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Mixed-Metal Supramolecular Complexes Coupling Phosphine-Containing Ru(II) Light Absorbers to a Reactive Pt(II) through Polyazine Bridging Ligands

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Supramolecular bimetallic Ru(II)/Pt(II) complexes $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ and their synthons $[(tpy)Ru(L)(BL)]^{n+}$ (where L = Cl^-, CH_3CN, or PEt_2Ph; tpy = 2,2′:6′,2′′-terpyridine; and BL = 2,2′-bipyrimidine (bpm) or 2,3-bis(2-pyridyl)pyrazine (dpp)) have been synthesized and studied by cyclic voltammetry, electronic absorption spectroscopy, mass spectral analysis, and ^{31}P NMR. The mixed-metal bimetallic complexes couple phosphine-containing Ru chromophores to a reactive Pt site. These complexes show how substitution of the monodentate ligand on the $[(tpy)RuCl(BL)]^+$ synthons can tune the properties of these light absorbers (LA) and incorporate a ^{31}P NMR tag by addition of the PEt_2Ph ligand. The redox potentials for the Ru(III/II) couples occur at values greater than 1.00 V versus the Ag/AgCl reference electrode and can be tuned to more positive potentials on going from Cl^- to CH_3CN or PEt_2Ph ($E_{1/2}$ = 1.01, 1.55, and 1.56 V, respectively, for BL = bpm). The $BL^{0/-}$ couple at –1.03 (bpm) and –1.05 V (dpp) for $[(tpy)Ru(PEt_2Ph)(BL)]^{2+}$ shifts dramatically to more positive potentials upon the addition of the $PtCl_2$ moiety to –0.34 (bpm) and –0.50 V (dpp) for the $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ bridged complex. The lowest energy electronic absorption for these complexes is assigned as the $Ru(d\pi) \rightarrow BL(\pi^*)$ metal-to-ligand charge transfer (MLCT) transition. These MLCT transitions are tuned to higher energy in the monometallic synthons when Cl^- is replaced by CH_3CN or PEt_2Ph (516, 452, and 450 nm, for BL = bpm, respectively) and to lower energy when $Pt^{II}Cl_2$ is coordinated to the bridging ligand (560 and 506 nm for BL = bpm or dpp). This MLCT state displays a broad emission at room temperature for all the dpp systems with the $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2]^{2+}$ system exhibiting an emission centered at 750 nm with a lifetime of 56 ns. These supramolecular complexes $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ represent the covalent linkage of TAG–LA–BL–RM assembly (TAG = NMR active tag, RM = Pt(II) reactive metal).

Introduction

Ruthenium(II) polypyridyl complexes have been extensively studied primarily because of their interesting photophysical and redox properties. Intermolecular excited state energy or electron transfer using such chromophores as the widely studied $[Ru(bpy)_3]^{2+}$ is limited by the need for a molecular collision prior to relaxation of the ^{3}MLCT excited state (bpy = 2,2′-bipyridine, MLCT = metal-to-ligand charge transfer).[1,2] This has led to the development and study of supramolecular polyazine bridged complexes.[3−7] One interesting class couples Ru(II) light absorbers (LA) to reactive metal (RM) centers.

Polyazine bridging ligands (BL) have been widely studied in the construction of polymetallic complexes.[3−7] These bridging ligands serve to connect two metal centers, bringing them into close proximity, and can serve as conduits for electron and energy transfer. Being good acceptors, these

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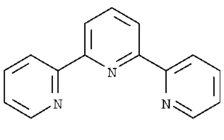
BLs impart interesting and useful spectroscopic and redox properties on polymetallic complexes. One of the more commonly used bridging ligands is 2,3-bis(2-pyridyl)pyrazine (dpp).[3−6,8−10] The dpp ligand binds to two metal centers through a pyridyl and a pyrazine nitrogen, acting as an AB chelate and possesses a lower lying π^* orbital than bpy. Much of the work using this AB chelate results in a mixture of stereoisomers not typically separated. The resulting supramolecular complexes are therefore studied as a mixture of sterioisomers. The less studied 2,2′-bipyrimidine (bpm) also acts as a good acceptor bridging ligand but binds to each metal center through two equivalent nitrogens, eliminating the stereoisomers that result from an asymmetric chelate.[7,11−13]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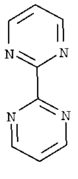
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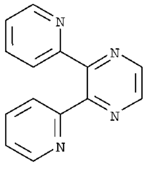
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Supramolecular complexes using bidentate polyazine BLs to couple Ru light absorbers to reactive metal centers also possess terminal ligands (TL). The most common TL is bpy. 2,2′:6′,2″-Terpyridine (tpy) can also be used as a terminal ligand on Ru centers but is less studied as the Ru → tpy MLCT excited state in $[\mathrm{Ru(tpy)}]^{2+}$ is short-lived.[14−16] One advantage of tpy as a terminal ligand is that it occupies three coordination sites, which results in some stereochemical control of supramolecular complexes by eliminating the Δ and Λ isomeric mixtures present in tris-bidentate systems. Recently it has been illustrated that polymetallic complexes incorporating the $\mathrm{Ru^{II}}$(tpy) chromophore can have long excited state lifetimes.[17−26] Combining a tpy TL with a polyazine BL that occupies two coordination sites leaves available the sixth coordination site to allow tuning of the ruthenium chromophore's properties $[\mathrm{(tpy)RuL(BL)}]^{n+}$ (L = monodentate ligand).

Introduction of tertiary phosphines into the coordination sphere of low valent ruthenium complexes has been extensively studied in the area of homogeneous catalysis, and therein ^{31}P NMR spectroscopy becomes an important characterization tool.[27−30] There is little mention in the literature of the effects of tertiary phosphines on the electronic properties of monometallic or bimetallic ruthenium(II) polyazine complexes.[31−34] One such study indicates that $\mathrm{PPh_3}$ in the trans position of $[\mathrm{(tpy)(PPh_3)RuCl_2}]$ stabilizes the Ru(dπ) orbital compared to the cis form of the complex, resulting in a blue shift for the MLCT.[33] Characterization of polymetallic polyazine bridged complexes could be aided by incorporation of tertiary phosphine ligands, as this would allow for the use of ^{31}P NMR spectroscopy, acting as an NMR tag for molecular structures.[35] Additionally, variation of the ligand used could modulate redox and spectroscopic properties of this important class of light absorbers, and this approach has been successfully applied in related osmium light absorbers.[35−37]

Investigations of ruthenium(II)/platinum(II) bridged complexes, $[\mathrm{(bpy)_2Ru(BL)PtCl_2}]^{2+}$ (BL = dpp,[38,39] dpq,[40] dpb,[40−42] or bpm;[43] dpq = 2,3-bis(2-pyridyl)quinoxaline and dpb = 2,3-bis(2-pyridyl)benzoquinoxaline) have shown that the Pt(II) center stabilizes the bridging ligand π^* orbitals upon coordination, resulting in lower energy MLCT transitions and BL-based reductions that occur at more positive potentials. Our motivation for incorporating the $\mathrm{PtCl_2}$ moiety into ruthenium polyazine chromophores stems from the potential reactivity of a $\mathrm{Pt^{II}}$ site and the known DNA binding ability of the *cis*-$\mathrm{PtCl_2}$ moiety, shown to be maintained in previous (μ-BL)$\mathrm{PtCl_2}$ complexes studied in our lab.[40−42]

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In this study supramolecular $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ complexes and their monometallic synthons $[(tpy)Ru(L)(BL)]^{n+}$, where L = Cl^-, CH_3CN, or PEt_2Ph and BL = bpm or dpp, have been synthesized and characterized by FAB mass spectral analysis, cyclic voltammetry (CV), ^{31}P NMR, and electronic absorption spectroscopy. The effect of the monodentate ligands and the platinum metal center on the electrochemical and spectroscopic properties of the complexes is discussed.

Experimental Section

Materials. 2,2′:6′,6′′-Terpyridine (tpy) (GFS chemicals), ruthenium(III) chloride hydrate and bipyrimidine (bpm) (Alfa), triethylamine (Acros), diethylphenylphosphine (PEt_2Ph), 2,3-bis(2-pyridyl)pyrazine (dpp) and deuterated acetonitrile (Aldrich), thallium hexafluorophosphate (Strem), potassium hexachloroplatinate(IV) (Alfa Aesar), (80−200 mesh) adsorption alumina (Fisher), and spectroquality grade acetonitrile and toluene (Burdick and Jackson) were used as received. Tetrabutylammonium hexafluorophosphate Bu_4NPF_6 (used as supporting electrolyte for electrochemistry experiments) was prepared by the aqueous metathesis of tetrabutylammonium bromide (Aldrich) with potassium hexafluorophosphate (Aldrich). After several recrystallizations from ethanol the white crystals were dried under vacuum and stored in a vacuum desiccator. $(tpy)RuCl_3$[33], $[(tpy)RuCl(dpp)](PF_6)$,[44] and $Pt(dmso)_2Cl_2$[45] were prepared as described previously. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis. $[(tpy)RuCl(bpm)](PF_6)$. To a solution containing 0.43 g (1.0 mmol) of $[(tpy)RuCl_3]$ and 0.24 g (1.5 mmol) of 2,2′-bipyrimidine in 40 mL of 2:1 (v/v) ethanol/water was added 4.0 mL (29 mmol) of triethylamine. The mixture was heated at reflux for 5 h, cooled to room temperature, and added to 10 mL of a saturated aqueous KPF_6 solution. The resulting black precipitate was filtered, dried, and chromatographed on adsorption alumina using a 3:2 toluene/acetonitrile mixture as eluent. A 30 cm column (2.5 cm diameter) is prepared with the eluent. The crude product is dissolved in a minimal amount (ca. 10 mL) of the eluent, filtered, and loaded on the column. The 3:2 toluene/acetonitrile eluent is used and all solvent eluting prior to the first colored band is discarded. The first band to elute was red and was collected and evaporated to dryness. The resulting product was dissolved in a minimum of acetonitrile (ca. 5 mL) flash precipitated in ca. 200 mL of ether and collected by vacuum filtration to yield a brown powder (0.45 g, 0.67 mmol, 67% yield). Anal. Calcd for $[(tpy)RuCl(bpm)](PF_6)$: C, 41.05; H, 2.55; N, 14.57. Found: C, 41.29; H, 2.74; N, 14.54. UV/vis (CH_3CN): λ_{max} (nm) [$\epsilon \times 10^{-4}/M^{-1}\ cm^{-1}$] = 240 [3.94], 266 [2.92], 316 [3.31], 370 [0.96], 516 [0.99]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)RuCl(bpm)]^+$ (528; 100), $[(tpy)Ru(bpm)]^+$ (492; 14), $[(tpy)Ru(CH_3CN)_3]^+$ (460; 24), $[(tpy)RuCl]^+$ (370; 19), $[Ru(tpy)]^+$ (334; 31).

$[(tpy)Ru(CH_3CN)(bpm)](PF_6)_2$. 0.67 g (1.0 mmol) of $[(tpy)RuCl(bpm)](PF_6)$ and 0.70 g (2.0 mmol) of $TlPF_6$ were heated at reflux in 30 mL of 1:1 (v/v) acetonitrile/water under argon in the dark for 24 h. After removal of the solvent the yellow solid that resulted was dissolved in a minimum of acetonitrile and TlCl was removed by vacuum filtration. The crude product was chromatographed, as described above, collecting the yellow product which elutes as the first colored band (0.77 g, 0.95 mmol, 95% yield). Anal. Calcd for $[(tpy)Ru(CH_3CN)(bpm)](PF_6)$: C, 36.46; H, 2.45; N, 13.61. Found: C, 36.19; H, 2.60; N, 13.27. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}/M^{-1}\ cm^{-1}$] = 268 [2.78], 304 [3.01], 332 [1.90], 452 [0.81]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(CH_3CN)(bpm)](PF_6)^+$ (679; 19), $[(tpy)Ru(CH_3CN)(bpm)]^+$ (533; 16), $[(tpy)Ru(bpm)F]^+$ (512; 100), $[(tpy)Ru(bpm)]^+$ (492; 82), $[Ru(tpy)]^+$ (334; 79).

$[(tpy)Ru(CH_3CN)(dpp)](PF_6)_2$. A solution of 0.75 g (1.0 mmol) of $[(tpy)RuCl(dpp)](PF_6)$ and 0.70 g (2.0 mmol) of $TlPF_6$ in 100 mL of a 1:1 (v:v) acetonitrile/water mixture was heated at reflux under argon in the dark for 24 h. After removal of the solvent, the solid was dissolved in a minimum of acetonitrile (ca. 5 mL) and TlCl was removed by vacuum filtration. The crude product was chromatographed, as described above, collecting the yellow product which elutes as the first colored band (0.85 g, 0.96 mmol, 96% yield). Anal. Calcd for $[(tpy)Ru(CH_3CN)(dpp)](PF_6)\cdot H_2O$: C, 40.58; H, 2.86; N, 12.21. Found: C, 40.94; H, 2.93; N, 12.17. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}/M^{-1}\ cm^{-1}$] = 272 [2.49], 302 [3.36], 333 [sh], 462 [0.93]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(CH_3CN)(dpp)](PF_6)^+$ (753; 12), $[(tpy)Ru(CH_3CN)(dpp)]^+$ (608; 13), $[(tpy)Ru(dpp)]^+$ (568; 29), $[(tpy)Ru(CH_3CN)_3]^+$ (460; 100), and $[Ru(tpy)]^+$ (334; 23).

$[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)_2$. 0.67 g (1.0 mmol) of $[(tpy)RuCl(bpm)](PF_6)$ and 0.70 g (2.0 mmol) of $TlPF_6$ were heated at reflux in 30 mL of 1:1 (v/v) ethanol/water under argon in the dark for 32 h. After 1 h, 180 μL (1.0 mmol) of PEt_2Ph was added to the reaction mixture. Subsequent additions were made at 6 h increments until the reaction was complete and a total of 1.08 mL (6.0 mmol) of PEt_2Ph had been added. The crude product was precipitated as the PF_6^- salt by adding the reaction mixture to 10 mL of a saturated aqueous solution of KPF_6. The resulting yellow solid was dissolved in a minimum of acetonitrile (ca. 5 mL) and TlCl was removed by vacuum filtration. The crude product was chromatographed as described above, collecting the yellow product which elutes as the second colored band following a red band, presumably a small amount of starting material (0.70 g, 0.75 mmol, 75% yield). Anal. Calcd for $[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)_2$: C, 41.56; H, 3.91; N, 10.28. Found: C, 41.44; H, 3.43; N, 10.45. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}/\ M^{-1}\ cm^{-1}$] = 234 [4.99], 268 [3.44], 308 [3.81], 334 [2.25], 450 [1.00]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)^+$ (804; 32), $[(tpy)Ru(PEt_2Ph)(bpm)]^+$ (659; 14), $[(tpy)Ru(bpm)F]^+$ (512; 61), $[(tpy)Ru(bpm)]^+$ (492; 100).^{31}P NMR (CD_3CN): −143.2 (m), 32.2 (s).

$[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)_2$. 0.75 g (1.0 mmol) of $[(tpy)RuCl(dpp)](PF_6)$ and 0.70 g (2.0 mmol) of $TlPF_6$ were heated at reflux in 30 mL of 1:1 (v/v) ethanol/water under argon in the dark for 32 h. After 1 h, 180 μL (1.0 mmol) of PEt_2Ph was added to the reaction mixture. Subsequent additions were made at 6 h increments until the reaction was complete and a total of 1.08 mL (6.0 mmol) of PEt_2Ph had been added. The crude product was precipitated as the PF_6^- salt by adding the reaction mixture to 10 mL of a saturated aqueous solution of KPF_6. The resulting yellow solid was dissolved in a minimum of acetonitrile (ca. 5 mL) and TlCl was removed by vacuum filtration. The crude product was chromatographed as described above, collecting the yellow product which elutes as the second colored band following a red band, presumably a small amount of unreacted starting material (0.76 g, 0.75 mmol, 75% yield). Anal. Calcd for $[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)_2\cdot H_2O$: C, 44.70; H, 4.14; N, 9.36. Found: C, 44.93; H, 3.93; N, 9.46. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}/M^{-1}\ cm^{-1}$] = 232 [3.75], 278 [3.02], 308 [3.87], 334 [0.60], 460 [0.96]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)^+$ (880; 31), $[(tpy)Ru(PEt_2Ph)(dpp)]^+$ (734; 16), $[(tpy)Ru(bpm)]^+$ (568; 94),

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$[Ru(tpy)]^+$ (334; 100). ^{31}P NMR (CD_3CN): −143.2 (m), 30.6 (s), 32.1 (s).

[(tpy)Ru(PEt$_2$Ph)(bpm)PtCl$_2$](PF$_6$)$_2$. Due to the lability of the chloride ligands, the $Pt^{II}Cl_2$ moiety was unstable under typical alumina chromatography. Careful development of synthetic methods is needed with alternative purification procedures. A solution of 0.19 g (0.20 mmol) of $[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)_2$ and 0.11 g (0.25 mmol) of $Pt(dmso)_2Cl_2$ was heated at reflux under argon in 140 mL of 100% ethanol for 4 h. After cooling to room temperature, the dark precipitate that formed was filtered and washed with 700 mL of hot 100% ethanol followed by 700 mL of diethyl ether. Unreacted $Pt(dmso)_2Cl_2$ was removed by dissolving the product in a minimum of acetonitrile (ca. 5 mL) followed by vacuum filtration. The solvent was evaporated from the filtrate to leave a dark green powder. This is dissolved in a minimum of acetonitrile (ca. 5 mL) and flash precipitated in diethyl ether, collected by vacuum filtration, and dried under vacuum (0.15 g, 0.12 mmol, 62% yield). Anal. Calcd for $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)_2 \cdot 2H_2O$: C, 31.56; H, 3.29; N, 7.81. Found: C, 31.42; H, 2.82; N, 8.07. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}$/ M^{-1} cm^{-1}] = 232 [5.61], 274 [4.71], 304 [4.01], 336 [3.14], 416 [1.52], 560 [0.61]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)^+$ (1072; 41), $[(tpy)Ru(PEt_2Ph)(bpm)Pt]^+$ (998; 18), $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2]^+$ (925; 100), $[(tpy)Ru(bpm)PtCl_2]^+$ (760; 40), $[(tpy)Ru(bpm)PtCl]^+$ (722; 87), $[(tpy)Ru(bpm)Pt]^+$ (685; 79), $[(tpy)Ru(PEt_2Ph)(bpm)]^+$ (658; 60). ^{31}P NMR(CD_3CN): −143.2 (m), 33.3 (s).

[(tpy)Ru(PEt$_2$Ph)(dpp)PtCl$_2$](PF$_6$)$_2$. Due to the lability of the chloride ligands, the $Pt^{II}Cl_2$ moiety was unstable under typical alumina chromatography. Careful development of synthetic methods is needed with alternative purification procedures. A solution of 0.21 g (0.20 mmol) of $[(tpy)Ru (PEt_2Ph)(dpp)](PF_6)_2$ and 0.11 g (0.25 mmol) of $Pt(dmso)_2Cl_2$ was refluxed under argon in 140 mL of 100% ethanol for 4 h. After cooling to room temperature, the dark precipitate that formed was filtered and washed with 700 mL of hot 100% ethanol followed by 700 mL of diethyl ether. Unreacted $Pt(dmso)_2Cl_2$ was removed by dissolving the product in a minimum of acetonitrile (ca. 5 mL) followed by vacuum filtration. The solvent was evaporated from the filtrate to leave a dark green powder. This powder is dissolved in a minimum of acetonitrile (ca. 5 mL), flash precipitated in diethyl ether, collected by vacuum filtration and dried under vacuum (0.14 g, 0.11 mmol, 55% yield). Anal. Calcd for $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2 \cdot 2H_2O$: C, 35.17; H, 3.41; N, 7.36. Found: C, 34.69; H, 2.92; N, 7.31. UV/vis (CH_3CN): λ_{max}(nm) [$\epsilon \times 10^{-4}$/M^{-1} cm^{-1}] = 234 [4.11], 276 [2.09], 3.08 [2.41], 336 [2.22], 424 [0.53], 506 [1.05]. FAB-MS ion (*m*/*z*; relative abundance): $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)^+$ (1146; 6), $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2]^+$ (1001; 21), $[(tpy)Ru(dpp)PtCl_2]^+$ (835; 12), $[(tpy)Ru(dpp)PtCl]^+$ (798; 17), $[(tpy)Ru(dpp)Pt]^+$ (763; 11). ^{31}P NMR(CD_3CN): −143.3 (m), 29.8 (s), 32.1 (s).

NMR Spectroscopy. ^{31}P NMR were run on a Bruker 360 MHz spectrometer using CD_3CN as the solvent and TMS as the internal standard.

FAB-MS Spectrometry. FAB mass spectral analysis was conducted on a Fisons VG Quattro triple-stage quadrupole mass spectrophotometer using *m*-nitrobenzyl alcohol as a matrix. The samples were dissolved in CH_3CN prior to introduction into the matrix.

Electronic Spectroscopy. UV/vis spectra were recorded at room temperature using a Hewlett-Packard 8452 diode array spectrophotometer with 2 nm resolution. Samples were run at room temperature (RT) in Burdick and Jackson UV-grade acetonitrile in 1 cm quartz cuvettes.

Emission Spectroscopy. Emission spectra were recorded at RT on deoxygenated, acetonitrile solutions of each analyte using a modified QuantaMaster Model QM-200-45E fluorometer from Photon Technology International. The system was modified to use a 150 W cooled xenon lamp excitation source with emission collected at right angle by a thermoelectrically cooled Hamamatsu 1527 photomultiplier tube operating in photon counting mode with 0.25 nm resolution. The acetonitrile solutions of each analyte were prepared to have an absorbance of ca. 0.1 at the wavelength of excitation (460 nm for $[(tpy)Ru(CH_3CN)(dpp)](PF_6)_2$ and $[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)_2$ and 500 nm for $[(tpy)RuCl(dpp)](PF_6)$ and $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$). The solutions were deoxygenated by bubbling with high purity argon for 20 min just prior to the collection of the emission spectra. Emission spectra are corrected for photomultiplier tube (PMT) response.

Emission quantum yields were measured relative to a $[Os(bpy)_3](PF_6)_2$ reference in deoxygenated CH_3CN at RT using Φ^{em} = 0.00462, $(area_{sample})(abs_{ref})/(area_{ref})(abs_{sample})$.[46] The monometallic complex $[(tpy)RuCl(dpp)](PF_6)$ and the bimetallic complex $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$ emit at relatively low energy, 770 and 750 nm, respectively. The Hamamatsu 1527 PMT response in this region is relatively weak and makes the absolute values of the emission quantum yields for these two complexes lower estimates.

Emission Lifetime Measurements. Laser induced emission lifetime measurements were obtained on the same solutions used for the emission spectroscopy. Emission decays were obtained as previously described using a Photon Technology International Pl-2300 nitrogen laser excitation source and a Hamamatsu R928 photomultiplier tube operating in direct analog mode.[10]

Electrochemistry. Cyclic voltammograms were recorded using a one-compartment, three-electrode cell, Bioanalytical Systems (BAS), equipped with a platinum wire auxiliary electrode. The working electrode was a 1.9 mm diameter glassy carbon disk from BAS. Potentials were referenced to a Ag/AgCl electrode (0.29 V vs NHE), which was calibrated against the $FeCp_2/FeCp_2^+$ redox couple (0.67 V vs NHE).[47] The supporting electrolyte was 0.1 M Bu_4NPF_6, and the measurements were made in Burdick and Jackson UV-grade acetonitrile, which was dried over 3 Å molecular sieves.

Results and Discussion

Synthesis. The supramolecular mixed-metal complexes, $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ (BL = bpm or dpp), have been prepared in good yields using a building block approach. Synthetic methods for the construction of the new $[(tpy)Ru(L)(BL)]^{n+}$ light absorbers have also been developed (L = Cl^-, CH_3CN, or PEt_2Ph). This new supramolecular architecture is of interest as it couples a phosphine-tagged light absorber to a reactive metal. This forms a TAG−LA−BL−RM framework (TAG = PEt_2Ph NMR tag, LA = ruthenium light absorber, BL = bpm or dpp bridging ligand, and RM = reactive metal site). Bridging ligand bound *cis*-$PtCl_2$ sites have been shown to function as reactive metals exhibiting avid DNA binding.[40−42]

Scheme 1 shows the building block approach used to synthesize the monometallic precursor complexes $[(tpy)RuCl(BL)](PF_6)$, $[(tpy)Ru(CH_3CN)(BL)](PF_6)_2$, and $[(tpy)Ru(PEt_2Ph)(BL)](PF_6)_2$ and the bimetallic complexes $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2](PF_6)_2$, where BL = bpm or dpp.

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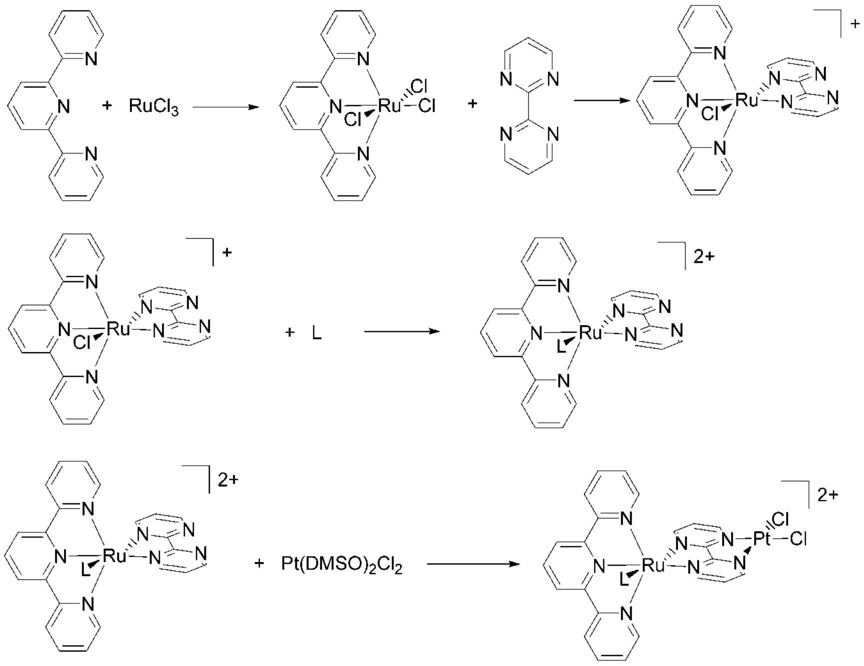
[46] Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

[47] Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787.

Scheme 1[a]



[a] L = PEt_2Ph.

This step-by-step method allows for high-purity products in good yields, developing generalized synthetic methods that allow for component modifications within this supramolecular architecture. The synthetic method described is dictated by the varying reactivity of the ruthenium(II) and platinum(II) metal centers. The platinum(II) reactions proceed under mild conditions, so construction of the TAG−LA−BL component is achieved first and then coupled to the platinum RM. The choice of tpy as the terminal ligand eliminates the Δ and Λ isomers that are typically present in tris-chelated systems.

Incorporating bpm as the bridging ligand eliminates stereochemical isomers possible with AB chelates, resulting in a pure complex free of isomeric mixtures. Analogous complexes using dpp as the bridging ligand were synthesized, giving a mixture of two (cis, trans type) stereoisomers.[44] These isomers were not detected by cyclic voltammetry or UV/vis spectroscopy but could be detected using the ^{31}P NMR probe (discussed below).

These new monometallic light absorbers allow substitution of the sixth coordination position, $[(tpy)Ru(L)(BL)]^{n+}$. This substitution modulates the electrochemical and spectroscopic properties (discussed below). Substitution of PEt_2Ph or CH_3CN for Cl^- (Scheme 1) was achieved by abstraction of the chloride ligand using thallium(I). Subsequent additions of PEt_2Ph over a 32 h period produced the PEt_2Ph complex. This procedure greatly improved the yield of the complex over a simple single addition of phosphine. The phosphine ligand will serve to tune the properties of these LAs and provides an NMR tag of molecular structure.

The monometallic complexes, $[(tpy)RuCl(BL)](PF_6)$, $[(tpy)Ru(CH_3CN)(BL)](PF_6)_2$, and $[(tpy)Ru(PEt_2Ph)(BL)](PF_6)_2$, are purified by column chromatography. Because of the lability of the chloride ligands on the $Pt^{II}Cl_2$ fragment, the bimetallic Ru−Pt complexes were not stable under typical alumina chromatography procedures. Through optimization of reaction conditions good purity mixed-metal complexes are isolated in reasonable yield without the need for chromatographic separations. This requires careful attention to stoichiometry, reaction time, and solvent choice.

Both mono- and bimetallic complexes are effectively characterized by FAB mass spectroscopy. For solubility reasons the complexes must first be dissolved in CH_3CN and then introduced into the *m*-nitrobenzyl alcohol matrix. Molecular ions with loss of a single PF_6^- are observed in all cases. Additional peaks are observed for loss of Cl^-, Pt (in the case of the bimetallics), and intact BLs. All MS data support the proposed structures of these systems.

The monometallic $[(tpy)Ru(L)(dpp)](PF_6)_2$ (L = Cl^-, CH_3CN, or PEt_2Ph) and bimetallic $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$ complexes exist as cis and trans isomers, which typically go undetected. The presence of PEt_2Ph allows ^{31}P NMR to be used to detect these cis and trans isomers. This results in two peaks separated by ca. 2 ppm in the coordinated phosphine region of the ^{31}P NMR spectrum.

Electrochemistry. Ruthenium(II) polyazine complexes are characterized by a reversible ruthenium oxidation and reversible ligand reductions, with the bpm or dpp BL being easier to reduce than the tpy terminal ligand.[3,5,7,16,32,44] This behavior is consistent with the Ru(dπ) nature of the highest occupied molecular orbital (HOMO) and BL(π*) nature of the lowest unoccupied molecular orbital (LUMO). Typically dpp and bpm bridged polymetallic complexes display $BL^{0/-}$ and $BL^{-/2-}$ couples prior to terminal ligand reductions.[3,5−7,9] Redox potentials for the bpm and dpp ruthenium based light absorbers and mixed-metal complexes are compared in Table 1. The cyclic voltammograms of the bpm complexes are very similar to the analogous complexes incorporating dpp owing to the similarity of the π* orbital energies of the two ligands.

Table 1. Redox Potentials for a Series of Ru(II) and Ru(II)/Pt(II) Complexes of the General Formula [(tpy)RuL(BL)](PF_6) and [(tpy)RuL(BL)PtCl_2](PF_6)$_2$, Where L = Cl^-, CH_3CN, or PEt_2Ph, BL = bpm (2,2′-Bipyrimidine) or dpp (2,3-Bis(2-pyridyl)pyrazine), and tpy = 2,2′:6′,2″-Terpyridine

complex	$E_{1/2}{}^{a}$/V	assignment
[(tpy)RuCl(bpm)](PF_6)	1.01	$Ru^{III/II}$
	−1.15	$bpm^{0/-}$
	−1.56	$tpy^{0/-}$
[(tpy)RuCl(dpp)](PF_6)[36]	1.00	$Ru^{III/II}$
	−1.21	$dpp^{0/-}$
	−1.54	$tpy^{0/-}$
[(tpy)Ru(CH_3CN)(bpm)](PF_6)$_2$	1.55	$Ru^{III/II}$
	−1.06	$bpm^{0/-}$
	−1.42	$tpy^{0/-}$
[(tpy)Ru(CH_3CN)(dpp)](PF_6)$_2$	1.56	$Ru^{III/II}$
	−1.06	$dpp^{0/-}$
	−1.40	$tpy^{0/-}$
[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)$_2$	1.56	$Ru^{III/II}$
	−1.03	$bpm^{0/-}$
	−1.38	$tpy^{0/-}$
[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)$_2$	1.57	$Ru^{III/II}$
	−1.05	$dpp^{0/-}$
	−1.42	$tpy^{0/-}$
[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)$_2$	$E_p{}^{a}$ = 1.82	$Pt^{IV/II}$
	1.63	$Ru^{III/II}$
	−0.34	$bpm^{0/-}$
	−1.04	$bpm^{-/2-}$
	−1.45	$tpy^{0/-}$
[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)$_2$	$E_p{}^{a}$ = 1.70	$Pt^{IV/II}$
	$E_p{}^{a}$ = 1.55	$Ru^{III/II}$
	−0.50	$dpp^{0/-}$
	−1.15	$dpp^{-/2-}$
	−1.40	$tpy^{0/-}$

[a] Potentials reported versus the Ag/AgCl (0.29 V vs NHE) reference electrode in 0.1 M in TBAH CH_3CN. $E_{1/2}$ values obtained from cyclic voltammetry except where indicated.

Previous studies[44] of [(tpy)RuCl(dpp)](PF_6) indicate that the $Ru^{III/II}$ redox couple has an $E_{1/2}$ value of 1.04 V vs Ag/AgCl while the $dpp^{0/-}$ and $tpy^{0/-}$ redox couples have $E_{1/2}$ values of −1.07 and −1.27 V vs Ag/AgCl, respectively, consistent with Table 1. For the bpm complex the initial reduction wave (−1.00 V vs Ag/AgCl) is assigned as a one-electron reduction of the bpm ligand.

Substitution of strong field ligands (PEt_2Ph and CH_3CN) for the weak field Cl^- ligand to form [(tpy)Ru(PEt_2Ph)(BL)]$^{2+}$ and [(tpy)Ru(CH_3CN)(BL)]$^{2+}$ should stabilize the Ru(dπ)-based HOMO, making it more difficult to oxidize Ru(II) to Ru(III).[32] As expected, positive shifts in the $Ru^{III/II}$ redox couple of greater than 500 mV are observed on going from Cl^- to PEt_2Ph or CH_3CN for both the bpm- and dpp-based systems. The BL and tpy reductions are influenced only slightly by this substitution with the BL, seeing positive shifts of up to 100 mV on going from Cl^- to PEt_2Ph or CH_3CN. This indicates some stabilization of the bpm and dpp (π*) based LUMOs by either PEt_2Ph or CH_3CN being substituted for Cl^-. Overall, this substitution dramatically increases the HOMO−LUMO energy gap owing to the larger impact of ligand variation on the Ru(dπ)-based HOMO. The variation of BL (bpm vs dpp) for [(tpy)Ru(PEt_2Ph)(BL)]$^{2+}$ and [(tpy)Ru(CH_3CN)(BL)]$^{2+}$ results in quite similar redox properties. There also appears to be little difference in this structural motif between the electronic effects of PEt_2Ph vs CH_3CN. This is in marked contrast to that observed for related Os(II) systems[35−37] but consistent with the very limited study of ruthenium light absorbers.[31,32]

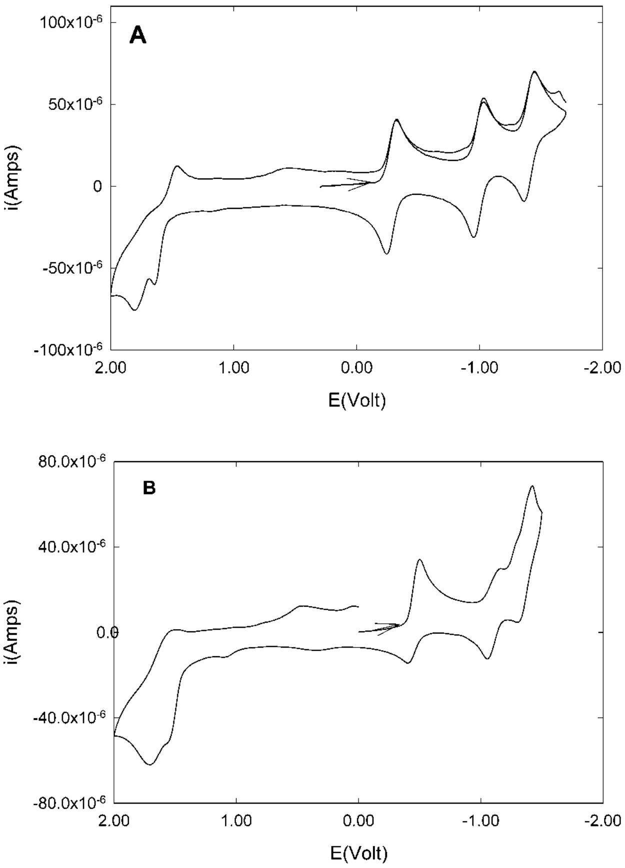


Figure 1. Cyclic voltammograms run at RT in 0.1 M NBu_4PF_6/CH_3CN, ν = 200 mV/s, potentials reported vs the Ag/AgCl reference electrode. (A) [(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)$_2$ and (B) [(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)$_2$.

Figure 1 shows the cyclic voltammograms for [(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)$_2$ (A) and [(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)$_2$ (B) run in acetonitrile versus the Ag/AgCl reference electrode. Both bimetallic complexes, [(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)$_2$ and [(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)$_2$, show broad overlapping oxidations. The bpm-based complex shows three well-defined reduction processes. The dpp-based complex shows only one well-defined reduction wave and two overlapping reductions. These differences appear to result from the cathodic shift of the dpp couples relative to bpm. Osteryoung square wave voltammetry (OSWV) was used to locate the last two reductions for [(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)$_2$.

Platinum(II) coordination stabilizes the π* orbitals on the bridging ligands relative to the monometallic synthons, making them easier to reduce; see Table 1. This stabilization is more dramatic for the bpm complex. Three reduction waves are observed for each bimetallic complex and are assigned as sequential bpm (dpp) reductions, $BL^{0/-}$, $BL^{-/2-}$ followed by reduction of the terminal ligand $tpy^{0/-}$. These

Scheme 2[a]

$[(tpy)Ru^{III}(PEt_2Ph)(BL)Pt^{IV}Cl_2]^{5-}$

$-2e^- \uparrow$

$[(tpy)Ru^{III}(PEt_2Ph)(BL)Pt^{II}Cl_2]^{3+}$

$-1e^- \uparrow\downarrow +1e^-$

$[(tpy)Ru^{II}(PEt_2Ph)(BL)Pt^{II}Cl_2]^{2+}$

$-1e^- \uparrow\downarrow +1e^-$

$[(tpy)Ru^{II}(PEt_2Ph)(BL^-)Pt^{II}Cl_2]^{+}$

$-1e^- \uparrow\downarrow +1e^-$

$[(tpy)Ru^{II}(PEt_2Ph)(BL^{2-})Pt^{II}Cl_2]^{0}$

$-1e^- \uparrow\downarrow +1e^-$

$[(tpy^-)Ru^{II}(PEt_2Ph)(BL^{2-})Pt^{II}Cl_2]^{-}$

[a] BL = bpm or dpp, with the synthesized oxidation state in bold.

assignments are consistent with assignments made for similar complexes with the occurrence of $BL^{-/2-}$ couples prior to the terminal ligand reductions indicative of the bimetallic formulation of these complexes.[9,40] The first two reductions of the bpm BL occur at -0.34 and -1.04 V, respectively, whereas the sequential one-electron reductions of dpp are at more negative potentials, -0.50 and -1.15 V (Table 1). This difference indicates coordination of the $Pt^{II}Cl_2$ to the remote sites of the BL has a more dramatic effect on the π^* orbital energy of the bpm-based system.

The oxidative behavior of these bimetallic complexes is complicated by nearly degenerate Ru($d\pi$) and Pt($d\pi$) orbitals and the irreversible nature of the Pt(II) oxidation. The oxidation of $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)_2$ ($E_p^a = 1.64$ V, Figure 1A) is coupled to a reduction wave at 1.47 V and is tentatively assigned as a $Ru^{III/II}$ quasireversible redox couple. The irreversible oxidation at 1.80 V is believed to be due to oxidation of the platinum(II) center. Scanning anodically in a solution of $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$ (Figure 1B) shows two overlapping oxidation processes with a much less pronounced reduction process upon switching the scan cathodically. We tentatively assign the first oxidation as Ru(II) based and the second oxidation as Pt(II) based. Scheme 2 suggests an electrochemical scheme for the Ru/Pt bimetallic complexes.

The electrochemical data indicate that the bimetallic complexes $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2](PF_6)_2$ and $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$ and the monometallic synthons have a Ru($d\pi$)-based HOMO and a bridging ligand (π^*) based LUMO whose energy can be modulated. The overlapping oxidation waves in the bimetallics are attributed to the Pt-based orbitals being very close in energy to the Ru-based orbitals.

Electronic Absorption Spectroscopy. The electronic absorption spectra in acetonitrile of the new monometallic and bimetallic complexes are summarized in Table 2. These systems have many chromophoric units leading to complex spectroscopy. Typically intense, high energy intraligand n → π^* and $\pi \rightarrow \pi^*$ transitions for each polyazine ligand dominate the ultraviolet with MLCT transitions to each acceptor ligand occurring in the visible region of the electronic spectrum.[1−3,38,40,43] Higher energy MLCT transitions often are seen in the UV overlapping the typically more intense intraligand bands in this region.

A comparison of the electronic absorption spectra of the monometallic complexes, $[(tpy)Ru(L)(BL)]^{n+}$, reveals some interesting features. Within a set of complexes, where the monodentate ligands are the same, the spectra are very similar for the bpm and dpp analogues. The systems with L $= CH_3CN$ and PEt_2Ph also display remarkably similar spectroscopy. The UV region of all the monometallic complexes display similar spectroscopy, with L $= CH_3CN$, PEt_2Ph, or Cl^- and BL = dpp or bpm. We have made some tentative assignments of major peaks in the UV by comparison of our systems and the known $[Ru(tpy)_2]^{2+}$ [16] and $[Ru(bpm)_3]^{2+}$ [12] complexes; see Table 2. The intense transition observed near 300 nm for the $[(tpy)Ru(PEt_2Ph)(BL)]^{2+}$ and $[(tpy)Ru(CH_3CN)(BL)]^{2+}$ complexes are most likely due to an overlapping tpy($\pi \rightarrow \pi^*$) transition with a higher energy Ru($d\pi$) → tpy(π^*) charge transfer (CT) transition.[48]

On the basis of the electrochemical studies the HOMO is Ru($d\pi$) based and the LUMO is BL(π^*). The lowest energy transition for all the complexes is overlapping Ru($d\pi$) → BL(π^*) and Ru($d\pi$) → tpy(π^*) CT transitions, with the Ru($d\pi$) → BL(π^*) CT transition being the lower energy component. This transition blue shifts when the weak field Cl^- ligand is replaced by the strong field PEt_2Ph or CH_3CN ligand as a result of stabilization of the Ru($d\pi$) orbitals. The bands at 370 nm for $[(tpy)RuCl(BL)]^+$ are assigned as a higher energy Ru($d\pi$) → tpy(π^*) CT transition. The greater intensity observed in this region for $[(tpy)RuCl(bpm)]^+$ is most likely the result of a high energy Ru($d\pi$) → bpm(π^*) CT transition which overlaps the Ru($d\pi$) → tpy(π^*) CT transition.

Figure 2 compares the electronic absorption spectra of $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2]^{2+}$ and $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2]^{2+}$ in acetonitrile at room temperature. The UV region contains major peaks very similar to the monometallic complexes described above. Changes in relative intensity occur in this series, consistent with many overlapping transitions shifting slightly with structural variations. The visible region of the spectra of the $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ systems varies as a function of BL and displays transitions substantially red-shifted relative to the monometallic synthons. A weak absorption band at 424 nm in the dpp system corresponds to a Ru($d\pi$) → tpy(π^*) CT transition. A broad more intense band at 416 nm for $[(tpy)Ru(PEt_2Ph)(bpm)PtCl_2]^{2+}$ is due to overlapping Ru($d\pi$) → tpy(π^*) and Ru($d\pi$) → bpm(π^*) CT transitions.

When the visible spectra of the monometallic $[(tpy)Ru(PEt_2Ph)(BL)]^{2+}$ and the bimetallic $[(tpy)Ru(PEt_2Ph)(BL)PtCl_2]^{2+}$ complexes, containing the same BLs, are compared,

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(48) Jones, S. W.; Vrana, L. M.; Brewer, K. J. *J. Organomet. Chem.* **1998**, *554*, 29.

Table 2. Electronic Absorption Spectroscopy Results for a Series of Ru(II) and Ru(II)/Pt(II) Complexes of the General Formula [(tpy)RuL(BL)](PF$_6$) and [(tpy)Ru(PEt$_2$Ph)(BL)PtCl$_2$](PF$_6$)$_2$, Where L = Cl$^-$, CH$_3$CN, or PEt$_2$Ph, BL = bpm (Bipyrimidine) or dpp (2,3-Bis(2-pyridyl)pyrazine), and tpy = 2,2′:6′,2″-Terpyridine[a]

complex	λ_{max} (nm)	$\epsilon \times 10^{-4}$ (M^{-1} cm^{-1})	assignment
[(tpy)RuCl(bpm)](PF$_6$)	516	0.99	Ru(dπ) $\rightarrow$ bpm(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	370	0.96	Ru(dπ) $\rightarrow$ tpy(π^*) CT
	316	3.31	tpy ($\pi \rightarrow \pi^*$)
	266	2.92	tpy ($\pi \rightarrow \pi^*$)
	240	3.94	bpm ($\pi \rightarrow \pi^*$)
[(tpy)RuCl(dpp)](PF$_6$)	514	0.89	Ru(dπ) $\rightarrow$ dpp(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	370	0.44	Ru(dπ) $\rightarrow$ tpy(π^*) CT
	314	2.91	tpy ($\pi \rightarrow \pi^*$)
	276	2.00	tpy ($\pi \rightarrow \pi^*$)
	238	2.32	dpp ($\pi \rightarrow \pi^*$)
[(tpy)Ru(CH$_3$CN)(bpm)](PF$_6$)$_2$	452	0.81	Ru(dπ) $\rightarrow$ bpm(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	332	1.90	tpy ($\pi \rightarrow \pi^*$)
	304	3.01	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	268	2.78	tpy ($\pi \rightarrow \pi^*$)
	234	3.05	bpm ($\pi \rightarrow \pi^*$)
[(tpy)Ru(CH$_3$CN)(dpp)](PF$_6$)$_2$	462	0.93	Ru(dπ) $\rightarrow$ dpp(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	332 (sh)		tpy ($\pi \rightarrow \pi^*$)
	302	3.36	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	272	2.49	tpy ($\pi \rightarrow \pi^*$)
	232 (sh)		dpp ($\pi \rightarrow \pi^*$)
[(tpy)Ru(PEt$_2$Ph)(bpm)](PF$_6$)$_2$	450	1.00	Ru(dπ) $\rightarrow$ bpm(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	334	2.25	tpy ($\pi \rightarrow \pi^*$)
	308	3.81	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	268	3.44	tpy ($\pi \rightarrow \pi^*$)
	234	4.99	bpm ($\pi \rightarrow \pi^*$)
[(tpy)Ru(PEt$_2$Ph)(dpp)](PF$_6$)$_2$	460	0.96	Ru(dπ) $\rightarrow$ dpp(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	334 (sh)	0.60	tpy ($\pi \rightarrow \pi^*$)
	308	3.87	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	278	3.02	tpy ($\pi \rightarrow \pi^*$)
	232	3.75	dpp ($\pi \rightarrow \pi^*$)
[(tpy)Ru(PEt$_2$Ph)(bpm)PtCl$_2$](PF$_6$)$_2$	560	0.61	Ru(dπ) $\rightarrow$ bpm(π^*) CT
	416	1.52	Ru(dπ) $\rightarrow$ bpm(π^*) CT
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	336	3.14	tpy ($\pi \rightarrow \pi^*$)
	304	4.01	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	274	4.71	tpy ($\pi \rightarrow \pi^*$)
	232	5.61	bpm ($\pi \rightarrow \pi^*$)
[(tpy)Ru(PEt$_2$Ph)(dpp)PtCl$_2$](PF$_6$)$_2$	506	1.05	Ru(dπ) $\rightarrow$ dpp(π^*) CT
	424 (sh)	0.53	Ru(dπ) $\rightarrow$ dpp(π^*) CT
	336	2.22	tpy ($\pi \rightarrow \pi^*$)
	308	2.41	tpy ($\pi \rightarrow \pi^*$)
			Ru(dπ) $\rightarrow$ tpy(π^*) CT
	276	2.09	tpy ($\pi \rightarrow \pi^*$)
	234	4.11	dpp ($\pi \rightarrow \pi^*$)

[a] Absorption spectra run in acetonitrile at room temperature (23 ± 1 °C).

it is clear that addition of the platinum(II) metal center stabilizes the BL (π^*) LUMO shifting the BL-based MLCT to lower energy. The absorption band at 540 nm for [(tpy)Ru(PEt$_2$Ph)(bpm)PtCl$_2$]$^{2+}$ is assigned as a Ru(dπ) $\rightarrow$ bpm(π^*) CT transition which has red-shifted nearly 100 nm compared to the monometallic synthon, [(tpy)Ru(PEt$_2$Ph)(bpm)]$^{2+}$. This is consistent with the observed shift in the bpm reduction when PtCl$_2$ is coordinated to [(tpy)Ru(PEt$_2$Ph)(bpm)]$^{2+}$.

Spectral differences between [(tpy)Ru(PEt$_2$Ph)(bpm)PtCl$_2$]$^{2+}$ and [(tpy)Ru(PEt$_2$Ph)(dpp)PtCl$_2$]$^{2+}$ become apparent when comparing the lowest energy MLCT transitions. The lowest energy electronic transition at 506 nm in [(tpy)Ru(PEt$_2$Ph)(dpp)PtCl$_2$]$^{2+}$, assigned as a Ru(dπ) $\rightarrow$ dpp(π^*) CT, is 54 nm higher in energy than the bpm analogue. This suggests that the impact of Pt coordination on the BL π^* is more dramatic for bpm than for dpp, in agreement with the electrochemical data.

In the [(tpy)Ru(PEt$_2$Ph)(dpp)PtCl$_2$]$^{2+}$ system, the Ru(dπ) and Pt(dπ) orbitals appear to be similar in energy, but the spectroscopic properties are dominated by the ruthenium chromophore. This is not surprising given the higher energy

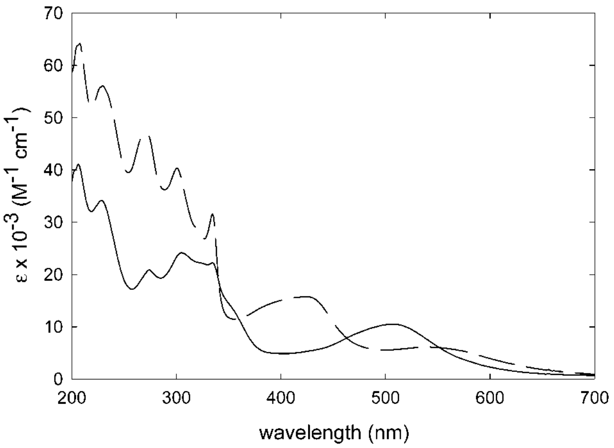

Figure 2. Electronic absorption spectra in acetonitrile at RT for [(tpy)Ru(PEt_2Ph)(bpm)$PtCl_2$](PF_6)$_2$ (— —) and [(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$](PF_6)$_2$ (—).

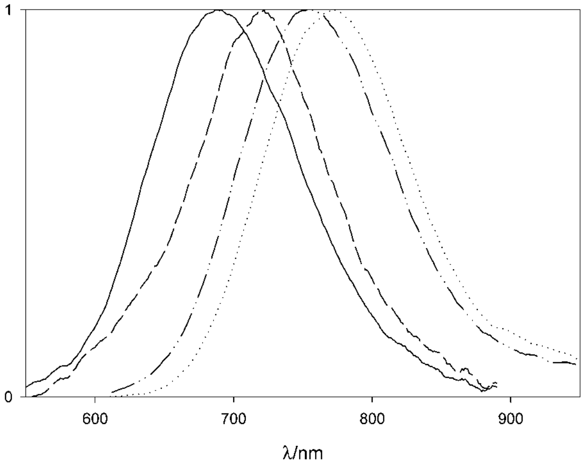

Figure 3. Emission spectra in deoxygenated acetonitrile at RT for [(tpy)Ru(CH_3CN)(dpp)](PF_6)$_2$ (—), [(tpy)Ru(PEt_2Ph)(dpp)](PF_6)$_2$ (---), [(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$](PF_6)$_2$ (— ·· —), and [(tpy)RuCl(dpp)](PF_6) (···).

and less intense MLCT of [Pt(dpp)Cl_2] vs [(bpy)$_2$Ru(dpp)]$^{2+}$.[4,5,49] The Pt(dπ) → dpp(π^*) CT likely occurs as a high energy shoulder on the lower energy, more intense Ru(dπ) → dpp(π^*) CT band.

Excited State Properties. The RT excited state properties of these complexes have been investigated using emission spectroscopy, emission quantum yields, and excited state lifetime measurements, summarized in Figure 3 and Table 3. All of the dpp complexes display easily detectable emissions at RT, while none of the bpm complexes display detectable emissions under our conditions. This is not unexpected as [(bpy)$_2$Ru(dpp)]$^{2+}$ displays a more intense, higher energy emission than does the bpm analogue [(bpy)$_2$Ru(bpm)]$^{2+}$ under similar conditions.[6,10,12] Our complexes, owing to the coordination of the tpy ligand to the ruthenium chromophore, are expected to display somewhat shortened excited state lifetimes and lower quantum yields for emission relative to bpy-containing systems due to the presence of low-lying ligand field states.[14−26] The low energy emission of the [(tpy)RuCl(dpp)](PF_6) at 770 nm ($\tau = 20$ ns) shifts to higher energy in the [(tpy)Ru(CH_3CN)(dpp)](PF_6)$_2$ (690 nm, $\tau = 14$ ns) and [(tpy)Ru(PEt_2Ph)(dpp)](PF_6)$_2$ (720 nm, $\tau = 6$ ns) systems with a slight decrease in the emission lifetime. The mixed-metal bimetallic system, [(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$](PF_6)$_2$, emits at lower energy than the monometallic synthon, displaying an emission centered at 750 nm with a lifetime of 56 ns. This lengthening of the excited state lifetime in bimetallic complexes relative to the monometallic synthons has been observed in bridging ligand complexes of tpy and is attributed to a decreased thermal activation of the low-lying ligand field state due to a lowering in the energy of the emissive MLCT state.[18]

Table 3. Photophysical Data for a Series of Ru(II) and Ru(II)/Pt(II) Complexes of the General Formula [(tpy)RuL(dpp)](PF_6) and [(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$](PF_6)$_2$, Where L = Cl^-, CH_3CN, or PEt_2Ph, dpp = (2,3-Bis(2-pyridyl)pyrazine), and tpy = 2,2′:6′,2″-Terpyridine

complex	$\lambda_{max}^{abs\,a}$ (nm)	$\lambda_{max}^{em\,b}$ (nm)	τ (ns)	$\Phi^{em\,c}$
[(tpy)RuCl(dpp)](PF_6)	514	770	20	1.3×10^{-4}
[(tpy)Ru(CH_3CN)(dpp)](PF_6)$_2$	462	690	14	5.6×10^{-5}
[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)$_2$	460	720	6	3.1×10^{-5}
[(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$](PF_6)$_2$	506	750	56	1.8×10^{-4}

[a] For the lowest lying transition (^{1}Ru → dpp charge transfer). [b] Emission spectra collected at RT in acetonitrile solution and corrected for PMT response. [c] Measured relative to [Os(bpy)$_3$](PF_6)$_2$.[46]

Conclusions

A building block approach was used to synthesize a new type of supramolecular assembly [(tpy)Ru(PEt_2Ph)(BL)$PtCl_2$]$^{2+}$ and the monometallic light absorbers [(tpy)RuL(BL)]$^{n+}$ (BL = bpm or dpp and L = Cl^-, CH_3CN, or PEt_2Ph). These systems assemble an NMR-active TAG, an intense LA, and a reactive Pt metal center. By using a tridentate capping ligand (tpy) and a bidentate bridging ligand (bpm or dpp), the sixth coordination site of the ruthenium center can be substituted with a variety of monodentate ligands.

The substitution of the ligand in this sixth coordination site results in tunable and interesting electrochemical and spectroscopic behavior. Substitution of Cl^- with PEt_2Ph substantially destabilizes the lowest energy Ru → BL CT excited state. This substitution also allowed ^{31}P NMR to be used to help identify the complexes and observe the two stereoisomers for the dpp systems. Stabilization of the Ru(dπ) orbitals, resulting in more positive Ru$^{III/II}$ redox couples and higher energy MLCT transitions, resulted when Cl^- was substituted by PEt_2Ph or CH_3CN. There is a remarkable similarity in the electrochemical and spectroscopic properties for the bpm and dpp systems with both CH_3CN and PEt_2Ph ligands.

The bimetallic complexes display characteristics consistent with their formulation. The bridging ligand π^* orbitals are stabilized by coordination of $PtCl_2$, shifting the Ru(dπ) → BL(π^*) CT transitions to lower energy and making the BL easier to reduce. This effect was more pronounced for [(tpy)Ru(PEt_2Ph)(bpm)$PtCl_2$]$^{2+}$ vs [(tpy)Ru(PEt_2Ph)(dpp)$PtCl_2$]$^{2+}$, suggesting greater orbital overlap between the Pt and bpm orbitals.

These mixed-metal complexes represent a TAG−LA−BL−RM assembly. The [(tpy)Ru(L)BL]$^{n+}$ motif provides the

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(49) Ng, Y.-Y.; Che, C.-M.; Peng, S.-M. *New J. Chem.* **1996**, *20*, 781.

ability to easily and effectively tune the properties of the ruthenium chromophore by substitution of the sixth coordination site of the ruthenium center. The bimetallic complexes possess a $PtCl_2$ active site of potential biological and catalytic importance. The $[(tpy)Ru(PEt_2Ph)(dpp)PtCl_2](PF_6)_2$ system is emissive at RT in acetonitrile solution, allowing a potential probe of the reactivity of this system. Studies are currently underway exploring the reactivity of these complexes in more detail including their interaction with DNA.[50]

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Supporting Information Available: Electronic absorption spectra and cyclic voltammograms for $[(tpy)RuCl(bpm)](PF_6)$, $[(tpy)RuCl(dpp)](PF_6)$, $[(tpy)Ru(CH_3CN)(bpm)](PF_6)_2$, $[(tpy)Ru(CH_3CN)(dpp)](PF_6)_2$, $[(tpy)Ru(PEt_2Ph)(bpm)](PF_6)_2$, and $[(tpy)Ru(PEt_2Ph)(dpp)](PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) Swavey, S.; Fang, Z.; Winkel, B. S.; Brewer, K. J. Work in progress.