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Ruthenium(II)-Polyazine Light Absorbers Bridged to Reactive *cis*-Dichlororhodium(III) Centers in a Bimetallic Molecular Architecture

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Bimetallic complexes of the form $[(bpy)_2Ru(BL)RhCl_2(phen)](PF_6)_3$, where bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and BL = 2,3-bis(2-pyridyl)pyrazine (dpp) or 2,2′-bipyrimidine (bpm), were synthesized, characterized, and compared to the $[\{(bpy)_2Ru(BL)\}_2RhCl_2](PF_6)_5$ trimetallic analogues. The new complexes were synthesized via the building block method, exploiting the known coordination chemistry of Rh(III) polyazine complexes. In contrast to $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$, $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ have a single visible light absorber subunit coupled to the *cis*-$Rh^{III}Cl_2$ moiety, an unexplored molecular architecture. The electrochemistry of $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ showed a reversible oxidation at 1.61 V (vs Ag/AgCl) ($Ru^{III/II}$), quasi-reversible reductions at −0.39 V, −0.74, and −0.98 V. The first two reductive couples corresponded to two electrons, consistent with Rh reduction. The electrochemistry of $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ exhibited a reversible oxidation at 1.76 V ($Ru^{III/II}$). A reversible reduction at −0.14 V ($bpm^{0/-}$), and quasi-reversible reductions at −0.77 and −0.91 V each corresponded to a one electron process, $bpm^{0/-}$, $Rh^{III/II}$, and $Rh^{II/I}$. The dpp bridged bimetallic and trimetallic display $Ru(d\pi)\rightarrow dpp(\pi^*)$ metal-to-ligand charge transfer (MLCT) transitions at 509 nm (14,700 $M^{-1}\ cm^{-1}$) and 518 nm (26,100 $M^{-1}\ cm^{-1}$), respectively. The bpm bridged bimetallic and trimetallic display $Ru(d\pi)\rightarrow bpm(\pi^*)$ charge transfer (CT) transitions at 581 nm (4,000 $M^{-1}\ cm^{-1}$) and 594 nm (9,900 $M^{-1}\ cm^{-1}$), respectively. The heteronuclear complexes $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ had ^{3}MLCT emissions that are $Ru(d\pi)\rightarrow dpp(\pi^*)$ CT in nature but were red-shifted and lower intensity than $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$. The lifetimes of the ^{3}MLCT state of $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ at room temperature (30 ns) was shorter than $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$, consistent with favorable electron transfer to Rh(III) to generate a metal-to-metal charge-transfer (^{3}MMCT) state. The reported synthetic methods provide means to a new molecular architecture coupling a single Ru light absorber to the Rh(III) center while retaining the interesting *cis*-$Rh^{III}Cl_2$ moiety.

Introduction

Platinum group metal polyazine complexes have been extensively studied for their rich photophysical and redox properties.[1,2] Ru(II) polyazine complexes often are potent visible light absorbers with low lying metal to ligand charge transfer excited states (MLCT).[3] The lowest ^{3}MLCT state is often long-lived, emissive, and reactive, finding application in energy conversion schemes and sensing applications.[4−7] The ^{3}MLCT excited states of these complexes are easily tuned by the ligand set bound to the Ru(II) center.

Complexes of the form *cis*-$[(NN)_2RhCl_2]^+$ and $[Rh(NN)_3]^{3+}$, where NN = a chelating polyazine ligand, are typically not efficient visible light absorbers, often absorbing light well only in the ultraviolet region of the spectrum.[8]

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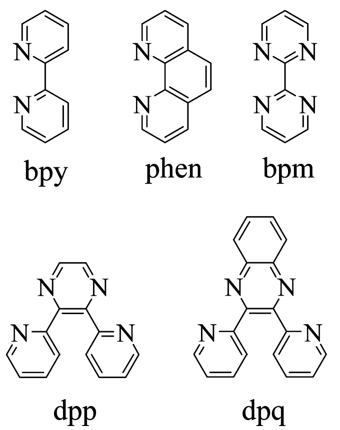

Figure 1. Polyazine ligands commonly used in the construction of supramolecular complexes; bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, bpm = 2,2′-bipyrimidine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline.

The lowest lying excited states are typically Rh centered ligand field (^{3}LF) states for *cis*-$[(NN)_2RhCl_2]^+$ systems and internal ligand (^{3}IL) states for the $[Rh(NN)_3]^{3+}$ motif.[3,4,8−11] The ^{3}LF state of *cis*-$[(phen)_2RhCl_2]^+$, phen = 1,10-phenanthroline, undergoes chloride substitution in fluid solution impeded in solid matrixes allowing for an observable emission at 723 nm.[12,13] The photophysics of the $[(NN)_2RhCl_2]^+$ complexes are modulated by the polyazine ligands coordinated to the Rh center.[13] The *cis*-$[(5,6\text{-}Me_2phen)_2RhCl_2]^+$, where 5,6-Me$_2$phen = 5,6-dimethyl-1,10-phenanthroline, displays a ^{3}LF emission at 710 nm blue-shifted by methylation of the phen ligand.[11]

The redox properties of rhodium(III) polyazine complexes also have been studied. Both *cis*-$[(bpy)_2RhCl_2]^+$ and $[Rh(bpy)_3]^{3+}$, bpy = 2,2′-bipyridine, exhibit an irreversible Rh$^{III/II/I}$ reduction process at −0.87 and −0.86 (V vs Ag/AgCl), respectively. This Rh$^{III/II/I}$ reduction is followed by ligand loss giving $[Rh(bpy)_2]^+$ as the product.[14] The multielectron reduction of Rh(III) polyazine complexes has prompted interest in their ability to act as electron acceptors, capable of multiple electron collection. The electrochemical properties of Rh(III) polyazine complexes can be tuned by changing the coordination environment of the Rh(III) center. Brewer and co-workers reported a series of *cis*-$[(NN)_2RhBr_2]^+$ complexes where NN was a series of chelating polyazine ligands with increasingly stabilized π^* acceptor orbitals including bpy, 2,3-bis(2-pyridyl)pyrazine (dpp), 2,2′-bipyrimidine (bpm), and 2,3-bis(2-pyridyl)-quinoxaline (dpq), Figure 1.[10] For the complex *cis*-$[(dpq)_2RhBr_2]^+$ the first reduction potential is shifted significantly to more positive potential versus the bpy analogue, occurring at −0.44 V (vs Ag/AgCl). Interestingly, the ^{3}LF emission of *cis*-$[(dpq)_2RhBr_2]^+$ at 77 K ($\lambda_{max}^{em} = 737$ nm) is red-shifted relative to *cis*-$[(bpy)_2RhBr_2]^+$ ($\lambda_{max}^{em} = 660$ nm), providing a correlation between Rh$^{III/II/I}$ reduction potential and ^{3}LF excited-state energy.

Syntheses of heteroleptic Rh(III) polyazine complexes have been reported using a $[(NN)RhCl_4]^-$ starting material reacting with 1 equiv of another polyazine ligand.[15−17] Morrison and co-workers recently reported the synthesis of *cis*-$[(phen)RhCl_2(dppz)]^+$ from K[(phen)RhCl$_4$] and dipyrido [3,2*a*-2′,3′*c*]phenazine (dppz) in dimethylformamide (DMF).[12] Tseng et al. prepared *cis*-$[(bpy)RhCl_2(HDPA)]^+$, where HDPA = bis(2-pyridyl)amine, from K[(bpy)RhCl$_4$] and HDPA in acidified refluxing methanol.[16] The same group prepared cyclometallated complexes *cis*-[(NN)RhCl$_2$(bzpy)], where NN = bpy or phen and bzpy = 2-(2-pyridylcarbonyl)phenylate, from a neat molten mixture of the appropriate K[(NN)RhCl$_4$] and Hbzpy.[17]

The ^{3}MLCT excited state of Ru(II) polyazine complexes are known to undergo bimolecular electron transfer quenching with Rh(III) polyazine complexes. The prototypical example was studied in detail by Creutz and Sutin.[7] The ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ was quenched by $[Rh(bpy)_3]^{3+}$ ($k_q \approx 2.0 \times 10^9$ M^{-1} s^{-1}) to give $[Ru(bpy)_3]^{3+}$ and $[Rh(bpy)_3]^{2+}$.[18,19] This excited-state chemistry was exploited in the presence of colloidal platinum and a sacrificial electron donor to catalyze the reduction of water to hydrogen. The $[Rh(bpy)_3]^{3+}$ in this system behaves as an electron relay, transferring an electron from the ^{3}MLCT excited $[Ru(bpy)_3]^{2+}$ to the Pt particle where catalysis occurs.

Polyazine bridging ligands (BLs) have been utilized to build multimetallic supramolecules containing Ru(II) centered light absorbers with Rh(III) centered electron acceptors.[20−24] These supramolecules undergo interesting intramolecular interactions governed by the nature of the connecting linkage.[25−28] The Ru(II) centered ^{3}MLCT state emission is quenched by intramolecular excited-state electron transfer to generate the Ru(dπ)→Rh(dσ^*) CT state (metal-to-metal

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charge-transfer state, MMCT).[29−38] Electronic coupling of the Ru(II) donor and Rh(III) acceptor and thermodynamic driving force dictate the rate of electron transfer.[39−41] Endicott and co-workers reported one of the first Ru, Rh dyads in this forum, $[(CN)(bpy)_2Ru(\mu\text{-}CN)Rh(NH_3)_4(L)]^{n+}$ with L = NH_3 (n = 3) or L = Br^-, I^-, CN^- (n = 2).[42] Furue et al. reported the heterodyad $[(bpy)_2Ru(Mebpy\text{-}CH_2CHOHCH_2\text{-}Mebpy)Rh(NN)_2]^{5+}$, NN = bpy or phen, which exhibited an intramolecular electron transfer rate constant (k_{et}) of about 10^6 s^{-1}.[31] The shorter alkyl tether of $[(4,7\text{-}Me_2phen)_2Ru(Mebpy\text{-}CH_2CH_2\text{-}Mebpy)Rh(dmb)]^{5+}$, where dmb = 4,4′-dimethyl-2,2′-bipyridine, reported by Indelli et al. had $k_{et} = 1.7 \times 10^8$ s^{-1}.[33] Decreasing the distance between excited-state donor and electron acceptor appeared to enhance intramolecular excited-state electron transfer. A series of complexes of the form $[(ttpy)Ru(tpy\text{-}Ph_n\text{-}tpy)Rh(ttpy)]^{5+}$, where ttpy = 4′-($p$-tolyl)-2,2′:6′,2″-terpyridine and n = 1, or 2, also exhibit a distance dependent k_{et}.[27,36,37]

Systems with polyazine BLs between the Ru(II) and Rh(III) have photophysical characteristics unlike either monometallic analogue and often are compared to the Ru−BL−Ru analogues. Indelli et al. studied the complex $[(ttpy)Ru(tpy\text{-}tpy)Rh(ttpy)]^{5+}$, which has a lowest MLCT state red-shifted relative to $[Ru(ttpy)_2]^{2+}$.[36,37] The complex $[(ttpy)Ru(tpy\text{-}tpy)Ru(ttpy)]^{4+}$ has a 600 ns excited-state lifetime, which upon changing a Ru(II) to Rh(III) decreases to 17 ns.[37] The excited-state lifetimes measured at 77 K were similar (ca. 12.5 μs). Kalyanasundaram and co-workers reported similar results for the complex $[(bpy)_2Ru(dpp)Rh(bpy)_2]^{5+}$ when compared to $[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$.[34] In solid matrix at 77 K, both the Ru,Rh complexes and Ru,Ru analogue display broad, somewhat structured emissions centered at about 700 nm. At room temperature $[(bpy)_2Ru(dpp)Rh(bpy)_2]^{5+}$ had an emission significantly lower in intensity and red-shifted relative to the model complex, which the authors attribute to the presence of additional emissive excited-state decay pathways, $k_q = 1.48 \times 10^7$ s^{-1}.

Mixed metal supramolecules have found utility as photochemical molecular devices with particular interest in molecular architectures that allow for multiple electron collection.[43−50] Major research has focused on aromatic BLs capable of multiple electron collection.[51] More recently, incorporation of redox active metals, e.g. Rh(III), have resulted in complexes that act as photocatalysts for hydrogen production from water and act to photocleave DNA.[52−56] The trimetallic complex of the form $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ is photochemically active in this regard.[53–55,57] The cis-$Rh^{III}Cl_2$ center is thought to be essential to the functioning of the complex both as a photocatalyst for hydrogen production from water and as an oxygen independent photocleavage agent of DNA.[55,56] The Ru(II) based ^{3}MLCT emission of this trimetallic is quenched relative to the homobinuclear $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$, consistent with excited-state electron transfer to the Rh(III) center.[34,35,55] Changing the bridge to a ligand with a lower energy π^* acceptor orbital inhibits intramolecular electron transfer by way of making the ^{3}MLCT to ^{3}MMCT state transition energetically uphill.[41,55,56]

Herein we report a synthetic strategy that combines the tendency of Rh(III) to form cis-$[(NN)_2RhX_2]^+$ polyazine structural motifs with a building block approach to make Ru, Rh dyads which retain the cis-$Rh^{III}Cl_2$ reactive site (NN = bidentate polyazine ligand, X = halide). The complexes synthesized were of the form $[(bpy)_2Ru(BL)RhCl_2(phen)](PF_6)_3$, where BL = dpp or bpm, Figure 2. We report the spectroscopic and electrochemical properties of these complexes compared to the previously studied trimetallic analogues illustrating the electronic consequence of exchanging an entire LA−BL subunit with a terminal polyazine

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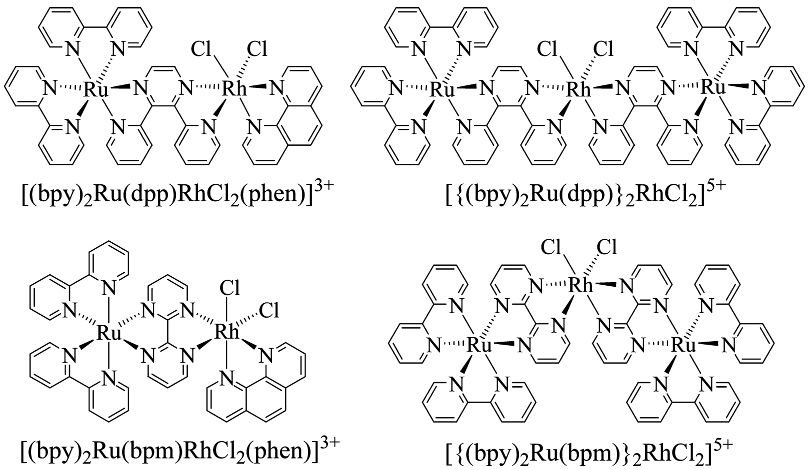

Figure 2. Structures of the title mixed bimetallic complexes and related trimetallic complexes used in this study (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, bpm = 2,2′-bipyrimidine, phen = 1,10-phenanthroline).

ligand on the Rh(III) center. These are the first reported Ru(II)−Rh(III) dyads which contain a *cis*-$Rh^{III}Cl_2$ site. This new molecular architecture will allow for better control of stereochemistry and tuning excited-state energetics while maintaining the interesting *cis*-$Rh^{III}Cl_2$ subunit.

Experimental Section

Materials. All commercial materials and solvents were used without further purification. The inorganic starting material $[(bpy)_2RuCl_2]\cdot 2H_2O$ was purchased from Strem Chemical (Newburyport, MA). The bridging ligand 2,3-bis(2-pyridyl)pyrazine (dpp) and starting material $RhCl_3\cdot xH_2O$ were purchased from Sigma-Aldrich (St. Louis, MO). The bridging ligand 2,2′-bipyrimidine (bpm) was purchased from Alfa-Aesar (Ward Hill, MA). The terminal ligand 1,10-phenanthroline monohydrate (phen) and supporting electrolyte tetra(*n*-butyl)ammonium hexafluorphosphate (Bu_4NPF_6, electrochemical grade) were from Fluka (Steinheim, Switzerland). Ethanol (200 proof) was from Aaper Alcohol and Chemical Company (Shelbyville, KY). Adsorption alumina (80−200 mesh), diethyl ether, 12 M HCl and HPLC grade methanol, acetonitrile, toluene, and acetone were all from Fisher (Fair Lawn, NJ). The complexes $[(bpy)_2Ru(dpp)](PF_6)_2$,[58] $[(bpy)_2Ru(bpm)](PF_6)_2$,[59] $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$,[49] and $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$[59] were prepared using literature procedures.

Syntheses. $K[(phen)RhCl_4]\cdot 3H_2O$. Synthetic procedures for $K[(phen)RhCl_4]\cdot 3H_2O$ were adapted from McKenzie and Plowman.[60] **Caution!** *This synthesis requires the heating of hydrochloric acid solutions in an open vessel, liberating HCl gas. All chemical manipulations were performed in a fume hood. All heating was performed using a stirring hot water bath.* Trichlororhodium(III) hydrate (1.33 g, ∼5.00 mmol) was dissolved in 100 mL of hot 2 M HCl. After heating for about 2 h at 95 °C, 1,10-phenanthroline monohydrate (3.76 g, 19.0 mmol) in 50 mL of 2 M HCl was added dropwise with vigorous stirring. The opaque salmon colored mixture was stirred for 2.5 h at 95 °C and then cooled to room temperature. The resulting orange-pink solid was removed via vacuum filtration. The damp solid was heated at 95 °C in 75 mL of 10 M HCl for 1 h with stirring, followed by hot vacuum filtration to remove any insoluble material. The deep orange filtrate was returned to 95 °C, allowed to cool slowly to room temperature, then plunged into a $CaCl_2$/ice water bath. The shimmering orange-red crystals were removed by vacuum filtration and rinsed with about 20 mL of cold 10 M HCl followed by about 20 mL of acetone. The acid salt was dissolved in a minimal amount (ca. 50 mL) of hot 5 M HCl. A saturated solution of KCl in 5 M HCl, about 15 mL, was added dropwise to cause precipitation of a bright orange solid. Continued heating followed by slow cooling, vacuum filtration, and an acetone rinse (ca. 20 mL) yielded bright orange needles of $K[(phen)RhCl_4]\cdot 3H_2O$ (1.89 g, 3.66 mmol, 71%). Rh analysis: Calcd Rh 19.9%, Determined 19.9%. The analysis of $K[(phen)RhCl_4]\cdot 3H_2O$ by NMR proved difficult as the spectrum indicated ligand exchange over time in DMSO-d_6. Product analysis was performed by the above Rh analysis and by reacting $K[(phen)RhCl_4]\cdot 3H_2O$ and 4,4′-dimethyl-2,2′-bipyridine (dmb) in a 1:1 stoichiometry with subsequent analysis of the ^1H NMR spectrum.

$[(phen)RhCl_2(dmb)](PF_6)$. $K[(phen)RhCl_4]\cdot 3H_2O$ (0.050 g, 0.11 mmol) and 4,4′-dimethyl-2,2′-bipyridine (0.021 g, 0.11 mmol) were added to 55 mL of stirring, deoxygenated 2:1 ethanol:water. The solution was heated at reflux for 1 h and then cooled. Metal complex precipitation was induced by slow addition to a 2 M aqueous solution of NH_4PF_6 (ca. 10 mL). The solid was removed by vaccum filtration and washed with about 20 mL each of water, ethanol, and diethyl ether. The pale-yellow $[(phen)RhCl_2(dmb)](PF_6)$ was dried in vacuo (0.053 g, 0.076 mmol, 69%) and analyzed by ^1H NMR. ^1H NMR (d_6-acetone) $\delta = 10.11$ (1H, dt, $J = 5.4$, 1.0 Hz), 9.80 (1H, d, $J = 5.9$ Hz), 9.23 (1H, dd, $J = 8.3$, 1.2 Hz), 8.94 (1H, dd, $J = 8.3$, 1.2 Hz), 8.80 (1H, weak dd), 8.66 (1H, weak dd), 8.54 (1H, d, $J = 8.9$ Hz), 8.51 (1H, dd, $J = 8.2$, 5.2 Hz), 8.43 (1H, d, $J = 8.9$ Hz), 8.36 (1H, dt, $J = 5.4$, 1.0 Hz), 8.04 (1H, ddd, $J = 5.9$, 1.9, 0.8 Hz), 7.95 (1H, dd, $J = 8.2$, 5.4 Hz), 7.71 (1H, d, $J = 6.0$ Hz), 7.27 (1H, ddd, $J = 6.0$, 1.8, 0.7 Hz), 2.84 (3H, s), 2.53 (3H, s) ppm.

$[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3\cdot 3H_2O$. $K[(phen)RhCl_4]\cdot 3H_2O$ (0.20 g, 0.38 mmol, 1.2 equiv) was dissolved in deoxygenated 2:1 v/v ethanol/water (45 mL) with continuous stirring under argon flow. To the stirring bright yellow solution was added 0.30 g of $[(bpy)_2Ru(dpp)](PF_6)_2$ (0.32 mmol, 1.0 eq) followed by 15 mL of 2:1 ethanol/water. The reaction mixture was slowly heated to reach reflux, ensuring all $[(bpy)_2Ru(dpp)](PF_6)_2$ had dissolved prior to reaching reaction temperature. The solution was heated for 45 min at reflux. The crude mixed metal complex was precipitated using NH_4PF_6 and isolated via vacuum filtration. The crude $[(bpy)_2Ru(dpp)$-

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$RhCl_2$(phen)]$(PF_6)_3$ was taken into a minimal amount of acetone (ca. 15 mL), syringe filtered and precipitated in diethyl ether (ca. 400 mL). The crude purple solid, 0.44 g, was stirred in 100 mL of boiling absolute ethanol for 15 min, followed by slow cooling and vacuum filtration to give a microcrystalline solid. The violet solid was dissolved in about 15 mL of acetone, syringe filtered and precipitated into about 400 mL of diethyl ether. Vacuum filtration and drying under vacuum afforded the complex $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3 \cdot 3H_2O$ (0.34 g, 0.23 mmol, 72%). Combustion analysis: Calcd C 37.06, H 2.70, N 9.40%; Found C 37.61, H 2.89, N 9.45%. (+)ESI-TOF MS: m/z = 1291.0 ($[M - PF_6]^+$, theor. 1291.0).

$[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3 \cdot 3H_2O$. The above synthesis was repeated using 0.28 g of $K[(phen)RhCl_4] \cdot 3H_2O$ (0.54 mmol, 1.2 equiv) and 0.40 g of $[(bpy)_2Ru(bpm)](PF_6)_2$ (0.46 mmol, 1.0 equiv) to afford 0.42 g of $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3 \cdot 3H_2O$ (0.30 mmol, 65%) as a dark green powder. Combustion analysis: Calcd C 33.96, H 2.56, N 9.90; Found C 34.34, H 2.74, N 9.96%. (+)ESI-TOF MS: m/z = 1215.0 ($[M - PF_6]^+$, 100% rel. abundance, theor. 1215.0), 1089.0 ($[\{M + F^-\} - 2PF_6]^+$, 28% rel abundance, theor. 1089.0).

Methods. Electrochemistry. Cyclic voltammetry was performed using a Bioanalytical Systems (BAS) Epsilon potentiostat and three-electrode, single chamber cell. Solutions were made in 0.1 M tetra-*n*-butylammonium hexafluorphosphate (Bu_4NPF_6) in spectrophotometric grade acetonitrile (Burdick and Jackson, Muskegon, MI). The working electrode was a Pt disk, the auxiliary electrode was a Pt wire, and potentials were measured against a Ag/AgCl reference electrode calibrated against $FeCp_2^{0/+}$ internal standard (0.46 V vs Ag/AgCl 3 M NaCl).[61] Cyclic voltammetry was typically performed at a scan rate of 100 mV/s.

Bulk electrolysis was performed in a two compartment cell with a platinum coil counter electrode separated from the working solution by fritted glass. Bulk electrolysis was performed with a graphite cloth working electrode in 0.3 M Bu_4NPF_6 in acetonitrile using a Ag/AgCl reference electrode. Solutions were magnetically stirred and continuously deoxygenated with solvent saturated argon during bulk electrolysis. Analyte solutions were typically about 8 mL and about 2 mM in $[(bpy)_2Ru(BL)RhCl_2(phen)](PF_6)_3$, BL = bpm or dpp. Current decay curves (i vs t) were integrated to calculate the charge passed, after subtracting the charge due to the capacitive current. Cyclic voltammetry was performed in situ using a Pt disk working electrode to assay free chloride in solution.

Electronic Absorption Spectroscopy. The electronic absorption spectra of $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ were collected using standard techniques. All electronic absorption spectra were obtained in room temperature spectrophotometric grade acetonitrile and using a 1 cm path length quartz cuvette (Starna Cells, Inc.; Atascadero, CA). Spectra were collected using an Agilent 8453 UV−vis spectrophotometer using a solvent reference. Extinction coefficients were determined by averaging the absorption spectra of gravimetric solutions of the title complexes prepared in triplicate.

Luminescence Spectroscopy. Steady state emission spectra were measured using standard techniques and recorded with a modified QuantaMaster Model QM-200-4E fluorimeter from Photon Technology International, Inc. (Birmingham, NJ). The system was modified to use a water cooled 150 W xenon arc lamp excitation source, and the emission was collected at 90° to the irradiation source by a thermoelectrically cooled Hamamatsu 1527 photomultiplier tube operating in photon counting mode with 0.25 nm resolution. The instrument was controlled with the factory standard Felix Software suite. Emission spectra were recorded in room temperature spectroscopic grade acetonitrile. The emission quantum yield is reported in room temperature acetonitrile against $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_2$ when exciting absorbance matched solutions at 520 nm ($\Phi^{em} = 0.00138$).[50] Low temperature emission spectra were obtained from 4:1 v/v ethanol/methanol glass solutions immersed in a liquid N_2 filled finger Dewar flask (77 K). Spectra were corrected for PMT response.

Excited State Lifetime Measurements. Excited state lifetimes were determined using a Photon Technology International, Inc. PL-2300 nitrogen laser equipped with a PL-201 continuously tunable dye laser (Coumarin 500, 490−540 nm) excitation source. Emissions were passed at a right angle from the excitation source through a monochromator and detected using a Hamamatsu R928 photomultiplier tube operating in direct analog mode. The signal was recorded using a LeCroy 9361 oscilloscope, averaging the results of 300 pulses, and transferred to a computer for data analysis. Room temperature measurements were made in acetonitrile solutions, exciting at 520 nm and observing the emission decay at 770 nm. Low temperature measurements were made in 4:1 v/v ethanol/methanol glass solutions immersed in a liquid N_2 filled finger Dewar flask (77 K), exciting at 520 nm, and measuring emission decay at 715 nm.

Results and Discussion

Synthesis. The previously unexplored molecular architecture containing polyazine bridged Ru,Rh dyads with *cis*-$Rh^{III}Cl_2$ moieties have been prepared and studied. The title complexes were synthesized from $[(bpy)_2Ru(BL)](PF_6)_2$ (BL = bridging ligand = dpp or bpm) and $K[(phen)RhCl_4] \cdot 3H_2O$, Figure 3, taking advantage of the facile formation of the *cis*-$[(NN)_2Rh^{III}Cl_2]^+$ coordination motif. The complex $K[(phen)RhCl_4] \cdot 3H_2O$ was synthesized using methods adapted from McKenzie and Plowman.[60,62] The $K[(phen)RhCl_4] \cdot 3H_2O$ was recovered as a bright orange crystalline material determined to contain 19.9% Rh by mass. $K[(phen)RhCl_4] \cdot 3H_2O$ undergoes rapid ligand substitution in solution at low chloride concentrations.[60] Further determination of the identity and reactivity of $K[(phen)RhCl_4] \cdot 3H_2O$ was performed byproduct analysis of the reaction of the metal complex with 4,4′-dimethyl-2,2′-bipyridine (dmb). Reaction of $K[(phen)RhCl_4] \cdot 3H_2O$ with 1 equiv of dmb in refluxing ethanol, following addition of NH_4PF_6, gave *cis*-$[(dmb)RhCl_2(phen)](PF_6)$ as a pale yellow solid in good yield as the only product observed by ^1H NMR in d_6-acetone.

The mixed metal dyads were synthesized using a building block approach. The reaction conditions used in the synthesis of *cis*-$[(phen)RhCl_2(dmb)](PF_6)$ were optimized and employed in the synthesis of the bimetallic complexes, Figure 3. The complexes $[(bpy)_2Ru(dpp)](PF_6)_2$ and $[(bpy)_2Ru(bpm)](PF_6)_2$ were each reacted with a slight excess of $K[(phen)RhCl_4] \cdot 3H_2O$ to give the deeply colored mixed metal supramolecule in good yield. The mixed metal supramolecules were purified by stirring in hot ethanol followed by syringe filtration and reprecipitation of the recovered material. Electrospray ionization-time-of-flight mass spectrometry (ESI-TOF MS) confirmed the presence of the title complexes $[M - PF_6]^+$, with experimental isotopic distribution patterns matching the theoretical values. The ESI-

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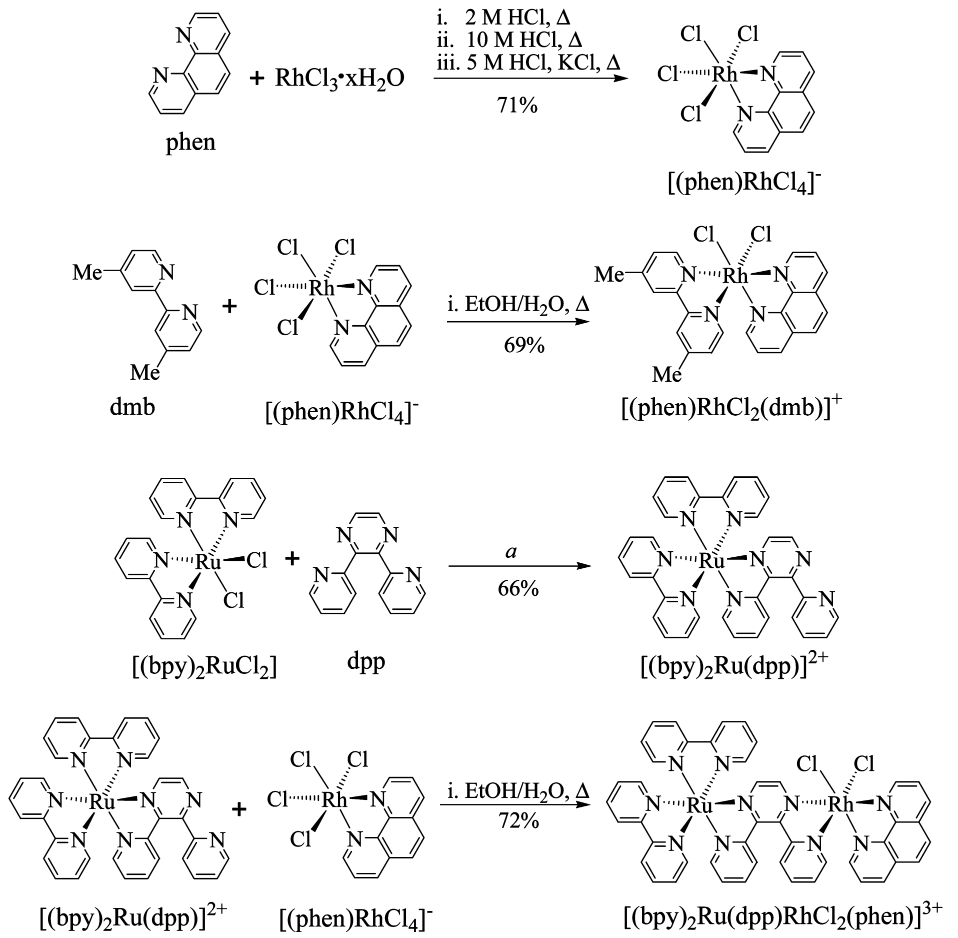

Figure 3. Synthetic method used to prepare Ru,Rh polyazine complexes. [a] From Gafney et al.[58]

TOF mass spectra of each dyad at higher *m*/*z* did not show any peaks assigned to possible $[\{(\mathrm{bpy})_2\mathrm{Ru(BL)}\}_2\mathrm{Rh(phen)}](\mathrm{PF}_6)_7$ trimetallic impurities, consistent with previous reports that the *cis*-$[(\mathrm{NN})_2\mathrm{Rh^{III}Cl_2}]$ moiety is favored under these reaction conditions.[63−65] The pure hetero dyads displayed no monometallic emission when excited into the maximal absorbance of the $[(\mathrm{bpy})_2\mathrm{Ru(BL)}](\mathrm{PF}_6)_2$ starting material.

The developed synthetic strategy provides means to this new structural motif, providing varied coordination at the Rh(III) center while retaining the interesting *cis*-$\mathrm{Rh^{III}Cl_2}$ moiety. These Ru,Rh bimetallic complexes provide limited stereoisomerization relative to their previously reported Ru,Rh,Ru trimetallic analogues.

Electrochemistry. The electrochemical properties of the title Ru,Rh polyazine complexes and related Ru,Rh,Ru trimetallics are summarized in Table 1. Potentials for all complexes are reported in 0.1 M $\mathrm{Bu_4NPF_6}$ in acetonitrile versus Ag/AgCl. Mixed metal supramolecules with Ru(II) and Rh(III) centered polyazine subunits typically are characterized by reversible $\mathrm{Ru^{III/II}}$ based oxidations, reversible ligand based reductions, and irreversible Rh based reductions. BLs such as dpp often are reduced prior to terminal ligands (TLs) such as bpy or phen because of lower lying π^* acceptor orbitals that are stabilized upon binding two electropositive metal centers. The substitution of bpm for dpp leads to a positive potential shift of the $\mathrm{Ru^{III/II}}$ redox couple. The $\mathrm{Rh(d\sigma^*)}$ orbital energy is sensitive to the Rh ligand set, modulated by ligand σ-bonding ability.[10]

Table 1. Electrochemical Properties of the Title Ru, Rh Bimetallic Complexes and the Previously Reported Ru, Rh, Ru Trimetallic Analogues

complex[a]	$E_{1/2}$[b] (V)	assignment
$[\{(\mathrm{bpy})_2\mathrm{Ru(dpp)}\}_2\mathrm{RhCl_2}](\mathrm{PF}_6)_5$[c]	1.60	$2\mathrm{Ru^{III/II}}$
	−0.39[e]	$\mathrm{Rh^{III/II/I}}$
	−0.79	$\mathrm{dpp^{0/-}}$
	−1.02	$\mathrm{dpp^{0/-}}$
$[(\mathrm{bpy})_2\mathrm{Ru(dpp)RhCl_2(phen)}](\mathrm{PF}_6)_3$	1.61	$\mathrm{Ru^{III/II}}$
	−0.39	$\mathrm{Rh^{III/II}}$
	−0.74[e]	$\mathrm{Rh^{II/I}}$
	−0.98	$\mathrm{dpp^{0/-}}$
$[\{(\mathrm{bpy})_2\mathrm{Ru(bpm)}\}_2\mathrm{RhCl_2}](\mathrm{PF}_6)_5$[d]	1.70	$2\mathrm{Ru^{III/II}}$
	−0.13	$\mathrm{bpm^{0/-}}$
	−0.26	$\mathrm{bpm^{0/-}}$
	−0.78[e]	$\mathrm{Rh^{III/II/I}}$
$[(\mathrm{bpy})_2\mathrm{Ru(bpm)RhCl_2(phen)}](\mathrm{PF}_6)_3$	1.76	$\mathrm{Ru^{III/II}}$
	−0.14	$\mathrm{bpm^{0/-}}$
	−0.77[e]	$\mathrm{Rh^{III/II}}$
	−0.91	$\mathrm{Rh^{II/I}}$

[a] bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline, bpm = 2,2′-bipyrimidine. [b] Potentials were measured in 0.1 M $\mathrm{Bu_4NPF_6}$ acetonitrile with Pt-disk working and Pt-wire auxiliary electrode, and are reported versus Ag/AgCl (3 M NaCl), ± 0.03 V, v = 100 mV/s. Reversible couples routinely had a peak potential separation (ΔE_p) of 80 ± 15 mV, likely due to uncompensated solutions resistance. [c] From ref 41. [d] From ref 58. [e] E_p^c for an irreversible process.

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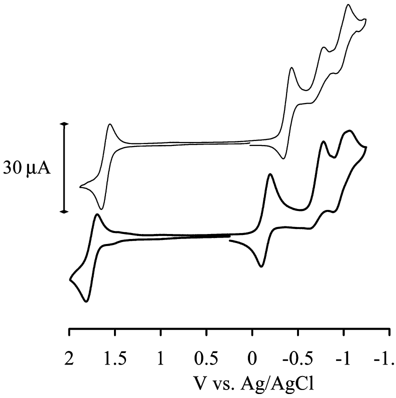

Figure 4. Cyclic voltammetry of $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ (thin line) and $[(bpy)_2Ru(bpm)RhCl_2(bpm)](PF_6)_3$ (thick line) in 0.1 M Bu_4NPF_6 acetonitrile solution using a platinum disk working electrode and platinum wire auxiliary electrode, bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline, bpm = 2,2′-bipyrimidine.

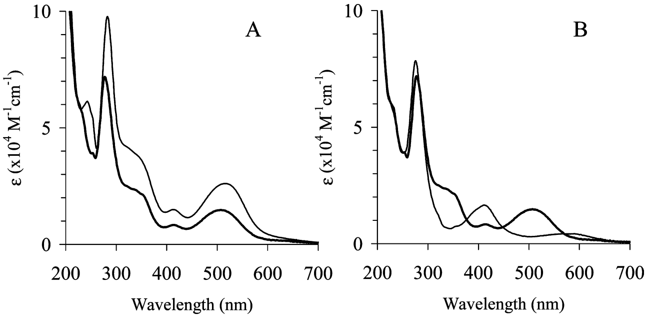

Figure 5. Electronic absorption spectroscopy of $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ (thick line) and (A) $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ (thin line), or (B)$[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ (thin line) in room temperature acetonitrile. bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, bpm = 2,2′-bipyrimidine, phen = 1,10 phenanthroline.

The title bimetallic complexes possess the same structural subunits as their known trimetallic analogues displaying related redox processes. Oxidatively, the complexes $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ display a reversible oxidation at 1.61 and 1.60 V, respectively. This represents overlapping $Ru^{III/II}$ redox processes for the trimetallic and analogous $Ru^{III/II}$ couple for the bimetallic. The first reduction of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ at −0.39 V has been assigned as the irreversible $Rh^{III/II/I}$ process. Ligand loss is known to occur upon reduction of octahedral *cis*-$Rh^{III}Cl_2$ moieties generating free halide and a square-planar Rh^I.[14] Subsequent reversible redox couples follow for each of the bridging dpp ligands at −0.79 and −1.02 V. This electrochemical mechanism is consistent with DeArmond's study of $[(bpy)_2RhCl_2]^+$ and $[(phen)_2RhCl_2]^+$ showing a similar ECECEE reductive mechanism.[14,66] The bimetallic $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ however shows three reductions at −0.39, −0.74, and −0.98 V, Figure 4. Constant potential electrolysis with coulometry past the first or second reduction results in passage of 2 electrons with evidence of chloride in solution, consistent with Rh based reductions. Conducting cyclic voltammetry at slower scan rates leads to an increase in the cathodic current for the couple at −0.39 V and decrease the reversibility of this couple. Constant potential electrolysis at −1.10 V results in passage of a third reducing equivalent. The first two couples are therefore assigned as Rh based reductions, followed by reduction of the dpp bridge at −0.98 V.

Mixed metal supramolecules bridged by bpm display similar redox processes to those bridged by dpp, modulated by the lower lying π^* orbitals on bpm versus dpp. The trimetallic $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$ displays a reversible oxidative couple at $E_{1/2} = 1.70$ V assigned as the two overlapping $Ru^{III/II}$ processes, more positive than the 1.60 V for the dpp bridged $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$.[59] Oxidatively, the complex $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ exhibits a reversible wave at $E_{1/2} = 1.76$ V corresponding to a $Ru^{III/II}$ redox couple, Figure 4. The first two reductions of $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$ at −0.13 and −0.26 V are sequential $bpm^{0/-}$ couples for each bpm bridge.[59] The irreversible $Rh^{III/II/I}$ couple is at −0.79 V for $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$. The complex $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ exhibits a first reduction that is reversible at −0.14 V, followed by two quasi-reversible couples at −0.77 and −0.91 V. Constant potential electrolysis with coulometry indicates each of the three reductive couples represents passage of a one reducing equivalent. The process corresponding to the first couple is reversible. The second and third couples are irreversible and lead to loss of chloride. This is consistent with $bpm^{0/-}$ couple, followed by $Rh^{III/II}$ and $Rh^{II/I}$ couples.

The electrochemical properties of the bimetallic complexes predict a Ru(dπ) based highest occupied molecular orbital (HOMO) in both the dpp and bpm based systems, with the relative energy modulated by BL identity. The lowest unoccupied molecular orbital (LUMO) of $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ is predicted to be bpm based, while electrochemistry suggests a Rh centered LUMO for $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$. Together these electrochemical properties predict low lying Ru(dπ)→BL(π^*) MLCT states with a lowest lying Ru(dπ)→Rh(dσ^*) MMCT state for $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$.

Electronic Absorption Spectroscopy. The electronic absorption spectra of the bimetallic complexes $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ differ significantly but are similar to the absorption spectra of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$, respectively. The electronic absorption spectra are presented in Figure 5 and summarized in Table 2. The spectroscopic properties of Ru,Rh polyazine complexes are dominated in the UV with $\pi \rightarrow \pi^*$ transitions based on each polyazine ligand and Ru based MLCT transitions in the visible to each acceptor ligand with Ru(dπ)→BL(π^*) occurring at the lowest energy. The complex $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ absorbs strongly in the visible region at 509 nm ($\varepsilon = 14{,}700\ M^{-1}\ cm^{-1}$) and 418 nm ($\varepsilon = 8{,}100\ M^{-1}\ cm^{-1}$) and in the UV region at 279 nm ($\varepsilon = 71{,}300\ M^{-1}\ cm^{-1}$) with a shoulder at 338 nm ($\varepsilon = 23{,}400\ M^{-1}\ cm^{-1}$). The complex $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ is a weaker visible light absorber at lower energy with a broad absorption appearing at 581 nm ($\varepsilon =$

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Table 2. Summary of the Electronic Absorption Spectral Data for Ru,Rh Polyazine Supramolecules

complex[a]	λ_{max} (nm)[b]	ε (10^3 M^{-1} cm^{-1})	assignment
$[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$[c]	284	99.0	bpy $\pi\rightarrow\pi^*$
	338(sh)	41.4	dpp $\pi\rightarrow\pi^*$
	416	16.4	Ru(dπ)→bpy(π^*) CT
	518	26.1	Ru(dπ)→dpp(π^*) CT
$[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$	279	71.3	bpy $\pi\rightarrow\pi^*$ phen $\pi\rightarrow\pi^*$
	338(sh)	23.4	dpp $\pi\rightarrow\pi^*$
	418	8.1	Ru(dπ)→bpy(π^*) CT
	509	14.7	Ru(dπ)→dpp(π^*) CT
$[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$[d]	278	90.0	bpy $\pi\rightarrow\pi^*$ bpm $\pi\rightarrow\pi^*$
	412	37.0	Ru(dπ)→bpy(π^*) CT Ru(dπ)→bpm(π^*) CT
	594	9.9	Ru(dπ)→bpm(π^*) CT
$[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$	276	78.4	bpy $\pi\rightarrow\pi^*$ phen $\pi\rightarrow\pi^*$ bpm $\pi\rightarrow\pi^*$
	393(sh)	14.2	Ru(dπ)→bpm(π^*) CT
	412	16.6	Ru(dπ)→bpy(π^*) CT
	581	4.0	Ru(dπ)→bpm(π^*) CT

[a] In room temperature acetonitrile. [b] bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline,bpm = 2,2′-bipyrimidine. [c] From ref 57. [d] From ref 59.

Table 3. Photophysical Properties of Di- And Trinuclear Metal Complexes Bridged by dpp

complex[a]	λ_{max}^{em} (RT)[b] (nm)	Φ^{em} (RT)[c]	τ (RT) (ns)	λ_{max}^{em} (77 K)[d] (nm)	τ (77 K) (μs)
$[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$	758	1.4×10^{-3}	124	696	2.45
$[(bpy)_2Ru(dpp)Rh(bpy)_2](PF_6)_5$[e]	778		37	686	1.71
$[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$	786	1.9×10^{-4}	32	730	1.86
$[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$	786	2.3×10^{-4}	30	716	1.80

[a] bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenantroline. [b] Room temperature (RT) emission data reported in aerated acetonitrile corrected for PMT response. [c] Quantum yield measured versus $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ using absorbance matched solutions. [d] 77 K emission data reported in 4:1 v/v ethanol/methanol glass corrected for PMT response. [e] From ref 34.

4,000 M^{-1} cm^{-1}) but displays higher absorptivity at 412 nm (ε = 16,600 M^{-1} cm^{-1}).

The trimetallic and bimetallic mixed metal complexes possesses absorptions in the UV and near-UV region of the spectrum that are $\pi\rightarrow\pi^*$ internal ligand (IL) based. The bpy and phen $\pi\rightarrow\pi^*$ transitions are at about 280 nm region with dpp $\pi\rightarrow\pi^*$ transitions appearing as low energy shoulders at 340 nm. The intensity of the IL absorption bands reflects the type and number of TLs and BLs.

The complexes $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ and $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ are both efficient visible light MLCT absorbers. Typical for $(bpy)_2Ru^{II}(dpp)$ subunits, the Ru(dπ)→bpy(π^*) CT transition occurs at about 410 nm for the $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ complex and displays significantly lower absorptivity than the Ru(dπ)→dpp(π^*) CT transition. Low energy absorption bands assigned to a Ru(dπ)→dpp(π^*) CT transition occur at λ_{max} = 518 nm and λ_{max} = 509 nm for the trimetallic and bimetallic, respectively, with extinction coefficients consistent with the number of Ru(II) centered chromophores. The heterobinuclear complex $[(bpy)_2Ru(dpp)Rh(bpy)_2](PF_6)_5$ displays a lowest lying MLCT transition centered at 514 nm (ε = 14,400 M^{-1} cm^{-1})[34] while the Ru,Ru homobimetallic $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ displays Ru(dπ)→dpp(π^*) CT transition at 526 nm (ε = 24,800 M^{-1} cm^{-1}).[35] The similar energy of these Ru(dπ)→dpp(π^*) CT transitions indicates that $Ru^{II}(bpy)_2$, $Rh^{III}(bpy)_2$, $Rh^{III}Cl_2(phen)$, or $Rh^{III}Cl_2(dpp)$ have similar impact on the energy and oscillator strength of the Ru(dπ)→ dpp(π^*) CT transitions.

The bpm bridged complexes $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$ and $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$ have strikingly similar electronic absorption properties as well. The intensity of the electronic absorption bands for each complex reflects the number of Ru(II) light absorbers attached to the Rh(III) center. The lowest lying visible absorbance is Ru(dπ)→bpm(π^*) CT in nature and lower energy than the dpp bridged supramolecules with λ_{max} = 594 nm (ε = 9,900 M^{-1} cm^{-1}) and λ_{max} = 581 nm (ε = 4,000 M^{-1} cm^{-1}) for $[\{(bpy)_2Ru(bpm)\}_2RhCl_2](PF_6)_5$ and $[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3$, respectively. The lower energy π^*-acceptor orbital of the bpm bridge relative to dpp leads to the red shift of this absorption. Typical of bpm bridged complexes, a higher energy CT band is seen at 412 nm with higher absorptivity, consistent with overlapping Ru(dπ)→bpy(π^*) CT and Ru(dπ)→bpm(π^*) CT transitions in this region. Both bimetallic complexes display lowest lying absorptions assigned as Ru(dπ)→BL(π^*) CT transitions, with the energy of these transitions being quite similar to the previously studied trimetallic analogues.

Steady State Emission Spectroscopy. The emission spectra of the $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ were measured in room temperature acetonitrile and in 4:1 ethanol/methanol glass at 77 K and compared to the homobimetallic $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$ lacking the Rh^{III} acceptor, Table 3. A broad, weak emission was observed for $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ at 786 nm (Φ^{em} = 2.3×10^{-4}) at room temperature. The room temperature emission of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ was centered at 786 nm with Φ^{em} = 1.9×10^{-4}, consistent with the previously reported photophysics of this complex when corrected for PMT response.[50] In alcoholic glass at 77 K the emission peak remained broad but shifted to 716 nm for $[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3$ and to 730 nm for [{(bpy)$_2$-

$\mathrm{Ru(dpp)\}_2RhCl_2](PF_6)_5}$. The bpm complexes did not display detectable emissions consistent with weaker and more red-shifted emission from Ru(II) complexes bridged by bpm.[35]

The room temperature emission spectra of the Ru,Rh complexes are weaker than those of the Ru,Ru model complex. Both $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ and $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ have broad, structureless emissions at 786 nm, consistent with emission from a stabilized $\mathrm{Ru}(d\pi)\rightarrow\mu\text{-dpp}(\pi^*)$ CT (^{3}MLCT) state. The complex $\mathrm{[(bpy)_2Ru(dpp)Rh(bpy)_2](PF_6)_5}$ possesses a similar reported emission ($\lambda_{\max}^{\mathrm{em}} = 778$ nm) at room temperature.[35] The homonuclear complex $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$ emission is slightly blue-shifted, centered at 758 nm with significantly higher intensity. The quantum yield of the emission of the mixed metal complexes is significantly reduced compared to the homonuclear analogue. The Rh containing complexes possess low lying $\mathrm{Rh}(d\sigma^*)$ acceptor orbitals. This provides energetically feasible intramolecular electron transfer to give the $\mathrm{Ru}(d\pi)\rightarrow\mathrm{Rh}(d\sigma^*)$ CT excited state (^{3}MMCT), leading to quenching of the ^{3}MLCT emission.

The ^{3}MLCT emission of the dpp bridged mixed metal supramolecules in alcoholic glass was studied and compared to the analogous emission of $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$. The emission of $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$ at 77 K displays some broad structure centered at 696 nm, consistent with previous reports.[35] The previously studied Ru,Rh dyad $\mathrm{[(bpy)_2Ru(dpp)Rh(bpy)_2](PF_6)_5}$ displayed a similar emission at 77 K, blue-shifted 10 nm relative to the Ru,Ru analogue.[34] The *cis*-$\mathrm{Rh^{III}Cl_2}$ containing complexes, however, have emission maxima red-shifted versus $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$. The complex $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ had an emission centered at 716 nm, while the emission at 77 K from $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ was centered at 730 nm.

Excited State Decay. Excited state lifetimes were determined by measuring emission decay in acetonitrile at room temperature and in 4:1 ethanol/methanol glass at 77 K, Table 3. The decay of the ^{3}MLCT emission fits well to a single exponential decay. In room temperature, fluid solution the excited-state lifetime of $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ was measured to be 30 ns, and the lifetime of $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ was determined to be 32 ns. In alcoholic glass at 77 K the excited-state lifetimes were 1.80 and 1.86 μs for $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$, respectively.

The lifetime of the emitting states of $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ in room temperature solution are significantly shorter than that of $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$. At room temperature, the lifetimes of the emission from the ^{3}MLCT states of $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ are about 30 ns, similar to the previously reported Ru,Rh complex $\mathrm{[(bpy)_2Ru(dpp)Rh(bpy)_2](PF_6)_5}$ ($\tau = 37$ ns).[34] The Ru,Rh complexes all display shorter ^{3}MLCT excited-state lifetimes relative to $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$ ($\tau = 124$ ns). This is reflective of quenching of the ^{3}MLCT state by intramolecular electron transfer to generate the ^{3}MMCT state. In alcoholic glass at 77 K the excited-state lifetime of $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ increase significantly to about 1.8 μs, compared to 2.45 μs measured for $\mathrm{[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4}$. Excited state electron transfer is known to be inhibited in rigid matrixes because of the large reorganizational energy associated with charge redistribution. For example, the ^{3}MLCT emission of $\mathrm{[(Me_2phen)_2Ru(Mebpy\text{-}CH_2CH_2\text{-}Mebpy)Rh(dmb)_2]^{5+}}$ increases from 30 ns to 6.8 μs when studied at 77 K in frozen solution.[33] The large increase in ^{3}MLCT emission for $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5}$ at 77 K versus room temperature is indicative of intramolecular electron transfer at room temperature being impeded at 77 K in rigid media.

Conclusions

The first polyazine bridged Ru,Rh dyads containing the *cis*-$\mathrm{Rh^{III}Cl_2}$ moiety were synthesized and characterized. The complexes were synthesized using a building block approach that exploited the known tendency of Rh(III) to form bis-bidentate polyazine units, *cis*-$\mathrm{[(NN)_2RhCl_2]^+}$. This strategy was tested by synthesizing the simple heteroleptic complex, $\mathrm{[(phen)RhCl_2(dmb)](PF_6)}$. Under similar conditions, $\mathrm{[(bpy)_2Ru(dpp)](PF_6)_2}$ and $\mathrm{[(bpy)_2Ru(bpm)](PF_6)_2}$ were each reacted with $\mathrm{K[(phen)RhCl_4]\cdot 3H_2O}$ to give $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3}$, respectively. Both $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3}$ exhibit a $\mathrm{Ru}(d\pi)$ based HOMO. The reductive processes for the Ru,Rh dyads suggest a $\mathrm{Rh}(d\sigma^*)$ based LUMO for $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{bpm}(\pi^*)$ based LUMO for $\mathrm{[(bpy)_2Ru(bpm)RhCl_2(phen)](PF_6)_3}$, similar to the Ru,Rh,Ru triads. The electronic absorption spectra of the bimetallic complexes were unique compared to each other but contained features similar to the trimetallic analogues. The absorptivity of the complexes depends on the number of Ru(II) polyazine subunits appended to the Rh(III) core. The spectral similarity between the newly prepared bimetallics and previously reported trimetallics indicated that exchange of a Ru(II) polyazine subunit for a terminal phen ligand had little impact on observed electronic spectroscopy consistent with the Ru subunit dominated light absorbing properties. The emission spectroscopy of $\mathrm{[(bpy)_2Ru(dpp)RhCl_2(phen)](PF_6)_3}$ and $\mathrm{[\{(bpy)_2Ru(dpp)\}_2\text{-}RhCl_2](PF_6)_5}$ indicated significant quenching of the $\mathrm{Ru}(d\pi)\rightarrow\mathrm{dpp}(\pi^*)$ ^{3}MLCT emission, consistent with intramolecular electron transfer to generate a ^{3}MMCT state. The title complexes represent a new structural motif related to known photochemical molecular devices with promising photochemistry.

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