group has recently developed supramolecular structures that rely solely on metal ion coordination to form metal-linked artificial oligopeptide duplexes.\textsuperscript{65-73} Replacing the phosphate backbone with oligopeptides and nucleic acids with metal-ligand interactions to drive assembly of supramolecular structures retains the advantages of using a programmable and expandable backbone, resolves the issues such as metal binding to nucleobases and backbone phosphates, and furthermore avoids base pairs’ undesired electrochemical properties. The oligopeptides have been built from an aminoethylglycine (aeg) backbone with only pendant ligands using either solid or solution phase peptide coupling chemistries. The pendant ligands including pyridine (py), bipyridine (bpy), 8-hydroxyquinoline (HQ), terpyridine (tpy), phenyl-terpyridine (Φ-tpy) were chosen based on their denticity and the coordination number of the resulting metal complex. For example, a tetracoordinate metal requires two bidentate ligands to form a $[2 \times 2]$ complex or a tridentate ligand and a monodentate ligand to form a $[3 \times 1]$ complex. A hexacoordinate metal requires two tridentate ligands or three bidentate ligands to form a $[3 \times 3]$ or a $[2 \times 2 \times 2]$ motif. These metal-linked oligopeptide duplexes with multiple metal centers can potentially
be used for catalysis, artificial photosynthesis and molecular electronics.

A bpy-substituted tripeptide with three pedant bpy ligands was first synthesized using solid phase peptide synthesis. Adding Fe$^{2+}$ to a solution containing this tripeptide led to the formation [Fe(bpy)$_3$]$^{2+}$ confirmed by UV-vis titration which showed a stoichiometric point at ~1:1 molar equivalence of Fe$^{2+}$: tripeptide. Mass spectrometry revealed the molecular ion peak of a complex consisting of two [Fe(bpy)$_3$]$^{2+}$ centers crosslinking the two tripeptide strands.

UV-vis emission titration of Cu$^{2+}$ to the same tripeptide showed an equivalence point of ~ 1.6 Cu$^{2+}$: tripeptide. Together with mass spectrometry, this confirmed two tripeptide strands were crosslinked by three Cu$^{2+}$ ions, forming three [Cu(bpy)$_2$]$^{2+}$ complexes. This is the first example using metal coordination as the only driving force to direct the self-assembly of oligopeptide duplex. (Figure 1-11A)

Φ-tpy containing artificial oligopeptides (n=1-4) have also been shown to form duplexes upon the addition of a hexacoordiante metal ion such as Fe$^{2+}$ or Co$^{2+}$. In these reported structures, the formation of geometric isomers (i.e., parallel and antiparallel structures, misalignment) is possible. To eliminate the formation of these isomers, three strategies have been applied: self-complementary heterofunctional sequences, palindromic synthetic routes, and hairpin structures.

Dipeptides containing py-tpy and py-Φ-tpy, as well as tripeptide containing py-bpy-tpy formed self-complementary duplexes up on the addition of Cu$^{2+}$. EPR studies of the Cu-crosslinked py-bpy-tpy tripeptide duplex revealed stronger Cu-Cu coupling comparing with the Cu-crosslinked dipeptide duplex, indicating the Cu-Cu
distance in the tripeptide duplex is more suitable for metal-metal interaction.

Another strategy to eliminate the formation of isomers is the palindromic synthetic scheme. Ligand-substituted aeg outside monomers were attached to a ligand-substituted iminodiacetic acid central monomer to create a homofunctional tripeptide in a one-pot reaction. The ligands used were bpy or HQ. Self-assembling of Cu\(^{2+}\) to the palindromic bpy-bpy-bpy tripeptide formed Cu-crosslinked tripeptide duplex with Cu-Cu distance larger than 6 Å suggested by EPR study\(^{65}\)(Figure 1-11D). Binding Zn\(^{2+}\) to the HQ ligands in the palindromic HQ-HQ-HQ tripeptide showed cooperative behavior.\(^{67}\) The luminescent HQ and Zn(HQ)\(_2\) complex provided an alternative way to study the metal binding kinetics. (Figure 1-11E)

Inspired from the self-complementary RNA hairpin loops, our group has also designed a Ru-hairpin motif using aeg-functionalized [Ru(bpy)\(_3\)]\(^{2+}\) with pendant bpy ligands (Scheme 1-1). These Ru-hairpin structures have 1-6 aeg chains with pedant bpy ligand(s) on each chain. Coordination of a tetracoordinate metal ion such as Cu\(^{2+}\), Pd\(^{2+}\) or Zn\(^{2+}\) crosslinks the aeg chains and closes the Ru-hairpin loop (Figure 1-12). Coordination of one Cu\(^{2+}\) to two bpy ligands from two Ru-ss molecules crosslinked these two molecules and formed a [Ru(bpy)\(_3\)]\(^{2+}\) -[Cu(bpy)\(_2\)]\(^{2+}\) -[Ru(bpy)\(_3\)]\(^{2+}\) trimetallic complex.\(^{68}\) Coordination of one Cu\(^{2+}\) or Zn\(^{2+}\) to a pair of bpy ligands in Ru-4 closed the hairpin loop and formed a [Ru(bpy)\(_3\)]\(^{2+}\) -[Cu(bpy)\(_2\)]\(^{2+}\) or [Ru(bpy)\(_3\)]\(^{2+}\) -[Zn(bpy)\(_2\)]\(^{2+}\) dimetallic complex.\(^{68}\) It has also been noticed that binding Cu\(^{2+}\) or Zn\(^{2+}\) quenched the emission intensity of [Ru(bpy)\(_3\)]\(^{2+}\). Cu\(^{2+}\) quenched about 97% of the emission intensity of [Ru(bpy)\(_3\)]\(^{2+}\) and Zn\(^{2+}\) quenched ~ 10%. The quenching caused by Cu\(^{2+}\) is likely to be an electron transfer process from [Ru(bpy)\(_3\)]\(^{2+}\)* to [Cu(bpy)\(_2\)]\(^{2+}\)*
Figure 1-11. (A) Bpy containing artificial tripeptide crosslinks with Cu$^{2+}$ and Fe$^{2+}$ depicting the antiparallel and parallel geometric isomers possible upon metal coordination. (Reprinted with permission from [71]. Copyright 2005 American Chemical Society.) (B) Φ-tpy containing oligopeptides of n=1-4 mers crosslinked by Co$^{2+}$ or Fe$^{2+}$ (Reprinted with permission from [69]. Copyright 2007 American Chemical Society.) (C) Self-complementary heterofunctional py-bpy-tpy tripeptides crosslinked with Cu$^{2+}$ (Reprinted with permission from [67]. Copyright 2011 American Chemical Society.) (D) Structure of palindromic tripeptide bpy-bpy-bpy (Reprinted with permission from [63]. Copyright 2011 Wiley and Sons.) (E) Palindromic tripeptides hq-hq-hq crosslinked by Zn$^{2+}$ (Reprinted with permission from [65]. Copyright 2012 American Chemical Society.)
Scheme 1-1. Structures of [Ru(bpy)$_3$]$^{2+}$ single strand and hairpin complexes
Figure 1.12. Cartoon representation of Cu$^{2+}$ binding crosslinks Ru-hairpin strands
and the quenching caused by Zn$^{2+}$ is likely due to the formation of [Zn(bpy)$_2$]$^{2+}$ which changes the chemical environment of [Ru(bpy)$_3$]$^{2+}$ as evident by our NMR studies.$^{74}$

The quenching of the emission intensity of [Ru(bpy)$_3$]$^{2+}$ caused by binding Cu$^{2+}$ was also found to be distance dependant.$^{66}$ The quenching efficiencies were 97%, 95% and 90%, for Ru-4, Ru-ds-2 and Ru-ds-3 respectively, likely reflecting the increased distance between [Ru(bpy)$_3$]$^{2+}$ and the quencher [Cu(bpy)$_2$]$^{2+}$. Compounds Ru-ds-4 and Ru-ds-5 contained two pair of bpy ligands capable of binding two Cu$^{2+}$ centers. Emission titration plots of Cu$^{2+}$ to Ru-ds-4 and Ru-ds-5 showed two distinct stages, and were attributed to two bound [Cu(bpy)$_2$]$^{2+}$. The quenching efficiencies of Ru-ds-4 and Ru-ds-5 were ~97% after two equivalents of Cu$^{2+}$ were added, similar to Ru-4. This was because the distance between [Ru(bpy)$_3$]$^{2+}$ and the nearest [Cu(bpy)$_2$]$^{2+}$ was roughly identical in these three compounds. The non-radiative decay rate ($k_{nr}$) and activation energy ($E_a$) were also obtained from temperature-dependant measurements. As the distance between Ru and Cu increased, $k_{nr}$ decreased and $E_a$ decreased. $k_{nr}$ and $E_a$ of Ru-ds-4(Cu)$_2$ and Ru-ds-5(Cu)$_2$ were similar to Ru-ds-1(Cu), because of the above-mentioned reason.

Ru hairpin structures with 4 and 6 aeg strands have also been synthesized with the purpose to form heterometallic heterofunctional structures (Scheme 1-2). Titration of Cu$^{2+}$, Zn$^{2+}$ or Pd$^{2+}$ to Ru(HP)$_2$ and Ru(HP)$_3$ formed [Ru(bpy)$_3$]$^{2+}$ linked to two metal or three metal center, respectively.
Scheme 1-2. Structure of Di-, and Tri-hairpin [Ru(bpy)$_3$]$^{2+}$ complexes
1.6 Overview of Thesis Research

[Ru(bpy)$_3$]$^{2+}$ has been studied as a photosensitizer and electron donor in artificial photosynthesis for decades because of its strong absorbance and emission bands in visible region of the spectrum, long-lived triplet excited state and reversible oxidative and reductive quenching. This thesis describes synthesis and characterization of oligopeptide-functionalized [Ru(bpy)$_3$]$^{2+}$ complexes for photoinduced electron/energy transfer and photocatalysis.

Chapter 2 is focused on a series of [Ru(bpy)$_3$]$^{2+}$ compounds linked to 1-3 Pd$^{2+}$ by aeg for use in photocatalytically dimerizing α-methylstyrene. This is the first example using the aeg chain to link a photosensitizer and a reaction center to perform chemical work. The Ru-Pd catalysts had faster reaction rates and better selectivity than conjugated linkers described in the literature. The catalytic efficiency when linking [Ru(bpy)$_3$]$^{2+}$ with 1-3 Pd$^{2+}$ centers was compared and it was found that the structure with three Pd centers had the lowest catalytic activity because of lower chemical stability. Further investigation was conducted to understand the excited state quenching mechanism. Solvent study of Ru-Pd catalysts showed a negative trend of the nonradiative decay rate vs. Pekar factor, which indicated an electron transfer process. Variable temperature study, which showed a large reorganization energy (>1 eV), with experiments using added sacrificial electron donor together indicated an electron transfer process from [Ru(bpy)$_3$]$^{2+*}$ to Pd$^{2+}$.

Chapter 3 and 4 focus on studying the impact of side chain change of different oligopeptide linkers (e.g. aminoethylglycine (gly), aminoethylvaline (val), aminoethylleucine (leu) and aminoethylphenylalanine (phe) ) on the emission photodynamics of a series of [Ru(bpy)$_3$]$^{2+}$-[M(bpy)$_2$]$^{2+}$ complexes (M = Cu, Pd or Zn). Photophysical data of the dimetallic
complexes showed for all the Ru-Cu complexes, the radiative decay rates were similar but the non-radiative decay rate decreased as the steric bulk of the side chain increased. A similar trend was observed for the Ru-Pd complexes. Temperature dependent non-radiative decay rates for all the Ru-M complexes were obtained to probe the activation energies of the non-radiative decay processes. For all the Ru-Cu complexes, Ru-7(Cu) had the highest activation energy, which agreed with the smallest non-radiative decay rate; the barrier decreased as the side chain got smaller. In the Ru-Pd complexes, the same trend was observed. In all cases, no trend was observed for the Ru-Zn complexes. Solvent study showed all the Ru-Cu and Ru-Pd complexes had a negative trend of non-radiative decay rates vs. Pekar factor but no trend was observed for the Ru-Zn complexes. Together these observations lead to our hypothesis that Ru-Cu and Ru-Pd had an electron transfer non-radiative decay mechanism and was different from the mechanism of Ru-Zn. The impact of side chain change on the non-radiative decay of Ru-Cu and Ru-Pd was probably due to the geometry change that accompanied the electron transfer process increased the electron transfer energy barrier.

Chapter 5 expanded our study of the Ru-hairpin system to hexacoordinate metal ions. We have developed a series of [Ru(bpy)_3]^{2+} complexes with three pendant bpy ligands that can directly coordinate to a hexacoordinate metal ion such as Fe^{2+}, Co^{2+}, Ni^{2+} or Mn^{2+} to form [Ru(bpy)_3]^{2+}-[M(bpy)_3]^{2+}. Spectrophotometric emission and absorption titrations confirmed a 1:1 metal binding stoichiometry, and the formation of [Fe(bpy)_3]^{2+} MLCT band. Spectrophotometric emission titrations also confirmed the 1:1 metal binding stoichiometry of Co^{2+}, Ni^{2+} and Mn^{2+}. The formation of Ru-M dimetallic complexes was supported by the cyclic voltammogram of [Ru(bpy)_3]^{2+}-[Fe(bpy)_3]^{2+} which showed the oxidative waves of both
Ru$^{III/II}$ and Fe$^{III/II}$. This was further supported by mass spectrometry and elemental analysis. The formation of [Ru(bpy)$_3$]$^{2+}$-[M(bpy)$_3$]$^{2+}$ also caused quenching of the excited state emission of [Ru(bpy)$_3$]$^{2+}$ by $\sim$ 40% - 90%. Energy transfer mechanism was speculated to be the plausible explanation for this nonradiative quenching because of the spectrum overlap and large energy barrier for electron transfer.

**Chapter 6** expended the ligand used in the Ru-hairpin system to hydroxyquinoline and studied the self-assembly of Cu$^{2+}$ and Zn$^{2+}$ to Ru-HQ and discussed possible energy transfer between [Ru(bpy)$_3$]$^{2+}$ and Zn(HQ)$_2$. Synthetic attempts to make triheterometallic complexes for redox cascades and heterofunctional structures have also been summarized. Future work such as using the Ru-Co complexes for water splitting is also proposed.

**1.7 Conclusion**

Enormous efforts have been made to design donor-acceptor systems with long-lived charge separated states for solar energy conversion. DNA duplexes with metal-ligand pairs lead to high ordered structures that have higher thermal stability. PNA duplexes with metal-ligand pairs have been developed to avoid the ionic interaction of metal ions with the backbone phosphate in DNA. Our metal-linked artificial oligopeptide duplexes doesn’t not only resolve the issues such as metal binding to nucleobases and backbone phosphates, but also exclude the base pairs’ undesirable electrochemical properties. Our approach using peptide coupling chemistry together with inorganic metal coordination provide a facile way to build modular, programmable, expendable and tunable large supramolecular structures that can potentially be used for artificial photosynthesis and molecular electronic devices.
1.8 References


Chapter 2

Aminoethylglycine-linked Ru-Pd Complexes Photocatalytically Dimerize α-methylstyrene

2.1 Introduction

Linking donors and acceptors together in distances, geometries, and conformations to enable charge separation that is useful to drive chemical transformations is centrally important in artificial photosynthesis. A number of synthetic approaches have been used to study and optimize the linker between donor and acceptor, which have primarily been through conjugated bridges.\(^1\)\(^-\)\(^3\) In contrast, natural complexes generally rely on tertiary structure to define the relative geometry of chromophores, redox components and catalyst interactions, and electron and energy transfer reactions, all of which occur over long distances or through space. Synthetic artificial systems that utilize analogous structural organization and transport mechanisms are comparatively rare in the literature, yet may offer advantages including the assembly of multifunctional arrays containing catalytic cascades,\(^4\)\(^-\)\(^5\) long distance proton shuttles,\(^6\)\(^-\)\(^7\) and multi-electron equivalents.\(^8\)\(^-\)\(^12\)

To begin to construct heterometallic complexes that self-assemble with linked flexible strands, our group has introduced a series of [Ru(bpy)\(_3\)]\(^{2+}\) complexes derivatized with aminoethylglycine (aeg) with varying oligopeptide sequences and geometries.\(^13\)\(^,\)\(^14\) When the aeg contains pendant bpy ligands, coordination of Cu\(^{2+}\) results in up to 98 % excited state quenching. This was found to depend on both the oligopeptide sequence, which controls the number of bound Cu\(^{2+}\), and distance between Ru and Cu\(^{2+}\).\(^13\)\(^,\)\(^14\) Given that the peptide brings the donor-acceptor distance close enough to induce excited state quenching, we reasoned that
this structural motif would be useful as an easily tailorable means with which sensitizer and
catalytic complex(es) could be joined.

Several recent reports describe linked $[\text{Ru(bpy)}_3]^{2+}-[\text{Pd(bpy)(CH}_3\text)(X)]^+$ (X is solvent) complexes that photocatalyze the dimerization of styrene and $\alpha$-methylstyrene when irradiated with light $> 455$ nm. In these examples, the Ru-Pd structures are linked by aromatic bridges, which were reported to facilitate sensitization of the Pd catalyst by either energy or electron transfer. Excited-state quenching mechanisms can be difficult to determine because either energy transfer or electron transfer process or a combination of both can occur. We have chosen $[\text{Ru(bpy)}_3]^{2+}$ functionalized with aeg strands bearing pendant bpy ligands to form heterometallic Ru-Pd structures (Scheme 2-1) to study the photocatalytic dimerization of $\alpha$-methylstyrene as a direct comparison to the literature and to further investigate the mechanism of the photocatalytic reaction, since the aeg bridge is unlikely to mediate electron transfer. Furthermore, observation of a photocatalytic reaction about the aeg backbone would represent a first example for our group and support that these systems can indeed act as scaffolds for artificial photosynthetic processes. In this chapter, we describe the use of the flexible, fully saturated aeg backbone to link a Ru sensitizer and Pd catalytic center(s). The quenching mechanism of our Ru-Pd catalysts is well studied and our observations support an electron transfer mechanism with faster reaction rates and better selectivity than prior reported Ru-Pd systems.
Scheme 2-1: Structures of Ru-Pd heterometallic complexes
2.2 Experimental Section

2.2.1 Chemicals and Reagents

N-Hydroxybenzotriazole (HOBT) was purchased from Advanced ChemTech. O-Benzotriazole-N,N,N',N'-tetramethyl-uronium hexafluorophosphate (HBTU) was purchased from NovaBiochem. Ethylamine (2.0 M in THF) was purchased from Aldrich. Tetrabutylammonium perchlorate (TBAP) was recrystallized three times from ethyl acetate. All solvents were used as received without further purification unless otherwise noted.

The syntheses of 4’-methyl-2,2’-bipyridine-4-acetic acid (MebpyAA), 26 4’-methyl-2,2’-bipyridine-4-carboxylic acid (MebpyCA), 27 4’-methyl-2,2’-bpy-4’-(aeg-OtButyl), 13 Ru(N-Et-4’-Me-2,2’-bpy-4-carboxamide)Cl₂, 28 [(Bz)Ru(N-Et-4’-Me-2,2’-bpy-4-carboxamide)Cl]Cl, 29 H₂N-aeg(bpy)-OButyl, 14 [Pd(COD)(CH₃)(Cl)] 30 were performed as previously reported.

2.2.2 Synthesis

2.2.2.1 Synthesis of N-Et-4’-Me-2,2’-bpy-4-carboxamide (1)

A 1.6 g amount of MebpyCA (7.5 mmol) was refluxed in a solution of 8 mL SOCl₂ and 100 mL CH₂Cl₂ overnight. The volume was reduced to 10 mL, and 80 mL of heptane was added to produce white precipitate. This was rinsed with another 30 mL of heptane and added immediately to a solution containing 30 mL ethylamine (2.0 M in THF) and 5 mL of Et₃N in 80 mL THF, and cooled in ice bath under N₂. The solution was stirred overnight. After
filtering the solid residue, the solvent was removed by rotary evaporation and the remaining solid purified by column chromatography on silica gel with 10% CH$_3$OH/CH$_2$Cl$_2$ to give 1.43 g of the pure product (79%). $^1$H NMR, 300 MHz, CDCl$_3$: 1.15 (t, $J = 9.5$ Hz, 3H); 2.39 (s, 3H); 3.46 (m, 2H); 6.63 (s, 1H); 7.14 (d, $J = 4.35$ Hz, 1H); 7.76 (d, $J = 4.88$ Hz, 1H); 8.23 (s, 1H); 8.47 (d, $J = 4.78$ Hz, 1H); 8.52 (s, 1H); 8.73 (d, $J = 4.52$ Hz, 1H). MS (ESI$^+$) [M+H$^+$] Calcd: 242.3; Found: 242.3.

2.2.2.2 Synthesis of
[Ru(Mebpy([aeg(bpy)-OtButyl])(N-Et-4'-Me-2,2'-bpy-4-carboxamide)$_2$](PF$_6$)$_2$ (Ru-1)

The synthesis is adapted from a procedure previously reported by our group,$^13$ except that N-Et-4'-Me-2,2'-bpy-4-carboxamide was used instead of bpy as the ligand (Scheme 2-2). This gave 0.351 g pure product (50.6%). $^1$H NMR, 300 MHz, CD$_3$CN: 1.13 (m, 6H); 1.27 - 1.50 (m, 9H); 2.09 - 2.72 (m, 12H); 3.16 - 3.42 (m, 5H); 3.44 - 3.78 (m, 4H); 3.78 - 3.98 (m, 2H); 4.12 (s, 1H); 7.00 - 7.29 (m, 4H); 7.29 - 7.51 (m, 6H); 7.51 - 7.65 (m, 3H); 7.65 - 7.98 (m, 4H); 7.98 - 8.32 (m, 3H); 8.47 (dt, $J = 28.7$, 15.1 Hz, 4H); 8.67 (s, 3H). MS (ESI$^+$) [M$^{2+}$ + PF$_6$] Calcd: 1309.4; Found 1309.2. [M$^{2+}$] Calcd: 582.2; Found 582.1. Elemental Anal [Ru-1 • 3 CH$_2$Cl$_2$] Calcd: 44.98 C; 4.25 H; 9.83 N. Found: 44.65 C; 4.43 H; 10.17 N.

2.2.2.3 Synthesis of
[Ru(Mebpy([aeg(bpy)-OtButyl])(N-Et-4'-Me-2,2'-bpy-4-carboxamide))(PF$_6$)$_2$ (Ru-2)

To a solution of ethanol was added 0.500 g [(Bz)Ru(N-Et-4'-Me-2,2'-bpy-4-carboxamide)Cl]Cl (1.02 mmol), 1.49 g of
4′-methyl-2,2′-bpy-4′-(aeg-OtButyl) (4.03 mmol) and 0.348 g AgNO₃ (2.30 mmol), and was refluxed over night. The following day the solution was filtered to remove AgCl and ethanol was removed by rotary evaporation. To the residue was added 5 mL ethanol, followed by 20 mL of saturated aqueous NH₄PF₆, which produced a red solid. This was filtered, washed with water, and purified by column chromatography on silica gel with 5:4:1 (volume ratio) CH₃OH: H₂O: sat KNO₃ (aq) solution. The solvent was removed by rotary evaporation, 2 mL CH₃CN and 15 mL CH₂Cl₂ were added, and the solution filtered to remove KNO₃. The red solution was dried over Na₂SO₄, and the solvent removed to give 0.632 g of the aeg modified Ru complex (2) (51.4% yield). After confirming identity by ¹H NMR spectroscopy the compound was used without further characterization.

A 50 mL solution containing 290 mg MebpyAA (1.27 mmol), 456 mg HBTU (1.2 mmol), and 184 mg HOBt (1.2 mmol) in CH₂Cl₂ was stirred for 15 min at 0 °C. After this time, 550 µL diisopropylethylamine (7.7 mmol) was added, and the solution was stirred for an additional hour. A 400 mg amount of the aeg-modified Ru complex (2) (0.332 mmol) was added and the solution stirred overnight, allowing it to reach room temperature. An additional 290 mg of MebpyAA was added, and the solution was stirred for another day (Scheme 2-3). The solvent was removed and the compound purified by column chromatography on silica gel with 5:4:1 (volume ratio) CH₃OH: H₂O: sat KNO₃ (aq) solution and isolated as above. The pure compound was dissolved in 5 mL 1:1 methanol: saturated aqueous NH₄PF₆, stirred for 2 hrs, and then 20 mL of saturated aqueous NH₄PF₆ was added to produce red solid which was collected, rinsed with water, dried under vacuum to give 0.273 g of the pure product (46% yield). ¹H NMR, 400 MHz, CDCl₃: 1.06 - 1.24 (m, 3H); 1.25 - 1.63 (m, 18H); 2.35 (m, 6H);
2.53 (m, 9H); 3.47 (m, 2H); 3.67 (m, 10H); 3.81 - 4.34 (m, 6H); 7.05 (d, \( J = 4.3 \) Hz, 2H); 7.10 - 7.34 (m, 5H); 7.34 - 7.61 (m, 3H); 7.61 - 7.99 (m, 5H); 8.05 (d, \( J = 10.6 \) Hz, 1H); 8.16 (t, \( J = 23.3 \) Hz, 1H); 8.24 - 8.72 (m, 7H); 8.80 - 9.21 (m, 4H); 9.43 (d, \( J = 61.5 \) Hz, 1H). MS (ESI\(^+\)) \([M^{2+}]\) Calcd: 751.8; Found 751.8. Elemental Anal. \([\text{Ru-}2 \cdot \text{CH}_2\text{Cl}_2]\) Calcd: 51.79 C; 4.78 H; 11.18 N. Found: 51.87 C; 5.00 H; 10.80 N.

2.2.2.4 Synthesis of 4-Methyl-4’methyl ester bpy (mbpyme) (3)

Esterification of MebpyCA was performed by refluxing 3.0 g of MebpyCA in 50 mL methanol with 3 mL H\(_2\)SO\(_4\) overnight. The solvent was then removed by rotary evaporation and then 100 mL water was added to the acid residue. The aqueous solution was neutralized with NaHCO\(_3\) to produce a white solid which was then extracted with CH\(_2\)Cl\(_2\) (4 x 15 mL). The organic layer was combined and dried with Na\(_2\)SO\(_4\) and the solvent was removed to yield 2.94 g pure product (92%). \(^1\)H NMR, 400 MHz, d6 dmso: 2.42 (s, 3H); 3.93 (s, 3H); 7.32 (d, \( J = 4.78 \) Hz, 1H); 7.86 (d, \( J = 4.78 \) Hz, 1H); 8.25 (s, 1H); 8.65 (d, \( J = 4.92 \) Hz, 1H); 8.81 (s, 1H); 8.87 (d, \( J = 4.92 \) Hz, 1H). MS (ESI\(^+\)) \([M + H^+]\) Calcd: 229.1; Found: 229.1
Figure 2-1: $^1$H NMR spectrum of Ru-1 at 300 MHz in CD$_3$CN. Solvent peaks are removed for clarity.
Figure 2-2: \( ^1H \) NMR spectrum of Ru-2 at 400 MHz in CD\(_3\)Cl. Solvent peaks are removed for clarity.
2.2.2.5 Synthesis of \([\text{Ru(mbpyme)}_3](\text{BF}_4)_2\) (4)

To 50 mL ethanol was added 0.394 g \(\text{RuCl}_3 \cdot 3\text{H}_2\text{O}\) (1.51 mmol), 0.882 AgBF\(_4\) (4.53 mmol), and 1.24 g mbpyme (5.44 mmol) and then refluxed overnight. The solution was filtered to remove AgCl and the solvent was evaporated. The residue was purified by column chromatography using silica gel with 10% methanol/CH\(_2\)Cl\(_2\). Collected 0.74 g (51%) \(^1\)H NMR, 360 MHz, CD\(_3\)CN: 2.55 (s, 9H); 3.97 (s, 9H); 7.27 (t, \(J = 6.29\) Hz, 3H); 7.51 (m, 3H); 7.74 (m, 3H); 7.86 (m, 3H); 8.54 (s, 3H); 8.89 (s, 3H). MS (ESI\(^+\)) \([\text{M}^{2+}\]) Calcd: 393.1; Found: 393.0

2.2.2.6 Synthesis of \([\text{Ru(MebpyCA)}_3](\text{PF}_6)_2\) (5)

A solution of 0.74 g (4) (0.69 mmol) in 100 mL aqueous 3 M NaOH was refluxed for 5 hours. After this time, the solution was cooled to room temperature and the pH was adjusted to 1 with conc. HCl. A saturated aqueous solution of NH\(_4\)PF\(_6\) was added, producing a red solid that was collected on a medium frit. This was rinsed with water and ether to give 0.62 g of pure compound (87% yield). \(^1\)H NMR, 360 MHz, d\(_6\) dmso: 2.52 (s, 9H); 7.34 - 7.39 (d - d, \(J = 5.96\) Hz 3H); 7.53-7.61 (d - d, \(J = 5.72\) Hz 3H); 7.57 - 7.95 (m-m, 6H); 8.99 (d, \(J = 6.46\) Hz 3H); 9.07 (s, 3H). MS (ESI\(^+\)) \([\text{M}^{2+}\]) Calcd: 372.0; Found: 371.8
2.2.2.7 Synthesis of \([\text{Ru(Mebpy}([\text{aeg(bpy)-OtButyl}])_3](\text{PF}_6)_2}\) (Ru-3)

A 0.62 g amount of (5) (0.6 mmol) was refluxed in 45 mL of CH$_2$Cl$_2$ and 5 mL SOCl$_2$ overnight. The next day the solvent was reduced to 10 mL by rotary evaporation and 100 mL heptane was added to produce a dark red solid which was quickly rinsed with 30 mL heptane and combined with 1.4 g H$_2$N-aeg(bpy)-OtButyl (3.64 mmol) and 4 mL triethylamine in 100 mL dry CH$_2$Cl$_2$ in an ice bath. The reaction was stirred overnight (Scheme 2-4). The following day, the solvent was removed by rotary evaporation, and the red residue dissolved in a minimal amount of methanol. To this, 20 mL of saturated aqueous NH$_4$PF$_6$ was added, which produced a red solid. The solid was filtered, dissolved in CH$_2$Cl$_2$ and dried with Na$_2$SO$_4$. The solvent was again removed, and the red residue was purified by column chromatography on silica gel with 5:4:1 (volume ratio) CH$_3$OH:H$_2$O:sat KNO$_3$ (aq) solution, then isolated as above for Ru-2. The pure compound was dissolved in 5 mL 1:1 methanol: saturated aqueous NH$_4$PF$_6$, stirred for 2 hrs, after which 20 mL of saturated aqueous NH$_4$PF$_6$ was added to the solution to produce red solid, which was collected, rinsed with water, and dried under vacuum to give 0.50 g of the pure product (39% yield). $^1$H NMR, 400 MHz CD$_3$Cl: 1.43 (m, 27H); 2.38 (m, 18H); 3.69 (m, 14H); 3.86 (m, 4H); 4.01 (s, 3H); 4.11 (s, 3H); 7.08 - 7.32 (m-m, 9H); 7.43 (m, 3H); 7.55 - 7.82 (m-m, 6H); 7.82 - 8.12 (m-m, 6H); 8.12 - 8.44 (m-m, 12H); 8.65 (m, 3H). MS (ESI$^+$) [M$^{2+}$] Calcd: 921.4; Found 921.2. Elemental Anal. [Ru-3 $\cdot$ 2 CH$_2$Cl$_2$] Calcd: 52.68 C; 4.90 H; 10.95 N. Found: 52.61 C; 5.54 H; 10.91 N.
Figure 2-3: $^1$H NMR spectrum of Ru-3 at 400 MHz in CD$_3$Cl. Solvent peaks are removed for clarity.
### 2.2.2.8 General synthetic method for Ru-Pd complexes

A sample of Ru-1, Ru-2 or Ru-3 was dissolved in dry CH$_2$Cl$_2$ and to this 1.1, 2.1, or 3.1 equivalents of [Pd(COD)(CH$_3$)(Cl)] was added, respectively, and the resulting solution stirred for 4 hrs. After this time, the solvent was removed by rotary evaporation and the solid was transferred to a fine frit where it was rinsed with copious amounts of 20% CH$_3$Cl / 80% ethyl acetate. The solid was dried and then stored in freezer under nitrogen in the dark. The resulting compounds contain the Pd complexes as [Pd(bpy)(CH$_3$)Cl]. Prior to use in catalytic reactions, Cl ligand was removed by adding a stoichiometric amount of AgBF$_4$ in nitrogen purged CH$_3$CN and stirring for 1 hr, which formed a white AgCl precipitate. This was removed by centrifugation and the red solutions concentrated by rotary evaporation to yield the final catalytic compound, which was used immediately.

### 2.2.2.9 Characterization of Ru-1[Pd(CH$_3$)Cl](PF$_6$)$_2$

$^1$H NMR, 400 MHz, CD$_3$CN: 0.42 - 0.71 (m, 1H); 0.72 - 0.86 (m, 2H); 1.13 - 1.30 (m, 6H); 1.36 - 1.53 (m, 9H); 2.36 (s, 4H); 2.72 (m-m, 8H) 3.45 (dt, $J = 12.6, 6.3$ Hz, 4H); 3.68 (d, $J = 27.7$ Hz, 4H); 4.06 (s, 3H); 4.26 (s, 1H); 7.20 - 7.38 (m, 3H); 7.40 - 7.64 (m, 6H); 7.64 - 7.78 (m, 3H); 7.78 - 7.96 (m-m, 4H); 7.96 - 8.45 (m, 4H); 8.53 (s, 3H); 8.79 (d, $J = 10.6$ Hz, 3H). MS (ESI$^+$) [M$^{2+}$] Calcd: 661.2; Found 661.1.
2.2.2.10 Characterization of Ru-1[Pd(CH₃)(CH₂CN)](PF₆)₂(BF₄) (Ru-1-(Pd))

¹H NMR, 400 MHz, CD₃CN: 0.42 - 0.71 (m, 1H); 0.72 - 0.86 (m, 2H); 1.13 - 1.30 (m, 6H); 1.36 - 1.53 (m, 9H); 1.98 (s, the peak of CH₂CN overlaps with the solvent peak); 2.36 (s, 4H); 2.72 (m-m, 8H) 3.45 (dt, J = 11.7, 6.1 Hz, 4H); 3.68 (d, J = 28.5 Hz, 4H); 4.06 (s, 3H); 4.26 (s, 1H); 7.20 - 7.38 (m, 3H); 7.40-7.64 (m, 6H); 7.64 - 7.78 (m, 3H); 7.78 - 7.96 (m-m, 4H); 7.96 - 8.45 (m, 4H); 8.53 (s, 3H); 8.79 (d, J = 9.1 Hz, 3H). MS (ESI⁺) [M⁺³⁺] Calcd: 442.1; Found 441.7. [M⁺³⁺ + PF₆⁻] Calcd: 735.7; Found 735.5.
Figure 2-4: $^1$H NMR spectrum of Ru-1[Pd(CH$_3$)Cl](PF$_6$)$_2$ at 400 MHz in CD$_3$CN. Solvent peaks are removed for clarity.
Figure 2-5: $^{13}$C NMR spectrum of Ru-1[Pd(CH$_3$)Cl](PF$_6$)$_2$ at 400 MHz in CD$_3$CN.
Figure 2-6: HMOC spectrum of Ru-I[Pd(CH$_3$)Cl](PF$_6$)$_2$ at 400 MHz in CD$_3$CN.
Figure 2-7: HMBC spectrum of Ru-1[Pd(CH$_3$)Cl](PF$_6$)$_2$ at 400 MHz in CD$_3$CN.
Figure 2-8: COSY spectrum of Ru-1[Pd(CH₃)Cl](PF₆)₂ at 400 MHz in CD₃CN.
Figure 2-9: $^1$H NMR spectrum of Ru-1-(Pd) at 400 MHz in CD$_3$CN.
Table 2-1: $^1$H and $^{13}$C shifts for Ru-1[Pd(CH$_3$)Cl](PF$_6$)$_2$

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Figure 2-10: $^1$H NMR spectrum of Ru-2[Pd(CH$_3$)Cl]$_2$(PF$_6$)$_2$ at 400 MHz in CD$_3$CN. Solvent peaks are removed for clarity.
Table 2-2: $^1$H shifts for Ru-2[Pd(CH$_3$)Cl]$_2$(PF$_6$)$_2$
2.2.2.11 Characterization of Ru-2[Pd(CH$_3$)Cl]$_2$(PF$_6$)$_2$

$^1$H NMR, 400 MHz, CD$_3$CN: 0.56 - 0.98 (m, 3H); 1.00 - 1.19 (m, 3H); 1.22 (m, 3H); 1.44 (m, 18H); 2.29 - 2.70 (m-m, 15H); 3.37 (d, $J = 55.45$, 3H); 3.71 (m, 9H); 4.02 (d, $J = 33.02$, 4H); 4.25 (s, 2H); 7.07 - 7.41 (m-m, 6H); 7.41 - 7.62 (m-m, 5H); 7.62 - 7.78 (m-m, 3H); 7.78 - 8.08 (m-m, 7H); 8.08 - 8.27 (m-m, 2H); 8.28 - 8.69 (m-m, 6H); 8.69 - 9.00 (m-m, 3H).

MS (ESI$^+$) [M$^{2+}$ + CH$_3$CN] Calcd: 928.2; Found 928.4.

2.2.2.12 Characterization of Ru-2[Pd(CH$_3$)(CH$_3$CN)]$_2$(PF$_6$)$_2$(BF$_4$)$_2$ (Ru-2-(Pd)$_2$)

$^1$H NMR, 400 MHz, CD$_3$CN: 0.56 - 0.98 (m, 3H); 1.00 - 1.19(m, 3H); 1.22 (m, 3H); 1.44 (m, 18H); 1.98 (s, the peak of CH$_3$CN overlaps with the solvent peak); 2.29 - 2.70 (m-m, 15H); 3.37 (d, $J = 53.22$, 3H); 3.71 (m, 9H); 4.02 (d, $J = 30.17$, 4H); 4.25 (s, 2H); 7.07 - 7.41 (m-m, 6H); 7.41 - 7.62 (m-m, 5H); 7.62 - 7.78 (m-m, 3H); 7.78 - 8.08 (m-m, 7H); 8.08 - 8.27 (m-m, 2H); 8.28 - 8.69 (m-m, 6H); 8.69 - 9.00 (m-m, 3H). MS (ESI$^+$) [M$^{4+}$ + 2 CH$_3$CN] Calcd: 457.1; Found 457.0.

2.2.2.13 Characterization of Ru-3[Pd(CH$_3$)Cl]$_3$(PF$_6$)$_2$

$^1$H NMR, 300 MHz CD$_3$CN: 0.34-1.02 (m, 9H) 1.45 (m, 27H); 2.43 (m, 18H); 3.71 (m, 14H); 3.87 (m, 4H); 4.03 (s, 3H); 4.12 (s, 3H); 6.68 - 7.52 (m-m, 13H); 7.52 - 7.73 (m, 6H); 7.73 - 8.00 (m-m, 7H); 8.00 - 8.32 (m-m, 6H); 8.33 - 8.64 (m-m, 5H); 8.78 (m, 2H). MS (ESI$^+$) [M$^{2+}$ + CH$_3$CN] Calcd: 1177.2; Found 1177.2.
Figure 2-11: $^1$H NMR spectrum of Ru-2-(Pd)$_2$ at 400 MHz in CD$_3$CN.
2.2.2.14 Characterization of Ru-3[Pd(CH$_3$)(CH$_3$CN)$_3$][PF$_6$]$_3$(BF$_4$)$_3$ (Ru-3-(Pd)$_3$)

$^1$H NMR, 400 MHz CD$_3$CN: 0.34 - 1.02 (m, 9H) 1.45 (m, 27H); 1.98 (s, the peak of CH$_3$CN overlaps with the solvent peak); 2.43 (m, 18H); 3.71 (m, 14H); 3.87 (m, 4H); 4.03 (s, 3H); 4.12 (s, 3H); 6.68 - 7.52 (m-m, 13H); 7.52 - 7.73 (m, 6H); 7.73 - 8.00 (m-m, 7H); 8.00 - 8.32 (m-m, 6H); 8.33 - 8.64 (m-m, 5H); 8.78 (m, 2H). MS (ESI$^+$) [M$^{5+}$ + 3 CH$_3$CN] Calcd: 466.1; Found 465.9.
Figure 2-12: $^1$H NMR spectrum of Ru-3[Pd(CH$_3$)Cl]$_2$(PF$_6$)$_2$ at 300 MHz in CD$_3$CN. Solvent peaks are removed for clarity.
Figure 2-13: \(^1\text{H} \) NMR spectrum of Ru-3-(Pd)$_3$ at 300 MHz in CD$_3$CN.
Table 2-3: $^1$H shifts for Ru-3[Pd(CH$_3$)$_3$Cl]$_3$(PF$_6$)$_2$

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Figure 2-14: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass (top) and isotopic splitting patterns (bottom) for 

Ru-1[Pd(CH₃)Cl](PF₆)₂ (A) [M²⁺] (B) [M²⁺ +H₂O].
Figure 2-15: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass (top) and isotopic splitting patterns (bottom) for

(A) $\text{Ru-2[Pd(CH}_3\text{Cl]}_2\text{(PF}_6\text{)}_2$ [M$^{2+}+$CH$_3$CN] and (B) $\text{Ru-3[Pd(CH}_3\text{Cl]}_3\text{(PF}_6\text{)}_2$ [M$^{2+}+$CH$_3$CN].

Figure 2-16: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass (top) and isotopic splitting patterns (bottom) for

$\text{Ru-1-(Pd)}$ (A) [M$^{1+}$] (B) [M$^{1+}+$PF$_6^{-}$].
Figure 2-17: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass (top) and isotopic splitting patterns (bottom) for (A) Ru-2-(Pd)$_2$ [M$^{4+}$] and (B) Ru-3-(Pd)$_3$ [M$^{5+}$].
2.2.3 Methods

UV-visible absorbance spectra were obtained with a double-beam spectrophotometer (Varian, Cary 500). Emission spectra were measured using a Photon Technology International (PTI) fluorescence spectrometer using a model 814 photomultiplier detection system. Time resolved emission decays were measured following excitation using a N\textsubscript{2} dye laser (PTI model GL-302), averaging 16 decays with a 50 µs collection time per point. Quantum yields and time resolved emission decays were determined using samples from which oxygen had been using removed in repetitive freeze-pump-thaw cycles, and finally measured in a sealed cell under nitrogen. Quantum yields were determined using the relationship:\textsuperscript{31}

\[
\Phi = \Phi_{\text{ref}} \frac{I / A}{I_{\text{ref}} / A_{\text{ref}}} \left( \frac{\eta}{\eta_{\text{ref}}} \right) \\
\text{Eq (2-1)}
\]

where \(\Phi\) is the radiative quantum yield of the sample; \(\Phi_{\text{ref}}\) is the known quantum yield of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} in acetonitrile = 0.062;\textsuperscript{32} \(I\) is the integrated emission, \(A\) is the absorbance at the excitation wavelength; and \(\eta\) is the dielectric constant of the solvent, which is assumed to be the same for the acetonitrile solutions of sample and reference.

Mass spectrometric analysis was performed on a Waters LCT Premier time-of-flight (TOF) mass spectrometer at the Penn State Mass Spectrometry Facility. Samples were introduced into the mass spectrometer using direct infusion via syringe pump and electrospray ionization (ESI). The mass spectrometer was scanned from 100-2500 m/z in positive ion mode.
NMR spectra were collected using either a 300, 360 or 400 MHz spectrometers (Bruker) in the Lloyd Jackman Nuclear Magnetic Resonance Facility. Elemental analyses were performed by Galbraith Laboratories.

All electrochemical measurements were obtained using a CH Instruments potentiostat (Model 660) with 0.31 cm diameter glassy carbon working and Pt wire counter electrodes with a Ag quasi reference electrode. Solutions of Ru-1, Ru-2, Ru-3, and [Pd(MebpǒMe)(CH₃)(CH₃CN)] were prepared from distilled CH₃CN containing 0.2 M TBAP supporting electrolyte. Solutions of Ru-1-(Pd), Ru-2-(Pd)₂ and Ru-3-(Pd)₃ were prepared from DMSO containing 0.2 M TBAP supporting electrolyte. All solutions were thoroughly deoxygenated by purging with solvent-saturated N₂. Potentials are reported versus saturated calomel electrode reference using Ferrocene as an internal potential reference standard.

High performance liquid chromatography (HPLC) was performed with a Varian system equipped with two quaternary pumps (Model 210), an autosampler (Model 410), a UV-vis detector (Model 320), and a Restek Pinnacle II C18 5 μm 150*4.6 mm column. The styrene monomer and reaction mixture were separately analyzed using a flow rate of 0.5 mL/min. The eluent contained 25:75 methanol: THF in volume ratio, respectively. Elution of the compounds was monitored at 260 nm.

Photocatalytic reactions were performed using a Newport lamp (Model 67005) equipped with a 300 W Xe lamp with a 455 nm long pass filter and IR filter. To monitor catalysis, samples were prepared in NMR tubes with 0.25 - 1% molar ratio of catalyst to α-methylstyrene in nitromethane-d₃ (CD₃NO₂) under N₂. Using NMR spectroscopy to monitor
the concentration of \(\alpha\)-methylstyrene, the percentage of styrene left was determined and plotted as a function time.

### 2.3 Results and Discussion

#### 2.3.1 Synthesis and Characterization of Ru Complexes

We have previously reported the synthesis and characterization of aeg-derivatized \(\text{[Ru(bpy)_3]^{2+}}\) complexes containing a single aeg strand.\(^{13, 14}\) Analogous approaches are used here to synthesize the modified Ru complexes shown in Scheme 2-1. Each Ru-coordinated bpy ligand contains one methyl and one carboxyamide at the 4 and 4' positions to maintain a constant electronic environment around \(\text{[Ru(bpy)_3]^{2+}}\) \((\textit{vide infra})\). The differences between \textbf{Ru-1}, \textbf{Ru-2}, and \textbf{Ru-3} are such that each contain one, two, and three aeg chains, respectively, connected through amide bonds. \textbf{Ru-1} and \textbf{Ru-2} were synthesized from Ru starting materials with two and one modified bpy ligand-1 around \textbf{Ru} center using modified literature methods (see Scheme 2-2, 2-3, and 2-4).\(^{13, 28, 29}\) Pendant bipyridine ligands were coupled to the aeg backbone using standard peptide coupling methods to give the final product \textbf{Ru-1} and \textbf{Ru-2} in 51.4 % and 50.6 % yield, respectively. \textbf{Ru-3} was synthesized by reacting an excess of mbpyme with \textit{RuCl}_3 to yield \(\text{[Ru(bpy)_3]^{2+}}\) with three methyl esters. After hydrolysis of the esters to form the carboxylic acid, acyl chloride compounds were synthesized through reaction with \textit{SOCl}_2. An excess of amine-terminated \(\text{H}_2\text{N-aeg(bpy)-Orbutyl}\) was quickly combined with \(\text{[Ru(MebpyCOCl)_3](PF}_6)_2\) and triethylamine to form the final product in \(\sim 40\) % yield.\(^5\) Molecular ion peaks of \textbf{Ru-1}, \textbf{Ru-2} and \textbf{Ru-3} observed in electrospray mass
spectrometry confirmed the identity of the compounds. Their purity was measured by elemental analysis and $^1$H NMR spectroscopy, through which we observed the expected elemental composition and relative aromatic-aliphatic proton integration ratios respectively.
Scheme 2-2: Synthetic steps toward Ru-1 (i) Ethanol reflux over night (ii) HOBT, HBTU, DIPEA in CH$_2$Cl$_2$, 2 days.
Scheme 2-3: Synthetic steps toward Ru-2 (i) AgNO₃ ethanol, reflux overnight (ii) HOBT, HBTU, DIPEA in CH₂Cl₂, 2 days.

Scheme 2-4: Synthetic steps toward Ru-3 (i) 50/50 ethylene glycol/ethanol, AgNO₃, reflux overnight (ii) 2.5 M NaOH, reflux 5 hours, HCl (iii) 10% v/v SOCl₂/CH₂Cl₂ reflux overnight (iv) excess H₂N-aeg(bpy)-OtBu, NEt₃ overnight.
Elemental analysis revealed the tendency to retain small amounts of solvents even after extensive drying. The slight differences between the expected and measured values in elemental analysis are attributed to the retention of some KNO₃ that is a result of the purification process.⁵

The redox and spectroscopic properties of Ru-1, Ru-2 and Ru-3 were measured to better understand the electronic and photophysical environment of the Ru chromophores. Figure 2-18 shows overlayed cyclic voltammograms for each complex. Each exhibited a one-electron oxidation assigned to the Ru₃/II couple at 1.25 V, and three sequential one-electron reductions that are assigned to reduction of the Ru-coordinated bpy ligands, which appear at -1.2, -1.4 and -1.65 V. The pendant bpy ligands on the aeg strands exhibit irreversible reductions well outside this potential window.¹⁴ Absorbance and emission spectra were measured for each of the Ru complexes in deoxygenated acetonitrile and are compared in Table 2-4; each exhibited a strong absorbance band centered at 464 nm assigned to the MLCT of [Ru(bpy)₃]²⁺. Following excitation at 464 nm, each compound exhibited similar emission maxima centered at 626 nm and a long-lived excited state (> 1 µsec).³³ The addition of aeg strands about the Ru center does not significantly impact the photophysical or electronic properties of the compounds. This makes it possible to evaluate the catalytic efficiency of each compound as a result of the number of attached Pd catalysts without altering the electronic structure of the Ru chromophores.
2.3.2 Synthesis and Characterization of Ru-Pd Catalyst Complexes

The Ru-(Pd)$_n$ (n = 1 - 3) compounds were synthesized by reacting Ru-1, Ru-2, and Ru-3 with a slight molar excess than 1 Pd(COD)(CH$_3$)(Cl) for each pendant bpy for 2 hours in CH$_3$CN, which caused formation of the [Pd(bpy)(CH$_3$)(Cl)] complex and loss of the COD ligand. Following removal of the COD and Pd starting material, the product was isolated and its identity and purity were confirmed by mass spectrometry and $^1$H NMR spectroscopy. The coordination of Pd to pendant bpy ligands for each compound was evaluated by comparing integration ratios in the $^1$H NMR spectrum between the Pd-CH$_3$ methyl group and bpy-CH$_3$ on aeg-bpy ligands, which were identified using 2D NMR techniques. Additionally, COSY, HMBC and HMQC were used to assign protons and carbons in each compound (See Table 2-1, 2-2 and 2-3). Photocatalytic compounds were formed by reacting Ru-PdCl complexes with a stoichiometric amount of AgBF$_4$ in acetonitrile to form the solvato complexes and AgCl. The products' identities were confirmed by mass spectrometry and $^1$H NMR spectroscopy. The Ru-Pd complexes were isolated and used immediately.

Cyclic voltammetry of the Ru-Pd complexes revealed four characteristic [Ru(bpy)$_3$]$^{2+}$ redox waves as reported above, together with a chemically irreversible reduction at -0.9 V (see Figure 2-19). The [Pd(MebpyMe)(CH$_3$)(CH$_3$CN)]$^+$ small molecule also exhibited an irreversible one electron reduction at this potential, which is consistent with literature reports of similar Pd complexes with a 4,4’-dimethyl substituted bpy ligand. We therefore assign this reduction in our systems to the reduction of the pendant Pd(bpy) complex. We further observed an increase in cathodic peak current of the reduction of the pendant Pd(bpy)
Figure 2-18: Cyclic voltammograms of 1.1 mM Ru-1, Ru-2, Ru-3 in CH$_3$CN with 0.2 M TBAP, 50 mV/s scan rate, with glassy carbon working and Pt counter electrodes and a Ag quasi reference electrode. Currents are normalized to Ru complex concentration.
Figure 2-19: Cyclic voltammograms of the complexes in acetonitrile or DMSO solutions containing 0.2 M TBAP (see experimental). Currents are normalized to the concentration of the complexes.
complex relative to the first Ru-bpy reduction as the number of Pd(bpy) complexes about the Ru center was increased through the series **Ru-1-(Pd)**, **Ru-2-(Pd)**, and **Ru-3-(Pd)**.

The photophysical properties of the Ru-Pd structures were measured for comparison with analogous monometallic Ru complexes to examine the impact of tethering 1 – 3 Pd to Ru, and these data are listed in **Table 2-4**. Upon Pd coordination to pendent bpy ligands in each compound, the quantum yield (Φ) decreased by ~ 2/3 and excited state lifetime (τ) decreased by ~500 ns. **Figure 2-20** and **2-21** show emission spectra of the Ru complexes and the absorption spectra of the [Pd(MebpyMe)(CH₃)(CH₃CN)]⁺ small molecule. It is evident that the Pd small molecule compound is spectroscopically silent and no absorption/emission overlap was observed.

Because the [Pd(MebpyMe)(CH₃)(CH₃CN)]⁺ complex is spectroscopically silent in the visible region and there is an accessible redox reaction, quenching of the excited state of the Ru complex most likely occurs by electron transfer from the excited state [Ru³⁺(bpy)₂(bpy⁻)]²⁺⁺ to the tethered Pd complex. The slight increase in Φ and longer τ with increasing number of tethered Pd complexes is minor, but may be related to the difference in ionic environment around the Ru.³⁴
Table 2-4: Summary of Photophysical Data\textsuperscript{a}

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<th>$\lambda_{\text{em, max}}$\textsuperscript{c} (nm)</th>
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<th>$\tau$\textsuperscript{e} (ns)</th>
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<td>980 ± 6</td>
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\textsuperscript{a}Measured in CH$_3$CN; oxygen was removed by several cycles of freeze-pump-thaw; \textsuperscript{b}Values are $\varepsilon$ = cm$^{-1}$M$^{-1}$/1000; \textsuperscript{c}Wavelength of the emission maxima; \textsuperscript{d}Quantum yield, determined using [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN as reference $\Phi = 0.062$; \textsuperscript{e}Excited state lifetimes.
Figure 2-20: UV-Vis absorbance spectra of 0.04 mM solutions of Ru-1, Ru-1-(Pd), Ru-2, Ru-2-(Pd)₂, Ru-3, Ru-3-(Pd)₃ and [Pd(MebpyMe)(CH₃)(CH₂CN)](BF₄) in CH₂CN.

Figure 2-21: Emission spectra of 0.02 mM solutions of Ru-1, Ru-1-(Pd), Ru-2, Ru-2-(Pd)₂, Ru-3, Ru-3-(Pd)₃ in CH₂CN, following excitation at 466 nm.
2.3.3 Catalytic Experiments

Analogous structures to ours containing Ru-Pd have been shown to be efficient photocatalysts toward the dimerization of α-methylstyrene. We conducted similar experiments to determine whether the aeg backbone would be an appropriate donor-acceptor linker for this reaction or if a conjugated linkage was necessary. In this regard, each catalyst was combined with a large molar excess of α-methylstyrene in deuterated nitromethane and irradiated as described above, monitoring the reaction by $^1$H NMR spectroscopy. Figure 2-22A (red) shows the $^1$H NMR spectrum of a solution of 1.8 M α-methylstyrene and 0.018 M (1%) Ru-1-(Pd); the proton peaks observed are characteristic of the Ru-Pd and α-methylstyrene starting materials. After 85 minutes of irradiation at wavelength > 455 nm, the spectrum shown in Figure 2-22A (black) was observed which showed a loss of the α-methylstyrene starting material and the apparent formation of a new set of peaks. In separate control experiments, no reaction was observed when Ru-1-(Pd) and α-methylstyrene were stirred in the dark for several hours. Further, irradiated samples of only Ru-1 (without any bound Pd) or [Pd(MebpyMe)(CH$_3$)(CH$_3$CN)]$^+$ (without bound Ru) or a mixture of Ru-0 (Ru-1 without pedant bpy ligand, see Figure 2-23) and [Pd(MebpyMe)(CH$_3$)(CH$_3$CN)]$^+$ did not show any evidence of catalytic activity (see Figure 2-23). To better illustrate this effect we normalized each spectrum to the intensity of the CD$_3$NO$_3$ solvent peak and subtracted the non-irradiated spectrum from the irradiated, shown in Figure 2-22B (black). Peaks orienting down indicate species that are no longer present in solution while peaks pointing upward are indicative of new compounds in solution. For further comparison, the
**Figure 2-22:** (A) $^1$H NMR spectra of a solution of Ru-1-(Pd) and α-methylstyrene in CD$_3$NO$_3$ before (red) and after exposure to light with wavelengths $>$ 455 nm for 85 minutes (black).

(B) Difference $^1$H NMR spectra following irradiation of this solution with wavelengths $>$ 455 nm for 85 minutes (black) and $^1$H NMR of purchased 2,4-diphenyl-4-methyl-1-pentene (red).

(C) HPLC of styrene monomer, reaction product and styrene dimer in 25 % methanol 75 % THF, 0.5mL/min flow rate. Inset: Mass spectra of the only peak from reaction mixture, showing molecular ion peak of 2,4-diphenyl-4-methyl-1-pentene(styrene dimer).
Figure 2-23: Results of control experiments. (◆) 1% solution of Ru-1-(Pd) with α-methylstyrene in dark for 2 hrs. (■) Solution of α-methylstyrene without catalyst, irradiated with light at wavelength > 455 nm for 2 hrs. (●) 1% solution of Ru-1 with α-methylstyrene, irradiated with light at wavelength > 455 nm for 2 hrs. (▼) 1% solution of [Pd(MeppyMe)(CH$_3$)(CH$_3$CN)]$^+$ with α-methylstyrene, irradiated with light at wavelength > 455 nm for 2 hrs. (▲) 1% solution of [Pd(MeppyMe)(CH$_3$)(CH$_3$CN)]$^+$ and 1% Ru[methyl bpy(4-potButyl)] (N-Et-4'-Me-2,2'-bpy-4-carboxamide)$_2$ (Ru-0) with α-methylstyrene, irradiated with light at wavelength > 455 nm for 2 hrs.
spectrum of 2,4-diphenyl-4-methyl-1-pentene (i.e., α-methylstyrene dimer, purchased from Sigma Aldrich), appears in Figure 1-22B (red). Comparison of the purchased dimer with the product (upward peaks) of our photocatalytic experiment shows excellent correlation.

The reaction mixture was further investigated by HPLC to separate and identify the product for comparison with the starting material and commercially available product, and the result is shown in Figure 2-22C. The α-methylstyrene monomer had a retention time of 3.05 min and the purchased dimer had a retention time of 3.45 minutes. Analysis of our reaction mixture exhibited only a single peak at 3.45 minutes, identical to that of the purchased dimer, indicating that this was the major product and very little starting material, if any, remained. Analysis of reaction product which eluted at 3.45 minutes by mass spectrometry revealed a molecular ion peak characteristic of the α-methylstyrene dimer at 236.1 m/z. These combined observations from $^1$H NMR, HPLC, and mass spectrometry conclusively identify the photocatalytic product as the α-methylstyrene dimer.

The catalytic activities of the three Ru-Pd complexes were compared by measuring the consumption of α-methylstyrene in solutions with constant molar ratio of styrene to Ru chromophore (100:1) as a function of time, shown in Figure 2-24. These data show that all three complexes completely consumed α-methylstyrene within 80 minutes, however a striking difference was observed in the rates. Although increasing the number of bound Pd from n = 1 to 2 consumes the styrene at a faster rate, the tetrametallic Ru-3-(Pd)$_3$ consumes styrene at a slower rate. In all three reactions, we observed formation of a black precipitate. In the case of Ru-3-(Pd)$_3$, the largest amount of precipitate was noted. This black precipitate was analyzed by elemental analysis and was found to contain a 31:1 molar ratio of Pd: Ru. The reaction
solution for **Ru-3-(Pd)₃** was further examined by cyclic voltammetry and the Pd-bpy₀⁻¹ reduction peak was not observed (**Figure 2-19**), providing evidence for the decomposition of the Pd center during the catalytic reaction, which reduces the reaction rate. Because the Pd centers are identical in these three complexes, we do not expect differences in their stability. The greater extent of decomposition in **Ru-3-(Pd)₃** likely reflects the higher concentration of Pd.

Integration of the alkene protons assigned to the α-methylstyrene dimer suggests a reaction yield that is less than 100 %. Although a small but measurable amount of styrene monomer starting material was consistently observed, the lower than expected yields of styrene dimer suggests that further reactions occur, for example formation of longer oligomers. Since this could result from the high concentrations used in these reactions, the experiments were repeated using several concentrations of the Ru-Pd catalysts. The high molar concentrations used in these studies are necessary for monitoring the reaction by ¹H NMR, and therefore only a narrow range of concentrations was examined. At the same 1.8 M concentration of α-methylstyrene, decreasing the concentration of the catalysts decreases the rate of consumption of α-methylstyrene, as shown in the inset of **Figure 2-24**.

Despite observation of a chemically irreversible reduction of the Pd complex in the cyclic voltammetry, there is no obvious detrimental impact on the catalytic rate for the styrene dimerization reaction. This is likely because the electrochemical experiment has a longer experimental time scale compared to the catalytic reaction. The lowest concentration of catalyst we used in catalytic reaction was 4.5 mM, which is 1:400 molar ratio of catalyst: α-methyl styrene and it was able to consume styrene monomer completely in 90 min. Based
on this, the turn over number is at least 400, so the time scale for one catalytic reaction is less than 13.5 s, comparing to ~2 min time scale of one cyclic voltammetry scan.
**Figure 2-24:** Plots of the molar percentage of α-methylstyrene remaining in the reaction mixture following irradiation with light > 455 nm in CD$_3$NO$_3$ solutions containing 1.8 M α-methylstyrene and (●) 0.018 M Ru-1-(Pd); (○) 0.018 M Ru-2-(Pd)$_2$; and (▼) 0.018 M Ru-3-(Pd)$_3$. Connecting lines are for guidance only. Inset: Plot of $k_{cat}$ versus Ru-Pd catalyst concentration.
2.3.4 The Mechanism of the Catalytic Reaction

Our results indicate that electronic conjugation between the metal centers is not essential for photosensitization of the Pd catalyst. To the contrary, the catalytic reaction proceeds at a higher rate than previously reported compounds containing conjugated bridging ligands.\textsuperscript{15-19} In conjugated bridged ligand-linked catalysts, the mechanism of the catalytic reaction is likely to be through-bond electron transfer. In our aeg-linked system, since the linker is much longer, the reaction rate is higher, the Pd fragment has no spectrum overlap with the Ru center and there is a favourable standard free energy $\Delta G^0 (-0.28 \text{ eV})$\textsuperscript{15} for electron transfer, we hypothesize it is a through-space electron transfer process from $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy}^-)]^{2+*}$ to Pd fragment in the catalytic reaction.

According to Marcus theory, if an electron transfer process dominates the non-radiative decay, the natural log of nonradiative rate constant ($k_{nr}$) of an electron-transfer process has a linear relationship with the Pekar factor ($D_{op}^{-1} - D_s^{-1}$) in a mixed valence system with a negative slope,\textsuperscript{36} where $D_{op}$ and $D_s$ are the optical and static dielectric constant of the solvent. However, a good correlation is not always found, and factors such as ion-pairing and specific solvation effects can cause unexpected solvent dependence.\textsuperscript{36} Although our complexes are not mixed valence systems, observation of a negative trend of $\ln k_{nr}$ vs. Pekar factor would still be indicative of an electron transfer process.\textsuperscript{36} Based on this, a series of solvents (dichloromethane, methanol, DMSO, THF, acetone, acetonitrile, propylene carbonate) were chosen because of their large range of dielectric constant. Time resolved emission spectra of the Ru-Pd compounds in different solvents were obtained to provide useful information of lifetimes and quantum yields to calculate $k_{nr}$. Natural log of $k_{nr}$ of
Ru-1-(Pd), Ru-2-(Pd)₂, and Ru-3-(Pd)₃ versus Pekar factor were plotted in Figure 2-25, and all show a negative trend. The magnitude of this negative trend is consistent with the magnitude of slopes reported in mixed valence systems\textsuperscript{37-40} and other homogeneous electron transfer reactions,\textsuperscript{41} which is evidence for an excited state electron transfer mechanism.

The temperature dependent nonradiative decay rate was also obtained for Ru-1-(Pd) to understand the dynamics and to determine the reorganization energy ($\lambda$) of the Ru-Pd complex. Electron-transfer processes generally have reorganization energy that is between 1 - 2 eV,\textsuperscript{42} depending on the nature of the donor and acceptor, and the solvent. However, Dexter energy transfer usually has considerably smaller reorganization energy due to the lack of a formal net transfer of charge associated in this process,\textsuperscript{42-46} so the order of reorganization energy could be used as evidence to distinguish energy and electron transfer. Lifetimes and quantum yields at different temperatures in the range from 0 - 35°C were obtained in acetonitrile. Figure 2-26 shows the Arrhenius plot of the non-radiative decay rate for Ru-1-(Pd) in acetonitrile. The slope of the Arrhenius plot determines free energy barrier $\Delta G^\theta$, which is 18 kJ/mol (0.18 eV), together with $\Delta G^0 = -0.28$ eV, to obtain reorganization energy $\lambda = 1.24$ eV from the well-known equation from Marcus theory (Eq(2-2)), which is additional supportive evidence for an electron transfer process.
Figure 2-25: Plots of the natural log of nonradiative decay rate \( (k_{nr}) \) of (●) Ru-1-(Pd); (■) Ru-2-(Pd)\(_2\); and (▲) Ru-3-(Pd)\(_3\) in different solvents at room temperature versus Pekar Factor (\( D_{\text{op}}^{-1} - D_{\text{s}}^{-1} \)) where \( D_{\text{op}} \) and \( D_{\text{s}} \) are the optical and static dielectric constants of the solvent.
Variable temperature transient emission of Ru-1-(Pd) was conducted to further investigate $\Delta G^\neq$ of relaxation in different solvents. Methanol, dichloromethane, and chloroform were used because their large range in Pekar factors. Arrhenius plots of the non-radiative decay rate for Ru-1-(Pd) in methanol, dichloromethane, and chloroform are shown in Figure 2-26 and $\Delta G^\neq$ are 16.8, 18.5 and 22.5 kJ/mol respectively, which increase as the Pekar factor of solvent change. This Pekar factor dependent behavior of $\Delta G^\neq$ can be due to the fact that $\lambda$ changes as Pekar factor changes, and thus causes change to $\Delta G^\neq$. A more direct way to compare change of $\lambda$ is to use Eq (2-3) from Marcus theory.

$$\ln k_{ET}T^{1/2} = \ln\left(\frac{2\pi\hbar^2}{\hbar}\right) + \ln\left(\frac{1}{4\pi\lambda R}\right)^{1/2} - \frac{\Delta G^\neq}{RT} \quad \text{Eq (2-3)}$$

In this equation, $k_{ET}$ is the electron transfer rate, $T$ is temperature, $\hbar$ is Planck's constant and $R$ is the ideal gas constant. The intercept is a combination of the coupling matrix ($H_{DA}$), which hardly changes in different solvents for the same donor and acceptor, and $\lambda$, so the change of the intercept in different solvents is indicative of change of $\lambda$. From Figure 2-26, the intercept of methanol is ~24, dichloromethane is ~26, and chloroform is ~27. Methanol has the largest Pekar factor (0.537) among the three and thus has the largest outside reorganization energy $\lambda_o$, which would lead to the smallest intercept. Chloroform, on the other side, has the smallest Pekar factor (0.24) and the smallest $\lambda_o$, and thus should have the largest intercept. The data we obtained follows the theoretical predication from Marcus theory and thus could be used as additional positive evidence for an electron transfer process.
Figure 2-26: (A) Arrhenius plots of the nonradiative relaxation rate for Ru-1-(Pd) in deaerated (●) methanol, (○) dichloromethane, (■) acetonitrile and (▼) chloroform solutions. (B) Plot of the natural log of nonradiative relaxation rate* $T^{1/2}$ vs. 1000/T for Ru-1-(Pd) in deaerated (●) methanol, (○) dichloromethane and (▼) chloroform solutions.
As a final piece of evidence, N,N-Diisopropylethylamine (i-PrNEt), which is widely used as sacrificial electron donor in [Ru(bpy)$_3$]$^{2+}$ photocatalytic systems, was added to our system to compare the catalytic efficiency. If the catalytic process occurs via energy transfer from [Ru$^{III}$]$^2$ to Pd fragment, adding a large molar ratio of sacrificial electron donor should dramatically decrease the catalytic efficiency, because [Ru$^{III}$] will be quenched by the electron donor, and the reaction rate will decrease. However, if it is an electron transfer dominated process, the produced [Ru($^{1+}$)] is still able to transfer one electron to the Pd fragment, and because $\Delta G^0$ is -0.4 eV, which is still favorable for one electron transferring from [Ru(bpy)$_3$]$^{1+}$ to Pd center, the reaction would still proceed.

Using a 1:100:100 molar ratio of Ru-I-(Pd): styrene: i-PrNEt, the reaction was monitored by $^1$H NMR, and percentage of styrene reactant remaining was plotted versus time in Figure 2-26. Comparison with the plot of Ru-I-(Pd) with no added sacrificial electron donor, the mixture with i-PrNEt shows similar catalytic efficiency even with excess sacrificial electron donor in the system. This experimental data conclusively eliminates an energy transfer quenching mechanism. The smaller difference in final consumption of styrene in the presence of electron donor may be due to a different electron donating efficiency between [Ru(bpy)$_3$]$^{1+}$ and [Ru$^{III}$]
Figure 2-27. Plots of the molar percentage of α-methylstyrene remaining in the reaction mixture following irradiation with light > 455 nm in CD$_3$NO$_3$ solutions containing 1.8 M α-methylstyrene and (●) 0.018 M Ru-I-(Pd) and (○) 0.018 M Ru-I-(Pd) and 1.8 M i-PrNEt.
2.4 Conclusion

In this chapter we have shown the use of flexible unsaturated artificial oligopeptide to link [Ru(bpy)$_3$]$^{2+}$ and a Pd center to accomplish a photocatalytic reaction for the first time with this structure motif. Varying numbers of Pd center linking to Ru center changes the catalytic efficiency but also changes the stability of the catalysts. The product of catalytic reaction was characterized with HPLC, $^1$H NMR and mass spectrometry, which confirms the catalysts selectively converted the styrene monomer to dimer. Solvent dependent emission studies and temperature dependent emission studies were used to support the proposed electron transfer mechanism and the system follows Marcus theory and has reorganization energy higher than 1 eV. Adding sacrificial electron donor to catalytic system doesn’t change the catalytic efficiency, which together with solvent study and reorganization energy rule out energy transfer as a mode of quenching. Our ongoing study is to optimize reactivity by modification of the flexible aeg linker, and expanding this motif to additional catalytic reactions.

2.5 Acknowledgements

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2.6 References


   12268-12269.


   *124*, 11923-11935.

   241-253.


12. Song, W.; Ito, A.; Binstead, R. A.; Hanson, K.; Luo, H.; Brennaman, M. K.; Concepcion,


Chapter 3

Oligopeptide-Derivatized [Ru(bpy)$_3$]$^{2+}$ with Pendant Bipyridines
Self-assemble Heterometallic Complexes by Cu, Pd and Zn Coordination

3.1 Introduction

Natural photosynthetic systems rely on highly ordered light-harvesting chromophores, electron donors and acceptors, as well as catalytic sites to efficiently convert solar energy. As with their natural counterparts, artificial photosynthetic systems must be able to collect solar energy, separate and then transport charge to reaction centers where multi-electron transfer reactions can be accomplished. Researchers have used large complex covalent molecular systems comprised of chromophores, electron donors and acceptors to mimic both the light-harvesting and charge separation functions of natural photosynthetic organisms.$^{1-2}$ In a recent paper, Suenobo and coworkers described creating long-lived charge separation in a covalent molecular system by adjusting the distance between porphyrin or Zn-porphyrin electron donors and fullerene electron acceptors.$^{8}$ These covalent molecular systems provided useful information on the dependencies of electron transfer rates on donor-acceptor distance and orientation, electronic interactions, and free energy of the reaction. However, covalent synthesis of large ordered molecular arrays can be inefficient and costly, making self-assembly a wise choice to build ordered complexes for artificial photosynthesis from functional building blocks. Recently there have been examples that use weak intermolecular interactions to build functional biomimetic structures.$^{9-14}$ These weak attractive forces generally include hydrogen bonding (bond energy = 1-5 kcal/mole), π-π interactions (bond energy = 0-10 kcal/mole), hydrophobic forces (bond energy = 0-10 kcal/mole), metal-ligand
interactions (bond energy = 10-30 kcal/mole) and van der Waals forces (bond energy = 0.5-1 kcal/mole). Wasielewski and coworkers have developed artificial photosynthetic systems in which supramolecular structures are made with π - π and/or metal-ligand attraction as the driving force. Inspired by the use of self-assembly to bring donors and acceptors together, our group introduced a modified Ru tris(bipyridine) system with pendant aminooethylglycine (aeg) chains and free bipyridine (bpy) ligands. Coordination of a transition metal ion such as Cu$^{2+}$ or Zn$^{2+}$ to the pendent bpy ligands formed “hairpin-loop” donor-acceptor structures and quenched the emission of [Ru(bpy)$_3$]$_{2+}$.

The advantage of the oligopeptide functionalized Ru-hairpin motif is the tunability of the structure: both the peptide linkers and the metal centers can be selected to optimize and promote electron transfer. We chose amino acid as the functional building block because with amide coupling chemistry we are able to construct expandable oligopeptides with pre-determined length, sequence and geometry.

We have previously studied the effect of distance on the electron transfer rate by utilizing linkers of varying aeg chain lengths. It was observed that the quenching of [Ru(bpy)$_3$]$_{2+}$ caused by [Cu(bpy)$_2$]$_{2+}$ was distance dependent. In addition to distance, substituents on the amino acid building blocks of the side chain could contribute to the excited state quenching dynamics because of possible impact on the conformation of the donor-acceptor system.

Another tunable component in this Ru-hairpin motif is the metal center. By introducing new metal centers to the donor-acceptor system with metal-ligand interactions, the metal binding geometry, metal ion liability and metal center redox states are synthetically
variable. We previously studied the quenching of [Ru(bpy)$_3$]$^{2+}$ caused by [Cu(bpy)$_2$]$^{2+}$ and [Zn(bpy)$_2$]$^{2+}$. In this chapter we introduce [Pd(bpy)$_2$]$^{2+}$ to this system; Pd$^{2+}$ was chosen for two primary reasons: (a) the redox potential of [Pd(bpy)$_2$]$^{2+}$ is ~ -0.5 V (vs. SCE) which would favor a [Ru(bpy)$_3$]$^{2+}$ excited state quenching by an electron transfer mechanism, as with Cu$^{2+}$; and (b) when attached closely to [Ru(bpy)$_3$]$^{2+}$, [Pd(bpy)$_2$]$^{2+}$ has been shown to yield compounds with photocatalytic properties.$^{17,18}$

In the chapter, we focus on the synthesis and detailed characterization of a series of Ru-hairpins with different side chains (e.g. aminoethyvaline (val), aminoethyleucine (leu) and aminoethyphenylalanine (phe)) (Scheme 3-1), that self-assemble to heterometallic structures upon addition of a second transition metal ion such as Cu$^{2+}$, Pd$^{2+}$ or Zn$^{2+}$. These syntheses provide molecules to study the quenching mechanism and impact of the side chain substituents on the emission photodynamics of the [Ru(bpy)$_3$]$^{2+}$, which is presented in the next chapter.
Scheme 3-1: Oligopeptide derivatized Ru complexes with different side chains. (aeg in Ru-4; val in Ru-5; leu in Ru-6; and phe in Ru-7)
3.2 Experimental Section

3.2.1 Chemicals and Reagents

N-Hydroxybenzotriazole (HOBT) was purchased from AdvancedChemTech. O-Benzotriazole-N,N,N’,N’-tetramethyl-uronium-hexafluorophosphate (HBTU) was purchased from NovaBiochem. Copper (II) nitrate (99.9%) was purchased from J. T. Baker. Tetrakis(acetonitrile)palladium (II) tetrafluoroborate (99%) was purchased from Strem Chemicals. Zinc acetate (99.98%) was purchased from Alfa Aesar. All solvents were used as received without further purification unless otherwise noted. Tetrabutylammonium perchlorate (TBAP) was recrystallized three times from ethyl acetate. The syntheses of 4’-Methyl-2,2’-bipyridine-4-acetic acid,\textsuperscript{19} cis-dichlorobis(2,2’-bipyridine)ruthenium (II) (e.g. [Ru(bpy)\textsubscript{2}Cl\textsubscript{2}]),\textsuperscript{20} [Ru(bpy)\textsubscript{2}(bpy[aeg(bpy)-Otbutyl]\textsubscript{2})]=(NO\textsubscript{3})\textsubscript{2} (Ru-4),\textsuperscript{16} [Ru-4(Cu)](PF\textsubscript{6})\textsubscript{4},\textsuperscript{16} [Ru-4(Zn)](PF\textsubscript{6})\textsubscript{4} \textsuperscript{16}and 4,4’-dimethoxycarbonyl-2,2’-bipyridine [(CO\textsubscript{2}CH\textsubscript{3})\textsubscript{2} bpy]\textsuperscript{20} were performed as previously reported.

3.2.2 Synthesis

3.2.2.1 Synthesis of 3-(fomc-amino)-1,2-propanediol (1)

Fmoc-OSu (9.26g, 27 mmol) suspended in a 4:1(v:v) dioxane:water mixture (75 mL) was added to a solution of 3-amino-1,2-propanediol (3.0 g, 33 mmol) dissolved in a 4:1(v:v) dioxane:water mixture (75 mL) and the reaction stirred at room temperature for 24 hrs. The solvent was removed by flash evaporation and dissolved in ethyl acetate (150 mL). The
solution was extracted successively with 5% (w/v) citric acid (3x50 mL), 10% (w/v) sodium bicarbonate (3x50 mL), and brine (3x50 mL). The organic layer was dried over Na$_2$SO$_4$ and the solvent was flash evaporated yielding a white solid. Yield = 8.1 g (94%). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 7.91 (d, $J = 7$Hz, 2H); 7.73 (d, $J = 7$Hz, 2H); 7.44 (t, $J = 7$Hz, 2H); 7.35 (t, $J = 7$Hz, 2H); 7.22 (t, $J = 6$Hz, 1H); 4.71 (d, $J = 5$Hz, 1H); 4.52 (t, $J = 6$Hz, 1H); 4.29 (d, $J = 6$Hz, 2H); 4.23 (t, $J = 6$Hz, 1H); 3.52-3.49 (m, 1H); 3.31 (t, $J = 7$Hz, 2H); 3.15-3.09 (m, 1H); 2.98-2.91 (m, 1H). MS (ESI+) [M+H$^+$] calcd 314.1, found 314.2.

### 3.2.2.2 Synthesis of Fmoc-Aminoacetaldehyde (2)

Adapted from a previously published method,$^{21}$ compound 1 (10.1 g, 32 mmol) was suspended in water (125 mL) and acetone (~ 200 mL) was added under vigorous stirring until the diol dissolved. Potassium m-periodate (7.42 g, 32 mmol) was added and the reaction was stirred at room temperature under N$_2$ for 2 hrs. The mixture was filtered and the solvent was removed via flash evaporation to give a white solid. The solid was dissolved in ethyl acetate (100 mL) and extracted with water (3x50 mL). The organic layer was dried over Na$_2$SO$_4$ and the solvent was flash evaporated yielding a white solid. Yield = 7.3 g (80%). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 9.68 (s, 1H); 7.79 (d, $J = 7$Hz, 2H); 7.62 (d, $J = 7$Hz, 2H); 7.43 (t, $J = 7$Hz, 2H); 7.34 (t, $J = 7$Hz, 2H); 5.46 (br, 1H); 4.46 (d, $J = 7$Hz, 2H); 4.26 (t, $J = 7$Hz, 1H); 4.19 (d, $J = 7$Hz, 2H). MS (ESI+) [M+H$^+$] calcd 281.1, found 281.2.
3.2.2.3 Synthesis of Fmoc-ae<sup>D</sup>v-<i>OtBu</i> (3)

NH<sub>2</sub>-<sup>D</sup>val-<i>OtBu</i> (1.0 g, 4.8 mmol) and 2 (1.12 g, 4.0 mmol) were combined in methanol (40 mL) and stirred at room temperature for 10 min. Acetic acid (0.30 mL, 5.2 mmol) and NaBH<sub>3</sub>CN (0.25 g, 4.0 mmol) were added sequentially and the reaction was stirred for 1 h at room temperature. The solvent was flash evaporated and the residue was dissolved in ethyl acetate (50 mL) and extracted with saturated NaHCO<sub>3</sub> (3x30 mL) and brine (3x30 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was flash evaporated yielding a clear oil. Yield = 1.5 g (86%). <sup>1</sup>H NMR (300 MHz, chloroform-d): δ 7.75 (d, <i>J</i> = 7Hz, 2H); 7.60 (d, <i>J</i> = 7Hz, 2H); 7.42-7.35 (t, <i>J</i> = 7Hz, 2H); 7.31-7.25 (t, <i>J</i> = 7Hz, 2H); 4.39-4.34 (m, 2H); 4.17-4.14 (m, 1H); 3.35-3.26 (m, 1H); 3.19-3.08 (m, 1H); 2.83-2.75 (m, 2H); 2.60-2.50 (m, 1H); 1.95 (m, 1H); 1.45 (s, 9H); 1.00-0.83 (m, 6H). MS (ESI+) [M+H<sup>+</sup>] calcd 439.3, found 439.3.

3.2.2.4 Synthesis of Fmoc-ae<sup>D</sup>v(bpy)-<i>OtBu</i> (4)

4'-Methyl-2,2'-bipyridine-4-acetic acid (1.67 g, 6.8 mmol), HBTU (2.59 g, 6.8 mmol), HOBT (0.92 g, 6.8 mmol), and DIPEA (2.26 mL, 13.7 mmol) were suspended in DCM (150 mL) and stirred at 0°C for 20 min. 3 (1.5 g, 3.4 mmol) dissolved in DCM (25 mL) was added and the reaction was stirred for 48 hrs at room temperature. The mixture was washed with water (3x50 mL), and dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was flash evaporated leaving a yellow oil. The oil was purified on a silica column with a mobile phase of 5% methanol in 95% DCM and a pale yellow band was collected and dried to give a yellow solid.
Yield = 1.2 g (55%)  
$^1$H NMR (300 MHz, chloroform-d): δ 8.54-8.41 (m, 2H); 8.33-8.11 (m, 2H); 7.68 (d, J = 7Hz, 2H); 7.53 (d, J = 7Hz, 2H); 7.32-7.26 (m, 2H); 7.23-7.17 (m, 5H); 7.08-6.98 (m, 1H); 4.43-4.29 (m, 2H); 4.25-4.10 (m, 1H); 3.91-3.83 (m, 1H); 3.66-3.58 (m, 2H); 3.40-3.21 (m, 2H); 3.20-3.16 (m, 2H); 2.41-2.35 (m, 3H); 2.16 (m, 1H); 1.43-1.33 (m, 9H); 0.92-0.67 (m, 6H). MS (ESI\(^+)\) [M+H\(^+\)] calcd 649.3, found 649.4.

3.2.2.5 Synthesis of Fmoc-ae\(^\alpha\)D-f-OtBu (5)

NH\(_2\)-\(^D\)phe-OtBu (2.20 g, 8.53 mmol) and 2 (2.0 g, 7.11 mmol) were combined in methanol (80 mL) and stirred at room temperature for 10 min. Acetic acid (0.53 mL, 9.24 mmol) and NaBH\(_3\)CN (0.45 g, 7.11 mmol) were added sequentially and the reaction was stirred for 1 h at room temperature. The solvent was flash evaporated and the residue was dissolved in ethyl acetate (50 mL) and extracted with saturated NaHCO\(_3\) (3x30 mL) and brine (3x30 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was flash evaporated yielding a clear oil. Yield = 2.85 g (82%). $^1$H NMR (300 MHz, chloroform-d): δ 7.81 (d, J = 7Hz, 2H); 7.67 (d, J = 7Hz, 2H); 7.5-7.16 (m, 9H); 4.40-4.33 (m, 2H); 4.12-4.01 (m, 1H); 3.45-3.36 (m, 1H); 3.21-3.03 (m, 2H); 2.78-2.65 (m, 2H); 2.63-2.51 (m, 1H); 2.33-2.48 (m, 1H); 1.45 (s, 9H). MS (ESI\(^+)\) [M+H\(^+\)] calcd 487.3, found 487.4.

3.2.2.6 Synthesis of Fmoc-ae\(^\alpha\)D(f(bpy))-OtBu (6)

4'-Methyl-2,2'-bipyridine-4-acetic acid (1.04 g, 4.2 mmol), HBTU (1.60 g, 4.2 mmol), HOBT (0.57 g, 4.2 mmol), and DIPEA (1.4 mL, 8.4 mmol) were suspended in DCM
(150 mL) and stirred at 0 °C for 20 min. 5 (1.04 g, 2.1 mmol) dissolved in DCM (25 mL) was added and the reaction was stirred for 48 hrs at room temperature. The mixture was washed with water (3x50 mL), and dried over Na₂SO₄ and the solvent was flash evaporated leaving a yellow oil. The oil was purified on a silica column with a mobile phase of 5% methanol in 95% DCM and a pale yellow band was collected and dried to give a yellow solid. Yield = 0.79 g (54%) ³H NMR (300 MHz, chloroform-d): δ 8.75-8.55 (m, 1H); 8.50-8.34 (m, 1H); 8.32-8.14 (m, 2H); 7.78 (d, J = 7Hz, 2H); 7.55 (d, J = 7Hz, 2H); 7.45-7.34 (m, 2H); 7.33-7.21 (m, 3H); 7.20-7.13 (m, 3H); 7.12-6.91 (m, 3H); 4.63-4.29 (m, 2H); 4.28-4.06 (m, 1H); 3.89-3.75 (m, 1H); 3.72-3.48 (m, 2H); 3.47-3.15 (m, 3H); 3.15-2.85 (m, 2H); 2.83-2.56 (m, 1H); 2.54-2.30 (m, 3H); 1.62-1.23 (m, 9H). MS (ESI+) [M+H⁺] calcd 697.3, found 697.0.

3.2.2.7 Synthesis of Fmoc-αDl-OtBu (7)

NH₂-Dl-leu-OtBu (2.86 g, 12.78 mmol) and 2 (3 g, 10.66 mmol) were combined in methanol (120 mL) and stirred at room temperature for 10 min. Acetic acid (0.80 mL, 13.9 mmol) and NaBH₃CN (0.67 g, 10.7 mmol) were added sequentially and the reaction was stirred for 1 h at room temperature. The solvent was flash evaporated and the residue was dissolved in ethyl acetate (50 mL) and extracted with saturated NaHCO₃ (3x50 mL) and brine (3x50 mL). The organic layer was dried over Na₂SO₄ and the solvent was flash evaporated yielding a clear oil. Yield = 3.36 g (70%). ¹H NMR (300 MHz, chloroform-d): δ 7.64 (d, J = 7Hz, 2H); 7.41 (d, J = 7Hz, 2H); 7.32-7.18 (t, J = 7Hz, 2H); 7.17-6.96 (t, J = 7Hz, 2H); 4.37-4.17 (m, 2H); 4.14-3.09 (m, 1H); 3.32-3.11 (m, 1H); 3.10-3.03 (m, 1H); 3.03-2.88 (m,
1H); 2.77-2.75 (m, 2H); 2.50-2.30 (m, 2H); 1.61 (m, 1H); 1.35 (s, 9H); 0.90-0.63 (m, 6H).

MS (ESI+) [M+H+] calcd 453.3, found 453.3.

3.2.2.8 Synthesis of Fmoc-α\textsuperscript{Dl}(bpy)-Ot\textsubscript{Bu} (8)

4'-Methyl-2,2'-bipyridine-4-acetic acid (3.62 g, 14.8 mmol), HBTU (5.64 g, 14.8 mmol), HOBT (2.27 g, 14.8 mmol), and DIPEA (5.5 mL, 27.4 mmol) were suspended in DCM (250 mL) and stirred at 0 °C for 20 min. 7 (3.36 g, 7.4 mmol) dissolved in DCM (25 mL) was added and the reaction was stirred for 48 hrs at room temperature. The mixture was washed with water (3x50 mL), and dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was flash evaporated leaving a yellow oil. The oil was purified on a silica column with a mobile phase of 5% methanol in 95% DCM and a pale yellow band was collected and dried to give a yellow solid.

Yield = 2.17 g (44%)

\textsuperscript{1}H NMR (300 MHz, chloroform-d): δ 8.73-8.41 (m, 2H); 8.43-8.07 (m, 2H); 7.74 (d, J = 7Hz, 2H); 7.55 (d, J = 7Hz, 2H); 7.46-7.31 (m, 1H); 7.39-7.15 (m, 4H); 7.15-6.99 (m, 1H); 4.65-4.29 (m, 2H); 4.25-4.02 (m, 2H); 4.01-3.83 (m, 1H); 3.82-3.77 (m, 2H); 3.54-3.13 (m, 3H); 2.47-2.22 (m, 3H); 1.81 (m, 1H); 1.61-1.26 (m, 9H); 1.01-0.58 (m, 6H). MS (ESI+) [M+H+] calcd 663.4, found 663.3.

3.2.2.9 Amine Deprotection

Fmoc deprotection was accomplished using a literature procedure.\textsuperscript{22} Briefly, a sample of Fmoc-protected oligopeptide was stirred overnight with 1 molar equivalent 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 10 molar equivalents 1-decanethiol in THF.
After this time, the solvent was removed by rotary evaporation and the product re-dissolved in 75 mL of 0.15 M HCl. The aqueous solution was extracted 5 times with 50 mL hexanes, the organic layers were combined and back-extracted with 0.15 M HCl and all aqueous portions combined. The acidic aqueous solution was adjusted to a pH of 9-10 with saturated Na₂CO₃ and the aqueous layer extracted 5 times with 50 mL CH₂Cl₂, the organic fractions combined and dried with Na₂SO₄. Dichloromethane was removed by rotary evaporation to give the pure amine-terminated oligopeptide. In each case, removal of the Fmoc was confirmed by mass spectrometry and by noting the absence of Fmoc proton peaks in the aromatic region of the ¹H NMR spectra.

3.2.2.10 Characterization of NH₂-aeαDv(bpy)-OtBu (9)

The Fmoc protecting group removed and the product isolated as described above, giving 1.20 g of solid (85 % yield). ¹H NMR (300 MHz, chloroform-d) δ 8.61-8.34 (dd, J = 5.4 Hz, 2H); 8.31-8.05 (d, J = 6 Hz, 2H); 7.27-6.91 (dd, J = 5.6 Hz, 2H); 3.92-3.81 (m, 2H); 3.75-3.70 (m, 1H); 3.62-3.35 (m, 2H); 3.33-3.06 (m, 1H); 2.91-2.75 (m, 1H); 2.73-2.53 (m, 1H); 2.31 (s, 3H); 1.50-1.33 (s, 9H); 0.92-0.67 (m, 6H). MS (ESI+) [M+H⁺] calcd 427.3, found 427.2.

3.2.2.11 Characterization of NH₂-aeαDf(bpy)-OtBu (10)

The Fmoc protecting group removed and the product isolated as described above, giving 0.72 g of solid (88 % yield). ¹H NMR (300 MHz, chloroform-d) δ 8.74-8.46 (dd, J = 6
Hz, 2H); 8.43-8.14 (d, J = 5 Hz, 2H); 7.45-7.21 (m, 2H); 7.20-6.99 (m, 5H) 3.98-3.79 (m, 2H); 3.47-3.24 (m, 3H); 2.85-2.60 (m, 2H); 2.58-2.50 (m, 1H); 2.48-2.34 (m, 3H); 1.60-1.33 (m, 9H). MS (ESI+) [M+H+] calcd 475.3, found 475.3.

### 3.2.2.12 Characterization of NH$_2$-ae$^{\beta\lambda}$(bpy)-OtBu (11)

The Fmoc protecting group removed and the product isolated as described above, giving 1.40 g of solid (97 % yield). $^1$H NMR (300 MHz, chloroform-d) $\delta$ 8.54-8.22 (dd, J = 6 Hz, 2H); 8.21-7.91 (d, J = 6 Hz, 2H); 7.20-6.82 (dd, J = 7.3 Hz, 2H); 4.24-3.85 (m, 1H); 3.84-3.51 (m, 2H); 3.50-3.29 (m, 1H); 3.29-3.13 (m, 1H); 3.12-2.80 (m, 2H); 2.80-2.47 (m, 2H); 2.22 (s, 3H); 1.47-1.35 (m, 1H); 1.34-1.13 (m, 9H); 0.96-0.45 (m, 6H). MS (ESI+) [M+H+] calcd 441.3, found 441.3.

### 3.2.2.13 General Approach for Ru Hairpin Complex Syntheses

All the Ru complexes were synthesized using a method previously reported$^{15}$ by reacting [Ru(bpy)$_2$(bpy(COCl)$_2$)]$^{2+}$ with Fmoc-deprotected bpy monomers.

### 3.2.2.14 Characterization of [Ru(bpy)$_2$(bpy[ae$^{\beta\lambda}$(bpy)-OtButyl)$_2$])(NO$_3$)$_2$ (Ru-5)

$^1$H NMR 400 MHz, chloroform-d: $\delta$ 9.65-9.40 (m, 2H); 9.40-9.04 (m, 2H); 8.76-8.44 (m, 5H); 8.44-8.35 (m, 2H); 8.35-8.19 (m, 2H); 8.19-8.07 (m, 2H); 8.07-7.93 (m, 5H); 7.93-7.77 (m, 2H); 7.77-7.52 (m, 4H); 7.52-7.32 (m, 5H); 7.27-7.14 (m, 1H); 7.14- 6.96 (m, 2H); 4.15-3.96 (m, 4H); 3.96-3.73 (m, 6H); 3.73-3.36 (m, 4H); 2.50-2.40 (m, 2H); 2.39-2.18
(m, 6H); 1.57-1.26 (m, 18H); 1.11-0.98 (m, 4H); 0.98-0.87 (m, 2H); 0.87-0.69 (m, 6H). MS (ESI$^+$) [M$^{2+}$] calcd, 737.3; found, 737.3. HRMS (ESI$^+$) [M$^{2+}$] calcd 737.2988; found 737.2950.

Elemental Anal. [Ru-5 • 2CH$_2$Cl$_2$] calcd: 55.69 C; 5.24 H; 12.67 N; found: 55.60 C; 5.67 H; 12.65 N.
Figure 3-1: $^1$H NMR spectrum of Ru-5 at 400 MHz in CDCl$_3$. 
Figure 3-2: $^{13}$C NMR spectrum of Ru-5 at 400 MHz in CDCl$_3$.

Figure 3-3: HMBC spectrum of Ru-5 at 400 MHz in CDCl$_3$. 
Figure 3-4: HMQC spectrum of **Ru-5** at 400 MHz in CDCl₃.

Figure 3-5: COSY spectrum of **Ru-5** at 400 MHz in CDCl₃.
3.2.2.15 Characterization of \([\text{Ru}(\text{bpy})_2(\text{bpy}[\text{ae}^{\text{ab}}-\text{(bpy)}-\text{OtButyl}]_2)](\text{NO}_3)_2\) (Ru-6)

\(^1\)H NMR 400 MHz, chloroform-d: \(\delta\) 9.65-9.06 (m, 3H); 8.72-8.54 (m, 4H); 8.53-8.44 (m, 2H); 8.44-8.35 (m, 2H); 8.34-8.15 (m, 2H); 8.14-7.93 (m, 7H); 7.93-7.77 (m, 2H); 7.76-7.54 (m, 4H); 7.54-7.34 (m, 4H); 7.34-7.16 (m, 2H); 7.16-6.99 (m, 2H); 4.63-4.16 (m, 2H); 4.15-3.93 (m, 2H); 3.91-3.65 (m, 6H); 3.64-3.27 (m, 3H); 3.27-2.90 (m, 1H); 2.54-2.22 (m, 6H); 1.96-1.65 (m, 4H); 1.65-1.45 (m, 2H); 1.45-1.17 (m, 18H); 1.08-0.65 (m, 12H). MS (ESI\(^+\)) \([M^{2+}\] calcd, 751.3; found, 751.3 HRMS (ESI\(^+\)) \([M^{2+}\] calcd 751.3145; found 751.3107. Elemental Anal. \([\text{Ru-6} \cdot 1.2\text{CH}_2\text{Cl}_2]\) calcd: 57.81 C; 5.50 H; 12.96 N; found: 57.79 C; 5.56 H; 12.98 N.

3.2.2.16 Characterization of \([\text{Ru}(\text{bpy})_2(\text{bpy}[\text{ae}^{\text{ab}}-\text{(bpy)}-\text{OtButyl}]_2)](\text{NO}_3)_2\) (Ru-7)

\(^1\)H NMR 400 MHz, chloroform-d: \(\delta\) 9.44-9.08 (m, 2H); 8.65-8.44 (m, 5H); 8.44-8.25 (m, 4H); 8.19-8.06 (m, 2H); 8.06-7.90 (m, 6H); 7.88-7.73 (m, 2H); 7.73-7.63 (m, 2H); 7.63-7.51 (m, 2H); 7.51-7.32 (m, 4H); 7.32-7.21 (m, 2H); 7.21-7.12 (m, 1H); 7.12-6.97 (m, 11H); 4.25-4.05 (m, 1H); 4.05-3.72 (m, 3H); 3.69-3.35 (m, 6H); 3.34-3.20 (m, 3H); 3.03-2.63 (m, 3H); 2.45-2.27 (m, 6H); 1.46-1.27 (m, 18H). MS (ESI\(^+\)) \([M^{2+}\] calcd, 785.3; found, 785.3. HRMS (ESI\(^+\)) \([M^{2+}\] calcd 785.2989; found 785.2990. Elemental Anal. \([\text{Ru-7} \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}]\) calcd: 59.46 C; 5.16 H; 12.47 N; found: 59.87 C; 5.16 H; 12.27 N.
3.2.2.17 Synthesis of Ruthenium-Copper, Ruthenium-Palladium and Ruthenium-Zinc Complexes

\[\text{[Ru-4}(\text{Pd})](\text{PF}_6)_4, \text{[Ru-5}(\text{M})](\text{PF}_6)_4, \text{[Ru-6}(\text{M})](\text{PF}_6)_4 \text{ and [Ru-7}(\text{M})](\text{PF}_6)_4\] (where M is Cu$^{2+}$ or Pd$^{2+}$) were synthesized by dissolving Ru-4, Ru-5, Ru-6 or Ru-7 in 1:1 CH$_3$CN:H$_2$O, adding 1.1 equivalents of the appropriate metal salt (Cu(NO$_3$)$_2$ or Pd(CH$_3$CN)$_4$(BF$_4$)$_2$), respectively. The reaction solutions were stirred for 2 hours, and a saturated aqueous solution of NH$_4$PF$_6$ was added to produce a dark precipitate. The solid was collected on a medium frit and washed with water and diethyl ether to yield the heterometallic complexes. The [Ru-5(Zn)](PF$_6$)$_4$, [Ru-6(Zn)](PF$_6$)$_4$ and [Ru-7(Zn)](PF$_6$)$_4$ complexes were similarly prepared, however because Zn(PF$_6$)$_2$ is insoluble in water, following addition of 1.1 molar equivalent of zinc (II) acetate, the reaction solutions (1:1 CH$_3$OH:H$_2$O) were stirred for 2 hours. NH$_4$PF$_6$ was then added and the solid filtered to give the red product. This powder was washed with H$_2$O and ether, re-dissolved in CH$_3$CN, and filtered again to remove Zn(PF$_6$)$_2$. The solvent was removed under vacuum to give the dry solid.

Identity and purity of these compounds were determined by $^1$H NMR, mass spectrometry and elemental analysis.
Figure 3-6: $^1$H NMR spectrum of Ru-6 at 400 MHz in CDCl$_3$.

Figure 3-7: $^{13}$C NMR spectrum of Ru-6 at 400 MHz in CDCl$_3$. 
Figure 3-8: HMBC spectrum of Ru-6 at 400 MHz in CDCl₃.

Figure 3-9: HMQC spectrum of Ru-6 at 400 MHz in CDCl₃.
Figure 3-10: COSY spectrum of Ru-6 at 400 MHz in CDCl$_3$.

Figure 3-11: $^1$H NMR spectrum of Ru-7 at 400 MHz in CDCl$_3$. CH$_2$Cl$_2$ peak is removed for clarity.
Figure 3-12: $^{13}$C NMR spectrum of Ru-7 at 400 MHz in CDCl$_3$.

Figure 3-13: HMBC spectrum of Ru-7 at 400 MHz in CDCl$_3$. 
Figure 3-14: HMQC spectrum of Ru-7 at 400 MHz in CDCl₃.

Figure 3-15: COSY spectrum of Ru-7 at 400 MHz in CDCl₃.
**Table 3-1: \(^1\)H and \(^{13}\)C shifts for Ru-5**

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### Table 3-2: $^1$H and $^{13}$C shifts for Ru-6

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3.2.2.18 Characterization of [Ru-4(Pd)](PF₆)₄

¹H NMR 400 MHz, acetonitrile-d₃: δ 9.24-8.84 (m, 2H); 8.84-8.70 (m, 1H); 8.70-8.53 (m, 6H); 8.53-8.29 (m, 3H); 8.29-8.09 (m, 6H); 8.09-7.92 (m, 3H); 7.92-7.66 (m, 8H); 7.66-7.21 (m, 5H); 4.48-3.87 (br, 8H); 3.87-3.32 (br, 8H); 2.38-2.13 (m, 6H); 1.73-1.06 (m, 18H). MS (ESI⁺) [M⁴⁺ + 2 PF₆⁻] calcd: 893.2; found: 893.2. [M⁴⁺ + PF₆⁻] calcd: 547.1; found: 547.1. [M⁴⁺] calcd: 374.1; found: 374.1. Elemental Analysis. calcd: 5.12 Pd; 4.87 Ru; found: 4.54 Pd; 4.10 Ru (1.05 mol Pd: 1 mol Ru).

3.2.2.19 Characterization of [Ru-5(Cu)](PF₆)₄

¹H NMR 400 MHz, acetonitrile-d₃: δ 9.17-8.58 (m, 2H); 8.58-8.13 (m, 4H); 8.13-7.94 (m, 3H); 7.94-7.70 (m, 3H); 7.70-7.43 (m, 6H); 7.43-7.06 (m, 4H); 4.41-3.85 (br, 3H); 3.82-3.23 (br, 7H); 1.62-1.09 (m, 18H); 1.09-0.47 (m, 12H). MS (ESI⁺) [M⁴⁺ + 2 PF₆⁻] calcd, 914.1; found, 914.3. [M⁴⁺ + 3 NO₃⁻] calcd, 1723.5; found, 1723.5. [M⁴⁺ + 2 NO₃⁻] calcd, 830.8; found, 830.7. Elemental Analysis. calcd: 3.00 Cu; 4.77 Ru; found: 2.88 Cu; 4.61 Ru (0.99 mol Cu: 1 mol Ru).

3.2.2.20 Characterization of [Ru-5(Pd)](PF₆)₄

¹H NMR 400 MHz, acetonitrile-d₃: δ 9.08-8.43 (m, 2H); 8.43-8.19 (m, 7H); 8.19-7.95 (m, 4H); 7.95-7.79 (m, 5H); 7.79-7.66 (m, 2H); 7.66-7.31 (m, 10H); 7.31-6.99 (m, 4H); 4.45-3.67 (br, 6H); 3.67-3.14 (br, 8H); 2.57-2.20 (m, 6H); 2.17-2.12 (m, 2H); 1.42-0.94 (m, 18H); 0.86-0.38 (m, 12H). MS (ESI⁺) [M⁴⁺ ] calcd: 395.1; found: 395.2 [M⁴⁺ + 1 PF₆⁻] calcd:
575.2; found: 575.3. [M^{4+} + 2PF_6^-] calcd: 935.2; found: 935.3. Elemental Analysis. calcd: 4.92 Pd; 4.68 Ru; found: 4.54 Pd; 4.40 Ru (0.98 mol Pd: 1 mol Ru).

3.2.2.21 Characterization of [Ru-5(Zn)](PF_6)_4

\[ ^1H \text{NMR } 400 \text{ MHz, acetonitrile-d}_3: \delta \] ^1H NMR 400 MHz, acetonitrile-d_3: \delta 9.20-8.61 (m, 3H); 8.61-8.21 (m, 8H); 8.21-7.99 (m, 4H); 7.99-7.59 (m, 12H); 7.59-7.27 (m, 7H); 4.41-3.85 (br, 6H); 3.85-3.29 (br, 8H); 2.75-2.43 (m, 6H); 2.41-2.36 (m, 2H); 1.71-1.17 (m, 18H); 1.16-0.72 (m, 12H). MS (ESI^+) [M^{4+} + 1 PF_6^-] calcd: 561.8; found: 561.9. [M^{4+}] calcd: 385.1; found: 385.2. Elemental Analysis. calcd: 3.08 Zn; 4.77 Ru; found: 2.88 Zn; 4.42 Ru (1.01 mol Zn: 1 mol Ru).

3.2.2.22 Characterization of [Ru-6(Cu)](PF_6)_4

\[ ^1H \text{NMR } 400 \text{ MHz, acetonitrile-d}_3: \delta \] ^1H NMR 400 MHz, acetonitrile-d_3: \delta 8.96-8.52 (m, 1H); 8.52-8.17 (m, 4H); 8.12-7.88 (m, 4H); 7.88-7.73 (m, 2H); 7.73-7.44 (m, 6H); 7.44-7.21 (m, 3H); 7.21-6.93 (m, 2H); 4.68-3.94 (br, 3H); 3.94-3.31 (br, 5H); 3.31-2.70 (br, 2H); 1.80-1.58 (m, 4H); 1.58-1.45 (m, 2H); 1.45-1.04 (m, 18H); 1.04-0.51 (m, 12H). MS (ESI^+) [M^{4+} + 2 PF_6^-] calcd: 927.7; found: 927.9; [M^{4+} + 1 PF_6^-] calcd: 570.2; found: 570.2. [M^{4+} + CH_3CN] calcd: 410.9; found: 410.7. Elemental Analysis. calcd: 2.96 Cu; 4.71 Ru; found: 2.63 Cu; 4.01 Ru (1.04 mol Cu: 1 mol Ru).
3.2.2.23 Characterization of [Ru-6(Pd)](PF$_6$)$_4$

$^1$H NMR 400 MHz, acetonitrile-d$_3$: δ 8.79-8.49 (m, 2H); 8.45-8.15 (m, 8H); 8.15-7.96 (m, 4H); 7.96-7.78 (m, 4H); 7.78-7.60 (m, 2H); 7.60-7.33 (m, 10H); 7.33-7.04 (m, 4H); 4.41-4.14 (br, 2H); 4.14-3.88 (br, 3H); 3.88-3.61 (br, 1H); 3.61-3.25 (br, 6H); 3.25-2.87 (br, 2H); 2.57-2.16 (m, 6H); 1.66-1.43 (m, 4H); 1.42-1.28 (m, 2H); 1.28-0.98 (m, 18H); 0.84-0.47 (m, 12H). MS (ESI$^+$) [M$^{4+}$] calcd: 402.1; found: 402.1. [M$^{4+}$ + 1 PF$_6$$^-$] calcd: 584.5; found: 584.5. [M$^{4+}$ + 2PF$_6$$^-$] calcd: 949.2; found: 949.2. Elemental Analysis. calcd: 4.86 Pd; 4.62 Ru; found: 4.31 Pd; 4.04 Ru (1.02 mol Pd: 1 mol Ru).

3.2.2.24 Characterization of [Ru-6(Zn)](PF$_6$)$_4$

$^1$H NMR 400 MHz, acetonitrile-d$_3$: δ 9.15-8.62 (m, 3H); 8.62-8.49 (m, 4H); 8.49-8.26 (m, 4H); 8.24-8.04 (m, 4H); 8.04-7.84 (m, 12H); 7.84-7.50 (m, 8H); 7.50-7.18 (m, 7H); 4.67-4.29 (br, 2H); 4.29-3.84 (br, 4H); 3.89-3.56 (br, 4H); 3.56-2.95 (br, 4H); 2.69-2.37 (m, 6H); 1.90-1.69 (m, 4H); 1.69-1.55 (m, 2H); 1.55-1.08 (m, 18H); 1.14-0.49 (m, 12H). MS (ESI$^+$) [M$^{4+}$] calcd: 571.2; found: 571.2. [M$^{4+}$ + 1 PF$_6$$^-$] calcd: 929.2; found: 929.2. Elemental Analysis. calcd: 3.04 Zn; 4.71 Ru; found: 4.22 Ru (1.02 mol Zn: 1 mol Ru).

3.2.2.25 Characterization of [Ru-7(Cu)](PF$_6$)$_4$

$^1$H NMR 400 MHz, acetonitrile-d$_3$: δ 9.03-8.53 (m, 1H); 8.53-8.18 (m, 4H); 8.18-7.88 (m, 4H); 7.88-7.72 (m, 2H); 7.72-7.40 (m, 7H); 7.40-6.60 (m, 14H); 4.94-4.43 (br, 1H); 4.43-3.84 (br, 4H); 3.84-3.56 (br, 4H); 3.56-2.95 (br, 4H); 2.69-2.37 (m, 6H); 1.90-1.69 (m, 4H); 1.69-1.55 (m, 2H); 1.55-1.08 (m, 18H); 1.14-0.49 (m, 12H). MS (ESI$^+$) [M$^{4+}$] calcd: 571.2; found: 571.2. [M$^{4+}$ + 1 PF$_6$$^-$] calcd: 929.2; found: 929.2. Elemental Analysis. calcd: 3.04 Zn; 4.71 Ru; found: 2.78 Zn; 4.22 Ru (1.02 mol Zn: 1 mol Ru).
4.43-3.84 (br, 2H); 3.82-2.48 (br, 13H); 1.62-0.82 (m, 18H). MS (ESI⁺) [M⁴⁺ + 1 PF₆⁻] calcd: 592.8; found, 592.8. [M⁴⁺ + 2 PF₆⁻] calcd: 961.7; found: 961.8. Elemental Analysis. calcd: 2.87 Cu; 4.56 Ru; found: 2.43 Cu; 4.07 Ru (0.95 mol Cu: 1 mol Ru).

3.2.2.26 Characterization of [Ru-7(Pd)](PF₆)₄

¹H NMR 400 MHz, acetonitrile-d₃; δ 9.07-8.72 (m, 1H); 8.72-8.26 (m, 10H); 8.26-8.02 (m, 5H); 8.02-7.83 (m, 3H); 7.83-7.65 (m, 7H); 7.65-7.33 (m, 8H); 7.33-6.84 (m, 10H); 4.60-3.77 (br, 5H); 3.77-3.10 (br, 10H); 3.10-2.88 (br, 1H); 2.86-2.51 (m, 6H); 1.52-1.23 (m, 18H). MS (ESI⁺) [M⁴⁺] calcd: 419.1; found: 419.1. [M⁴⁺ + 1 PF₆⁻] calcd: 607.2; found: 607.2. [M⁴⁺ + 2 PF₆⁻] calcd: 983.4; found: 983.4. Elemental Analysis. calcd: 4.71 Pd; 4.48 Ru; found: 4.51 Pd; 3.99 Ru (1.08 mol Pd: 1 mol Ru).

3.2.2.27 Characterization of [Ru-7(Zn)](PF₆)₄

¹H NMR 400 MHz, acetonitrile-d₃; δ 9.07-8.61 (m, 2H); 8.61-8.18 (m, 7H); 8.18-7.97 (m, 4H); 7.97-7.54 (m, 12H); 7.54-6.71 (m, 19H); 4.41-3.77 (br, 5H); 3.77-2.99 (br, 11H); 2.72-2.35 (m, 6H); 1.49-1.07 (m, 18H). MS (ESI⁺) [M⁴⁺] calcd: 409.1; found: 409.1. [M⁴⁺ + 1 PF₆⁻] calcd: 593.8; found: 593.9. [M⁴⁺ + 2 PF₆⁻] calcd: 963.2; found: 963.4. Elemental Analysis. calcd: 2.95 Zn; 4.56 Ru; found: 2.63 Zn; 4.11 Ru (0.99 mol Zn: 1 mol Ru).
Figure 3-16: $^1$H NMR spectrum of Ru-5(Cu) at 400 MHz in CD$_3$CN.

Figure 3-17: $^1$H NMR spectrum of Ru-5(Pd) at 400 MHz in CD$_3$CN.
Figure 3-18: $^1$H NMR spectrum of Ru-5(Zn) at 400 MHz in CD$_3$CN.

Figure 3-19: $^1$H NMR spectrum of Ru-6(Cu) at 400 MHz in CD$_3$CN.
Figure 3-20: $^1$H NMR spectrum of Ru-6(Pd) at 400 MHz in CD$_3$CN.

Figure 3-21: $^1$H NMR spectrum of Ru-6(Zn) at 400 MHz in CD$_3$CN.
Figure 3-22: $^1$H NMR spectrum of Ru-7(Cu) at 400 MHz in CD$_3$CN.

Figure 3-23: $^1$H NMR spectrum of Ru-7(Pd) at 400 MHz in CD$_3$CN.
Figure 3-24: $^1$H NMR spectrum of Ru-7(Zn) at 400 MHz in CD$_3$CN.
**Figure 3-25**: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for $[\text{Ru-5(Cu)}](\text{NO}_3)_4$.
Figure 3-26: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-5(Pd)](PF$_6$)$_4$.

Figure 3-27: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-5(Zn)](PF$_6$)$_4$.
Figure 3-28: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-6(Cu)](PF₆)₄.
Figure 3-29: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for \([\text{Ru-6(Pd)}](\text{PF}_6)_4\).
**Figure 3-30**: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-6(Zn)](PF₆)₄.
Figure 3-31: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-7(Cu)](PF₆)₄.
**Figure 3-32**: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for $[\text{Ru-7(Pd)}](\text{PF}_6)_4$. 
Figure 3-33: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-7(Zn)](PF₆)₄
3.2.3 Methods

Mass spectrometric analysis was performed on a Waters LCT Premier time-of-flight (TOF) mass spectrometer at the Penn State Mass Spectrometry Facility. Samples were introduced into the mass spectrometer using a Waters 2695 high performance liquid chromatograph. The samples were analyzed using flow injection analysis (FIA), in which the sample is injected into the mobile phase flow and passes directly into the mass spectrometer, where the analytes are ionized and detected. The mobile phase used was 100% acetonitrile (LC-MS grade). The flow rate was 0.20 mL/min. The nitrogen drying gas temperature was set to 300 °C at a flow of 6 L/min. The capillary voltage was 2400 V. The mass spectrometer was set to scan from 100-2000 m/z in positive ion mode, using electrospray ionization (ESI). NMR spectra were collected using 300, 360 or 400 MHz spectrometers (Bruker) in the Lloyd Jackman Nuclear Magnetic Resonance Facility. Elemental analysis was performed by Galbraith Laboratories.

3.3 Results and Discussion

3.3.1 Synthesis of Chiral Backbones and Oligopeptides

The synthesis of chiral backbones is different from the method used to synthesize regular aeg backbone as previously reported by our group. In this three-step synthesis (Scheme 3-2), the 3-amino-1,2-propanediol was Fmoc-protected first to produce 3-(fmc-amino)-1,2-propanediol, which was then converted to Fmoc-Aminoacetaldehyde using the method reported in the literature. The Fmoc-Aminoacetaldehyde was further
reacted with t-butyl protected chiral amine to produce the chiral backbones respectively at 70–80% yield. The pendant bpy ligand was then introduced to the backbones via standard liquid phase peptide coupling reactions at ~50% yield in grams scale. The identity and purity of the backbones and bpy monomers were confirmed by MS and $^1$H NMR.

3.3.2 Synthesis and Characterization of Ru Complexes

Ruthenium hairpin complexes Ru-5, Ru-6 and Ru-7 were synthesized by reaction of an excess amount of Fmoc-deprotected bpy monomer with [Ru(bpy)$_2$(bpy(COCl)$_2$)]$^{2+}$ with triethylamine in dry dichloromethane. (Scheme 3-2) This approach rapidly enabled yields of > 30 % in hundreds of mg scales. The identities of these Ru complexes were confirmed by observation of molecular ion peaks in the electrospray mass spectra. Purity of these compounds was assessed by $^1$H NMR, $^{13}$C NMR, 2D HMBC, HMQC, COSY spectroscopy (Figure 3-1 through Figure 3-15) and elemental analysis. $^1$H NMR spectra confirmed the expected relative integrations of protons for Ru complexes; $^{13}$C NMR, 2D HMBC, HMQC, COSY spectroscopy were used to assign the peaks of protons and carbons of different molecules (Table 3-1, 3-2 and 3-3); The protons and carbons in Ru-4 were fully assigned in a previously published paper, and the protons and carbons in Ru-5, Ru-6 and Ru-7 have been assigned by comparing the 1D and 2D NMR spectra with the NMR spectra of Ru-4. For example, in the $^1$H NMR of Ru-7, the peak at ~ 7 ppm was assigned to the protons of the phenyl ring by comparing the $^1$H NMR spectra of Ru-7 with the $^1$H NMR spectra of Ru-4 and NH$_2$-ae$_{ab}(bpy)$-O/tBu. After this proton peak was assigned, the chemical shift (~ 128 ppm) of the carbons in the phenyl ring was also determined by analyzing the correlations between
the proton signals and carbon signals in 2D HMQC and $^{13}$C NMR spectra. 2D $^1$H-$^1$H COSY and HMBC were used to confirm the assignment. Elemental analysis revealed the tendency to retain small amounts of solvent even after extensive drying. Slight differences between the calculated and observed mass percentages of C, H and N are likely the result of residual salt (KNO$_3$) from the final purification column.
Scheme 3-2: Synthetic steps toward Ru-hairpin complexes
3.3.3 Synthesis and Characterization of Ru-M dimetallic Complexes

To understand the photophysical behavior and characterization of the dimetallic complexes, Ru-Cu, Ru-Pd and Ru-Zn complexes were synthesized in preparative scale. Using a soft ionization method as mentioned in experimental section, we were able to obtain mass spectra for all the dimetallic complexes. In each case, molecular ion peaks of species with different charges ranging from +2 to +4 were observed. For example in Figure 3-29, peaks corresponding to $M^{2+}$, $M^{3+}$ and $M^{4+}$ molecular ions were observed for the dimetallic $[\text{Ru-6(Pd)}]^{4+}$ complex associated with decreasing numbers of PF$_6^-$ anions. In comparison with the calculated isotopic splitting patterns expected for these species, these data conclusively identify the dimetallic complexes. (Series of molecular ion peaks for each of the heterometallic complexes are shown in Figure 3-25 through Figure 3-33). Elemental analysis of the Ru-M dimetallic complexes isolated from bulk scale preparation also confirms the 1:1 metal binding stoichiometric point, and also confirms the purity of the dimetallic complexes.

We observed that in each of the dimetallic compound, the measured percentage of the two metals is lower than expected, and this could be a result of the retention of small amounts of solvent after extensive drying.
3.4 Conclusions

In this chapter, three different Ru-hairpin structures with different side chain substituents have been successfully synthesized. Their purities and identities have been confirmed with mass spectrometry, NMR as well as elemental analysis. Adding a second transition metal ion such as Cu$^{2+}$, Pd$^{2+}$ or Zn$^{2+}$ to the Ru complexes forms heterometallic complexes and their purities and identities have also been confirmed using mass spectrometry, NMR and elemental analysis. The formed heterometallic complexes could be used to study donor-acceptor interactions. Their photophysical properties will be discussed in next chapter.
3.5 References

1. Abrahamsson, M. L.; Baudin, H. B.; Tran, A.; Philouze, C.; Berg, K. E.;


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Chapter 4

Impact of Side Chain Substituents On the Emission Photodynamics of [Ru(bpy)$_3$]$^{2+}$ with Artificial Oligopeptide Linked [Cu(bpy)$_2$]$^{2+}$, [Pd(bpy)$_2$]$^{2+}$ or [Zn(bpy)$_2$]$^{2+}$

4.1 Introduction

The placement of chromophores, electron donors/acceptors and redox sites at specific distances and orientations to create a long-lived charge separated state and slow down back electron transfer is crucial to artificial photosynthesis. Self-assembly via weak non-covalent interactions such as metal-ligand coordinate bonds, hydrogen bonding, electrostatic or hydrophobic interactions is a popular approach to build large supramolecular structures with multiple functional sites.\(^1\) Metal complexes are commonly found in these functional moieties because of their unique photophysical and electrochemical properties.\(^2,\,3\) To construct multisite, multifunctional supramolecular structures for artificial photosynthesis, our group has introduced a modified Ru tris(bipyridine) system with pendant aminoethylglycine (aeg) chains and free bipyridine (bpy) ligands.\(^4,\,5\) Coordination of a transition metal ion such as Cu$^{2+}$ or Zn$^{2+}$ closes the “hairpin loop” and forms heterometallic structures. In Chapter 3, we presented the synthesis and detailed characterization of a series of Ru-hairpin structures with the side chain substituents aminoethylvaline (val), aminoethylleucine (leu) and aminoethylphenylalanine (phe) (shown in Scheme 4-1). We also presented the synthesis and characterization of the [Ru(bpy)$_3$]$^{2+}$-[M(bpy)$_2$]$^{2+}$ complexes (M = Cu, Pd, or Zn). In this chapter, the formation of the dimetallic complexes is further studied using spectrophotometric emission titrations.
Scheme 4-1: Oligopeptide derivatized Ru complexes with different side chains. (aeg for Ru-4, val for Ru-5, leu for Ru-6 and phe for Ru-7)
Metal binding stoichiometry obtained from emission titrations gives the molar ratio of a second metal binding to the Ru complexes. A 1:1 metal binding stoichiometry supports the formation of a dimetallic complex.

In our previous study, binding Cu$^{2+}$ to the free bpy ligands caused excited state emission quenching of the [Ru(bpy)$_3$]$^{2+}$, and likely due to electron transfer.$^{4,5}$ However, it is generally difficult to determine the quenching mechanism because excited state emission quenching of [Ru(bpy)$_3$]$^{2+}$ could be via electron transfer or energy transfer or a combination of both.$^{6,7}$ In this chapter, we use several methods to probe the dominant quenching mechanism in these systems.

Bridging linkers are essential in donor-acceptor systems, not only because they bring donors and acceptors close enough for electron/energy transfer to happen, but also because they impact electron/energy transfer energetically and topologically.$^8$ Conjugated bridging linkers are more rigid and exert influence mostly through bound electron transfer by fixing donor-acceptor distance and regulating electronic communication between donor(s) and acceptor(s).$^9$ They have been studied extensively in dye-sensitized solar cells$^{10-17}$ and other donor-acceptor systems.$^9,18-22$ Saturated linkers are more flexible, but still have distance and conformational effects on mostly through-space electron transfer, as shown in recent examples.$^{21-24}$ Our group has previously studied distance effects of linkers by varying the length of the aminoethylglycine chain and found distance dependent quenching of [Ru(bpy)$_3$]$^{2+}$ by [Cu(bpy)$_2$]$^{2+}$. In this report, we further extend those studies to the conformational effects of linkers by incorporating amino acid building blocks with different side chain substituents (e.g. val, leu and phe) into the “Ru-hairpin” system. The side chains
have different sizes, orientations, and conformational flexibility. They could potentially have structural constraints on the orientation of electron donors and acceptors, and thus have impact on the emission photodynamics of the dimetallic \([\text{Ru(bpy)}_3]^{2+} \cdot [\text{M(bpy)}_2]^{2+}\) complexes (\(M = \text{Cu, Pd or Zn}\)). These compounds utilize a facile way to vary the side chain substituents on the linkers and potentially lead to optimizing linkers and designing artificial photosynthetic systems.

4.2 Experimental Section

4.2.1 Methods

UV-visible absorbance spectra were obtained with a double-beam spectrophotometer (Varian, Cary 500). Emission spectra were measured using a Photon Technology International (PTI) fluorescence spectrometer using an 814 photomultiplier detection system. Time resolved emission decays were measured following excitation using a \(\text{N}_2\) pumped dye laser (800 ps excitation, PTI model GL-302), averaging 16 decays with a 50 µs collection time per point. Quantum yields and radiative and non-radiative decay rate constants\(^{25}\) at all temperatures were determined using samples from which oxygen had been removed in repetitive freeze-pump-thaw cycles and finally in a sealed cell under nitrogen. Quantum yields were determined using the relationship:\(^{26}\)

\[
\Phi = \Phi_{\text{ref}} \frac{(I / A)}{(I_{\text{ref}} A_{\text{ref}})} \left( \frac{\eta}{\eta_{\text{ref}}} \right)^2
\]

Eq (4-1)

where \(\Phi\) is the radiative quantum yield of the sample; \(\Phi_{\text{ref}}\) is the known quantum yield of \([\text{Ru(bpy)}_3]^{2+}\) in acetonitrile = 0.062;\(^{27}\) \(I\) is the integrated emission, \(A\) is the absorbance at the
excitation wavelength; and \( \eta \) is the dielectric constant of the solvent, which is assumed to be the same for the acetonitrile solutions of sample and reference. The rate constants of radiative \( (k_r) \) and nonradiative \( (k_{nr}) \) decay were determined using the measured excited state lifetime (\( \tau \)) and the equations: \(^{25}\)

\[
\Phi = \frac{k_r}{k_r + k_{nr}} \quad \text{Eq (4-2)}
\]

\[
\tau^{-1} = k_r + k_{nr} \quad \text{Eq (4-3)}
\]

Spectrophotometric emission titrations were conducted in CH\textsubscript{3}CN or CH\textsubscript{3}OH solutions at room temperature in the presence of air using known concentrations of Ru compounds. The compounds were excited at their MLCT absorbance maxima (\( \lambda_{\text{abs}} \) in Table 4-1) and monitored at their emission maxima (\( \lambda_{\text{em}} \) in Table 4-1). Spectra were obtained after stirring each with known volumes (10 – 19 \( \mu \)L) of standard Cu\textsuperscript{2+} solutions (4.36 mM), Pd\textsuperscript{2+} solutions (3 – 6 mM) in CH\textsubscript{3}CN or Zn\textsuperscript{2+} solutions (5 – 6 mM) in CH\textsubscript{3}OH for 15 min.

All electrochemical measurements were obtained using a CH Instruments potentiostat (Model 660) with 0.31 cm diameter glassy carbon working and Pt wire counter electrodes with a Ag quasi reference electrode. Solutions were prepared from distilled CH\textsubscript{3}CN containing 0.2 M TBAP supporting electrolyte; the solutions were deoxygenated by purging with solvent-saturated N\textsubscript{2}. Potentials are reported vs. a saturated calomel electrode (SCE) reference scale using ferrocene as an internal potential reference standard.
4.3 Results and Discussion

4.3.1 Redox and Photophysical Properties of Ru Complexes

Analysis of the redox properties of the Ru complexes was performed using cyclic voltammetry. Figure 4-1 shows cyclic voltammograms of Ru-5, Ru-6 and Ru-7. The one electron oxidation peak at ~ 1.23 V is assigned to the well-known oxidation of Ru$^{III/II}$ couple and three sequential one electron reduction peaks at ~ -1.25 V, ~ -1.60 V and ~ -1.85 V in the reduction region are assigned to the sequential reduction of three bpy ligands around the Ru center. The first reduction peak at ~ -1.25 V is the reduction of the diamide-substituted bpy ligand, which is shifted to more positive potential due to the electron withdrawing property of the amides. The reduction of the pendant bpy ligands is outside the scanned potential window at larger overpotentials. These data are summarized in Table 4-1, and exhibit only very minor differences in the redox couples across the four Ru complexes, which is a reflection of their similar central structure.

Absorbance and emission spectra were also measured for each of the Ru complexes in acetonitrile solutions. Each of the complexes has an absorbance band with a peak centered at 470 nm which is assigned to the well-known metal-to-ligand charge transfer band of [Ru(bpy)$_3$]$^{2+}$. The extinction coefficients ($\epsilon$) and peak maxima do not vary as the peptide chains linked to the Ru center changes: the peak emission of all Ru complexes is centered at 650 nm. The quantum yields of Ru-7, Ru-6 and Ru-5 in thoroughly deaerated acetonitrile solutions are ~ 50% higher than that of Ru-4 even though they have the same [Ru(bpy)$_3$]$^{2+}$ center. Ru-7, with the bulkiest and most non-polar side chain (phenyl), has the highest
quantum yield (0.065) followed by Ru-6 (0.059) and Ru-5 (0.058). The Ru-4 hairpin which has no side chain has the lowest quantum yield (0.041). The relationship of quantum yield and bulkiness of the side chain could be due a change in the local dielectric by the non-polar side chains (such as phenyl). To test this hypothesis, a control experiment using benzene as the solvent was carried out to mimic the low dielectric environment of Ru-7. The quantum yield of Ru-4 increases from 0.04 in acetonitrile to 0.08 in benzene, suggesting that the excited state dynamics of the Ru complex are sensitive indicators of solvent dielectric. The excited state lifetimes of all Ru complexes are roughly the same ~ 1 µs, and this is typical for [Ru(bpy)_3]^{2+} compounds. Using the quantum yields and lifetimes, the radiative and nonradiative decay rates \(k_r\) and \(k_{nr}\) were calculated. The non-radiative decay rates decrease slightly as the bulkiness of side chains increases, which was as expected from the low quantum yields of Ru-6 and Ru-7, indicating the dependency of nonradiative decay rates on the bulkiness of the side chains in the Ru complexes.
Figure 4-1: Cyclic voltammograms of 1.1 mM Ru-7, Ru-6, and Ru-5 in CH$_3$CN with 0.2 M TBAP, 100 mV/s scan rate, with glassy carbon working and Pt counter electrodes and a Ag quasi reference electrode. Currents are normalized to Ru complex concentration.
Table 4-1: Photophysical and Electrochemical Data for Ru Hairpin Complexes.

<table>
<thead>
<tr>
<th></th>
<th>Ru-7</th>
<th>Ru-6</th>
<th>Ru-5</th>
<th>Ru-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{abs, max}}$ (nm)$^a$</td>
<td>470 (13.5)</td>
<td>470 (13.6)</td>
<td>470 (13.5)</td>
<td>469 (13.4)</td>
</tr>
<tr>
<td>($\varepsilon$, $M^{-1} \text{cm}^{-1} \times 1000$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{em, max}}$ (nm)$^b$</td>
<td>650</td>
<td>650</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>$\Phi^c$</td>
<td>0.065 ± 0.003</td>
<td>0.059 ± 0.002</td>
<td>0.058 ± 0.003</td>
<td>0.0405 ± 0.004</td>
</tr>
<tr>
<td>$\tau^d$ (µsec)</td>
<td>1.22 ± 0.02</td>
<td>1.24 ± 0.02</td>
<td>1.21 ± 0.02</td>
<td>1.18 ± 0.02</td>
</tr>
<tr>
<td>$k_r \times 10^7$ (sec)$^{-1}$</td>
<td>0.0053</td>
<td>0.0050</td>
<td>0.0050</td>
<td>0.0034</td>
</tr>
<tr>
<td>$k_{nr} \times 10^7$ (sec)$^{-1}$</td>
<td>0.076</td>
<td>0.076</td>
<td>0.078</td>
<td>0.081</td>
</tr>
<tr>
<td>$E^f_{\text{Ru}^{3+/2+}}$ (V)$^f$</td>
<td>1.26</td>
<td>1.25</td>
<td>1.26</td>
<td>1.29</td>
</tr>
<tr>
<td>$E^f_{\text{Ru}^{2+/1+}}$ (V)$^f$</td>
<td>-1.24</td>
<td>-1.19</td>
<td>-1.32</td>
<td>-1.25</td>
</tr>
<tr>
<td>$E^f_{\text{Ru}^{1+/0}}$ (V)$^f$</td>
<td>-1.60</td>
<td>-1.57</td>
<td>-1.65</td>
<td>-1.66</td>
</tr>
<tr>
<td>$E^f_{\text{Ru}^{0/-1}}$ (V)$^f$</td>
<td>-1.82</td>
<td>-1.79</td>
<td>-1.89</td>
<td>-1.88</td>
</tr>
</tbody>
</table>

$^a$ Maximum absorbance wavelength and extinction coefficient for the metal to ligand charge transfer band. $^b$ Peak emission wavelength following excitation at $\lambda_{\text{max,abs}}$. $^c$ Emission quantum yields following excitation at $\lambda_{\text{max,abs}}$, determined using [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN ($\Phi = 0.062$) as a reference. $^d$ Excited state lifetime in deoxygenated CH$_3$CN solutions, determined from the emission decay following pulsed excitation at $\lambda_{\text{max,abs}}$. $^e$ Rates of radiative ($k_r$) and nonradiative decay ($k_{nr}$). $^f$ Reaction formal potentials vs. SCE, measured in 0.2 M TBAP in deoxygenated CH$_3$CN.
4.3.2 Copper, Palladium and Zinc Coordination Emission Titrations

Spectrophotometric titrations were previously used to confirm metal binding stoichiometry and quantify quenching efficiencies in the Ru-hairpin structures.\textsuperscript{4, 5} Emission titrations were therefore conducted to examine the effects of Cu\textsuperscript{2+}, Zn\textsuperscript{2+} and Pd\textsuperscript{2+} coordination on the emission of \textbf{Ru-4, Ru-5, Ru-6 and Ru-7}. The emission spectra of the Ru complexes following excitation at 469 nm were monitored at 650 nm as aliquots of Cu\textsuperscript{2+}, Zn\textsuperscript{2+} or Pd\textsuperscript{2+} solution was added sequentially to the solution of Ru complexes. We previously reported that coordination of Cu\textsuperscript{2+} or Zn\textsuperscript{2+} to the pendant bpy ligands of \textbf{Ru-4} resulted in excited state emission quenching of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}.\textsuperscript{5} The coordination of 1 molar equivalent of Cu\textsuperscript{2+} to \textbf{Ru-4} resulted in 97% excited state quenching of the [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} chromophore.\textsuperscript{5} The coordination of 1 molar equivalent of Zn\textsuperscript{2+} to \textbf{Ru-4} resulted in about 10% excited state emission quenching.\textsuperscript{5} The emission titration spectra of Cu\textsuperscript{2+} to \textbf{Ru-5, Ru-6, and Ru-7} also show quenching of the emission intensity by coordination of Cu\textsuperscript{2+}. Titration plots of Cu\textsuperscript{2+} to \textbf{Ru-5, Ru-6, and Ru-7} level out after 1 equiv. of Cu\textsuperscript{2+} is added to the Ru complex solutions (\textbf{Figure 4-2}), which indicates binding one Cu\textsuperscript{2+} to a pair of pendant bpy ligands forms [Cu(bpy)\textsubscript{2}\textsuperscript{2+} and closes the Ru-hairpin loop to produce the Ru-Cu dimetallic complex. Cu\textsuperscript{2+} coordination causes ~95% of the emission quenching of the Ru complexes.

Coordination of 1 equiv. Zn\textsuperscript{2+} also produces [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}-[Zn(bpy)\textsubscript{2}]\textsuperscript{2+} dimetallic complexes and causes 5% - 10% excited state quenching of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} (\textbf{Figure 4-2}). The quenching efficiency of Zn\textsuperscript{2+} in all chiral hairpins (\textbf{Ru-5, Ru-6, Ru-7}) is smaller than in the aeg hairpin (\textbf{Ru-4}). The quenching caused by coordination of Zn\textsuperscript{2+} is likely to be the formation of [Zn(bpy)\textsubscript{2}]\textsuperscript{2+} changes the chemical environment of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+}.\textsuperscript{29} The observed
low quenching efficiency in chiral hairpins (Ru-5, Ru-6, Ru-7) suggests the bulky side chains in between of [Ru(bpy)₃]²⁺ and [Zn(bpy)₂]²⁺ reduced the change of the chemical environment of [Ru(bpy)₃]²⁺ caused by formation of [Zn(bpy)₂]²⁺.

Pd²⁺ was also chosen to be studied based on two reasons: (a) the redox potential of [Pd(bpy)₂]²⁺ is ~ -0.5 V (vs. SCE) which would favor a [Ru(bpy)₃]²⁺ excited state quenching by an electron transfer mechanism, as with Cu²⁺; and (b) when attached closely to [Ru(bpy)₃]²⁺, [Pd(bpy)₂]²⁺ has been shown to yield compounds with photocatalytic properties. The titration plots of Pd²⁺ to Ru complexes are shown in Figure 4-5. Similar to the titrations of Cu²⁺ and Zn²⁺, the emission intensity of all Ru complexes levels out after about 1 molar equivalent of Pd²⁺ is added to the solution, which suggests the hairpin loop closes to form the Ru-Pd dimetallic complexes. However, the quenching efficiency varies among the Ru complexes: the aeg hairpin (Ru-4(Pd)) has the highest quenching efficiency (~40%) while the leu hairpin (Ru-6(Pd)) has the lowest (~15%). To quantitatively compare the differences in the quenching efficiency of binding Cu²⁺ and Pd²⁺ caused by the side chain substituents, the relative rates were measured in deaerated solutions and discussed below.
**Figure 4-2:** Emission spectra of CH$_3$CN solution containing 116 µM Ru-5 with addition of 14 µL aliquots of 4.36 mM Cu(NO$_3$)$_2$.

**Figure 4-3:** Plot of emission spectra of CH$_3$CN solution containing 122.6 µM Ru-5 with addition of 12 µL aliquots of 5.17 mM Pd(ACN)$_3$(BF$_4$)$_2$. 
Figure 4-4: Plot of emission spectra of methanol solution containing 142.1 µM Ru-5 with addition of 13 µL aliquots of 5.24 mM Zn(OAc)$_2$. 
Figure 4-5: Plot of normalized emission intensity of CH$_3$CN solution containing

(▼) 134.4 µM Ru-7 with addition of 12 µL aliquots of 4.36 mM Cu(NO$_3$)$_2$;

(▲) 144.0 µM Ru-6 with addition of 16 µL aliquots of 4.36 mM Cu(NO$_3$)$_2$;

(■) 116.0 µM Ru-5 with addition of 14 µL aliquots of 4.36 mM Cu(NO$_3$)$_2$.

(▼) 157.4 µM Ru-7 with addition of 12 µL aliquots of 5.17 mM Pd(ACN)$_4$(BF$_4$)$_2$;

(▲) 134.4 µM Ru-6 with addition of 19 µL aliquots of 3.51 mM Pd(ACN)$_4$(BF$_4$)$_2$;

(■) 122.6 µM Ru-5 with addition of 12 µL aliquots of 5.17 mM Pd(ACN)$_4$(BF$_4$)$_2$;

(●) 126.8 µM Ru-4 with addition of 12 µL aliquots of 5.17 mM Pd(ACN)$_4$(BF$_4$)$_2$.

Plot of emission intensity of methanol solution containing

(▼) 115.2 µM Ru-7 with addition of 11 µL aliquots of 5.24 mM Zn(acetate)$_2$;

(▲) 121.8 µM Ru-6 with addition of 10 µL aliquots of 5.77 mM Zn(acetate)$_2$;

(■) 142.1 µM Ru-5 with addition of 13 µL aliquots of 5.24 mM Zn(acetate)$_2$. 
Table 4-2: Photophysical Data for Ru-M Heterometallic Complexes

<table>
<thead>
<tr>
<th>M^{2+}</th>
<th>Ru-7</th>
<th>Ru-6</th>
<th>Ru-5</th>
<th>Ru-4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Zn</td>
<td>Pd</td>
<td>Cu</td>
</tr>
<tr>
<td>Φ&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0116</td>
<td>0.05</td>
<td>0.057</td>
<td>0.0081</td>
</tr>
<tr>
<td>τ&lt;sup&gt;a&lt;/sup&gt; (µsec)</td>
<td>0.053</td>
<td>1.01</td>
<td>0.571</td>
<td>0.047</td>
</tr>
<tr>
<td>k&lt;sub&gt;r&lt;/sub&gt; x 10&lt;sup&gt;7&lt;/sup&gt; (sec)&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.020</td>
<td>0.005</td>
<td>0.01</td>
<td>0.017</td>
</tr>
<tr>
<td>k&lt;sub&gt;nr&lt;/sub&gt; x 10&lt;sup&gt;7&lt;/sup&gt; (sec)&lt;sup&gt;-1&lt;/sup&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.85</td>
<td>0.094</td>
<td>0.165</td>
<td>2.1</td>
</tr>
<tr>
<td>E&lt;sub&gt;a,Arr&lt;/sub&gt; (kJ/mol)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>34.5</td>
<td>8.9</td>
<td>18.8</td>
<td>21.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Emission lifetime (τ), quantum yield (Φ), radiative and nonradiative (k<sub>r</sub> and k<sub>nr</sub>) rate constants at 25°C in deaerated CH<sub>3</sub>CN solutions.

<sup>b</sup>activation energy, determined from the slopes of Arrhenius plots as in Figure 4-7.
4.3.3 Time-Resolved Emission Spectroscopy

To quantitatively compare the photophysical properties of the Ru-M complexes, quantum yields and lifetimes of all the Ru-M complexes were obtained in deaerated acetonitrile solutions and are listed in Table 4-2. We begin with discussion of Ru-Cu to start the comparison. The quantum yield of Ru-4(Cu) is only 0.0001 whereas the quantum yields of Ru-5(Cu) and Ru-6(Cu) are about eight times larger. In the case of Ru-7(Cu), the quantum yield is ten-fold greater than Ru-4(Cu). The excited state lifetimes of the Ru-Cu complexes also increase as the size of the polyamide side chain increases: Ru-4(Cu) has a lifetime of ~30 ns, Ru-5(Cu) and Ru-6(Cu) have lifetimes of ~40 ns, and Ru-7(Cu) has the longest lifetime that is over 60 ns. Using the quantum yields and lifetimes together, the radiative and nonradiative decay rates of the Ru-Cu complexes were calculated. The radiative decay rates of Ru-5(Cu), Ru-6(Cu) and Ru-7(Cu) are nearly ten times greater than that of Ru-4(Cu), which indicates the radiative decay pathway is more favored for Ru-5(Cu), Ru-6(Cu) and Ru-7(Cu) comparing to Ru-4(Cu). The nonradiative decay rate dramatically decreases from 2.91x10^7 s\(^{-1}\) to 1.85x10^7 s\(^{-1}\) over the series of molecules, as the size of side chain increases. The radiative and nonradiative decay processes are two competing pathways when [Ru\(^{11+}\)(bpy\(^{3-}\))(bpy\(^{2+}\))]\(^{2+}\) is quenched. The greater radiative decay rates of Ru-5(Cu), Ru-6(Cu) and Ru-7(Cu) comparing to Ru-4(Cu) is likely to be a result of low nonradiative decay rates of Ru-5(Cu), Ru-6(Cu) and Ru-7(Cu) caused by the bulky side chains.

A similar trend was observed in the series of Ru-Pd complexes with varying oligoamide side chains: The radiative decay rates of Ru-5(Pd), Ru-6(Pd) and Ru-7(Pd) are
much higher than that of **Ru-4**(Pd), which agrees with the observed low quenching of **Ru-5**(Pd), **Ru-6**(Pd) and **Ru-7**(Pd). This trend could be explained the same way as in Ru-Cu species. No trend was observed in the analogous Ru-Zn complexes. The fact that such a trend has been observed for only Ru-Cu and Ru-Pd but not for Ru-Zn could be the result of different quenching mechanisms in these species. Quenching of the excited state Ru complex could occur by electron or energy transfer mechanism or a combination of both.\(^{6,32,33}\) For example, excited state electron transfers in the Ru-Cu and Ru-Pd species can occur by:

\[
[Ru^{III}(bpy)_2(bpy^*)]^- \rightarrow [Cu^{II}(bpy)_2] \rightarrow [Ru^{III}(bpy)_3] \rightarrow [Cu^{II}(bpy)_2] \quad \text{Eq (4-4)}
\]

\[
[Ru^{III}(bpy)_2(bpy^*)]^- \rightarrow [Pd^{II}(bpy)_2] \rightarrow [Ru^{III}(bpy)_3] \rightarrow [Pd^{II}(bpy)(bpy^*)] \quad \text{Eq (4-5)}
\]

The electron transfer process in Eq (4-4) has a favorable \(\Delta G_0\) of -0.7 eV and this is likely the major quenching pathway in the nonradiative decay process of Ru-Cu, although energy transfer remains a possible quenching mechanism because of weak extinction of \([Cu(bpy)_2]^{2+}\).\(^{34-38}\) For the Ru-Pd complexes, the electron transfer process in Eq (4-5) has a favorable \(\Delta G_0\) of -0.2 eV and there is no spectral overlap, so that electron transfer is likely the dominant quenching mechanism in the nonradiative decay process. However, \([Zn(bpy)_2]^{2+}\) is both redox and spectroscopically silent, so the quenching caused by Zn\(^{2+}\) is neither electron transfer nor energy transfer. A plausible explanation is the formation of \([Zn(bpy)_2]^{2+}\) changes the chemical environment of \([Ru(bpy)_3]^{2+}\).\(^{29}\)

To further investigate this hypothesis, a study of the effect of on the excited state dynamics was carried out. According to Marcus theory, if electron transfer dominates the
nonradiative decay process, the nonradiative decay rate should be inversely related to the solvent dielectric properties:

\[
\tilde{\lambda}_0 = (\Delta e)^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right)
\]

Eq (4-6)

where \(1/D_{op} - 1/D_s\) is the Pekar factor, and \(D_{op}\) and \(D_s\) are the optical and static dielectric constants of the solvent. In Figure 4-6, it is clear that the natural log of the nonradiative decay rate of each of the Ru-Cu and Ru-Pd complexes has a negative trend versus the Pekar factor, whereas no such a trend is observed for Ru-Zn complexes. This observation supports excited state quenching caused by electron transfer in the \([\text{Ru(bpy)}_3]^2+ - [\text{Cu(bpy)}_2]^2+\) and \([\text{Ru(bpy)}_3]^2+ - [\text{Pd(bpy)}_2]^2+\) structures.

Variable temperature studies of the time-resolved emission were used to better understand the emission photodynamics and non-radiative decay processes. Quantum yields and lifetimes of the Ru-M series of complexes in deaerated acetonitrile solutions were obtained; nonradiative decay rates \(k_{nr}\) were calculated and plotted in the Arrhenius plots in Figure 4-7. The varying slopes for the Ru-Cu and Ru-Pd complexes indicate differences in their activation energies for the nonradiative decay process. The activation energies are calculated and listed in Table 4-2. Comparison of the nonradiative decay activation energy of Ru-4(Cu) and Ru-7(Cu) reveals a striking difference in these structures. Whereas Ru-7(Cu) has the highest activation energy (34.5 kJ/mol), this is ~ 2 times greater than in Ru-4(Cu) (13.1 kJ/mol). The activation energies of Ru-5(Cu) and Ru-6(Cu) fit right in between of Ru-4(Cu) and Ru-7(Cu), and increase as the side chain increases its size from val to leu. This is in agreement with the observed trend in \(k_{nr}\), since a large activation energy barrier for nonradiative decay process leads to a small \(k_{nr}\). A similar trend in the activation energy and \(k_{nr}\)
was also observed with the Ru-Pd complexes, however the magnitude of the change was not as large as with the Ru-Cu complexes.

It is hypothesized that the change of activation energy and $k_{nr}$ in Ru-Cu and Ru-Pd complexes results from a change of local dielectric caused by substituents on the oligoamide side chains. For example, the phenyl groups in the phe-substituted complexes would create the lowest local dielectric constant in the environment immediately surrounding the Ru complex. To test the impact of a low dielectric constant on, the quantum yield and lifetime of Ru-4(Cu) were measured in a benzene solution. Under these conditions, the quantum yield of the Ru complex is 0.002, higher than in acetonitrile, and its lifetime is 12 ns, significantly shorter than in acetonitrile. Together this leads to a $k_{nr}$ of $8.32 \times 10^7 \text{s}^{-1}$ for Ru-4(Cu) in benzene and does not agree with our initial proposed hypothesis.

To mimic the change of local dielectric of Ru-7(Cu) caused by phenyl groups, Ru-4(Cu) in benzene is used as a control since the major structural difference between Ru-7(Cu) and Ru-4(Cu) is the phenyl ring. In Eq (4-6), $\lambda_o$ is the outer-sphere reorganization energy, while $D_{op}$ and $D_s$ are the optical and static dielectric and $1/D_{op} - 1/D_s$ is the Pekar factor of the solvent. Since benzene has a very small Pekar factor which is close to 0, it is expected that Ru-4(Cu) has a very small $\lambda_o$ in benzene. The small $\lambda_o$ leads to small total reorganization energy in Eq (4-7). $\lambda$ is the total reorganization energy and $\lambda_i$ is the inner sphere reorganization energy.

$$\lambda = \lambda_o + \lambda_i$$  \hspace{1cm} \text{Eq (4-7)}
Figure 4-6: Plots of the natural log of nonradiative decay rate ($k_{nr}$) of (▼) Ru-7(Cu); (▲)Ru-6(Cu); (■)Ru-5(Cu); (●)Ru-4(Cu); (▼)Ru-7(Pd); (▲)Ru-6(Pd) (■)Ru-5(Pd); (●)Ru-4(Pd); (▼)Ru-7(Zn); (▲)Ru-6(Zn); (■)Ru-5(Zn) and (●)Ru-4(Zn) in different solvents at room temperature versus Pekar Factor ($1/D_{op}-1/D_s$) where $D_{op}$ and $D_s$ are the optical and static dielectric constants of the solvent.
Figure 4-7: Arrhenius plot of the non-radiative relaxation rate ($k_{nr}$) for A: (●) Ru-7(Cu);
(■) Ru-6(Cu); (▲) Ru-5(Cu); (○) Ru-4(Cu); B(●) Ru-7(Pd);
(■) Ru-6(Pd); (▲) Ru-5(Pd); (○) Ru-4(Pd) in deoxygenated CH$_3$CN solutions.
In the normal region of Marcus theory, a small reorganization energy leads to small activation energy barrier, and a large nonradiative decay rate. If the change of the local dielectric caused by the non-polar side chains has an impact on the nonradiative decay process of Ru-7(Cu), it is expected that Ru-7(Cu) would have the smallest activation energy barrier and largest $k_{nr}$ among all Ru-Cu complexes. However, our data shows that Ru-7(Cu) has the largest activation energy barrier and smallest $k_{nr}$, so the change of local dielectric does not have a significant impact on the electron transfer process.

Another way to explain the trend in $k_{nr}$ is the bulky functional side chains could restrict the necessary geometry change that accompanies electron transfer. [Cu$^{ll}$(bpy)$_2$] has a d$^9$ electronic configuration and generally adopts a distorted square pyramidal or trigonal bipyramidal geometry resulting from an axial ligand from solvent or counter ion and [Cu$^{l}$(bpy)$_2$] has a d$^{10}$ electronic configuration and generally adopts a pseudo-tetrahedral geometry. When [Cu$^{ll}$(bpy)$_2$] is reduced to [Cu$^{l}$(bpy)$_2$], the geometry change is necessary, however, when there are bulky functional groups very close to [Cu$^{ll}$(bpy)$_2$], they could limit or inhibit the geometry change, and it is unlikely for [Cu$^{l}$(bpy)$_2$] to have a pseudo-tetrahedral geometry. The bulkier the side chains the more distorted the geometry of [Cu$^{l}$(bpy)$_2$] is from tetrahedral and the less stable [Cu$^{l}$(bpy)$_2$] is, assuming all else is the same. This means the electron transfer product with the bulkiest side chains has the highest energy level. As a result, the absolute value of $\Delta G_0$ for this electron transfer process decreases and the activation energy barrier increases and thus causes a decrease in the electron transfer rate. This is consistent with our observations in the Ru-Cu complexes. As the side chains
become more sterically hindered, the activation energy increases and the electron transfer rate decreases.

The photophysical properties of Ru-Pd follow similar trends, except that the magnitude of the trend is smaller which could be due to the fact that \( \Delta G_0 \) for electron transfer from \([\text{Ru(bpy)}_3]^{2+}\) to \([\text{Pd(bpy)}_2]^{2+}\) is much smaller than that from \([\text{Ru(bpy)}_3]^{2+}\) to \([\text{Cu(bpy)}_2]^{2+}\). Ru-7(Pd) has the highest quantum yield followed by Ru-6(Pd), which are all higher than 0.05. Ru-5(Pd) has a quantum yield of 0.044 followed by the smallest quantum yield of Ru-4(Pd) which is only \( \sim 0.02 \). The lifetimes of all Ru-Pd complexes are roughly the same, with Ru-7(Pd) being the longest and Ru-4(Pd) the shortest, which together lead to the \( k_r \) of Ru-7(Pd) the highest, followed by Ru-6(Pd) and Ru-5(Pd), with Ru-4(Pd) being the lowest. The \( k_{nr} \) decreases as the side chain gets bulkier, with Ru-4(Pd) the largest and Ru-7(Pd) the smallest.

A mechanism similar to the Ru-Cu complexes is invoked to explain what is observed in the Ru-Pd complexes. The small molecule \([\text{Pd(bpy)}_2]^{2+}\) favors a square planer geometry,\(^{54}\) however, there are no available structures of mononuclear \([\text{Pd(bpy)}_2]^+\), and all examples of the reduced species exist in a Pd-Pd dimer form.\(^{55-60}\) The cyclic voltammogram of \([\text{Pd(bpy)}_2]^{2+}\) shows two irreversible reduction peaks that are usually assigned to the reduction of the bpy ligand and the metal center. This irreversible behavior leads us to conclude that \([\text{Pd(bpy)}_2]^+\) is an unstable intermediate that may further undergo ligand dissociation, consistent with the literature.\(^{61}\) In this way, sterically hindered functional groups could also increase the activation energy by preventing ligand dissociation that accompanies electron transfer.
No such relationship is observed for the Ru-Zn complexes, as the size of the side chains on the oligopeptide is increased, which is likely due to a different excited state quenching mechanism in these species.

4.4 Conclusions

In this chapter, we utilize the compounds synthesized in the prior chapter to create a series of oligopeptide derivatized $[\text{Ru(bpy)}_3]^{2+}$ complexes with pendant bpy ligands, different side chain substituents, and coordinated Cu$^{2+}$, Pd$^{2+}$ or Zn$^{2+}$. The formation of dimetallic complexes causes excited state emission quenching of $[\text{Ru(bpy)}_3]^{2+}$. Electron transfer is the energetically favorable excited state quenching mechanism for the structures containing Cu$^{2+}$ and Pd$^{2+}$. Investigation of the impacts of solvent polarity also suggests that electron transfer could be the dominant quenching pathway for Cu$^{2+}$ and Pd$^{2+}$. Photophysical data show $k_{nr}$ decreases and activation energy increases as the size of side chain increases for all Ru-Cu and Ru-Pd complexes. This is likely due to the sterically-hindered functional groups restricting the necessary geometry change or ligand dissociation that accompanies the electron transfer. Our study gives an insight into the impact of side chain substituents on the donor-acceptor interactions and provides useful information on optimizing linkers between donors and acceptors.
4.5 References


57. Bonney, K. J.; Proutiere, F.; Schoenebeck, F. Chemical Science 2013, 4, 4434-4439.


Chapter 5

Self-assembly of Multimetallic Complexes Featuring Coordination of Hexacoordinate Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ or Mn$^{2+}$ to Aminoethylglycine Derivatized [Ru(bpy)$_3$]$_2^{2+}$ with Pendant Bipyridines

5.1 Introduction

Artificial photosynthetic systems require specific arrangement of photosensitizers, donors, acceptors, reaction centers and different redox sites to promote efficient conversion of solar energy to chemical energy.$^1$ Different approaches have been made to tether donors and acceptors together to induce electron/energy transfer.$^2$-$^{11}$ and most of them rely on covalent linking.$^4$-$^{11}$ These systems require challenging synthetic steps in which tailoring the properties using structural variations are generally daunting.$^4$-$^6, 8$-$^{11}$ An alternative approach to design donor-acceptor systems with tunable structures is to learn from nature and use modular repeating units such as amino acid building blocks. Structural variations such as changing donor-acceptor distance, or changing donor/accepter ratio could be easily achieved by varying the number and position of amino acid monomers or redox center-substituted monomers in a peptide backbone using amide coupling reactions. There have been several bio-inspired peptide nucleic acid structures designed to insert metal ions to peptide nucleic acid (PNA) duplexes and to study metal center interactions.$^{12-19}$ However because of the electrochemical irreversibility of the nucleic acid, using metal-containing PNA for redox cascades or long range electron transfer is greatly restricted. To eliminate the use of nucleic acid, our group has designed a modified [Ru(bpy)$_3$]$_2^{2+}$ system containing pendant aminoethylglycine (aeg) chains with free bipyridine (bpy) ligands,$^{20, 21}$ which relies solely on the metal-ligand interaction to
direct self-assembly of a second transition metal ion. The \([\text{Ru(bpy)}_3]^{2+}\) complexes are categorized as “Ru-single strand” complex,\(^{21}\) which has one pendant aeg chain with one free bpy ligand, or “Ru-hairpin” complex,\(^{20}\) with two pendant aeg chains and two free bpy ligands. (Scheme 5-1) Addition of a tetra-coordinate transition metal ion such as \(\text{Cu}^{2+}\) to a solution of “Ru-single strand” complex causes intermolecular cross-linking and self-assembly to form a \([\text{Ru(bpy)}_3]^{2+}-[\text{Cu(bpy)}_2]^{2+}-[\text{Ru(bpy)}_3]^{2+}\) trimetallic complex.\(^{21}\) Coordination of \(\text{Cu}^{2+}\) to the two free bpy ligands in a “Ru-hairpin” structure closes the hairpin loop, and forms \([\text{Ru(bpy)}_3]^{2+}-[\text{Cu(bpy)}_2]^{2+}\) complex.\(^{20}\) In each case, formation of \([\text{Cu(bpy)}_2]^{2+}\) causes ~95% excited state emission quenching of \([\text{Ru(bpy)}_3]^{2+}\) and this is likely to be caused by an electron transfer process. Other tetracoordinate transition metal ions such as \(\text{Zn}^{2+}\) or \(\text{Pd}^{2+}\) have also been incorporated to the Ru system,\(^{22}\) and also result in excited state emission quenching of \([\text{Ru(bpy)}_3]^{2+}\).

In designing the Ru-hairpin system, we considered the denticity of the free bpy ligand and the coordination number of the transition metal ion. Bpy is a bidentate ligand, and two bidentate ligands can only coordinate to a tetracoordinate transition metal ion to form a \([2 \times 2]\) metal center. We want to expand our study to hexacoordinate transition metal ions such as \(\text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}\) or \(\text{Mn}^{2+}\) because of their unique redox properties.

Literature has suggested that a solution containing a mixture of \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Co(bpy)}_3]^{2+}\) is able to photocatalyze water splitting via an electron transfer process with the addition of a sacrificial electron donor.\(^{23-26}\) There are also examples of tethering \([\text{Ru(bpy)}_3]^{2+}\) and manganese polypyridyl complexes to photo-induce electron transfer from manganese polypyridyl complexes to \([\text{Ru}^{III}(bpy)]^{3+}\) with the addition of a sacrificial electron.
Scheme 5-1: Structures of Ru-single strand (Ru-ss) and Ru-hairpin (Ru-ds-1) complexes.
To form analogous compounds using the aeg motif, incorporation of hexacoordinate metals could be accomplished by coordination of a metal ion by three bpy ligands. For example, a $[\text{Ru(bpy)}_3]^{2+}-[\text{M(bpy)}_3]^{2+}$ heterometallic complex, where M$^{2+}$ is a hexacoordinate transition metal ion, there must be three free bpy ligands in a Ru complex. To do this, we modified the Ru-single strand structure and designed the Ru-triple strand complex (Scheme 5-2). In this structure, each bpy around the Ru center is mono-aeg substituted, and there is a free bpy ligand on each pendant aeg chain. With the structural variations in Scheme 5-2, our aims here are two-fold: first, to direct the self-assembly of a hexacoordinate transition metal ion such as Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ or Mn$^{2+}$ to the Ru complex to form a $[\text{Ru(bpy)}_3]^{2+}-[\text{M(bpy)}_3]^{2+}$ heterometallic structures; and second, to study the impact of the distance and the spacing groups on the emission photodynamics of the $[\text{Ru(bpy)}_3]^{2+}-[\text{M(bpy)}_3]^{2+}$ dimetallic complexes.
Scheme 5-2: Structures of Ru-triple strand complexes
5.2 Experimental Section

5.2.1 Chemicals and Reagents

N-Hydroxybenzotriazole (HOBT) was purchased from AdvancedChemTech. O-Benzotriazole-N,N,N’,N’-tetramethyl-uronium-hexafluorophosphate (HBTU) was purchased from NovaBiochem. Iron (II) perchlorate hydrate, Manganese (II) perchlorate hexahydrate (99.995%) and Nickel (II) nitrate hexahydrate (98%) were purchased from Alfa Aesar. Cobalt (II) perchlorate hexahydrate was purchased from Aldrich Chemical Company. All solvents were used as received without further purification unless otherwise noted. Tetrabutylammonium perchlorate (TBAP) was recrystallized three times from ethyl acetate.

The syntheses of tert-butyl N-[2-(N-9-fluorenylmethoxycarbonyl)aminoethyl]glycinate hydrochloride (Fmoc-aeg-OtBu•HCl), \[\text{NH}_2\text{-}[\text{aeg(bpy)}]\text{-OtButyl}\], [Ru(4’-methyl-2,2’-bipyridine-4-carboxylic acid)(PF$_6$)$_2$]([Ru(MebpyCA)$_3$](PF$_6$)$_2$), [Ru(Mebpy([aeg(bpy)-OtButyl])$_3$](PF$_6$)$_2$] (Ru-1) were performed as described in Chapter 2.

5.2.2 Synthesis

5.2.2.1 Synthesis of Fmoc-aeg(ibu)-OtButyl (1)

Isobutyric acid (5g, 53.8 mmol), EDC (4.43g, 23 mmol), HOBT (3.53g, 23 mmol) were added to 200 mL dry dichloromethane in a round bottom flask stirred in an ice bath. The suspension was stirred for 15 min and DIPEA (15 mL, 86 mmol) was added. The solution was
stirred for another 15 min. Fmoc-aeg-OtBu•HCl (5g, 11.5 mmol) was dissolved in 50 mL dichloromethane and washed with 3x50 mL saturated NaHCO₃ aqueous solution. The organic layer was dried with Na₂SO₄ and the solvent was removed via flash evaporation. The yellow oil was redissolved in 10 mL dichloromethane and added to the solution containing isobutyric acid. The mixture was then stirred at room temperature for 2 days. The reaction mixture was washed with water (3x50 mL). The organic layer was dried with Na₂SO₄ and solvent was removed via flash evaporation. The crude product was purified on a silica column eluted with a solvent gradient (0.5% methanol in dichloromethane to 1% methanol in dichloromethane). Like fractions were combined and the solvent was evaporated to give a white solid (2.15g, 40% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.73 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 4.34 (dd, J = 13.8, 7.2 Hz, 2H), 4.19 (d, J = 6.7 Hz, 1H), 3.90 (s, 1H), 3.51 (dd, J = 15.7, 5.6 Hz, 2H), 3.40 – 2.98 (m, 2H), 2.85 (dt, J = 13.0, 6.3 Hz, 1H), 2.52 (s, 1H), 1.47 (s, 9H), 1.12 (d, J = 6.5 Hz, 6H). MS (ESI⁺) [M + H⁺] Calcd: 467.3; Found: 467.2.

5.2.2.2 Synthesis of Fmoc-aeg(phe)-OtButyl (2)

Benzoic acid (2.95g, 24 mmol), EDC (4.63g, 24 mmol), HOBT (3.70g, 24 mmol) were add to 200 mL dry dichloromethane in a round bottom flask stirred in an ice bath. The suspension was stirred for 15 min and DIPEA (15 mL, 86 mmol) was added. The solution was stirred for another 15 min. Fmoc-aeg-OtBu•HCl (5.23g, 12mmol) was dissolved in 50 mL dichloromethane and washed with 3x50 mL saturated NaHCO₃ aqueous solution. The organic layer was dried with Na₂SO₄ and the solvent was removed via flash evaporation. The yellow
oil was redissolved in 10 mL dichloromethane and added to the solution containing benzoic acid. The solution was then stirred at room temperature for 2 days. The reaction mixture was washed with water (3x50 mL). The organic layer was dried with Na$_2$SO$_4$ and solvent was removed via flash evaporation. The crude product was purified on a silica column, eluted with a solvent gradient (100% dichloromethane to 2% methanol in dichloromethane). Like fractions were combined and the solvent was evaporated to give a white solid (3.88g, 58%).

$^1$H NMR (360 MHz, CDCl$_3$): $\delta$ 7.87 – 7.68 (m, 2H), 7.62 (d, $J = 7.3$ Hz, 2H), 7.37 (d, $J = 6.6$ Hz, 5H), 7.28 (dd, $J = 17.6$, 8.1 Hz, 4H), 4.36 (d, $J = 7.1$ Hz, 1H), 4.30 – 4.15 (m, 2H), 4.11 (s, 1H), 3.90 (s, 1H), 3.72 (s, 1H), 3.51 (d, $J = 5.1$ Hz, 1H), 3.43 (s, 1H), 3.22 (d, $J = 4.8$ Hz, 1H), 1.75 – 1.12 (m, 9H). MS (ESI$^+$) [M + H$^+$] Calcd: 501.2; Found: 501.3.

5.2.2.3 Amine and Acid Deprotection

Fmoc deprotection was accomplished using a modified literature procedure.$^{25}$ Briefly, a sample of Fmoc-protected oligopeptide was stirred overnight with 1 molar equivalent 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 10 molar equivalents decane thiol in THF. After this time, the solvent was removed by rotary evaporation and the product redissolved in 75 mL of 0.15 M HCl. The aqueous solution was extracted 5 times with 50 mL hexanes, the organic layers were combined and back-extracted with 0.15 M HCl and all aqueous portions combined. The acidic aqueous solution was adjusted to a pH of 9-10 with saturated Na$_2$CO$_3$ and the aqueous layer extracted 5 times with 50 mL CH$_2$Cl$_2$, the organic fractions combined and dried with Na$_2$SO$_4$. Dichloromethane was removed by rotary evaporation to give the pure amine-terminated oligopeptide. In each case, removal of the Fmoc was confirmed by mass
spectrometry and by noting the absence of Fmoc proton peaks in the aromatic region of the $^1$H NMR spectra.

Cleavage of the tert-butyl protecting groups from select oligopeptides to form terminal carboxylic acids was accomplished by acid hydrolysis in a 50/50 (v/v) trifluoroacetic acid/dichloromethane solution. The solution was stirred for 2 hours and the solvent removed by rotary evaporation. Diethyl ether was added to precipitate a pale yellow solid. The ether was decanted and the solid dried by vacuum to give the pure carboxylic acid-terminated oligopeptide. In each case, removal of the t-butyl was confirmed by the absence of the proton peaks of the t-butyl group in the $^1$H NMR spectrum.

5.2.2.4 Synthesis of NH$_2$-[aeg(ibu)-aeg(bpy)]-O$^t$Butyl (3)

The acid terminus of the Fmoc-aeg(ibu)-O$^t$Butyl monomer was deprotected as described above, and 5.77 g of the product (Fmoc-aeg(ibu)-COOH, 14 mmol) was dissolved in 300 mL CH$_2$Cl$_2$ with 2.7 g EDC (14 mmol), 2.2 g HOBT (14 mmol) and 12 mL diisopropylethylamine (DIPEA, 68 mmol), and stirred for 15 min at 0°C. A 4.4 g amount of H$_2$N-aeg(bpy)-OrButyl (11.3 mmol) was added to the solution and stirred for 2 days at room temperature. Solvent was removed by rotary evaporation and the pale yellow residue purified by column chromatography with silica gel using 5/95 (v/v) CH$_3$OH/CH$_2$Cl$_2$ to give 3.59 g (40.7%) of the Fmoc-protected dipeptide 3. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.74 – 8.36 (m, 2H), 8.25 (dd, $J$ = 21.3, 8.4 Hz, 2H), 7.70 (d, $J$ = 7.8 Hz, 2H), 7.57 (d, $J$ = 7.6 Hz, 2H), 7.44 – 7.28 (m, 2H), 7.26 (m, 3H), 7.07 (dd, $J$ = 13.4, 3.8 Hz, 1H), 4.31 (d, $J$ = 7.5 Hz, 2H), 4.21 – 4.06 (m, 1H), 4.05 (s, 1H), 4.00 – 3.87 (m, 2H), 3.79 (d, $J$ = 20.4 Hz, 2H), 3.68 (s, 1H), 3.62 (d, $J$ = 10.6 Hz,
2H), 3.50 (s, 6H), 2.79 (m, 1H), 2.37 (d, \( J = 7.4 \) Hz, 3H), 1.51 – 1.28 (m, 9H), 1.04 (dt, \( J = 12.0, 6.2 \) Hz, 6H). MS (ESI\(^+\)) [M + H\(^+\)] Calcd: 777.4; Found: 777.5.

The Fmoc was cleaved and dipeptide 3 isolated as described above; a 2.02 g amount of the pure product was collected (79% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.36 (dd, \( J = 8.6, 4.7 \) Hz, 1H), 8.25 (t, \( J = 5.9 \) Hz, 1H), 8.13 – 7.79 (m, 2H), 7.18 – 6.96 (m, 1H), 6.96 – 6.67 (m, 1H), 3.81 (d, \( J = 4.7 \) Hz, 1H), 3.72 (dd, \( J = 8.7, 3.7 \) Hz, 2H), 3.68 – 3.55 (m, 2H), 3.55 – 3.34 (m, 2H), 3.22 (m, 6H), 2.80 – 2.48 (m, 2H), 2.19 (s, 3H), 1.20 (dd, \( J = 13.4, 7.2 \) Hz, 9H), 0.95 – 0.74 (m, 6H). MS (ESI\(^+\)) [M + H\(^+\)] Calcd: 555.3; Found: 555.3.

5.2.2.5 Synthesis of NH\(_2\)-[aeg(phe)-aeg(bpy)]-OtButyl (4)

The acid terminus of the Fmoc-aeg(phe)-OtButyl monomer was deprotected as described above, and 4.54 g of the product (Fmoc-aeg(phe)-COOH, 10.2 mmol) was dissolved in 300 mL CH\(_2\)Cl\(_2\) with 1.96 g EDC (10.2 mmol), 1.57 g HOBT (10.2 mmol) and 10 mL diisopropylethylamine (DIPEA, 57 mmol), and stirred for 15 min at 0 \(^\circ\)C. A 2.62 g amount of H\(_2\)N-aeg(bpy)-OtButyl (6.8 mmol) was added to the solution and stirred for 2 days at room temperature. Solvent was removed by rotary evaporation and the pale yellow residue purified by column chromatography with silica gel using 5/95 (v/v) CH\(_3\)OH/CH\(_2\)Cl\(_2\) to give 3.74 g (68%) of the Fmoc-protected dipeptide 4. \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 8.58 (dd, \( J = 11.0, 4.8 \) Hz, 1H), 8.46 (d, \( J = 4.9 \) Hz, 1H), 8.22 (t, \( J = 18.1 \) Hz, 2H), 7.74 (d, \( J = 7.2 \) Hz, 2H), 7.60 (t, \( J = 7.3 \) Hz, 2H), 7.37 (t, \( J = 7.0 \) Hz, 4H), 7.33 – 6.94 (m, 7H), 4.21 (dd, \( J = 33.4, 19.4 \) Hz, 3H), 4.00 (dd, \( J = 37.5, 19.0 \) Hz, 5H), 3.69 (d, \( J = 18.3 \) Hz, 2H), 3.60 – 3.33 (m, 5H), 3.28 (d, \( J = 25.6 \) Hz, 2H), 2.40 (d, \( J = 6.0 \) Hz, 3H), 1.49 (s, 9H). MS (ESI\(^+\)) [M + H\(^+\)] Calcd: 811.4; Found: 811.5.
The Fmoc was cleaved and dipeptide 4 isolated as described above; a 2.39 g amount of the pure product was collected (88 % yield). $^1$H NMR (300 MHz, CDCl$_3$): δ 8.43 (s, 1H), 8.33 (d, $J = 4.7$ Hz, 1H), 8.08 (dd, $J = 17.5$, 8.1 Hz, 2H), 7.45 – 7.09 (m, 5H), 7.08 – 6.78 (m, 2H), 3.92 (d, $J = 25.3$ Hz, 2H), 3.86 – 3.62 (m, 3H), 3.32 (m, 7H), 2.65 (dd, $J = 43.7$, 30.3 Hz, 2H), 2.26 (d, $J = 3.9$ Hz, 3H), 1.29 (t, $J = 9.8$ Hz, 9H). MS (ESI$^+$) [M + H$^+$] Calcd: 589.3; Found: 589.3.

5.2.2.6 General Approach for Ru Complex Syntheses.

The Ru complex [Ru(MebpyCA)$_3$](PF$_6$)$_2$ was refluxed in 50 mL CH$_2$Cl$_2$ and 2 mL SOCl$_2$ overnight to form the tri-acid chloride complex, [Ru(MebpyCOCl)$_3$]$^{2+}$. The solution was cooled to room temperature and filtered to give a red solid which was washed with cold, dry CH$_2$Cl$_2$ and used immediately. To form the Ru tri-single strand complexes, the [Ru(MebpyCOCl)$_3$]$^{2+}$ was combined with ~ 10 molar equivalents of an amine-terminated oligopeptide and 3 mL triethylamine in 100 mL dry CH$_2$Cl$_2$. The reaction was stirred overnight at room temperature and the solvent removed by rotary evaporation. The remaining red residue was purified first by column chromatography with alumina using a 10/90 (v/v) CH$_3$OH/CH$_2$Cl$_2$ mobile phase. The first red band was collected and further purified on silica using 5:4:1 (volume ratio) CH$_3$OH:H$_2$O:sat KNO$_3$ (aq) solution as the mobile phase. In all cases, the products were isolated using previously reported methods$^{20a}$ and characterized as below:
5.2.2.7 Characterization of [Ru(Mebpy( [aeg(ac)-aeg(bpy)-OtButyl])₃](NO₃)₂ (Ru-8)

The isolated product was a 0.230 g amount of red solid (58% yield). ¹H NMR (360 MHz, CDCl₃): δ 9.34 (d, J = 129.2 Hz, 2H), 8.97 (s, 3H), 8.67 (s, 1H), 8.57 – 8.29 (m, 9H), 8.29 – 7.99 (m, 7H), 7.99 – 7.64 (m, 7H), 7.41 (d, J = 33.1 Hz, 4H), 7.24 (d, J = 36.5 Hz, 5H), 7.09 (s, 3H), 4.65 – 3.73 (m, 16H), 3.73 – 2.85 (m, 26H), 2.70 – 2.23 (m, 18H), 2.23 – 1.59 (m, 9H), 1.53 – 1.22 (m, 27H). HRMS (ESI⁺) [M²⁺] Calcd: 1134.4862; Found: 1134.4844. Elemental Anal. [Ru-8• 2CH₂Cl₂] Calcd: 55.76 C; 5.58 H; 14.21 N. Found: 55.61 C; 5.24 H; 14.78 N.

5.2.2.8 Characterization of [Ru(Mebpy( [aeg(ibu)-aeg(bpy)-OtButyl])₃](NO₃)₂ (Ru-9)

The isolated product was a 0.158 g amount of red solid (44% yield). ¹H NMR (300 MHz, CDCl₃): δ 9.61 (s, 1H), 8.97 (s, 4H), 8.38 (dd, J = 24.3, 4.7 Hz, 9H), 8.21 – 7.95 (m, 6H), 7.95 – 7.53 (m, 7H), 7.36 (s, 4H), 7.30 – 6.78 (m, 10H), 3.94 (dd, J = 61.8, 18.6 Hz, 16H), 3.74 – 3.18 (m, 26H), 3.16 – 2.55 (m, 3H), 2.55 – 2.11 (m, 18H), 1.25 (dd, J = 52.0, 12.0 Hz, 27H), 0.94 (s, 18H). HRMS (ESI⁺) [M²⁺] Calcd: 1176.5314; Found: 1176.5280. Elemental Anal. [Ru-9• CH₂Cl₂] Calcd: 58.12 C; 5.98 H; 14.21 N. Found: 57.36 C; 5.77 H; 14.88 N.

5.2.2.9 Characterization of [Ru(Mebpy([aeg(phe)-aeg(bpy)-OtButyl])₃](NO₃)₂ (Ru-10)

The isolated product was a 0.212 g amount of red solid (52% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.40 (s, 1H), 9.14 (s, 1H), 8.94 (s, 3H), 8.74 – 8.20 (m, 9H), 8.20 – 7.98 (m, 6H), 7.80 (s, 8H), 7.37 (s, 8H), 7.23 (d, J = 37.0 Hz, 13H), 7.04 (s, 6H), 4.05 (dd, J = 77.8, 43.5 Hz, 10H), 3.83 – 3.55 (m, 13H), 3.46 (s, 14H), 3.07 (s, 5H), 2.35 (d, J = 5.2 Hz, 18H), 1.33 (t, J

[Ru-10 • CH$_2$Cl$_2$ • H$_2$O] Calcd: 59.54 C; 5.56 H; 13.57 N. Found: 55.79 C; 5.32 H; 14.11 N.
Figure 5-1: $^1$H NMR spectrum of Ru-8 at 400 MHz in CDCl$_3$. Solvent peaks are removed for clarity.

Figure 5-2: $^{13}$C NMR spectrum of Ru-8 at 400 MHz in CDCl$_3$. 
Figure 5-3: HMBC spectrum of Ru-8 at 400 MHz in CDCl₃.

Figure 5-4: HMQC spectrum of Ru-8 at 400 MHz in CDCl₃.
Figure 5-5: COSY spectrum of Ru-8 at 400 MHz in CDCl$_3$.

Figure 5-6: $^1$H NMR spectrum of Ru-9 at 400 MHz in CDCl$_3$. Solvent peaks are removed for clarity.
Figure 5-7: $^{13}$C NMR spectrum of Ru-9 at 400 MHz in CDCl$_3$.

Figure 5-8: HMBC spectrum of Ru-9 at 400 MHz in CDCl$_3$. 
**Figure 5-9**: HMQC spectrum of Ru-9 at 400 MHz in CDCl$_3$.

**Figure 5-10**: COSY spectrum of Ru-9 at 400 MHz in CDCl$_3$. 
Figure 5-11: $^1$H NMR spectrum of Ru-10 at 400 MHz in CDCl$_3$.

Figure 5-12: $^{13}$C NMR spectrum of Ru-10 at 400 MHz in CDCl$_3$. 
Figure 5-13: HMBC spectrum of Ru-10 at 400 MHz in CDCl₃.

Figure 5-14: HMQC spectrum of Ru-10 at 400 MHz in CDCl₃.
Figure 5-15: COSY spectrum of Ru-10 at 400 MHz in CDCl$_3$. 
**Table 5-1**: $^1$H and $^{13}$C shifts for Ru-8 in CDCl$_3$.

![Chemical Structure](image)

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5.2.2.10 Synthesis of Ruthenium-Iron, Ruthenium-Cobalt, Ruthenium-Nickel and Ruthenium-Manganese Complexes

\[ [\text{Ru-3}(M)](\text{PF}_6)_4, \quad [\text{Ru-8}(M)](\text{PF}_6)_4, \quad [\text{Ru-9}(M)](\text{PF}_6)_4 \text{ and } [\text{Ru-10}(M)](\text{PF}_6)_4 \] (where M is Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) or Mn\(^{2+}\)) were synthesized by dissolving Ru-3, Ru-8, Ru-9 or Ru-10 in CH\(_3\)CN, adding 1.2 equivalents of the appropriate metal salt (Fe(ClO\(_4\))\(_2\), Co(ClO\(_4\))\(_2\), Ni(NO\(_3\))\(_2\), or Mn(ClO\(_4\))\(_2\)) respectively. The reaction solutions were stirred for 2 hours, and a saturated aqueous solution of NH\(_4\)PF\(_6\) was added to produce a dark precipitate. The solid was collected on a medium frit and washed with water and diethyl ether to yield the heterometallic complexes.

Identity and purity of these compounds were determined by \(^1\)H NMR, mass spectrometry and elemental analysis.

5.2.2.11 Characterization of [Ru-3(Fe)](PF\(_6\))\(_4\)

\(^1\)H NMR 300 MHz, acetonitrile-d\(_3\): \(\delta 9.07 – 8.07 (\text{br, 8H}); 8.07 – 6.29 (\text{br, 28H}); 4.65 – 2.94 (\text{br, 24H}); 2.85 – 2.38 (\text{br, 18H}); 1.66 – 1.11 (m, 27H). MS (ESI\(^+\)) [M\(^{4+}\) + PF\(_6^-\)] Calcd: 681.2; Found: 681.3. [M\(^{4+}\)] Calcd: 477.7; Found: 477.8. Elemental Analysis. Calcd: 2.25 Fe; 4.08 Ru; Found: 2.56Fe; 4.10 Ru (1.12 mol Fe: 1 mol Ru).

5.2.2.12 Characterization of [Ru-3(Co)](PF\(_6\))\(_4\)

\(^1\)H NMR 300 MHz, acetonitrile - d\(_3\): \(\delta 9.60 – 8.13 (\text{br, 5H}); 8.16 – 6.41 (\text{br, 22H}); 4.65 – 3.00 (\text{br, 24H}); 3.00 – 2.28 (\text{br, 18H}); 1.69 – 1.08 (m, 27H). MS (ESI\(^+\)) [M\(^{4+}\) + ClO\(_4^-\) + PF\(_6^-\)] Calcd: 1072.8; Found: 1072.6. [M\(^{4+}\) + ClO\(_4^-\)] Calcd: 666.9; Found: 666.8. [M\(^{4+}\)] Calcd:
475.4; Found: 475.3. Elemental Analysis. Calcd: 2.37 Co; 4.07 Ru; Found: 2.21 Co; 4.10 Ru
(0.92 mol Co: 1 mol Ru).

5.2.2.13 Characterization of [Ru-3(Ni)](PF₆)₄

¹H NMR 300 MHz, acetonitrile – d₃: δ 9.14 – 8.13 (br, 7H); 8.13 – 6.19 (br, 28H);
4.97 – 3.13 (br, 24H); 3.05 – 2.46 (br, 18H); 1.64 – 1.08 (m, 27H). MS (ESI⁺) [M⁴⁺ + 2 NO₃⁻]
Calcd: 1012.3; Found: 1012.4. [M⁴⁺ + NO₃⁻] Calcd: 654.2; Found: 654.2. [M⁴⁺] Calcd: 475.2;
Found: 475.2. Elemental Analysis. Calcd: 2.37 Ni; 4.07 Ru; Found: 2.31 Ni; 4.13 Ru (0.96
mol Ni: 1 mol Ru).

5.2.2.14 Characterization of [Ru-3(Mn)](PF₆)₄

¹H NMR 300 MHz, acetonitrile – d₃: δ 9.42 – 6.89 (br, 38H); 4.61 – 2.95 (br, 24H);
2.95 – 2.11 (br, 18H); 1.65 – 0.97 (m, 27H). MS (ESI⁺) [M⁴⁺ + 2 PF₆⁻] Calcd: 1093.8; Found:
Elemental Analysis. Calcd: 2.22 Mn; 4.08 Ru; Found: 2.28 Mn; 4.17 Ru (1.00 mol Mn: 1 mol
Ru).
Figure 5-16: $^1$H NMR spectrum of [Ru-3(Fe)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-17: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-3(Fe)](PF$_6$)$_4$. 
Figure 5-18: $^1$H NMR spectrum of [Ru-3(Co)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-19: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-3(Co)](PF$_6$)$_4$

$[M^{4+}+ClO_4^-+PF_6^-]^2+$, $[M^{4+}+ClO_4^-]^3+$, $[M^{4+}]$. 
Figure 5-20: $^1$H NMR spectrum of [Ru-3(Ni)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-21: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-3(Ni)](NO$_3$)$_4$. 
**Figure 5-22:** $^1$H NMR spectrum of [Ru-3(Mn)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

**Figure 5-23:** Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-3(Mn)](PF$_6$)$_4$. 
5.2.2.15 Characterization of [Ru-8(Fe)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile – d$_3$: $\delta$ 9.21 – 8.01 (br, 10H); 8.01 – 7.45 (br, 8H);
7.45 – 6.32 (br, 18H); 4.47 – 3.68 (m, 18H); 3.68 – 2.81 (m, 24H); 2.81 – 2.31 (m, 18H); 1.67
– 0.88 (m, 36H). MS (ESI$^+$) [M$^{4+}$ + NO$_3$ + ClO$_4$] Calcd: 1243.4; Found: 1243.4. [M$^{4+}$ +
Calcld: 1.92 Fe; 3.48 Ru; Found: 1.88 Fe; 3.39 Ru (1.00 mol Fe: 1 mol Ru).

5.2.2.16 Characterization of [Ru-8(Co)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile – d$_3$: $\delta$ 9.45 – 8.04 (br, 4H); 8.04 – 6.35 (m, 18H);
5.97 – 3.34 (br, 42H); 2.80 – 2.09 (br, 18H); 1.61 – 0.41 (m, 36H). MS (ESI$^+$) [M$^{4+}$ + NO$_3$ +
ClO$_4$] Calcd: 1245.4; Found: 1245.4. [M$^{4+}$ + NO$_3$] Calcd: 796.6; Found: 796.6. [M$^{4+}$] Calcd:
582.0; Found: 582.0. Elemental Analysis. Calcld: 2.03 Co; 3.46 Ru; Found: 2.11 Co; 3.57 Ru
(1.01 mol Co: 1 mol Ru).

5.2.2.17 Characterization of [Ru-8(Ni)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile – d$_3$: $\delta$ 9.19 – 8.16 (br, 4H); 8.13 – 6.46 (m, 32H);
6.44 – 5.63 (br, 2H); 3.84 – 4.73 (br, 15H); 3.84 – 2.90 (br, 25H); 2.87 – 2.01 (m, 18H); 1.73
– 0.43 (m, 36H). MS (ESI$^+$) [M$^{4+}$ + 2 NO$_3$] Calcd: 1206.4; Found: 1206.4. [M$^{4+}$ + NO$_3$]
Calcd: 797.0; Found: 797.0. [M$^{4+}$] Calcd: 582.0; Found: 582.0. Elemental Analysis. Calcd:
2.02 Ni; 3.48 Ru; Found: 2.11 Ni; 3.52 Ru (1.03 mol Ni: 1 mol Ru).
5.2.2.18 Characterization of [Ru-8(Mn)](PF₆)₄

$^1$H NMR 300 MHz, acetonitrile - d₃: $\delta$ 9.75 - 8.09 (br, 14H); 8.09 - 5.88 (br, 22H); 4.86 - 2.90 (br, 42H); 2.90 - 2.31 (br, 18H); 1.67 - 0.13 (m, 36H). MS (ESI$^+$) [M$^{4+}$ + 2 PF$_6^-$]

Calcd: 1306.9; Found: 1306.9. [M$^{4+}$ + PF$_6^-$] Calcd: 823.0; Found: 823.0. [M$^{4+}$] Calcd: 581.0; Found: 581.0. Elemental Analysis. Calcd: 1.89 Mn; 3.48 Ru; Found: 1.78 Mn; 3.45 Ru (0.95 mol Mn: 1 mol Ru).
Figure 5-24: $^1$H NMR spectrum of $[\text{Ru-8(Fe)}](\text{PF}_6)_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-25: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for $[\text{Ru-8(Fe)}](\text{NO}_3)_4$ $[\text{M}^{4+}+\text{NO}_3^-+\text{ClO}_4^-]^{3+}$, $[\text{M}^{4+}+\text{NO}_3^-]^{3+}$, $[\text{M}^{4+}]$. 
Figure 5-26: $^1$H NMR spectrum of [Ru-8(Co)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-27: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-8(Co)](NO$_3$)$_4$

[M$^{4+}$+NO$_3^-$+ClO$_4^-$]$^{2+}$, [M$^{4+}$+NO$_3^-$]$^{3+}$, [M$^{4+}$].
Figure 5-28: $^1$H NMR spectrum of [Ru-8(Ni)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-29: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-8(Ni)](NO$_3$)$_4$. 
Figure 5-30: $^1$H NMR spectrum of $[\text{Ru-8(Mn)}](\text{PF}_6)_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-31: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for $[\text{Ru-8(Mn)}](\text{PF}_6)_4$. 
5.2.2.19 Characterization of [Ru-9(Fe)](PF₆)₄

1H NMR 300 MHz, acetonitrile – d₃: δ 9.21 – 8.01 (br, 10H); 8.01 – 7.45 (br, 8H); 7.45 – 6.32 (br, 18H); 4.47 – 3.68 (m, 24H); 3.68 – 2.31 (m, 18H); 1.67 – 0.88 (m, 36H). MS (ESI⁺) [M⁴⁺ + NO₃⁻ + ClO₄⁻] Calcd: 1285.5; Found: 1285.4. [M⁴⁺ + NO₃⁻] Calcd: 823.7; Found: 823.6. [M⁴⁺] Calcd: 602.2; Found: 602.3. Elemental Analysis. Calcd: 1.87 Fe; 3.38 Ru; Found: 1.95 Fe; 3.35 Ru (1.05 mol Fe: 1 mol Ru).

5.2.2.20 Characterization of [Ru-9(Co)](PF₆)₄

1H NMR 300 MHz, acetonitrile – d₃: δ 9.38 – 8.05 (br, 6H); 8.05 – 6.04 (br, 18H); 4.50 – 2.97 (br, 42H); 2.88 – 2.50 (m, 21H); 1.69 – 1.14 (m, 27H); 1.10 – 0.56 (m, 18H). MS (ESI⁺) [M⁴⁺ + NO₃⁻ + PF₆⁻ + CH₃CN] Calcd: 1307.5; Found: 1307.5. [M⁴⁺ + ClO₄⁻ + CH₃CN] Calcd: 851.0; Found: 851.0. [M⁴⁺] Calcd: 613.2; Found: 613.2. Elemental Analysis. Calcd: 1.97 Co; 3.38 Ru; Found: 2.03 Co; 3.28 Ru (1.03 mol Co: 1 mol Ru).

5.2.2.21 Characterization of [Ru-9(Ni)](PF₆)₄

1H NMR 300 MHz, acetonitrile – d₃: δ 9.56 – 8.20 (br, 16H); 8.20 – 6.24 (m, 20H); 4.64 – 2.95 (br, 42H); 2.93 – 2.12 (br, 21H); 1.74 – 1.15 (br, 27H); 1.15 – 0.13 (m, 18H). MS (ESI⁺) [M⁴⁺ + 2 NO₃⁻] Calcd: 1268.5; Found: 1268.5. [M⁴⁺ + NO₃⁻] Calcd: 825.0; Found: 825.0. [M⁴⁺] Calcd: 603.2; Found: 603.3. Elemental Analysis. Calcd: 1.96 Ni; 3.38 Ru; Found: 2.05 Ni; 3.30 Ru (1.06 mol Ni: 1 mol Ru).
5.2.2.22 Characterization of [Ru-9(Mn)](PF₆)₄

\[^1\text{H} \text{NMR 300 MHz, acetonitrile - d₃; } δ 9.45 \sim 8.21 (\text{br, 16H}); 8.21 \sim 6.72 (\text{br, 20H}); 4.76 \sim 2.96 (\text{br, 42H}); 2.91 \sim 2.32 (\text{br, 21H}); 1.69 \sim 1.09 (\text{br, 27H}); 1.03 \sim 0.32 (\text{br, 18H}).\] MS (ESI⁺) [M⁴⁺ + 2 PF₆⁻] Calcd: 1349.0; Found: 1349.0. [M⁴⁺ + PF₆⁻] Calcd: 851.0; Found: 851.0. [M⁴⁺] Calcd: 602.0; Found: 602.0. Elemental Analysis. Calcd: 1.84 Mn; 3.38 Ru; Found: 1.92 Mn; 3.29 Ru (1.07 mol Mn: 1 mol Ru).
Figure 5-32: $^1$H NMR spectrum of [Ru-9(Fe)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-33: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-9(Fe)](ClO$_4$)$_4$

$[M^{4+} + NO_3^- + PF_6^-]^2^+, [M^{4+} + ClO_4^-]^3^+, [M^{4+}]$. 
Figure 5-34: $^1$H NMR spectrum of [Ru-9(Co)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-35: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-9(Co)](PF$_6$)$_4$ [M$^{4+}$+NO$_3^-$+PF$_6^-+CH_3CN]^{2+}$, [M$^{4+}$+ClO$_4^-$+CH$_3$CN]$^{3+}$, [M$^{4+}$+CH$_3$CN].
Figure 5-36: $^1$H NMR spectrum of [Ru-9(Ni)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-37: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-9(Ni)](NO$_3$)$_4$. 
**Figure 5-38:** $^1$H NMR spectrum of [Ru-9(Mn)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN. Solvent is removed for clarity.

**Figure 5-39:** Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-9(Mn)](PF$_6$)$_4$. 
5.2.2.23 Characterization of [Ru-10(Fe)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile - d$_3$: $\delta$ 9.02 - 8.03 (br, 12H); 8.03 - 7.43 (br, 12H);
7.43 - 6.24 (br, 27H); 4.41 - 2.73 (br, 42H); 2.78 - 2.31 (m, 18H); 1.70 - 1.01 (m, 27H). MS (ESI$^+$) [M$^{4+}$+NO$_3$ +ClO$_4$]$^-$ Calcd: 1336.4; Found: 1336.4. [M$^{4+}$+ClO$_4$]$^-$ Calcd: 870.3; Found:
870.3. [M$^{4+}$] Calcd: 628.0; Found: 628.0. Elemental Analysis. Calcd: 1.81 Fe; 3.27 Ru;
Found: 1.89 Fe; 3.22 Ru (1.06 mol Fe: 1 mol Ru).

5.2.2.24 Characterization of [Ru-10(Co)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile - d$_3$: $\delta$ 9.54 - 8.04 (br, 15H); 8.04 - 6.19 (br, 30H);
4.60 - 3.17 (br, 42H); 2.87 - 2.10 (br, 18H); 1.67 - 1.04 (m, 27H). MS (ESI$^+$) [M$^{4+}$ + ClO$_4$ +
NO$_3$]$^-$ Calcd: 1338.4; Found: 1338.4. [M$^{4+}$ + NO$_3$]$^-$ Calcd: 859.0; Found: 859.0. [M$^{4+}$] Calcd:
628.7; Found: 628.7. Elemental Analysis. Calcd: 1.90 Co; 3.27 Ru; Found: 1.95 Co; 3.25 Ru
(1.03 mol Co: 1 mol Ru).

5.2.2.25 Characterization of [Ru-10(Ni)](PF$_6$)$_4$

$^1$H NMR 300 MHz, acetonitrile - d$_3$: $\delta$ 9.36 - 8.15 (br, 9H); 8.15 - 6.35 (br, 42H);
4.68 - 2.81 (br, 42H); 2.81 - 2.10 (br, 18H); 1.54 - 1.29 (m, 27H). MS (ESI$^+$) [M$^{4+}$ + 2 NO$_3$]$^-$
Calcd: 1319.5; Found: 1319.5. [M$^{4+}$ + NO$_3$]$^-$ Calcd: 859.0; Found: 859.0. [M$^{4+}$] Calcd: 628.7;
Found: 628.8. Elemental Analysis. Calcd: 1.90 Ni; 3.27 Ru; Found: 1.96 Ni; 3.22 Ru (1.04
mol Ni: 1 mol Ru).
5.2.2.26 Characterization of [Ru-10(Mn)](PF₆)₄

¹H NMR 300 MHz, acetonitrile – d₃: δ 9.45 – 6.90 (br, 52H); 4.70 – 2.88 (br, 42H); 2.89 – 2.31 (br, 18H); 1.59 – 1.14 (m, 27H). MS (ESI⁺) [M⁴⁺ + 2 PF₆⁻] Calcd: 1400.4; Found: 1400.4. [M⁴⁺ + PF₆⁻] Calcd: 885.3; Found: 885.3. [M⁴⁺] Calcd: 627.7; Found: 627.7.

Elemental Analysis. Calcd: 1.78 Mn; 3.27 Ru; Found: 1.84 Mn; 3.31 Ru (1.02 mol Mn: 1 mol Ru).
Figure 5-40: $^1$H NMR spectrum of [Ru-10(Fe)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-41: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [Ru-10(Fe)](NO$_3$)$_4$ [M$^{4+}$+NO$_3^-$+ClO$_4^-$]$^{2+}$, [M$^{4+}$+ClO$_4^-$]$^{3+}$, [M$^{4+}$].
Figure 5-42: $^1$H NMR spectrum of [Ru-10(Co)](PF$_6$)$_4$ at 300 MHz in CD$_3$CN.

Figure 5-43: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for

$[\text{Ru-10(Co)}](\text{NO}_3)_4 \ [\text{M}^{2+} + \text{NO}_3^- + \text{ClO}_4^- ]^{2+}$, $[\text{M}^{3+} + \text{NO}_3^- ]^{3+}$, $[\text{M}^{4+}$].
**Figure 5-44:** $^1$H NMR spectrum of $[\text{Ru-10(Ni)}](\text{PF}_6)_4$ at 300 MHz in CD$_3$CN.

**Figure 5-45:** Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for

$[\text{Ru-10(Ni)}](\text{NO}_3)_4$. 
Figure 5-46: $^1$H NMR spectrum of [(Ru-10(Mn))(PF$_6$)$_4$] at 300 MHz in CD$_3$CN. Solvent peak is removed for clarity.

Figure 5-47: Molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [(Ru-10(Mn))(PF$_6$)$_4$].
5.2.3 Methods

UV-visible absorbance spectra were obtained with a double-beam spectrophotometer (Varian, Cary 500). Emission spectra were measured using a Photon Technology International (PTI) fluorescence spectrometer using an 814 photomultiplier detection system. Time resolved emission decays were measured following excitation using a N$_2$ pumped dye laser (800 ps excitation, PTI model GL-302), averaging 16 decays with a 50 µs collection time per point. Quantum yields and radiative and non-radiative decay rate constants at all temperatures were determined using samples from which oxygen had been removed in repetitive freeze-pump-thaw cycles and finally in a sealed cell under nitrogen. Quantum yields were determined using the relationship:

\[
\Phi = \Phi_{ref} \frac{(I / A)}{(I_{ref} A_{ref})} \left( \frac{\eta}{\eta_{ref}} \right)^2 \tag{5-1}
\]

where \( \Phi \) is the radiative quantum yield of the sample; \( \Phi_{ref} \) is the known quantum yield of [Ru(bpy)$_3$]$_{2+}$ in acetonitrile = 0.062; \( I \) is the integrated emission, \( A \) is the absorbance at the excitation wavelength; and \( \eta \) is the dielectric constant of the solvent, which is assumed to be the same for the acetonitrile solutions of sample and reference. The rate constants of radiative \( (k_r) \) and nonradiative \( (k_{nr}) \) decay were determined using the measured excited state lifetime \( (\tau) \) and the equations.

\[
\Phi = \frac{k_r}{k_r + k_{nr}} \tag{5-2}
\]

\[
\tau^{-1} = k_r + k_{nr} \tag{5-3}
\]

Spectrophotometric absorbance and emission titrations were conducted in CH$_3$CN solutions at room temperature in the presence of air using known concentrations of Ru
compounds. In the emission titrations, the compounds were excited at their MLCT absorbance maxima ($\lambda_{\text{abs}}$ in Table 5-4) and monitored at their emission maxima ($\lambda_{\text{em}}$ in Table 5-4).

During the spectrophotometric titrations, absorbance and emission spectra were obtained after stirring each with known volumes (5 - 15 µL) of standard Fe$^{2+}$ solutions (6 - 10 mM), Co$^{2+}$ solutions (3 - 6 mM), Ni$^{2+}$ solutions (4.84 mM) and Mn$^{2+}$ solutions (4.14 mM) in CH$_3$CN for 15 min.

Mass spectrometric analysis was performed on a Waters LCT Premier time-of-flight (TOF) mass spectrometer at the Penn State Mass Spectrometry Facility. Samples were introduced into the mass spectrometer using direct infusion via a syringe pump. The mass spectrometer scanned from 100-2000 m/z in positive ion mode using electrospray ionization (ESI$^+$).

NMR spectra were collected using either a 300, 360 or 400 MHz spectrometers (Bruker) in the Lloyd Jackman Nuclear Magnetic Resonance Facility. Elemental analysis was performed by Galbraith Laboratories.

All electrochemical measurements were obtained using a CH Instruments potentiostat (Model 660) with 0.31 cm diameter glassy carbon working and Pt wire counter electrodes with a Ag quasi reference electrode. Solutions were prepared from distilled CH$_3$CN containing 0.2 M TBAP supporting electrolyte; the solutions were deoxygenated by purging with solvent-saturated N$_2$. Potentials are reported vs. a saturated calomel electrode (SCE) reference scale using ferrocene as an internal potential reference standard.
5.3 Results and Discussion

5.3.1 Synthesis of Peptide Monomers and Dimers

The spacing groups were introduced to the aeg backbone using standard solution phase peptide coupling reactions. This produced peptide monomers with different spacing groups at a yield of 40 - 60%. We observed that the ibu monomer has the lowest yield even with excess amount of acid, which may be due to the high pKa of the acid. The formation of a amide bond involves two steps. The first step which is the activation of the carboxyl group of the acid could be slow if the acid has a high pKa and the coupling reagents will be degraded and will no longer be able to activate the carboxyl function, leading to a low yield.33 The monomers with spacing groups were then t-butyl deprotected to give the acid terminated monomers. The dipeptides were synthesized using standard peptide coupling reagents (Scheme 5-2). For example, reaction of H₂N-aeg(bpy)-OrButyl with Fmoc-aeg(ibu)-COOH with EDC, HOBT, and DIPEA produced Fmoc-protected dipeptide 3 with 40.7% yield. Analogous reaction of H₂N-aeg(bpy)-OrButyl with Fmoc-aeg(phe)-COOH gave Fmoc-protected dipeptide 4 in 68% yield. Each of the desired products were made in gram-scale quantities, and the purity and identity of the oligopeptides were confirmed by ¹H NMR spectroscopy and mass spectrometry, respectively. The Fmoc protecting group was then cleaved to give the amine-terminated dipeptides.
5.3.2 Synthesis and Characterization of Ru Complexes

Ruthenium “triple strand” complexes Ru-8, Ru-9, and Ru-10 were synthesized using the same method as previously described for Ru-3 in Chapter 2 by reacting ~ 10 equivalents of amine-terminated dipeptide with [Ru(MebpyCOCl)\(_3\)]\(^{2+}\) with triethyl amine in dry dichloromethane (Scheme 5-3). This rapid approach enabled yields of > 40 % of the product in hundreds of mg scales. Molecular ion peaks observed in the positive electrospray mass spectra conclusively identified the products of these reactions, and their purities were assessed by NMR spectroscopy and elemental analysis. \(^1\)H NMR spectra confirmed the expected relative integrations of protons for the Ru complexes; further analysis by \(^{13}\)C NMR, 2D HMBC, HMQC, and COSY were used to assign individual proton and carbon resonances in the spectra for each compound, allowing us to conclusively determine the structures. Elemental analyses revealed the tendency to retain small amounts of solvent even after extensive drying, and slight differences between the theoretical and observed mass percentages of C, H and N. The latter are likely the result of residual salt (KNO\(_3\)) from the final purification column.

Analysis of the redox properties of the Ru complexes was performed using cyclic voltammetry in acetonitrile electrolyte solutions, such as in Figure 5-48 for the Ru-8, Ru-9 and Ru-10 complexes. The reversible one electron oxidation peak at ~1.26 V is the well-known metal centered Ru\(^{III/II}\) couple. Three ligand-centered one-electron reductions at -1.26 V, -1.46 V, -1.67 V are observed in the voltammograms, are assigned to the [Ru(bpy)\(_3\)]\(^{2+}\) core (the pendant bpy ligands on the aeg strands exhibit irreversible reductions well outside this potential window\(^{20}\)). These data are summarized in Table 5-4, and indicate only very
minor differences in the redox couples across the four Ru complexes, reflecting their similar central structure.

Absorbance and emission spectra were measured for each of the Ru complexes in deoxygenated acetonitrile and are compared in Table 5-4; each exhibited a strong absorbance peak centered at 466 nm, which is assigned to the MLCT band of [Ru(bpy)$_3$]$^{2+}$. Following excitation at 466 nm, each compound exhibited similar emission maxima, centered at 626 nm, and a long-lived excited state (> 1 µsec).\textsuperscript{34} We have observed that as the length of the oligopeptide linkers increases, or as the size of the spacing groups becomes larger, the quantum yield of the Ru complexes slightly increases. For example, Ru-3 has a quantum yield of 8.9%, Ru-8 has a quantum yield of 9.4%, and Ru-10 has the highest quantum yield of 11%. We have observed a similar trend in different systems (see Chapter 3),\textsuperscript{20} and this may be due to the introduction of nonpolar substituents on the oligopeptide backbone.
Scheme 5-3: Synthetic steps toward dipeptides.

Scheme 5-4: Synthetic steps toward Ru complexes.
Figure 5-48: Cyclic voltammograms of 1.75 mM Ru-8, Ru-9, and Ru-10 in CH$_3$CN vs. SCE, with 0.2 M TBAP supporting electrolyte, a 100 mV/s scan rate, and using glassy carbon working and Pt counter electrodes, and a Ag quasi-reference electrode. Currents are normalized to Ru complex concentration.
Table 5-4: Photophysical and Electrochemical Data for Ru Complexes.

<table>
<thead>
<tr>
<th></th>
<th>Ru-3</th>
<th>Ru-8</th>
<th>Ru-9</th>
<th>Ru-10</th>
</tr>
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<tbody>
<tr>
<td>λ_{abs, max} (nm)^a</td>
<td>466 (15.3)</td>
<td>466 (15.3)</td>
<td>466 (15.3)</td>
<td>466 (15.3)</td>
</tr>
<tr>
<td>(ε, M^{-1}cm^{-1} x 1000)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ_{em, max} (nm)^b</td>
<td>626</td>
<td>626</td>
<td>626</td>
<td>626</td>
</tr>
<tr>
<td>Φ^c</td>
<td>0.089</td>
<td>0.094</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>τ^d (μsec)</td>
<td>1.32</td>
<td>1.27</td>
<td>1.39</td>
<td>1.39</td>
</tr>
<tr>
<td>k_r x 10^7 (sec)^{-1}e</td>
<td>0.0067</td>
<td>0.0074</td>
<td>0.0072</td>
<td>0.0079</td>
</tr>
<tr>
<td>k_{nr} x 10^7 (sec)^{-1}e</td>
<td>0.069</td>
<td>0.071</td>
<td>0.065</td>
<td>0.064</td>
</tr>
<tr>
<td>E° Ru^{3+/2+} (V)</td>
<td>1.26</td>
<td>1.27</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>E° Ru^{2+/1+} (V)</td>
<td>-1.26</td>
<td>-1.26</td>
<td>-1.24</td>
<td>-1.26</td>
</tr>
<tr>
<td>E° Ru^{1+/0} (V)</td>
<td>-1.46</td>
<td>-1.47</td>
<td>-1.43</td>
<td>-1.46</td>
</tr>
<tr>
<td>E° Ru^{0/-1} (V)</td>
<td>-1.67</td>
<td>-1.66</td>
<td>-1.63</td>
<td>-1.67</td>
</tr>
</tbody>
</table>

^a Maximum absorbance wavelength and extinction coefficient for the metal to ligand charge transfer band.  ^b Peak emission wavelength following excitation at λ_{max,abs}.  ^c Emission quantum yields following excitation at λ_{max,abs}, determined using [Ru(bpy)_{3}]^{2+} in CH_{3}CN (Φ = 0.062) as a reference.  ^d Excited state lifetime in deaired CH_{3}CN solutions, determined from the emission decay following pulsed excitation at λ_{max,abs}.  ^e Rates of radiative (k_r) and nonradiative decay (k_{nr}).  ^f Reaction formal potentials vs. SCE, measured in 0.2 M TBAP in deoxygenated CH_{3}CN.
5.3.3 Synthesis and Characterization of Ru-M Complexes

The Ru-M dimetallic complexes were characterized with mass spectrometry, \(^1\)H NMR spectroscopy and elemental analysis. With the help of positive ion electrospray mass spectrometry we were able to observe the molecular ion peaks for all Ru-M complexes. In each case, molecular ion peaks for species with charges ranging from +2 up to +4 were observed. For example, in Figure 5-49, peaks corresponding to \(M^{2+}\), \(M^{3+}\) and \(M^{4+}\) molecular ions are observed for the dimetallic \([\text{Ru-3(Mn)}]^{4+}\) complex associated with differing numbers of \(\text{PF}_6^-\) anions (e.g. \([\text{Ru-3(Mn)}]^{4+}\), \([\text{Ru-3(Mn)}]\text{PF}_6^{3+}\), \([\text{Ru-3(Mn)}](\text{PF}_6)^{2+}\)). In comparison with the calculated isotopic splitting patterns expected for these species, the observed mass spectral data conclusively identify the dimetallic complexes.

\(^1\)H NMR spectra has also been obtained for all heterometallic complexes. The aromatic proton signals of the bpy ligands around the second metal are broadened, split, and shifted downfield by metal coordination, but the relative integrations are consistent with the pure heterometallic species. Elemental analysis of the heterometallic compounds also confirms the 1:1 metal binding stoichiometry and the purity of the complexes.

5.3.4 Iron, Cobalt, Nickel and Manganese Coordination Titrations

We have previously used spectrophotometric titrations to confirm metal binding stoichiometry of a tetra-coordinate transition metal ion such as \(\text{Cu}^{2+}\), \(\text{Zn}^{2+}\) or \(\text{Pd}^{2+}\) to the Ru-hairpin system.\(^{20-22}\) Emission and absorption titrations were therefore conducted to study the metal binding stoichiometry and quantify the quenching efficiency of a hexacoordinate
transition metal ion such as Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ or Mn$^{2+}$ binding to the Ru triple strand complexes. Figure 5-50 shows the UV-vis absorption titration spectra of Fe$^{2+}$ to Ru-3, Ru-8, Ru-9 and Ru-10. As aliquots of Fe$^{2+}$ solution is added to the solution of Ru complex in acetonitrile, a new peak centered at 530 nm forms, which is due to the MLCT band of [Fe(bpy)$_3$]$^{2+}$. Presence of this peak in the spectrum indicates the formation of [Fe(bpy)$_3$]$^{2+}$ and therefore coordination of one Fe$^{2+}$ to three bpy ligands. The intensity of the peak at 530 nm for [Fe(bpy)$_3$]$^{2+}$ levels after ~ 1 equiv. of Fe$^{2+}$ is added to the solution, which indicates stoichiometric binding of Fe$^{2+}$ to the Ru complex.

The emission titration spectra in Figure 5-51 shows the emission intensity of [Ru(bpy)$_3$]$^{2+}$ decreases until ~ 1 equiv. of Fe$^{2+}$ is added to the solution, consistent with the binding stoichiometry observed in the absorbance spectra. Binding Fe$^{2+}$ quenches about 95% of the emission intensity of excited state [Ru(bpy)$_3$]$^{2+}$. Since the complexes [Co(bpy)$_3$]$^{2+}$, [Ni(bpy)$_3$]$^{2+}$ or [Mn(bpy)$_3$]$^{2+}$ have either very weak extinction in the UV-visible region, only emission titrations (i.e., not UV-Vis absorbance titrations) were conducted to evaluate the binding stoichiometry of Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$. The emission titrations of Co$^{2+}$ to Ru complexes are also consistent with a 1:1 metal binding stoichiometry, which suggests formation of the [Co(bpy)$_3$]$^{2+}$ complex the Ru-Co dimetallic complex. Co$^{2+}$ quenches about 80% of the exited state emission intensity of [Ru(bpy)$_3$]$^{2+}$. The emission titrations of Ni$^{2+}$ and Mn$^{2+}$ both show the 1:1 metal binding stoichioemtric point as we expect, but for different Ru compound, the quenching efficiency is different. Binding Ni$^{2+}$ quenches ~ 55% of the emission intensity of Ru-3, but only ~ 45% of the emission intensity of Ru-8. Binding Mn$^{2+}$ quenches ~ 60% of the emission intensity of
Ru-10, but only ~ 40% of the emission intensity of Ru-3. The difference in quenching efficiency is likely caused by the different distances between [Ru(bpy)_3]^{2+} and the second metal center. Donor-acceptor distance has impact on both energy and electron transfer process. The impact of distance and side chain substitutes on the excited state decay rates obtained in deaerated acetonitrile solutions is quantitatively analyzed in Section 5.3.5.
Figure 5-49. (A) UV-vis absorbance spectra for the titration of 3.5 mL, 34.5 µM Ru-3 with addition of 1.3 µL aliquots of 10.1 mM Fe(ClO$_4$)$_2$ in CH$_3$CN. (B) UV-vis absorbance spectra for the titration of 3.0 mL, 18.0 µM Ru-8 with addition of 6.7 µL aliquots of 1.37 mM Fe(ClO$_4$)$_2$ in CH$_3$CN. (C) UV-vis absorbance spectra for the titration of 2.5 mL, 17.2 µM Ru-9 with addition of 4.0 µL aliquots of 1.37 mM Fe(ClO$_4$)$_2$ in CH$_3$CN. (D) UV-vis absorbance spectra for the titration of 2.5 mL, 25.2 µM Ru-10 with addition of 5.4 µL aliquots of 1.37 mM Fe(ClO$_4$)$_2$ in CH$_3$CN. Insets: Titration curves, monitored at 530 nm.
Figure 5-50. (A) Plot of normalized emission intensity of a CH$_3$CN solution containing 200 µM Ru-3 with addition of 9.0 µL aliquots of 10 mM Fe(ClO$_4$)$_2$; 81 µM Ru-8 with addition of 7.0 µL aliquots of 6.0 mM Fe(ClO$_4$)$_2$; 86 µM Ru-9 with addition of 5.5 µL aliquots of 7.3 mM Fe(ClO$_4$)$_2$; 75 µM Ru-10 with addition of 5.5 µL aliquots of 6.7 mM Fe(ClO$_4$)$_2$. Inset: Plot of emission spectra of 81 µM Ru-8 with addition of 7.0 µL aliquots of 6.0 mM Fe(ClO$_4$)$_2$. (B) Plot of normalized emission intensity of CH$_3$CN solution containing 68 µM Ru-3 with addition of 6.0 µL aliquots of 5.3 mM Co(ClO$_4$)$_2$; 61 µM Ru-8 with addition of 10 µL aliquots of 3.4 mM Co(ClO$_4$)$_2$; 72 µM Ru-9 with addition of 7.2 µL aliquots of 5.0 mM Co(ClO$_4$)$_2$; 55 µM Ru-10 with addition of 6.9 µL aliquots of 4.0 mM Co(ClO$_4$)$_2$. Inset: Plot of emission spectra of 61 µM Ru-8 with addition of 10 µL aliquots of 3.4 mM Co(ClO$_4$)$_2$. (C) Plot of normalized emission intensity of CH$_3$CN solution containing 49 µM Ru-3 with addition of 4.5 µL aliquots of 4.8 mM Ni(NO$_3$)$_2$; 60 µM Ru-8 with addition of 6.0 µL aliquots of 4.8 mM Ni(NO$_3$)$_2$; 100 µM Ru-9 with addition of 10 µL aliquots of 4.8 mM Ni(NO$_3$)$_2$; 39 µM Ru-10 with addition of 3.7 µL aliquots of 4.8 mM Ni(NO$_3$)$_2$. Inset: Plot of emission spectra of CH$_3$CN solution containing 60 µM Ru-8 with addition of 6.0 µL aliquots of 4.8 mM Ni(NO$_3$)$_2$. (D) Plot of normalized emission intensity of CH$_3$CN solution containing 31 µM Ru-3 with addition of 3.3 µL aliquots of 4.1 mM Mn(ClO$_4$)$_2$; 39.2 µM Ru-8 with addition of 3.7 µL aliquots of 4.1 mM Mn(ClO$_4$)$_2$; 26 µM Ru-9 with addition of 2.2 µL aliquots of 4.1 mM Mn(ClO$_4$)$_2$; 33 µM Ru-10 with addition of 3.1 µL aliquots of 4.1 mM Mn(ClO$_4$)$_2$. Inset: Plot of emission spectra of 39 µM Ru-3 with addition of 3.7 µL aliquots of 4.1 mM Mn(ClO$_4$)$_2$. 
5.3.5 Possible Quenching Mechanism

We have observed emission intensity quenching of the Ru complexes caused by coordination of Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ but determining the possible quenching mechanism is generally difficult. There are usually two quenching pathways: electron transfer and energy transfer. The quenching pathway could be either of these, or a combination of both.$^{36}$ In the Ru-Fe complexes, for the oxidative quenching mechanism in Eq (5-4), the energy barrier is + 0.47 eV, which is energetically uphill and unfavorable. However a reductive quenching mechanism as in Eq (5-5), has an energy barrier of + 0.03 eV, which could happen.

$$[\text{Ru}^{III}(bpy)_3(bpy^*)]^+ - [\text{Fe}^{II}(bpy)_3] \rightarrow [\text{Ru}^{III}(bpy)_3] - [\text{Fe}^{I}(bpy)_3]$$  \hspace{1cm} \text{Eq (5-4)}

$$[\text{Ru}^{III}(bpy)_3(bpy^*)]^+ - [\text{Fe}^{II}(bpy)_3] \rightarrow [\text{Ru}^{I}(bpy)_3] - [\text{Fe}^{III}(bpy)_3]$$  \hspace{1cm} \text{Eq (5-5)}

However, spectral overlap between the emission of excited state $[\text{Ru(bpy)}_3]^{2+}$ and the absorption of $[\text{Fe(bpy)}_3]^{2+}$ makes it feasible for energy transfer to play a non-trivial role in the excited state quenching in the Ru-Fe species.

In the case of $[\text{Co(bpy)}_3]^{2+}$, the energy barrier is + 0.16 eV for oxidative quenching in Eq (5-6). For reductive quenching in Eq (5-7), the energy barrier is - 0.49 eV, which is favorable. However, the oxidation of $[\text{Co}^{II}(bpy)_3]$ to $[\text{Co}^{III}(bpy)_3]$ is slow because of the spin crossover and therefore is unlikely to happen.

$$[\text{Ru}^{III}(bpy)_3(bpy^*)]^+ - [\text{Co}^{II}(bpy)_3] \rightarrow [\text{Ru}^{III}(bpy)_3] - [\text{Co}^{I}(bpy)_3]$$  \hspace{1cm} \text{Eq (5-6)}

$$[\text{Ru}^{III}(bpy)_3(bpy^*)]^+ - [\text{Co}^{II}(bpy)_3] \rightarrow [\text{Ru}^{I}(bpy)_3] - [\text{Co}^{III}(bpy)_3]$$  \hspace{1cm} \text{Eq (5-7)}

To probe the possible quenching mechanism of $[\text{Fe(bpy)}_3]^{2+}$ and $[\text{Co(bpy)}_3]^{2+}$, we varied the solvent to investigate the effects of solvent polarity (dielectric) on the excited state dynamics. According to Marcus theory, if an electron transfer process dominates the
Figure 5-51: Plots of the natural log of nonradiative decay rate ($k_{nr}$) of Ru-8(Co) and Ru-8(Fe) in different solvents at room temperature versus Pekar Factor ($D_{op}^{-1}D_{s}^{-1}$) where $D_{op}$ and $D_{s}$ are the optical and static dielectric constants of the solvent.
nonradiative decay process, then the natural log of the nonradiative decay rate should have a negative trend when it is plotted vs. the Pekar factor of the solvents. We have obtained the nonradiative decay rates of Ru-8(Co) and Ru-8(Fe) in different solvents and they are plotted vs. the Pekar Factor of different solvents in Figure 5-51. In the case of Ru-8(Co), there is a clear, positive trend; the corresponding plot for Ru-8(Fe) appears to lack any trend. For both of these compounds, these observations indicate that electron transfer is not a dominant quenching pathway for the excited state Ru complex. This is consistent with previously reported examples, which invoked an energy transfer relaxation mechanism in systems containing [Fe(bpy)_3]^{2+} and [Ru(bpy)_3]^{2+} 35, 37 or [Co(bpy)_3]^{2+} and [Ru(bpy)_3]^{2+} 38, 39. In the example that a solution containing a mixture of [Ru(bpy)_3]^{2+} and [Co(bpy)_3]^{2+} is able to photocatalyze water splitting via an electron transfer process, a sacrificial electron donor is needed to reduce [Ru(bpy)_3]^{2+*} to [Ru(bpy)_3]^{1+} first and then the electron transfer from [Ru(bpy)_3]^{1+} to [Co(bpy)_3]^{2+} could happen. 23-26

For [Ni(bpy)_3]^{2+}, neither oxidative or reductive quenching is energetically favorable: in the processes in Eq (5-8) and (5-9), the energy barriers are + 0.52 eV and + 0.87 eV, respectively. In addition there is also spectral overlap between the absorption of the [Ni(bpy)_3]^{2+} complex and emission of [Ru(bpy)_3]^{2+}. Together, these make energy transfer the likely pathway for [Ru(bpy)_3]^{2+} excited state quenching in the dimetallic structures.

\[
[Ru^{III}(bpy)_2(bpy^{*\cdot})]^{\cdot}\rightarrow [Ni^{II}(bpy)_3] \rightarrow [Ru^{II}(bpy)_3]^{\cdot} [Ni^{I}(bpy)_3] \quad \text{Eq (5-8)}
\]

\[
[Ru^{III}(bpy)_2(bpy^{*\cdot})]^{\cdot}\rightarrow [Ni^{II}(bpy)_3] \rightarrow [Ru^{I}(bpy)_3]^{\cdot} [Ni^{III}(bpy)_3] \quad \text{Eq (5-9)}
\]
The reaction free energies for \([\text{Mn(bpy)}_3]^{2+}\) are similarly uphill for electron transfer quenching of the Ru excited state; both reactions in Eq (5-10) and Eq (5-11) have energy barriers greater than 0.5 eV. Energy transfer could be a more favorable mechanism for excited state \([\text{Ru(bpy)}_3]^{2+}\) quenching.\(^2\) A sacrificial electron acceptor is needed to oxidize \([\text{Ru(bpy)}_3]^{2+}\) to \([\text{Ru(bpy)}_3]^{3+}\) for electron transfer from manganese polypyridyl complexes to \([\text{Ru(bpy)}_3]^{3+}\) to happen in reported examples.\(^27\)-\(^29\)

\[
[\text{Ru}^{III}(\text{bpy})_2(\text{bpy}^\ast)] - [\text{Mn}^{II}(\text{bpy})_3] \rightarrow [\text{Ru}^{III}(\text{bpy})_3] - [\text{Mn}^{I}(\text{bpy})_3] \quad \text{Eq (5-10)}
\]

\[
[\text{Ru}^{III}(\text{bpy})_2(\text{bpy}^\ast)] - [\text{Mn}^{II}(\text{bpy})_3] \rightarrow [\text{Ru}^{I}(\text{bpy})_3] - [\text{Mn}^{III}(\text{bpy})_3] \quad \text{Eq (5-11)}
\]

### 5.3.6 Time-resolved Spectroscopy

To quantitatively compare the rates of excited state decay in the Ru-M complexes, and to evaluate the impact of the length of the peptide linkers as well as the size of the spacing groups of the peptide linkers on the emission photodynamics, the quantum yields and lifetimes of the series of dimetallic complexes were obtained in completely deaerated acetonitrile solutions. The dimetallic complexes were excited with an 800 ps excitation pulse and the emission transients fit with monoexponential decays to give the exited state lifetimes listed in Table 5-5. Compared to the monometallic Ru complexes, the excited state lifetimes of the dimetallic complexes are 1- 2 orders of magnitude shorter. The Ru quantum yields decrease drastically upon Fe\(^{2+}\), Co\(^{2+}\) or Ni\(^{2+}\) binding, whereas Mn\(^{2+}\) causes a more modest 20% ~ 30% decrease of the quantum yield compared to monometallic Ru complex.

The quantum yields and lifetimes were used to calculate the radiative \((k_r)\) and nonradiative \((k_{nr})\) rates of the excited state relaxation. Although the magnitude of \(k_r\) is largely
unaffected by the presence of a second metal ion in relative proximity to the Ru center, $k_{nr}$ in the dimetallic complexes is 1 --2 orders of magnitude larger than in the monometallic Ru complex. This observation suggests that the presence of the second metal ion creates new excited state quenching pathways, which based on the reasoning above, are mostly likely to be via energy transfer.

The structural variations in Scheme 5-1 were designed to study the impact of the distance and the spacing groups on the emission photodynamics of Ru-M dimetallic complexes. Crystallization attempts are still ongoing in our lab; however, considering the flexibility of the peptide chain, its dynamic motions on the timescale of excited state relaxation may play a significant role in this process. Therefore, we rely on molecular models to qualitatively understand the relative molecular structures and dynamics in solution. In a fully extended aminoethylglycine chain, the (through-space) distance between substituents (e.g. bpy and ac) is ~ 7 Å, and we use this as the approximate distance between the tethered metal center and the spacing groups (acetyl, isobutyl or phenyl). The approximate distance between Ru center and the tethered metal center is ~ 9 Å. In solution, because of the flexibility of the peptide chain, this distance will vary, however electrostatic repulsions between the charged metal centers together with bulkiness of the oligopeptide linkers put some restraints on the dynamical motions. As the distance between Ru and the tethered metal center is increased from ~ 9 Å in Ru-3(M) to ~ 16 Å in Ru-8(M), the experimental data indicate a slight decrease of $k_{nr}$ (i.e., $2.0 \times 10^7$ s$^{-1}$ versus $1.7 \times 10^7$ s$^{-1}$) and the trend is also observed in the corresponding Ru-Co, Ru-Ni, and Ru-Mn complexes. These are consistent with the known distance dependence of excited state energy transfer. However, the shallow
distance-dependence of $k_{nr}$ that is observed does not follow either an exponential (e.g. $\propto e^{-r}$) or inverse distance ($\propto r^6$) relationship, as it would be expected for energy transfer. This leads us to consider that the actual distance between Ru and the tethered metal center in Ru-8(M), Ru-9(M), and Ru-10(M) can be shorter than the simple extended model: the flexibility of longer peptide chains allows these to at least partially fold and bring the metal centers closer together. Excited state quenching will therefore occur in these dynamic structures over a range of possible distances, at greater reaction rates when the motions of the chains bring the species closer together in space.

Consistent with this picture, when the spacer groups on the oligopeptide increase in size, there is a slight decrease in $k_{nr}$ (see Table 5-5) for each of the metal complexes in the series. Steric bulkiness of the side groups impact the conformational flexibility of the backbone, and thus the motions which bring the metal reactants together. That is, bulkier substituents force an average donor-acceptor distance that is larger, decreasing $k_{nr}$. 
<table>
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<td>Mn</td>
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^a Maximum absorbance wavelength and extinction coefficient for the metal to ligand charge transfer band. ^b Peak emission wavelength following excitation at λ_{max,abs}. ^c Emission quantum yields following excitation at λ_{max,abs}, determined using [Ru(bpy)]^{2+} in CH₃CN (Φ = 0.062) as a reference. ^d Excited state lifetime in deaired CH₃CN solutions, determined from the emission decay following pulsed excitation at λ_{max,abs}. ^e Rates of radiative (k_r) and nonradiative decay (k_{nr}).
5.4 Conclusions

In this chapter we have introduced a modified \([\text{Ru(bpy)}_3]^{2+}\) triple strand system with one free bpy ligand on each of three pendant oligopeptide strands that extend from the Ru core. Coordination of a hexacoordinate transition metal ion such as Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) or Mn\(^{2+}\) to these \([\text{Ru(bpy)}_3]^{2+}\) structures forms \([\text{Ru(bpy)}_3]^{2+}\)-[M(bpy)_3]^{2+} dimetallic complexes and also results in the addition of new excited state emission quenching pathways of \([\text{Ru(bpy)}_3]^{2+}\).

High energy barriers for electron transfer and spectral overlap suggest that the likely mechanism for excited state quenching will occur by energy transfer; data from experiments obtain in a range of solvents indicates this to be the case. The \(k_{nr}\) of Ru-M complexes in the relaxation process has a shallow distance dependence that is also impacted by the presence of side substituents on the oligopeptide chain. These observations of the structural impacts on the nonradiative relaxation process provide evidence for dynamic conformations of the dimetallic structures.
5.5 References


2. Abrahamsson, M. L.; Baudin, H. B.; Tran, A.; Philouze, C.; Berg, K. E.;


Chapter 6

Mixed-Ligand Heterometallic [Ru(bpy)$_3$]$^{2+}$ Hairpin Structures for Redox Cascades and Future Directions

6.1 Coordination of Zn and Cu to Aminoethylglycine-Functionalized [Ru(bpy)$_3$]$^{2+}$ with Pendant 8-Hydroxyquinolines

6.1.1 Introduction

One advantage of using inorganic coordination chemistry to construct multimetallic complexes for artificial photosynthesis is the redox properties and photophysical properties are both tunable based on the metal ion and the ligand. In previous chapters, the emission photodynamics of a series of [Ru(bpy)$_3$]$^{2+}$-[M(bpy)$_2$]$^{2+}$ (M = Cu, Pd or Zn) or [Ru(bpy)$_3$]$^{2+}$-[M(bpy)$_3$]$^{2+}$ (M = Fe, Co, Ni or Mn) heterometallic complexes was studied. Different metal centers have unique redox potentials, and when closely linked to [Ru(bpy)$_3$]$^{2+}$, can quench the excited state emission of [Ru(bpy)$_3$]$^{2+}$ either by electron transfer, energy transfer, or a combination of both. Another way to tune the redox and photophysical properties of these metal complexes is to introduce a different ligand. We chose 8-hydroxyquinoline (HQ) as another ligand to incorporate into our aeg system for several reasons: [Cu(HQ)$_2$] has a redox potential that enables it to function as an electron acceptor from excited state [Ru(bpy)$_3$]$^{2+}$. Zn(HQ)$_2$ is fluorescent and the emission spectra of Zn(HQ)$_2$ overlaps the absorption spectra of [Ru(bpy)$_3$]$^{2+}$, so energy transfer from Zn(HQ)$_2$ to [Ru(bpy)$_3$]$^{2+}$ is possible. In our previous work, there is only one fluorophore which is [Ru(bpy)$_3$]$^{2+}$ in the heterometallic complexes. In the [Ru(bpy)$_3$]$^{2+}$-[Zn(HQ)$_2$]
system, there are two fluorophores and energy transfer could be complex. HQ ligand and Zn(HQ)$_2$ both have broad absorbance spectra in UV region and [Ru(bpy)$_3$]$^{2+}$ has broad absorption in the UV-visible region. Using self-assembly to make molecules with two fluorophores provides a facile way to make efficient light harvesting compounds. Zn(HQ)$_2$ is charge neutral and is unlikely to quench the excited state emission of [Ru(bpy)$_3$]$^{2+}$ by changing its chemical environment like [Zn(bpy)$_2$]$^{2+}$, so [Ru(bpy)$_3$]$^{2+}$ - [Zn(HQ)$_2$] might also be used to support the quenching mechanism of [Zn(bpy)$_2$]$^{2+}$ if no quenching caused by Zn(HQ)$_2$ is observed.
Scheme 6-1: Ru-HQ Hairpin
6.1.2 Synthesis

6.1.2.1 Synthesis of Ru-HQ-hairpin (Ru-HQ)

NH$_2$-aeg(HQ)-OtBu was synthesized as described in literature.$^{19}$ Ru-HQ was synthesized using method previously reported$^{20}$ by reacting [Ru(bpy)$_2$(bpy(COCl)$_2$)]$^{2+}$ with 8 equiv. of NH$_2$-aeg(HQ)-OtBu in dry DCM with Et$_3$N. This compound was purified using literature reported methods,$^{20}$ yielding 236 mg of red compound (46% Yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.43 – 8.98 (m, 3H), 8.82 (d, $J$ = 43.5 Hz, 1H), 8.73 – 8.40 (m, 6H), 8.40 – 8.14 (m, 2H), 8.06 (d, $J$ = 5.6 Hz, 4H), 7.96 – 7.73 (m, 4H), 7.66 (d, $J$ = 4.0 Hz, 4H), 7.52 – 7.10 (m, 8H), 6.81 (dd, $J$ = 20.6, 7.7 Hz, 2H), 4.36 – 4.09 (m, 3H), 4.02 (s, 3H), 3.92 (d, $J$ = 9.7 Hz, 3H), 3.77 (s, 4H), 3.64 (s, 3H), 1.53 – 1.23 (m, 18H). MS (ESI$^+$) [M$^{2+}$] calcd: 670.2; found: 670.2.

6.1.3 Cu and Zn Emission Titrations

5.25 mM Zinc acetate dissolved in methanol was added to methanol solution containing 0.162mM Ru-HQ to study the coordination of Zn$^{2+}$ to pendant HQ ligands and the formation of [Ru(bpy)$_3$]$^{2+}$-Zn(HQ) heterometallic complex. The emission intensity of Ru-HQ is quenched by $\sim$70% and levels after 1 equiv. of Zn$^{2+}$ is added, which indicates binding one Zn$^{2+}$ to one pair of HQ ligands and the formation of the Ru-Zn dimetallic complex. (Figure 6-2) And we discussed in a previous study that the quenching of the emission intensity of [Ru(bpy)$_3$]$^{2+}$ by coordination of Zn$^{2+}$ to a pair of pendant bpy ligands
Figure 6-1: $^1$H NMR spectrum of Ru-HQ at 300 MHz in CDCl$_3$. 
in a Ru hairpin system was likely due to the formation of \([\text{Zn(bpy)}_2]^{2+}\). This changes the chemical environment of the Ru center because \([\text{Zn(bpy)}_2]^{2+}\) has two positive charges, and that causes about 10\% quenching of the emission intensity of \([\text{Ru(bpy)}_3]^{2+}\). Since \(\text{Zn(HQ)}_2\) is charge neutral, and it quenches about 70\% of the emission intensity of \([\text{Ru(bpy)}_3]^{2+}\), we hypothesize that there are other quenching pathways. There is no spectral overlap between the emission spectrum of \([\text{Ru(bpy)}_3]^{2+}\) and the absorption spectrum of \(\text{Zn(HQ)}_2\) (Figure 6-3), and it is unlikely that there is an electron transfer process from \([\text{Ru(bpy)}_3]^{2+}\) to \(\text{Zn(HQ)}_2\) because Zn is electrochemically inert and the high redox potential needed to reduce the HQ ligand. We are still investigating the quenching mechanism. Experiments such as solvent study or variable temperature study could be used to probe the possible quenching mechanism.

The HQ ligand has peak absorption at 325 nm and emission at 423 nm, whereas \(\text{Zn(HQ)}_2\) has a peak absorption at 390 nm and peak emission at 565 nm. However, when \textbf{Ru-HQ} was excited at 325 nm, no emission peak was observed at 423 nm. As \(\text{Zn}^{2+}\) was added to \textbf{Ru-HQ}, the solution was also excited at 390 nm but still no peak was observed at 565 nm. By comparing the absorption spectrum of \textbf{Ru-HQ} and emission spectrum of HQ monomer and \(\text{Zn(HQ)}_2\) (Figure 6-3), the spectral overlap that makes it likely that there is energy transfer from HQ and/or \(\text{Zn(HQ)}_2\) to \([\text{Ru(bpy)}_3]^{2+}\). In summary, there are likely two processes in the emission titration of \(\text{Zn}^{2+}\) to \textbf{Ru-HQ}: (1) there is energy transfer from HQ and/or \(\text{Zn(HQ)}_2\) to \([\text{Ru(bpy)}_3]^{2+}\), (2) and the emission intensity decreases due to excited state quenching of \([\text{Ru(bpy)}_3]^{2+}\) by \(\text{Zn(HQ)}_2\).
Figure 6-2: (A) Emission spectra of 5 mL 0.162mM Ru-HQ in CH₃OH upon incremental additions of 10 µL of 5.25 mM Zn(acetate)₂ in CH₃OH. (B) Plot of emission intensity at 657 nm of 5 mL 0.162 mM Ru-HQ in CH₃OH upon incremental additions of 10 µL of 5.25 mM Zn(acetate)₂ in CH₃OH versus Zn/Ru molar ratio.

Figure 6-3: Normalized emission spectra of HQ monomer, Zn(HQ)₂ and normalized absorption spectra of Ru-HQ.
Cu$^{2+}$ was also titrated to the solution of Ru-HQ to study the self-assembly of Cu$^{2+}$ to HQ and to determine if there is quenching caused by the formation of Cu(HQ)$_2$. As in the case of Zn$^{2+}$, the titration plot levels after ~1 equivalent of Cu(NO$_3$)$_2$ is added to solution, the emission intensity of [Ru(bpy)$_3$]$_2^{2+}$ is quenched by ~95% (Figure 6-4), which is likely to be an electron transfer process. One interesting observation in the titration plot of Cu$^{2+}$ is that the emission is quenched in two different phases. In Figure 6-4, the initial turning point is at ~0.5 equiv. of Cu$^{2+}$, and the slope is subsequently shallower. This was observed in several repeated titration experiments. Our hypothesis is that in the process of Cu$^{2+}$ titration, Cu$^{2+}$ binds to two HQ ligands, which is accompanied by disassociation of two H$^+$ as in:

$$Cu^{2+} + 2HQ \rightleftharpoons Cu(HQ)_2 + 2H^+ \quad \text{Eq (6-1)}$$

As Cu$^{2+}$ binds to HQ, H$^+$ accumulates in the solution until the reaction reaches equilibrium. The reaction differs in the case of the Zn$^{2+}$ titration because acetate is in the solution the counter anion of Zn$^{2+}$, which is a weak acid. When H$^+$ is produced, it prefers binding to an acetate anion, and forms acetic acid. However, the counter anion is nitrate in the Cu$^{2+}$ titration, so that there is no shift in the equilibrium because of the buffer. We hypothesize that the shape of the curve in the Cu titration is a result of the acetate buffer; to test this hypothesis, 10 equiv. of sodium acetate was added to the Ru-HQ solution and the titration was conducted again. The resulting titration plot is shown in Figure 6-5, which shows a lack of a second quenching phase.

Photophysical data of Ru-HQ, Ru-Cu(HQ)$_2$, and Ru-Zn(HQ)$_2$ have been collected in completely deaerated CH$_3$CN solutions and the results of those experiments are listed in Table 6-1. Introduction of a new ligand to the Ru hairpin system does not change the photophysical
behavior of the $[\text{Ru(bpy)}_3]^{2+}$ center: Ru-HQ has a quantum yield of 7.6% and a lifetime that is about 1 $\mu$s, typical for $[\text{Ru(bpy)}_3]^{2+}$. It has been observed that the maximum absorbance wavelength for Ru-Cu(HQ)$_2$ and Ru-Zn(HQ)$_2$ shifts to \( \sim \) 440 nm, which is because of the overlap of the absorbance of the MLCT band of $[\text{Ru(bpy)}_3]^{2+}$ and the $\pi - \pi^*$ transition of Cu(HQ)$_2$ and Zn(HQ)$_2$ complexes. The non-radiative decay rates ($k_{nr}$) of Ru-Zn(HQ)$_2$ and Ru-Cu(HQ)$_2$ are larger than $k_{nr}$ of the monometallic Ru-HQ, indicating new non-radiative quenching pathways in the heterometallic complexes.
Figure 6-4: (A) Emission spectra of 5 mL 0.153 mM Ru-HQ in CH$_3$CN upon incremental additions of 12 µL of 5.39 mM Cu(NO$_3$)$_2$in CH$_3$CN. (B) Plot of emission intensity at 657 nm of 5 mL 0.153 mM Ru-HQ in CH$_3$CN upon incremental additions of 12 µL of 5.39 mM Cu(NO$_3$)$_2$in CH$_3$CN versus Cu/Ru molar ratio.

Figure 6-5: Plot of emission intensity at 657 nm of 5 mL 0.121 mM Ru-HQ with 1.21 mM CH$_3$COONa in CH$_3$CN upon incremental addition of 9.5 µL of 5.39 mM Cu$^{2+}$ in CH$_3$CN versus Cu/Ru molar ratio.
Table 6-1: Photophysical Data for Ru-HQ and Heterometallic Complexes.

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$^a$ Maximum absorbance wavelength  $^b$ Peak emission wavelength following excitation at $\lambda_{\text{max,abs}}$.  
$^c$ Emission quantum yields following excitation at $\lambda_{\text{max,abs}}$, determined using [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN ($\Phi = 0.062$) as a reference.  
$^d$ Excited state lifetime in deaerated CH$_3$CN solutions, determined from the emission decay following pulsed excitation at $\lambda_{\text{max,abs}}$.  
$^e$ Rates of radiative ($k_r$) and nonradiative decay ($k_{nr}$).
6.2 Mixed-Ligand and Multimetallic [Ru(bpy)$_3^{2+}$] Complexes as Photoinduced Redox Cascades

6.2.1 Introduction

When a series of photosensitizer(s), electron donor(s) and acceptor(s) are connected in an order to create a redox gradient, photoinduced electron transfer can follow the direction of this redox gradient to form different charge separated states and create a photoinduced redox cascade$^{22-26}$ Photoinduced redox cascades can be potentially used in promoting photoinduced energy/electron transfer,$^{22-27}$ photo-sensing and signaling,$^{28-31}$ as photo-switches,$^{32-34}$ as well as photosynthetic reactions.$^{35-38}$ The advantage of photo-induced redox cascades is (i) the redox potential difference between different electron acceptors could reduce the back electron transfer rate and increase the lifetime of the charge-separated state.$^{22, 39-43}$ (ii) it provides multiple catalytic centers and multiple electron transfer processes which could be used in complicated photocatalytic reactions.$^{44-46}$

With the help of coordination chemistry, there are several ways to tune the redox potentials of different metal-coordinated centers to create a redox gradient in the Ru-hairpin structure with two pairs of pendant ligands: (i) the two pairs of ligands can be the same ligands such as bpy. By coordinating two different metal centers with different redox potentials to two pairs of bpy ligands respectively, a redox gradient can be created. But the synthesis of this multimetallic complex could be challenging. (ii) An alternative method is to synthesize a Ru hairpin structure with two pairs of different ligands such as bpy and HQ. By selecting a metal ion $M^{2+}$ that forms $M(HQ)_2$ and $M(bpy)_2$ with different redox potentials, a redox gradient could also been created.
6.2.2 Mixed-Ligand Ru-Hairpin

[Ru(bpy)$_3$]$^{2+}$ has been used as a photo-sensitizer to generate photo-excited electrons for several decades. The redox potential of [Ru(bpy)$_3$]$^{2+}$/[Ru(bpy)$_3$]$^{3+}$ is $\sim -0.8$ V vs. SCE, so the redox potential for the electron acceptors must be both higher than -0.8 V to cause electron transfer and the electron accepter that is furthest from [Ru(bpy)$_3$]$^{2+}$ must have the highest redox potential of all of them to create the redox gradient. We chose [Cu(bpy)$_2$]$^{2+}$ and [Cu(HQ)$_2$] as electron acceptors not only because the information such as spectroscopic and redox properties we have obtained from previous study about [Cu(bpy)$_2$]$^{2+}$ and [Cu(HQ)$_2$] but also because of their different redox potential.

$$[\text{Ru}^{III}(\text{bpy})_2(\text{bpy}^-)]^+ - [\text{Cu}^{II}(\text{HQ})_2] - [\text{Cu}^{II}(\text{bpy})_2] \quad \text{Eq (6-2)}$$

$$\rightarrow [\text{Ru}^{III}(\text{bpy})_2(\text{bpy})] - [\text{Cu}^{I}(\text{HQ})_2] - [\text{Cu}^{II}(\text{bpy})_2]$$

$$[\text{Ru}^{III}(\text{bpy})_2(\text{bpy})] - [\text{Cu}^{I}(\text{HQ})_2] - [\text{Cu}^{II}(\text{bpy})_2] \quad \text{Eq (6-3)}$$

$$\rightarrow [\text{Ru}^{III}(\text{bpy})_2(\text{bpy})] - [\text{Cu}^{II}(\text{HQ})_2] - [\text{Cu}^{I}(\text{bpy})_2]$$

$$[\text{Ru}^{III}(\text{bpy})_2(\text{bpy})] - [\text{Cu}^{II}(\text{HQ})_2] - [\text{Cu}^{I}(\text{bpy})_2] \quad \text{Eq (6-4)}$$

$$\rightarrow [\text{Ru}^{II}(\text{bpy})_2(\text{bpy})] - [\text{Cu}^{II}(\text{HQ})_2] - [\text{Cu}^{II}(\text{bpy})_2]$$

$\Delta G$ for electron transfer process in Eq (6-2) is $\sim -0.3$ eV, for Eq (6-3) is $\sim -0.5$ eV, which are both favorable. For the back electron transfer process in Eq (6-4), $\Delta G$ is $\sim -1.3$ eV, which seems to be large, but large $\Delta G$ for back electron transfer process could fall into the inverted region of Marcus theory, and slows the back electron transfer rate. To assemble this $[\text{Ru(bpy)}_3]^{2+} - [\text{Cu(HQ)}_2] - [\text{Cu(bpy)}_2]^{2+}$ complex, a mixed ligand hairpin Ru-HQ-BPY (Scheme 6-2) has been synthesized.
Scheme 6-2: Structure of Ru-HQ-BPY
6.2.3 Synthesis

6.2.3.1 Synthesis of Fmoc-aeg(HQ)-aeg(bpy)-OtBu (1)

The t-butyl of Fmoc-aeg(HQ)-OtBu was deprotected using previously reported method\textsuperscript{20} to give Fmoc-aeg(HQ)-COOH. In an ice bath and under N\textsubscript{2} protection, 2.22g (4.2 mmol) Fmoc-aeg(HQ)-COOH, 0.65g HOBT, (4.2 mmol), 1.6 g HBTU (4.2 mmol) and 2.3 mL (12 mmol) DIPEA were added to 100 mL dry DCM and was stirred for 15 min. To this, 1.28g (3.3 mmol) NH\textsubscript{2}-aeg(bpy)-OtBu was added and the reaction was stirred under N\textsubscript{2} at room temperature for 2 days. The reaction mixture was washed with water (3* 50 mL ). The organic layer was dried with Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed under vacuum. The crude product was purified using a silica column chromatography with 5% MeOH in DCM as mobile phase to give 0.51 g product. (17.2% yield). \textsuperscript{1}H NMR 300MHz in CD\textsubscript{3}Cl: 1.51 (s, 9H); 2.46 (s, 3H); 3.11-3.75(m, 9H); 3.78-4.18(m, 6H); 4.20-4.62 (m, 4H); 6.61-7.46(m, 10H); 7.50-8.44(m, 9H). MS (ESI\textsuperscript{+}) [M+H]\textsuperscript{+} calcd: 892.4; found: 892.4

6.2.3.2 Synthesis of Fmoc-aeg(HQ)-aeg(HQ)-OtBu (2)

In an ice bath and under N\textsubscript{2} protection, 1.98g (3.75 mmol) Fmoc-aeg(HQ)-COOH, 0.6g HOBT, (3.75 mmol), 1.4g HBTU (3.75 mmol) and 2 mL (10 mmol) DIPEA were added to 100 mL dry DCM and was stirred for 15 min. To this, 0.9g (2.5 mmol) NH\textsubscript{2}-aeg(HQ)-OtBu was added and the reaction was stirred under N\textsubscript{2} at room temperature for 2 days. The reaction mixture was washed with water (3* 50 mL ). The organic layer was dried with Na\textsubscript{2}SO\textsubscript{4} and
the solvent was removed under vacuum. The crude product was purified using a silica column chromatography with 5% MeOH in DCM as mobile phase to give 0.89 g product. (41% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (ddd, $J = 50.0, 20.6, 4.2$ Hz, 2H), 8.43 – 7.82 (m, 2H), 7.70 (d, $J = 4.1$ Hz, 2H), 7.64 – 7.45 (m, 2H), 7.30 (dddd, $J = 35.7, 25.2, 11.2, 5.1$ Hz, 5H), 7.15 – 6.81 (m, 3H), 6.81 – 6.53 (m, 2H), 4.33 (t, $J = 18.0$ Hz, 2H), 4.14 (dd, $J = 24.7, 17.4$ Hz, 2H), 3.94 (dd, $J = 29.1, 9.4$ Hz, 4H), 3.85 – 3.63 (m, 5H), 3.63 – 2.81 (m, 7H), 1.62 – 1.19 (m, 9H).

MS (ESI$^+$) [M+H]$^+$ calcd: 867.4; found: 867.4
Figure 6-6: $^1$H NMR spectrum of 1 at 300 MHz in CDCl$_3$.

Figure 6-7: $^1$H NMR spectrum of 2 at 400 MHz in CDCl$_3$. 
6.2.3.3 Synthesis of Ru-HQ-BPY

The dipeptide 1 was Fmoc deprotected to give the amine-terminated dipeptide. Ru-HQ-BPY was synthesized using previously reported method.\textsuperscript{20} A 189 mg amount of product was collected (42% yield). \textsuperscript{1}H NMR (360 MHz, CD$_2$Cl$_2$) $\delta$ 9.60 – 8.57 (m, 4H), 8.57 – 7.87 (m, 16H), 7.60 (dd, $J$ = 63.2, 33.4 Hz, 12H), 7.35 – 6.76 (m, 11H), 6.52 (s, 2H), 3.90 (dd, $J$ = 46.5, 27.1 Hz, 15H), 3.70 – 2.97 (m, 17H), 2.25 (d, $J$ = 9.3 Hz, 6H), 1.47 – 0.99 (m, 18H). MS (ESI\textsuperscript{+}) [M$^{2+}$] calc: 980.4; found: 980.4.
Figure 6-8: $^1$H NMR spectrum of Ru-HQ-BPY at 360 MHz in CDCl$_3$. 
6.2.4 Results and Discussions

6.2.4.1 Synthesis of Dipeptides

The mixed ligand dipeptide was synthesized using standard solution phase peptide coupling reaction by reacting 1.5 equiv of the acid-terminated monomer with 1.0 equiv of the amine-terminated monomer. (Scheme 6-3)

6.2.4.2 Emission Titration of Cu\(^{2+}\) to Ru-HQ-BPY

Ru-HQ-BPY contains four pendant ligands that are available for Cu\(^{2+}\) coordination: one pair of HQ ligands and one pair of bpy ligands. Cu\(^{2+}\) emission titration was used to study the metal binding stoichiometry and quenching efficiency. In Figure 6-9B, the normalized emission intensity of Ru-HQ-BPY is plotted versus the relative amount of added Cu\(^{2+}\). When comparing the titration plot of Cu\(^{2+}\) to Ru-HQ and Ru-HQ-BPY, a striking difference is the titration curve of Ru-HQ-BPY has two distinct phases, and the turning point is when ~ 1 equiv Cu\(^{2+}\) has been added to the solution. In the first phase, the emission intensity decreases until ~ 1 equiv. of Cu\(^{2+}\) is added to the solution. When [Cu] = [Ru], the emission intensity is quenched by ~75%. As more Cu\(^{2+}\) is added to the solution, the emission intensity continues to decrease until ~ 2 equiv. Cu\(^{2+}\) is added, and after that, the emission intensity levels. But in the second phase, the titration curve is shallower. After 2 equiv. Cu\(^{2+}\) is added, the emission is quenched by ~98% for Ru-HQ-BPY.
Scheme 6-3: Synthesis of Fmoc-aeg(HQ)-aeg(bpy)-OtBu

Figure 6-9: (A) Emission spectra of 5 mL 157.6 µM Ru-HQ in CH₃CN upon incremental additions of 14 µL of 5.90 mM Cu²⁺ in CH₃CN. (B) Plot of emission intensity at 649 nm of 5 mL 157.6 µM Ru-HQ in CH₃CN upon incremental additions of 14 µL of 5.90 mM Cu²⁺ in CH₃CN versus Cu/Ru molar ratio. Inset: Expended region of the titration curve at higher Cu²⁺ concentrations.
We attribute the two distinct phases in the titration curve of Ru-HQ-BPY to the sequential binding of Cu$^{2+}$ to HQ and bpy ligands and this has been observed in our previous study where there are multiple free bpy binding sides available. During the titration, the first Cu$^{2+}$ ion to bind can either form Cu(HQ)$_2$ or [Cu(bpy)$_2$]$^{2+}$ by coordination of a pair of HQ ligands or bpy ligands. In our previous study, we found that the quenching efficiency of [Ru(bpy)$_3$]$^{2+}$ by [Cu(bpy)$_2$]$^{2+}$ is distance dependent. The lower observed quenching efficiency of Ru-HQ-BPY at one equiv. of Cu$^{2+}$ is likely due to a mixture of Cu(HQ)$_2$ and [Cu(bpy)$_2$]$^{2+}$. The addition of second equivalent of Cu$^{2+}$ led to a quenching efficiency of 98%. This was due to the coordination of the free HQ and bpy ligands with the additional Cu$^{2+}$. In Ru-Cu(HQ)$_2$ and Ru-Cu(HQ)$_2$-Cu(bpy)$_2$, the closest Ru-Cu distance is equivalent, so the ultimate quenching efficiencies are approximately the same.
6.2.5 Mixed-Ligand Triheterometallic Complexes for Redox Cascades

The introduction of a second transition metal to the Ru hairpin system is an alternative way to create a redox cascade. We have chosen Pd$^{2+}$ as our choice of metal due to reasons that (i) [Pd(bpy)$_2$]$^{2+}$ has a different redox potential than [Cu(bpy)$_2$]$^{2+}$ and [Cu(HQ)$_2$], and (ii) when closely attached to [Ru(bpy)$_3$]$^{2+}$, Pd complexes have been shown to have catalytic activity. Based on recent study of BPY-HQ-BPY and HQ-BPY-HQ tripeptide in our group, HQ has a higher affinity to bind Cu$^{2+}$ than bpy in basic solution (~pH=10). And HQ binding sides can be fully saturated with Cu$^{2+}$ in basic solution leaving bpy sides still available for binding another metal ion. So we should be able to make mixed-ligand, heterometallic hairpin with Ru-HQ-BPY by controlling the pH of solution. For example in basic solution one equiv. Cu$^{2+}$ can be titrated to Ru-HQ-BPY. The higher affinity of Cu$^{2+}$ to bind in basic solution will allow Cu$^{2+}$ to bind with the HQ binding sites to produce Ru-Cu(HQ)$_2$-BPY. Then the pH of solution is carefully adjusted to 7 and Pd$^{2+}$ is titrated to solution which will bind only with bpy. The redox potential for [Cu(HQ)$_2$] is ~ - 0.5V and redox potential for [Pd(bpy)$_2$]$^{2+}$ is ~ - 0.6V, which means Ru-Cu(HQ)$_2$-[Pd(bpy)$_2$]$^{2+}$ would function as a redox cascade. This will also provide information on the impact of pH in directing metal coordination to a specific pair of binding sides and could serve as an easy way to direct the arrangement of different redox species to form photoinduced redox cascades.
6.2.6 Triheterometallic Complexes Constructed from Di-Hairpin System

Our group has previously developed a di- and tri-hairpin system shown in Scheme 6-4. We desire total control over metal species and binding location but our current scaffolds contain many identical binding sites so metal coordination to a particular location cannot be adequately controlled. To illustrate the complexity in this challenge with our current system, we attempted to synthesize a tri-heterometallic complex using Ru(HP)₂ to form [Ru(HP)₂(Pd)(Cu)]⁶⁺ by taking the following steps:

\[
\text{Ru(HP)}_2 + Pd^{2+} \rightarrow \text{Ru(HP)}_2(Pd) \quad \text{Eq (6-5)}
\]

\[
\text{Ru(HP)}_2(Pd) + Cu^{2+} \rightarrow \text{Ru(HP)}_2(Pd)(Cu) \quad \text{Eq (6-6)}
\]

To a sample of Ru(HP)₂, one equivalent of Pd²⁺ was added and the solution was stirred for one hour after which one equivalent of Cu²⁺ was added and stirred for an additional hour. The product was precipitated through anion exchange with NH₄PF₆ and then identified through mass spectrometry as the desired tri-heterometallic complex, shown in Figure 6-10, compared with predicted mass-to-charge ratio and isotopic splitting patterns. Using this method of sequential metal ion addition, it is possible to synthesize tri-heterometallic complexes. However, as shown in Figure 6-10, this method does not prevent Ru(HP)₂(Cu)₂ or Ru(HP)₂(Pd)₂ as a by-product. To further purify the mixture, we used column chromatography. We used silica as the stationary phase and 5:4:1 volume ratio of CH₃CN:H₂O:sat KNO₃ as the mobile phase to purify the mixture.
Scheme 6-4: Ru-(HP)$_2$

Figure 6-10: Selected molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [[Ru-(HP)$_2$(2M)](PF$_6$)$_3$]$^{3+}$ showing evidence of Ru-(HP)$_2$ coordinated with two Cu, two Pd, and one Cu and one Pd.
After the purification, the purified heterotrimeetallic complex was characterized by mass spectrometry again, shown in Figure 6-11. The molecular ion peak of Ru(HP)₂(Pd)(Cu) is again seen in the spectra but the peaks corresponding to Ru(HP)₂(Pd)₂ and Ru(HP)₂(Cu)₂ are not shown in the spectra. This might suggest that the mixture has been purified and could be used to study its photophysical properties.
Figure 6-11: Selected molecular ion peaks observed by positive ion electrospray mass spectrometry, plotted together with the calculated mass and isotopic splitting patterns for [[Ru-(HP)(2M)](PF$_6$)$_3$]$^{3+}$ showing evidence of Ru-(HP)$_2$ coordinated with one Cu and one Pd.
6.3 Future Directions: Photochemical Generation of Hydrogen by Reduction of Water under Visible Light Irradiation with Aminoethylglicine - linked [Ru(bpy)₃]²⁺ -[Co(bpy)₃]³⁺ Complexes

The visible-light induced water splitting to form hydrogen is of great interest because of the production of clean energy. In a lot of systems that are designed to split water, [Ru(bpy)₃]²⁺ is commonly used as the photosensitizer, and generally another metal center which serves as the catalytic center is required. The photosensitizer and reaction center must be brought close enough for photo-induced electron transfer to happen. We have demonstrated in our system that the aeg chain is a good linker to bring donors and acceptors together. In our previous studies, the Ru-Pd catalysts system is able to photocatalyze the dimerization of styrene with an electron transfer mechanism. The quenching in Ru-hairpin system caused by coordination of Cu²⁺ and Pd²⁺ is also likely to be an electron transfer mechanism. To construct a catalyst that is able to photocatalyze the formation of hydrogen from water with our system, we need to incorporate an efficient catalytic reaction center.

Literatures have suggested that under irradiation of visible light, a mixture of [Ru(bpy)₃]²⁺ and [Co(bpy)₃]³⁺ is able to reduce water and produce hydrogen. A sacrificial electron donor such as triethylamine is necessary in this catalytic reaction to reduce [Ru(bpy)₃]²⁺ to [Ru(bpy)₃]⁺. The proposed mechanism is described as follows:

\[
[\text{Ru}^{	ext{I}}(\text{bpy})_3] + [\text{Co}^{	ext{II}}(\text{bpy})_3] \rightleftharpoons [\text{Ru}^{	ext{II}}(\text{bpy})_3] + [\text{Co}^{	ext{I}}(\text{bpy})_3] \quad \text{Eq (6-7)}
\]

\[
[\text{Co}^{	ext{I}}(\text{bpy})_3] + [\text{H}_3\text{O}]^+ \rightleftharpoons [\text{Co}^{	ext{II}}(\text{bpy})_2(\text{H}_2\text{O})(\text{H}^-)]^{2+} + \text{bpy} \quad \text{Eq (6-8)}
\]

\[
[\text{Co}^{	ext{III}}(\text{bpy})_2(\text{H}_2\text{O})(\text{H}^-)]^{2+} + \text{H}^+ + \text{bpy} \rightleftharpoons [\text{Co}^{	ext{III}}(\text{bpy})_3] + \text{H}_2\text{O} + \text{H}_2 \quad \text{Eq (6-9)}
\]

The produced [Co(bpy)₃]³⁺ is then reduced to [Co(bpy)₃]²⁺ by the sacrificial electron donor.
By linking \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Co(bpy)}_3]^{2+}\) together with oligopeptide chains, the intermolecular electron transfer in Eq (6-7) is converted to intramolecular electron transfer which promotes the electron transfer rate. Also we have noticed that in Eq (6-8) and (6-9), there is ligand dissociation and association that accompanies the catalytic reaction. With a free bpy ligand on aeg chain that is close to the Co center, it could also accelerate the ligand association, and the catalytic reaction. The motif we plan to use as the photocatalyst is the Ru-Co complexes synthesized in Chapter 5 and the 3D structure is shown in Figure 6-12. The \([\text{Ru(bpy)}_3]^{2+}\) center is closely attached to the \([\text{Co(bpy)}_3]^{2+}\) center by three aeg chains.

The experimental condition we plan to use is 0.5 mmol of the Ru-Co complex in 10 mL solution which contains 6:2:2 volume ratio of acetonitrile: water: triethylamine. The solution has to be deaired to remove oxygen that can quench the excited state of \([\text{Ru(bpy)}_3]^{2+}\). The light source is equipped with a 400 nm long filter and an IR filter to guarantee it is in the wavelength range of visible light. The produced gas can be analyzed qualitatively and quantitatively using GC and GC-MS. Other tunable conditions could be the reaction time, and different electron donors.

In Chapter 5 we have synthesized four different Ru-Co complexes with different Ru-Co distance and different spacers on the aeg chain. This proposed experiment will provide a chance for us to investigate the impact of donor-acceptor distance as well as the spacer on the catalytic reaction with an electron transfer mechanism.
Figure 6-12: 3D Structure of Ru-8(Co)
6.4 References


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Publications
Sun, S.; Myers, C. P.; Williams, M. E.* "Aminoethylglycine-linked Ru-Pd Complexes Photocatalytically Dimerize α-methylstyrene” submitted to JACS.

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Sun, S.; Myers, C. P.; Williams, M. E.*” Self-assembly of Multimetallic Complexes Featuring Coordination of Hexacoordinate Fe2+, Co2+, Ni2+ or Mn2+ to Aminoethylglycine Derivatized Ru(bpy)32+ with Pendant Bipyridines” in preparation.


Zhang, T.; Huang, X.* Xue, J.; Sun, S.” Ring expansion reaction of α-sulfonyl cyclic ketones via insertion of arynes into C-C: a facile and mild access to medium-and large-sized benzannulated carbocycles.” Tetrahedron Lett. 2009, 50, 1290-1294