Supplementary Materials

Ruthenium Dihydroxybipyridine Complexes are Tumor Activated Prodrugs Due to Low pH and Blue Light Induced Ligand Release

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IR Spectroscopy

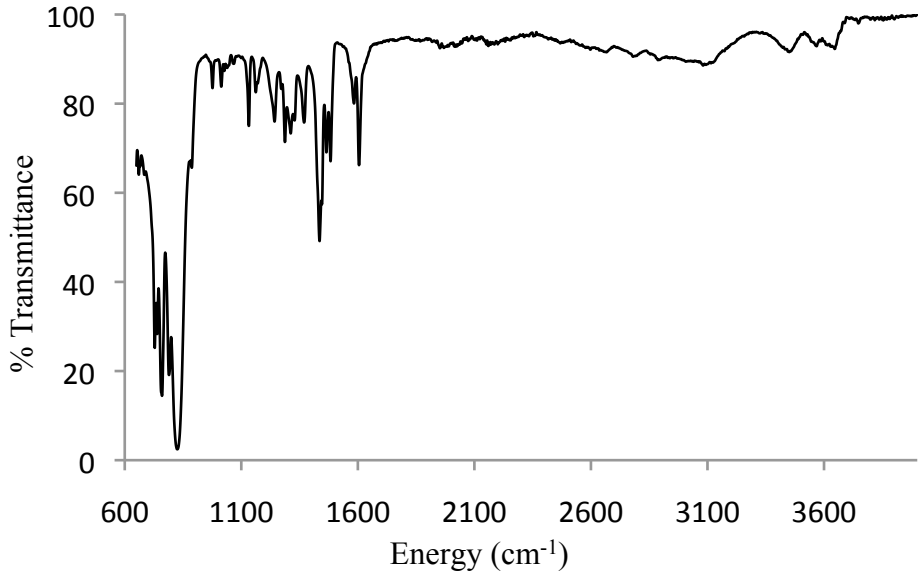


Figure S1 – FT-IR Spectrum of $[Ru(bpy)_2(66'bpy(OH)_2)][PF_6]_2$.

NMR Spectroscopy

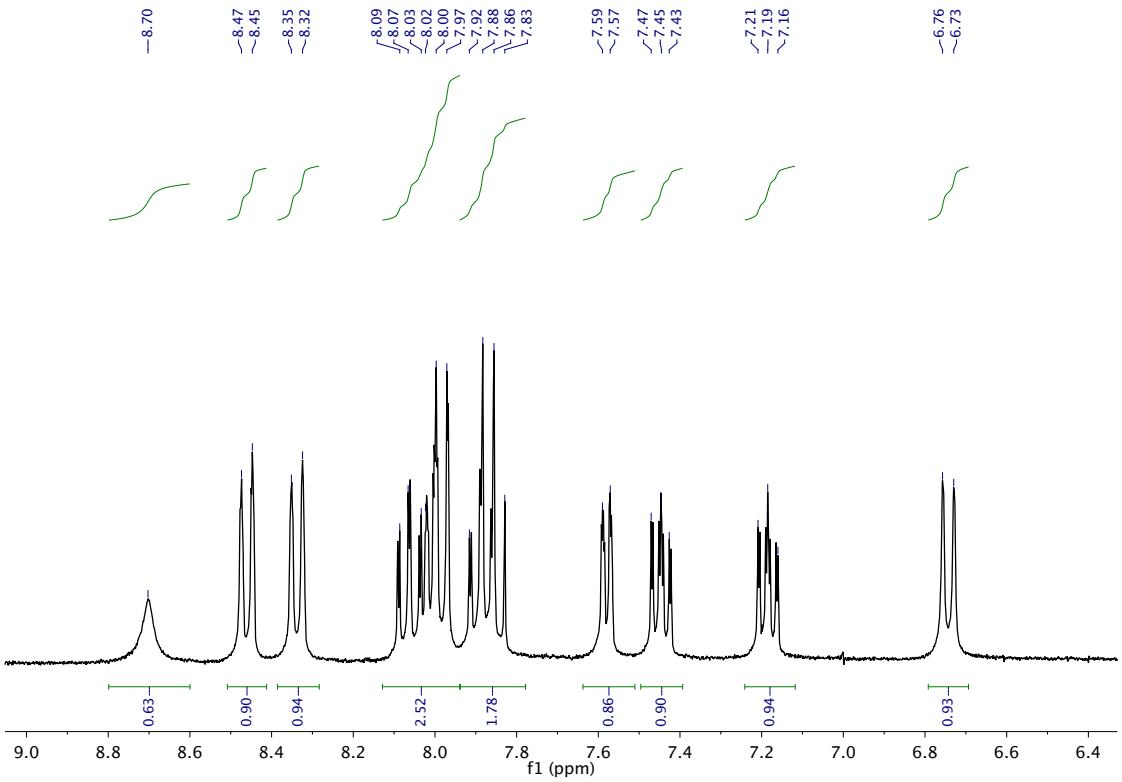


Figure S2 – ^{1}H-NMR Spectrum of $[Ru(bpy)_2(66'bpy(OH)_2)][PF_6]_2$ in CD_3CN.

pH Titration

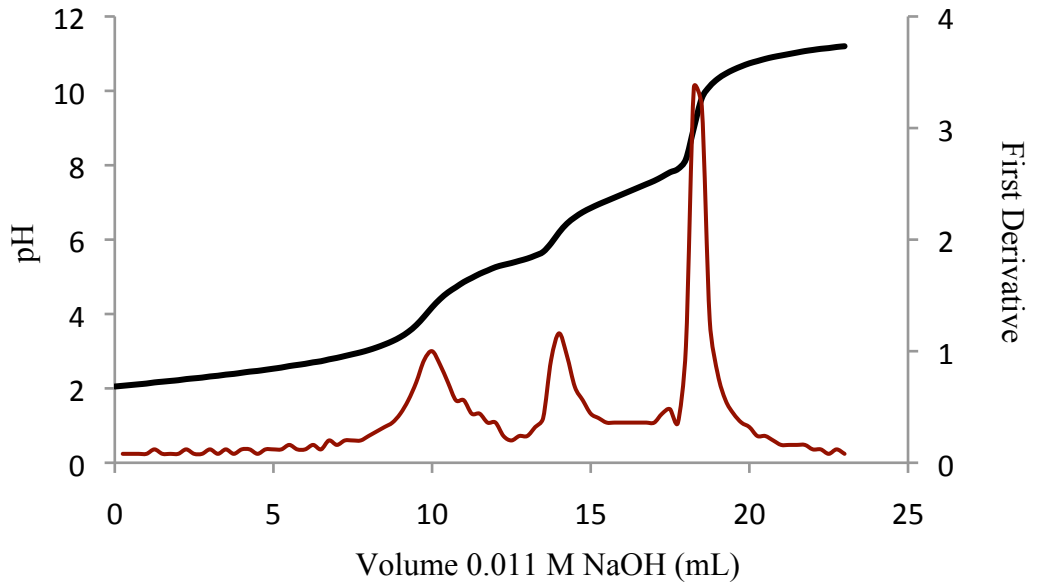


Figure S3 – pH Titration of 4.9 mM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in 0.01 M HCl with 0.011 M NaOH at 25 ^{o}C. The first equivalence point is due to neutralization of the excess HCl used to ensure full protonation of the metal complex.

Electrochemistry

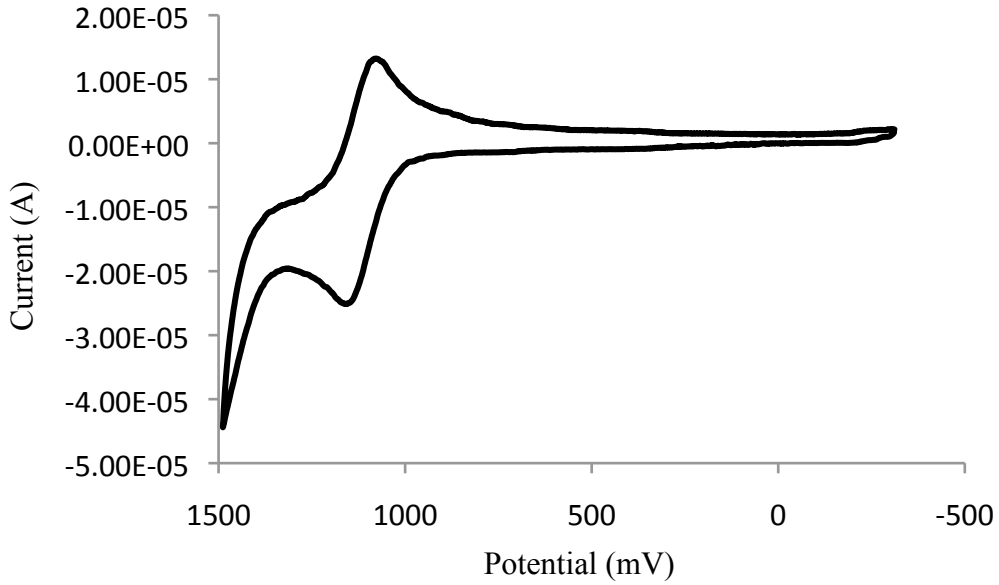


Figure S4 – Cyclic voltammogram (oxidative scan) of 1.3 mM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in acetonitrile with 0.1M tetrabutylammonium hexafluorophosphate with glassy carbon working electrode at 25 ^{o}C. Scan rate was 200 mV/s. Potentials corrected vs. SCE.

Absorbance Spectroscopy

UV/visible absorbance spectra were also collected in varying solvents. The solvents: acetonitrile, 1,2-dichloroethane, methanol, and ethanol were chosen for their varying dielectric constants and hydrogen bonding properties. The structure of the protonated form of the complex, $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ are similar between solvents with ≤ 5 nm shifts for all corresponding peak maxima. For example, the lowest energy MLCT band appears at $\lambda_{max} = 459$ nm in acetonitrile and 1,2-dichloroethane, and $\lambda_{max} = 462$ nm in methanol. These small shifts were also observed for the protonated $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ and also $[Ru(bpy)_3]^{2+}$, lacking the hydroxyl groups.[1, 2]

More dramatic solvent effects were observed when the $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ complex was deprotonated using tetrabutylammonium hydroxide. All peak maxima at wavelengths greater than 300 nm shift to the red upon deprotonation. As observed with $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$, the extent of lowest energy MLCT band shift is a function of the combination of 1) hydrogen bonding ability and 2) dielectric constant of the solvent. The peak maxima for the lowest energy band shifts between protonated and deprotonated complex range from 1900 cm^{-1} in water to 3500 cm^{-1} in 1,2-dichloroethane. The hydrogen bonding solvents on average do not shift as greatly as the non-hydrogen bonding solvents. For the hydrogen bonding solvents, the λ_{max} of the lowest energy band scale with the dielectric constant of the solvent from ethanol ($\lambda_{max} = 519$ nm) to methanol ($\lambda_{max} = 513$ nm) to water ($\lambda_{max} = 504$ nm). In general the non-hydrogen bonding solvents have larger shifts that are dependent upon the dielectric constant with $\lambda_{max} = 546$ nm in 1,2-dichloroethane and $\lambda_{max} = 543$ nm in acetonitrile. The largest is shift is 1500 cm^{-1} when comparing water to 1,2-dichloroethane and comparable to the 1600 cm^{-1} shift observed from water to 1,2-dichloroethane in $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$.[1] The hydrogen bonding solvents can interact with the deprotonated pyridinolate in the complex, resulting in less pyridinolate character of the complex, and therefore, less of a shift in wavelength.

The structure of the lowest energy MLCT of protonated complex, $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$, reveals a major peak at 459 nm with a shoulder at 428 nm. This separation of ~1600 cm^{-1} is on the order of the separation observed for $[Ru(44'bpy(OH)_2)_3]^{2+}$ (~1500 cm^{-1}) and $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ (~1400 cm^{-1}).[1, 3] Upon deprotonation of $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in acetonitrile, there appears to be two peaks, one at 543 nm and another at 480 nm, corresponding to 2400 cm^{-1} peak to peak separation. The deprotonated $[Ru(bpy)_2(44'bpy(O^-)_2)]$ complex has similar band structure with a peak to peak separation of 2500 cm^{-1} in acetonitrile. Of note is that the structure of the more highly symmetrical deprotonated $[Ru(44'bpy(O^-)_2)_3]^{4-}$ complex does not change significantly from the protonated complex.[3] This observation is due to the divergence of types of electronic transitions occurring in the varying complexes during deprotonation, discussed in the computation section of the manuscript.

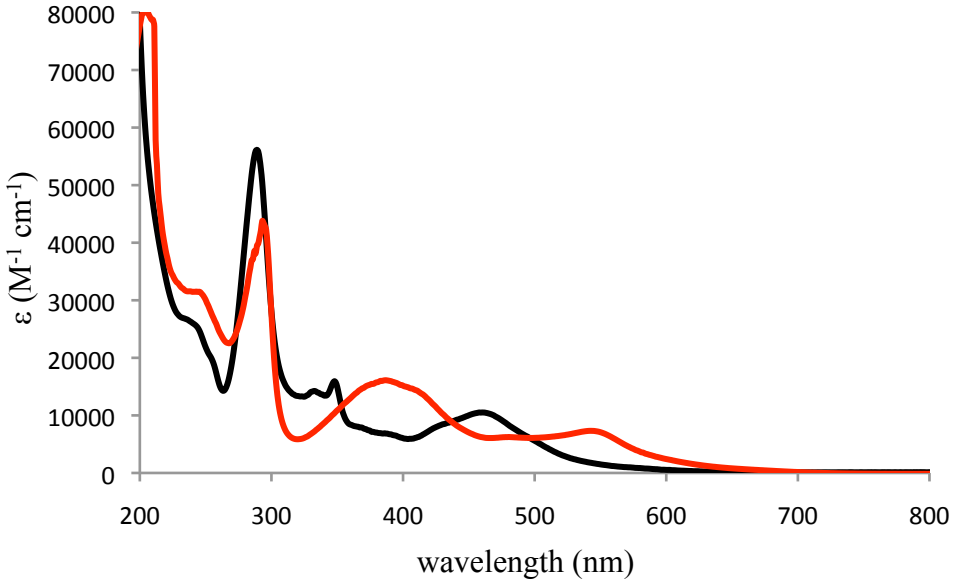


Figure S5 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in acetonitrile solvent at 25 ^oC.

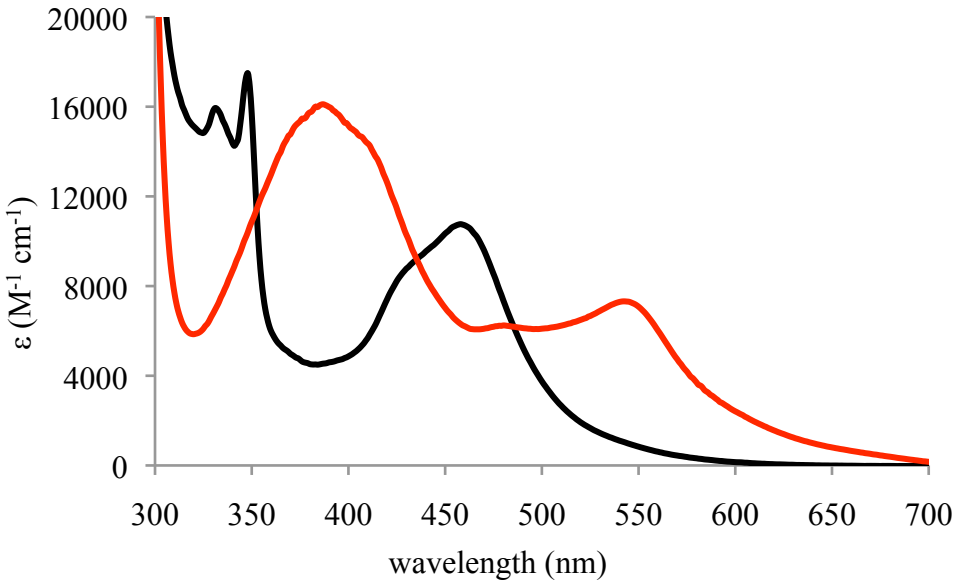


Figure S6 – UV/Visible spectrum of (black line) $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in acetonitrile at 25 ^oC.

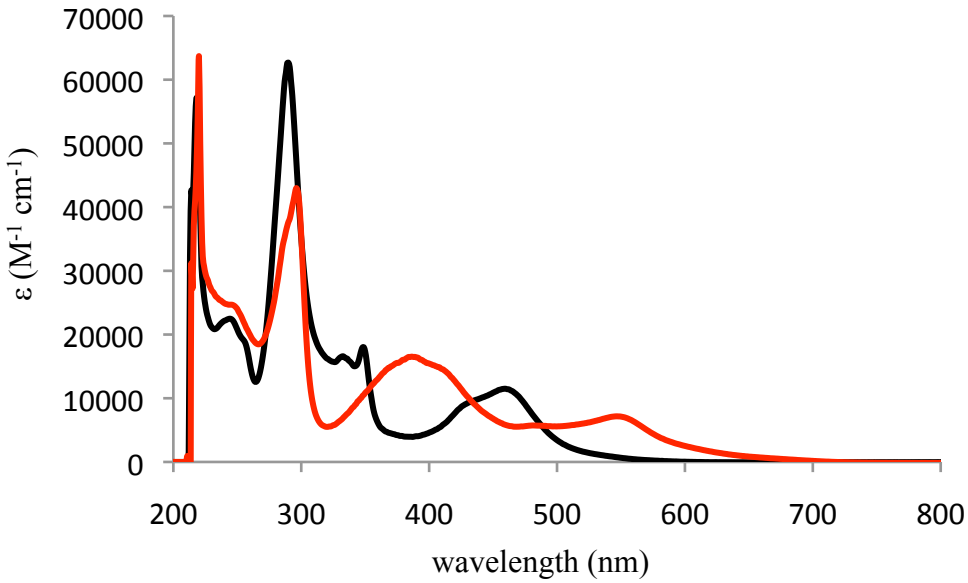


Figure S7 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in 1,2-dichloroethane solvent at 25 ^oC.

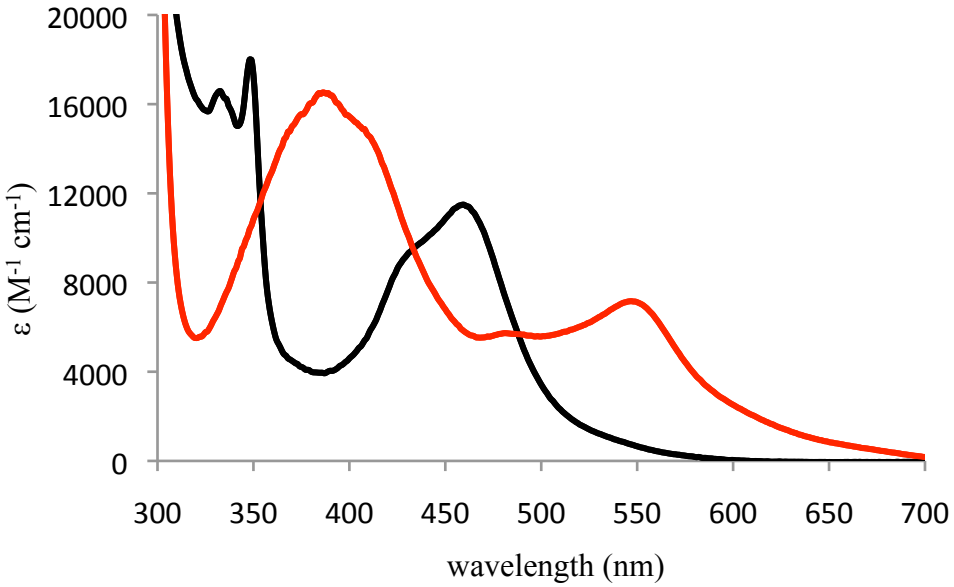


Figure S8 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in 1,2-dichloroethane solvent at 25 ^oC.

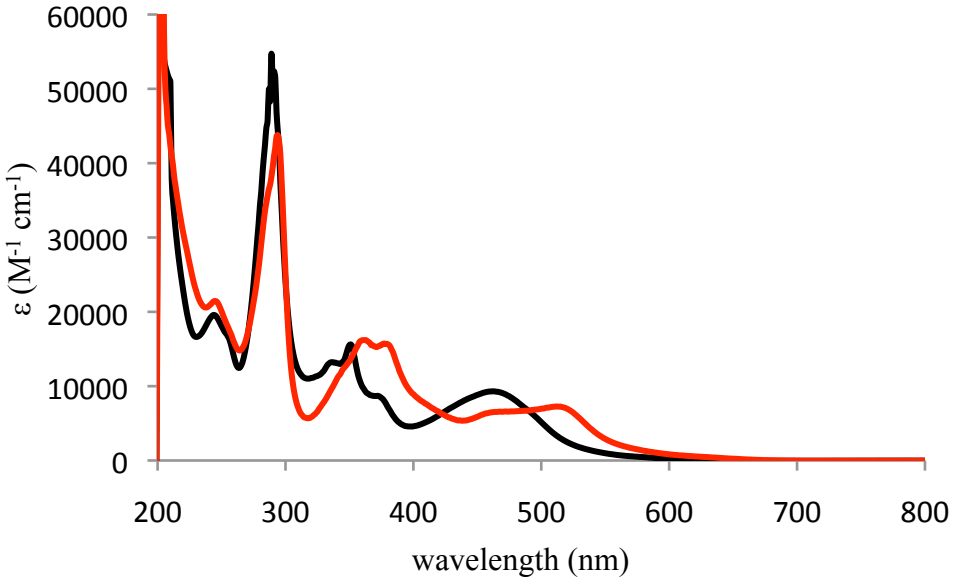


Figure S9 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in methanol solvent at 25 ^oC.

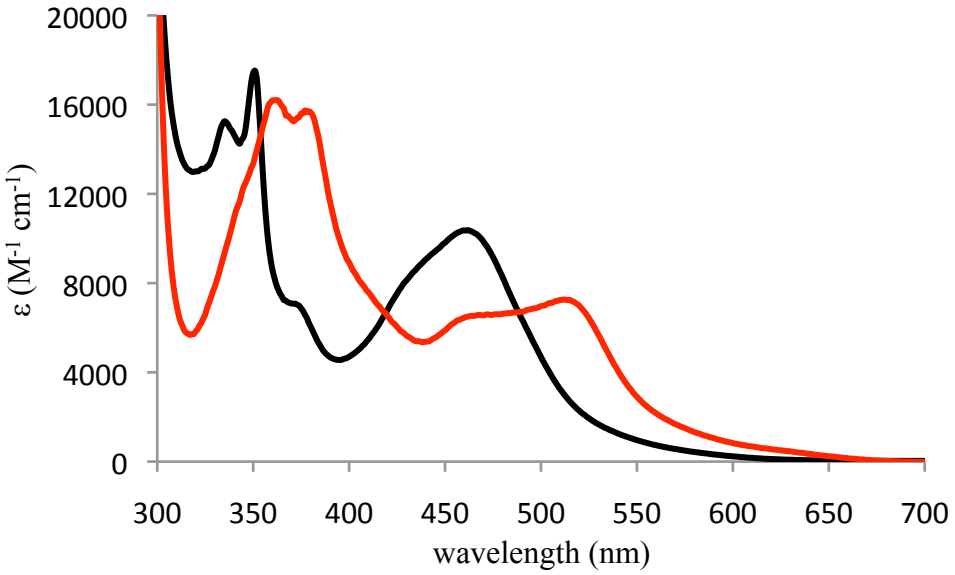


Figure S10 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in methanol solvent at 25 ^oC.

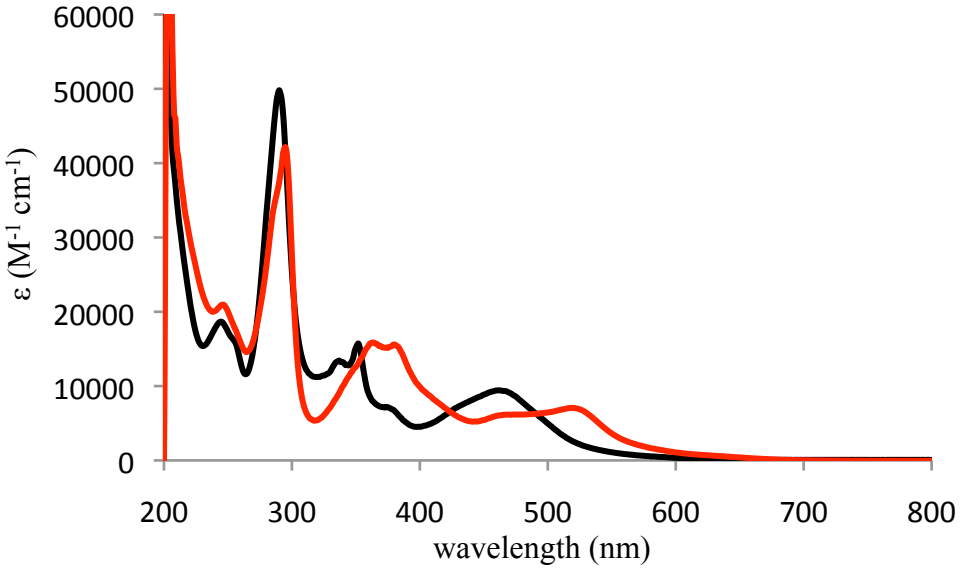


Figure S11 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in ethanol solvent at 25 ^oC.

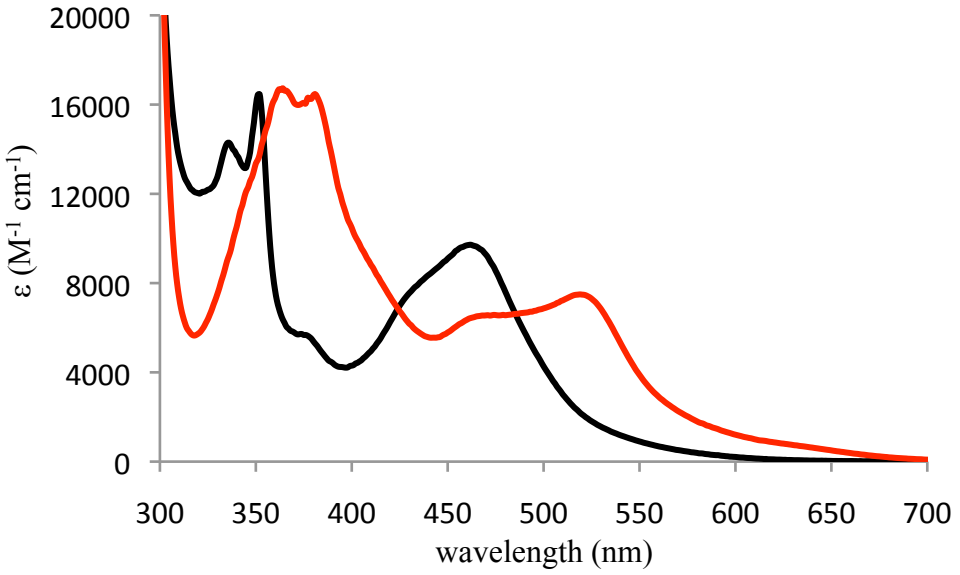


Figure S12 – UV/Visible spectrum of (black line) protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and (red line) deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in ethanol solvent at 25 ^oC.

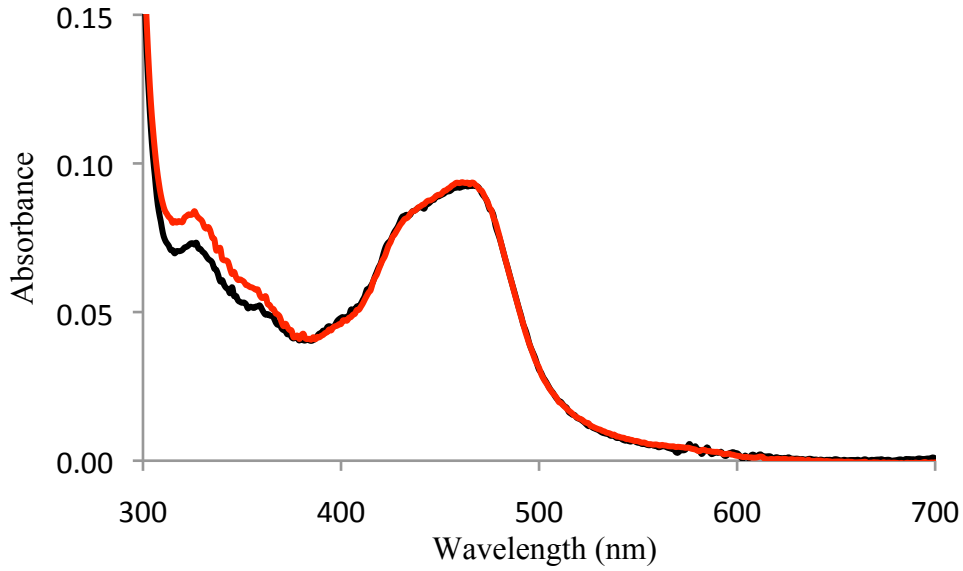


Figure S13 – UV/Visible spectrum of 8.3 μM $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ in 0.1 M HCl and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that no photodecomposition is occurring during the experiment timeframe.

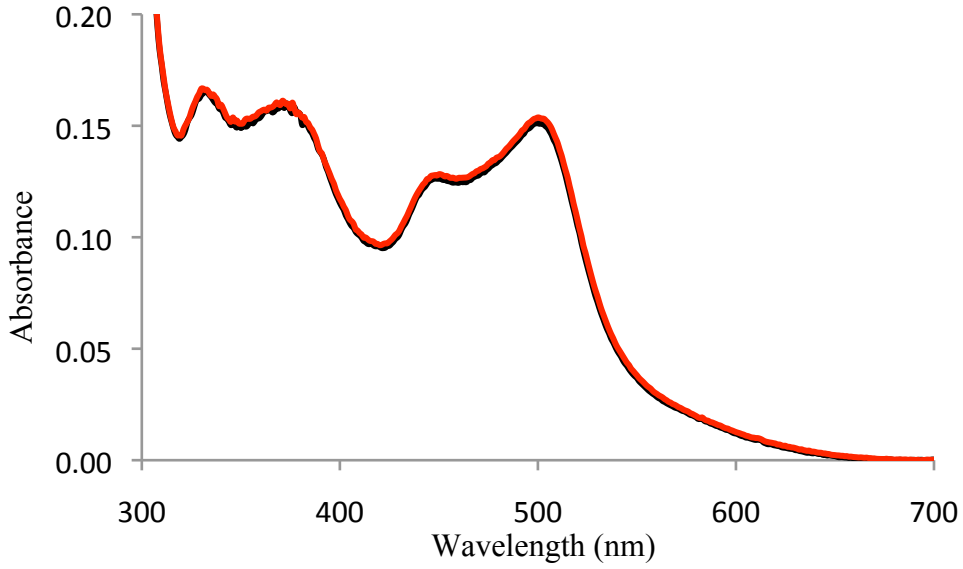


Figure S14 – UV/Visible spectrum of 17 μM $[Ru(bpy)_2(44'bpy(O^-)_2)]$ in 0.1 M NaOH and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that no photodecomposition is occurring during the experiment timeframe.

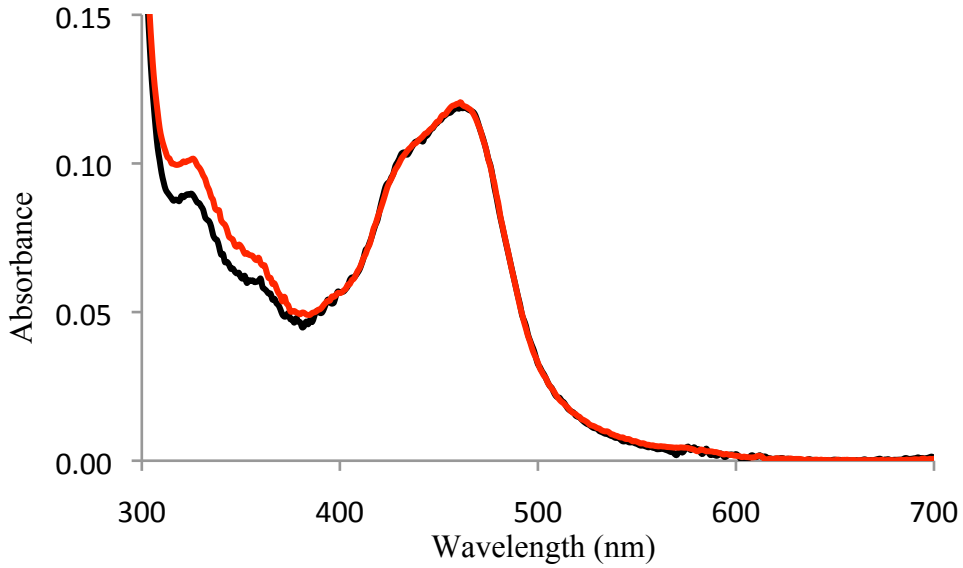


Figure S15 – UV/Visible spectrum of 9.1 μM $[Ru(bpy)_2(44'bpy(OMe)_2)]^{2+}$ in 0.1 M HCl and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that no photodecomposition is occurring during the experiment timeframe.

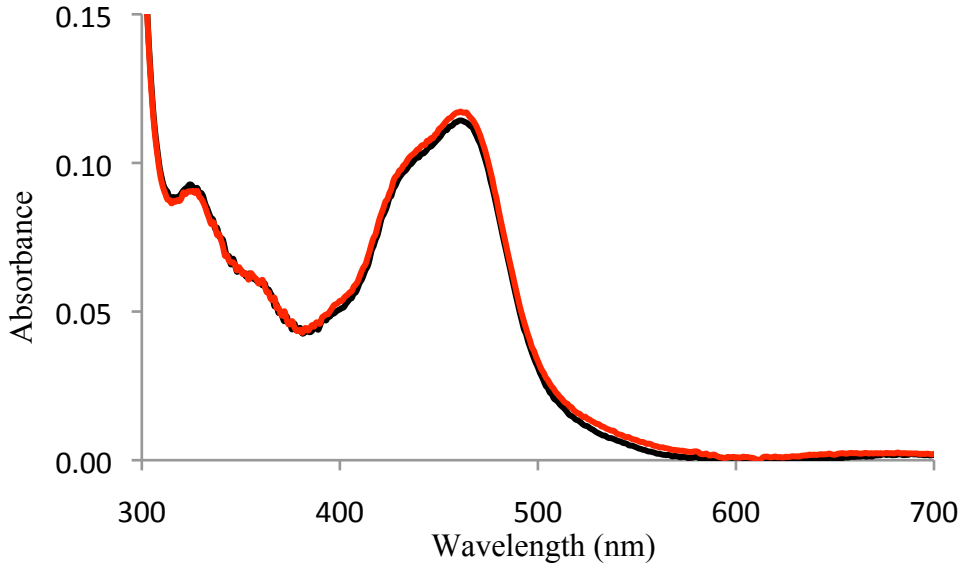


Figure S16 – UV/Visible spectrum of 9.1 μM $[Ru(bpy)_2(44'bpy(OMe)_2)]^{2+}$ in 0.1 M NaOH and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that no photodecomposition is occurring during the experiment timeframe.

Figure S17 – UV/Visible spectrum of 8.9 μM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in 0.1 M HCl and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that photodecomposition is occurring during the experiment timeframe.

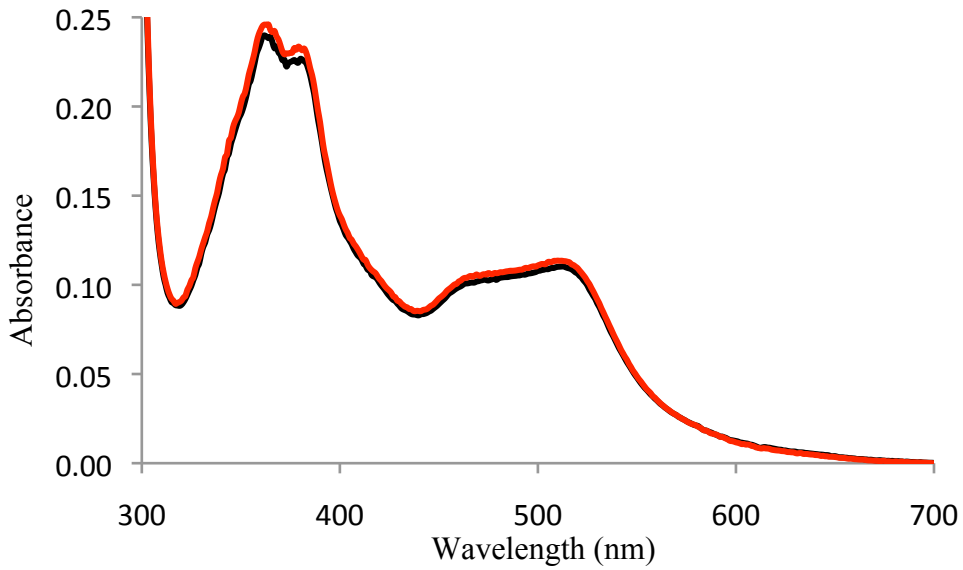


Figure S18 – UV/Visible spectrum of 14 μM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in 0.1 M NaOH and 1:1 mixture acetonitrile:water (black) before luminescence studies and (red) after luminescence studies at 25 ^{o}C. Demonstrates that no photodecomposition is occurring during the experiment timeframe.

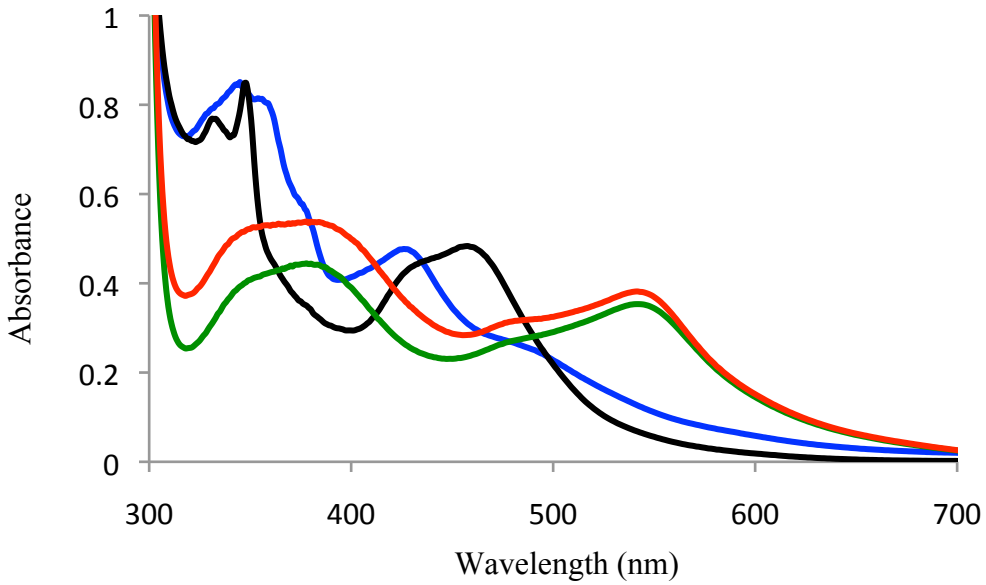


Figure S19 - UV/Visible spectrum of (black line) protonated 50 μM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ kept in dark, (blue line) protonated 50 μM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ kept in light, (red line) deprotonated 50 μM $[Ru(bpy)_2(66'bpy(O^-)_2)]$ kept in dark, and (green line) deprotonated 50 μM $[Ru(bpy)_2(66'bpy(O^-)_2)]$ kept in light. All data collected in acetonitrile solvent at 25 ^oC and spectra collected after 18 days in solution.

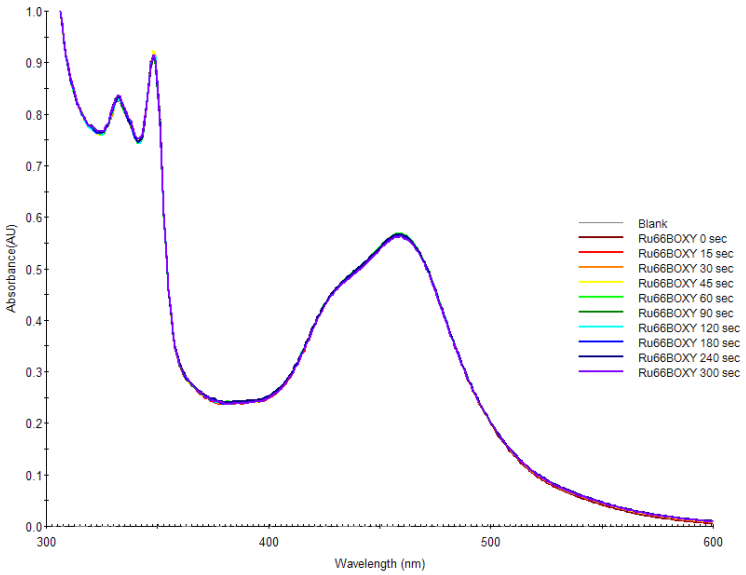


Figure S20 – UV/Visible spectra of protonated 50 μM $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ irradiated with 720 nm red light from 0 to 5 minutes in acetonitrile solvent at 25 ^oC.

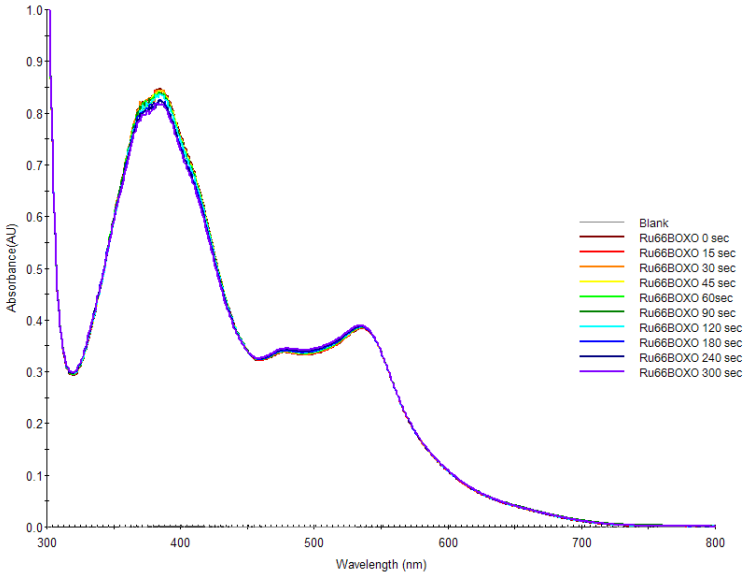


Figure S21 – UV/Visible spectra of deprotonated 50 μM $[Ru(bpy)_2(66'bpy(O^-)_2)]$ irradiated with 720 nm red light from 0 to 5 minutes in acetonitrile solvent at 25 ^oC.

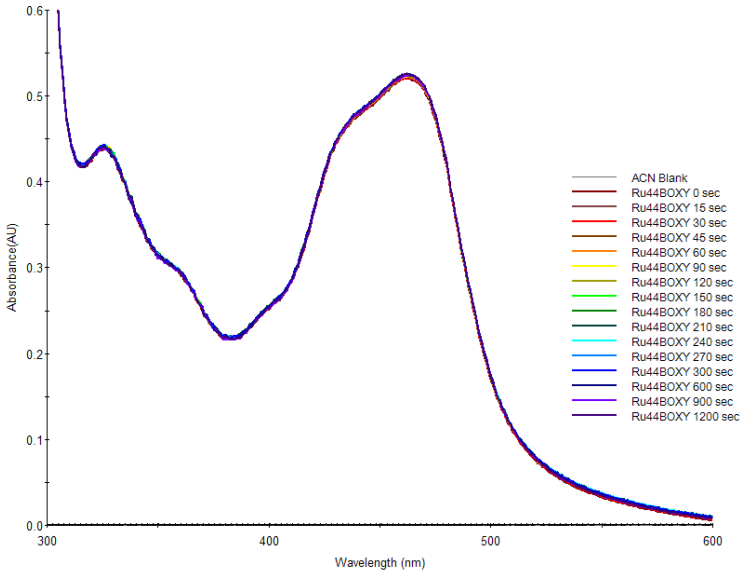


Figure S22 – UV/Visible spectra of protonated 50 μM $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ irradiated with 450 nm blue light from 0 to 20 minutes in acetonitrile solvent at 25 ^oC.

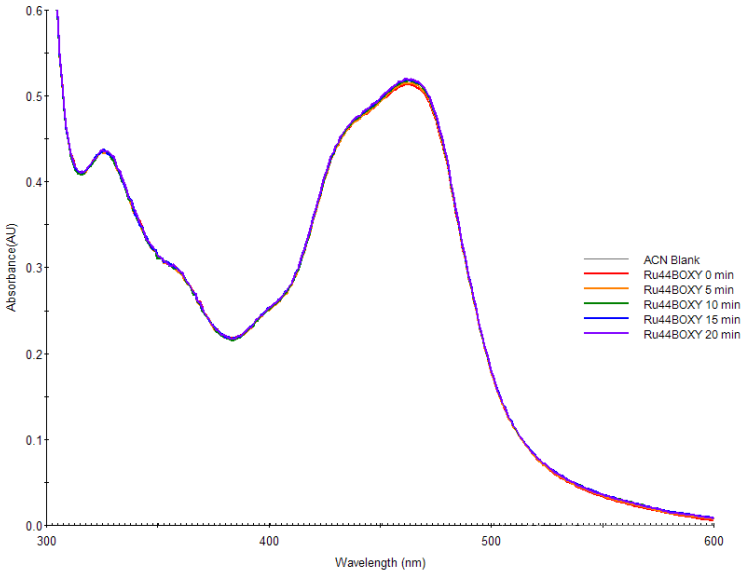


Figure S23 – UV/Visible spectra of protonated 50 μM $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ irradiated with 720 nm red light from 0 to 20 minutes in acetonitrile solvent at 25 ^{o}C.

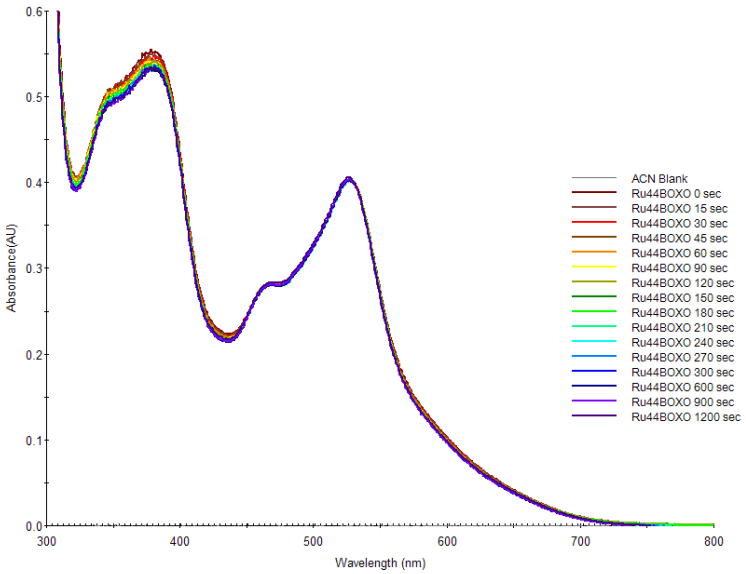


Figure S24 – UV/Visible spectra of deprotonated 50 μM $[Ru(bpy)_2(44'bpy(O^-)_2)]$ irradiated with 450 nm blue light from 0 to 20 minutes in acetonitrile solvent at 25 ^{o}C.

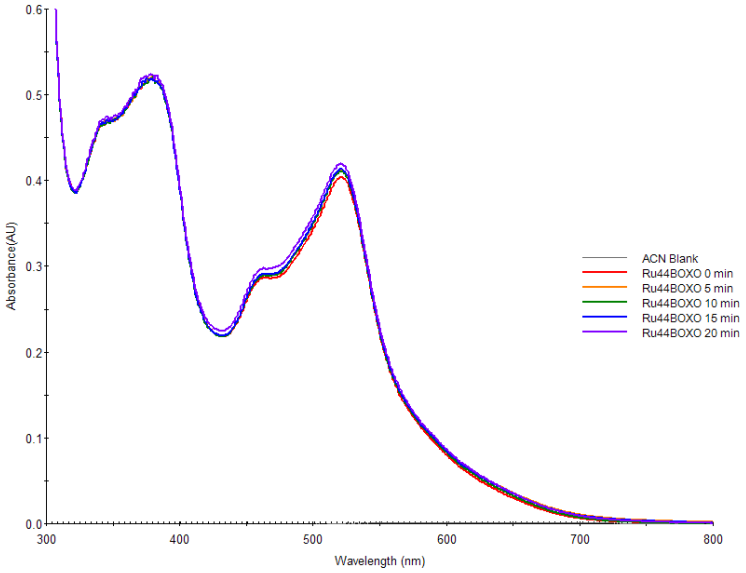


Figure S25 – UV/Visible spectra of deprotonated 50 μM [Ru(bpy)$_2$(44'bpy(O$^-$)$_2$)] irradiated with 720 nm red light from 0 to 20 minutes in acetonitrile solvent at 25 ^{o}C.

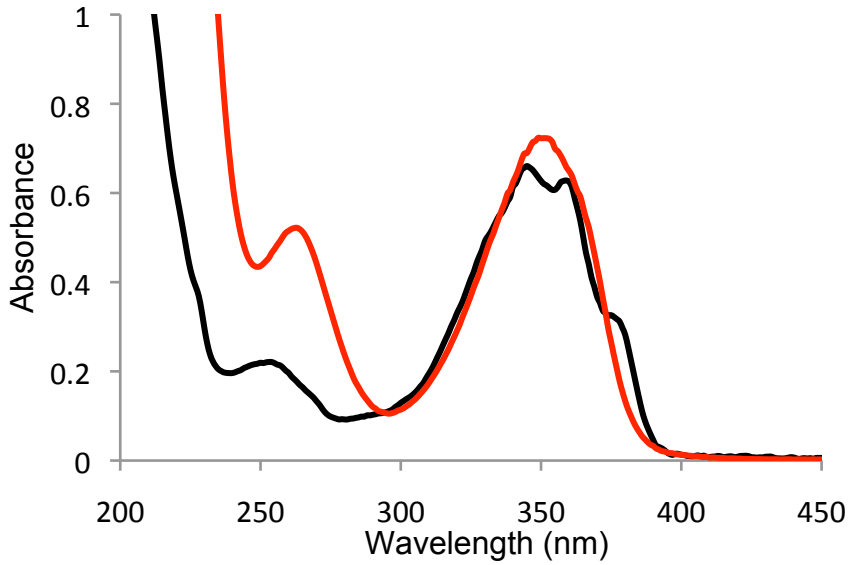


Figure S26 – UV/Visible spectra of (black line) protonated 50 μM 66'bpy(OH)$_2$ ligand and (red line) deprotonated 50 μM 66'bpy(O$^-$)$_2$ in acetonitrile solvent. A 20:1 mole ratio of tetrabutylammonium hydroxide to ligand was used to deprotonate the ligand at 25 ^{o}C.

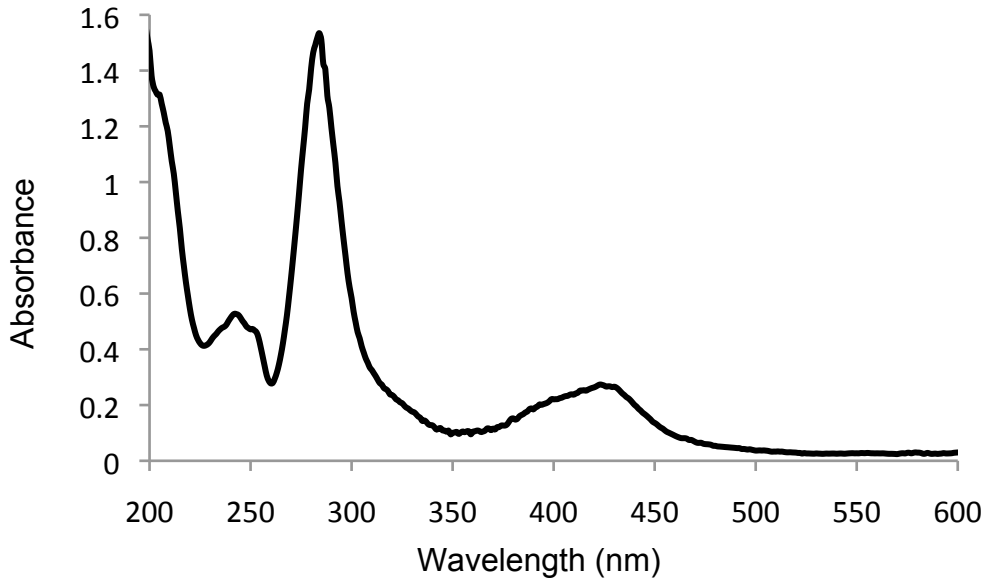


Figure S27 – UV/Visible spectrum of 25 μM $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ in acetonitrile solvent at 25 ^oC.

Table S1. UV/Visible Absorption Data for Protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and Deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in acetonitrile.

protonated			deprotonated		
energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})	energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})
5.061	245	20300	5.020	247	24300
4.305	288	63700	4.217	294	43700
3.746	331	17500	3.195	388	17100
3.563	348	19400	3.024	410(sh)	14900
2.897	428(sh)	9010	2.583	480	6480
2.701	459	11200	2.283	543	7580

Table S2. UV/Visible Absorption Data for Protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and Deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in 1,2-dichloroethane.

protonated			deprotonated		
energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})	energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})
5.061	245	19900	5.040	246	27500
4.881	254(sh)	18600	4.189	296	43000
4.275	290	63000	3.212	386	18700
3.734	332	17300	3.009	412(sh)	15800
3.563	348	19400	2.271	546	8070
2.890	429(sh)	9290			
2.701	459	11700			

Table S3. UV/Visible Absorption Data for Protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and Deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in methanol.

protonated			deprotonated		
energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})	energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})
5.081	244	21000	5.061	245	22000
4.881	254(sh)	19600	4.232	293	46000
4.246	292	46200	3.425	362	17100
3.690	336	18000	3.271	379	16500
3.532	351	19300	2.672	464	6710
3.306	375(sh)	4960	2.417	513	7480
2.863	433(sh)	9740			
2.684	462	11800			

Table S4. UV/Visible Absorption Data for Protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and Deprotonated $[Ru(bpy)_2(66'bpy(O^-)_2)]$ in ethanol.

protonated			deprotonated		
energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})	energy (eV)	λ (nm)	ε (M^{-1} cm^{-1})
5.061	245	19900	5.040	246	22200
4.881	254(sh)	17400	4.217	294	42000
4.275	290	53300	3.416	363	17000
3.690	336	17200	3.263	380	17100
3.522	352	19900	2.661	466	6600
3.297	376(sh)	3810	2.389	519	7510
2.877	431	8660			
2.689	461	10800			

Kinetics of Ligand Loss

Studies in Acetonitrile: 1. Neutral conditions. The conversion of $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ to $[Ru(bpy)_2(CH_3CN)_2)]^{2+}$ in acetonitrile upon irradiation with blue light was fit as an A → B process at 457 nm. The extinction coefficients were measured as follows at 457 nm:

$\varepsilon_A = 11{,}300\ M^{-1}cm^{-1}$

$\varepsilon_B = 4{,}500\ M^{-1}cm^{-1}$

The concentration of B as a function of time, $[B]_t$, was calculated as such in excel:

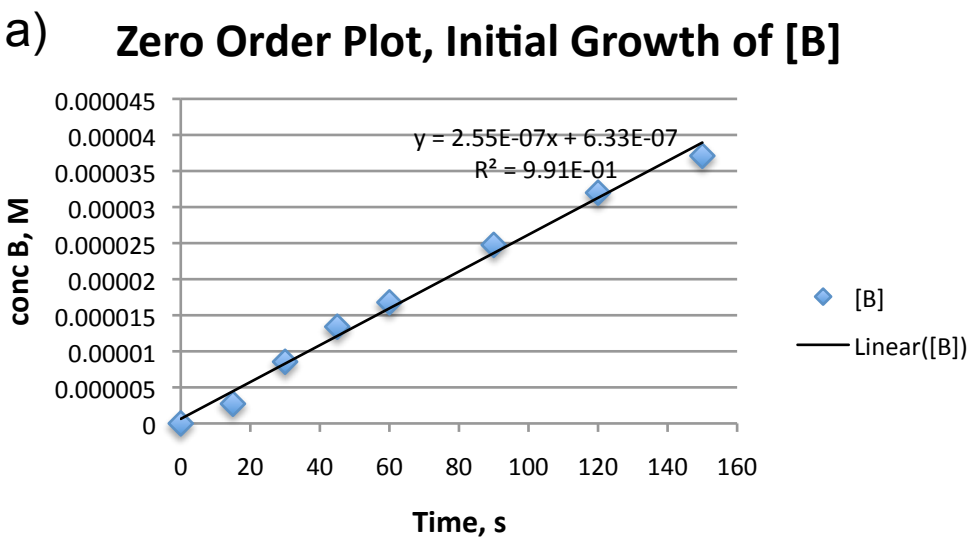
$$[B]_t = (A_{457nm} - (\varepsilon_A \times [A]_0)) / (\varepsilon_B - \varepsilon_A) \qquad (1)$$

The above equation (1) results from solving the two equations below for $[B]_t$:

$$[A]_t + [B]_t = [A]_0 \qquad (2)$$

$$A_{457nm} = [A]_t \times \varepsilon_A + [B]_t \times \varepsilon_B \qquad (3)$$

The results of this analysis are shown in Figure S28. The first order ($\ln([B]_t)$ vs. time) and second order ($(1/([B]_t)$ vs. time)) plots gave curved plots in all time regimes, rather than linear results, and thus initial rate constants dependent on $[A]_t$ or $[A]_t^2$ were ruled out.



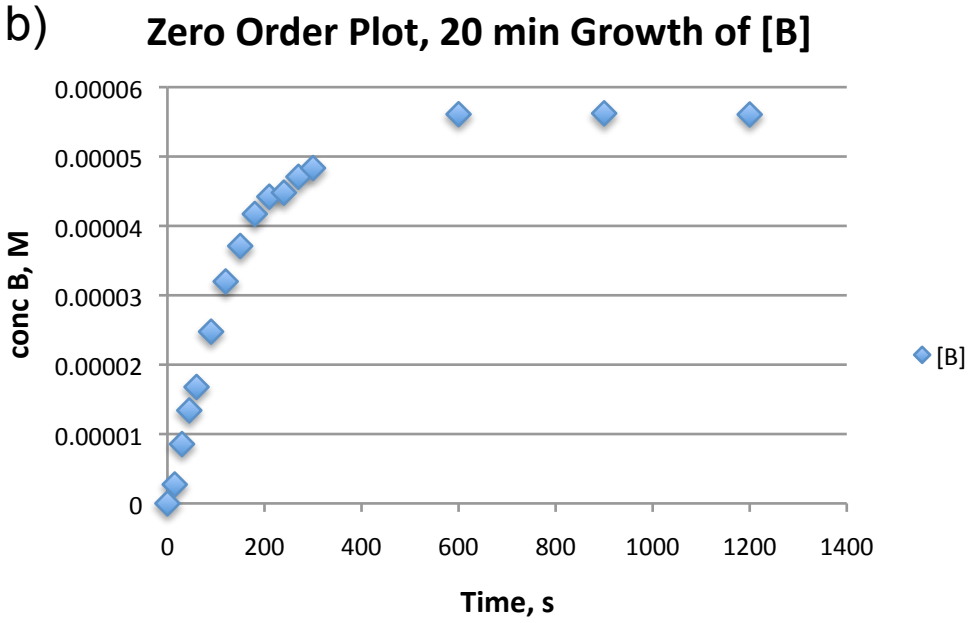


Figure S28 - Zero order plot of concentration of B, $[Ru(bpy)_2(CH_3CN)_2)]^{2+}$, as a function of time. Part a) Shows the initial rise, which was used to calculate an initial rate constant, $k_{obs} = 2.6 \times 10^{-7}$ M/s . Part b) show the long term growth of the product.

Studies in Acetonitrile: 2. Basic Conditions. Similarly, we attempted to study the photo-dissociation of $[Ru(bpy)_2(66'bpy(O^-)_2)]$ with base present in acetonitrile, Figure S29. However, the presence of a strong base led to substitution kinetics rather than photo-dissociation, as the products formed are clearly not the same as under neutral conditions. Due to the absence of strong base *in vivo*, this reaction is not biologically relevant, however it is interesting and will be studied further for a separate paper.

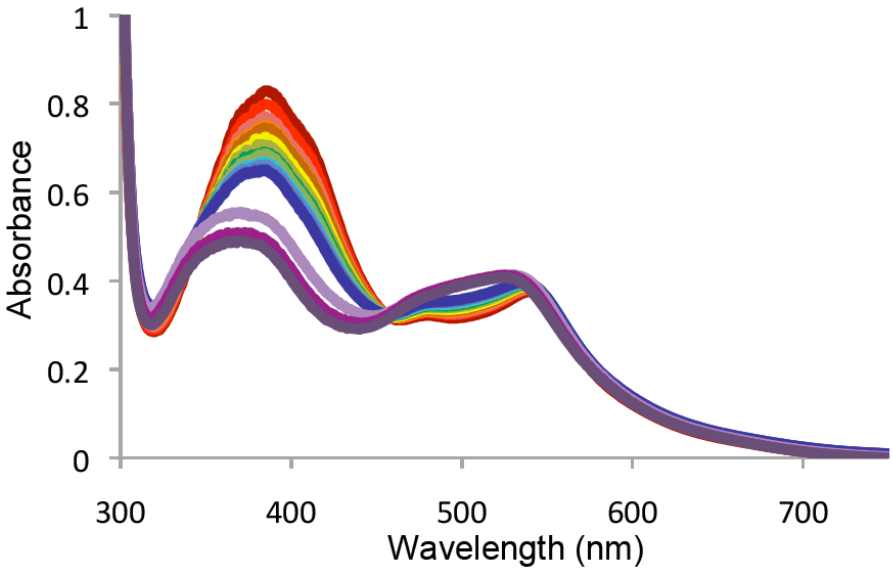
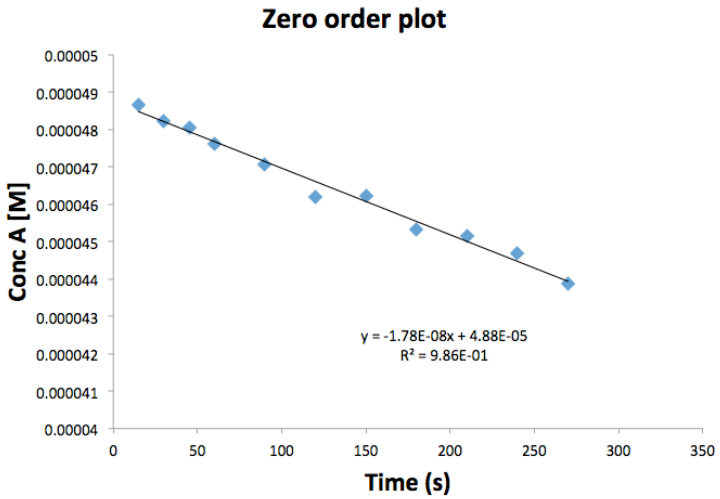


Figure S29 - UV/Visible spectra of deprotonated 50 μM $[Ru(bpy)_2(66'bpy(O\text{-})_2)]$ in acetonitrile with 10 fold excess of $[NBu_4]OH$ irradiated with 450 nm blue light from (red = —) 0 minutes to (purple = —) 20 minutes at 25 °C.

Aqueous studies at pH 5. In a similar fashion to that done with protonated $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in acetonitrile, the reaction of $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ in water at pH 5 was monitored by UV/Vis spectroscopy for 60 minutes. The peak at 461 nm undergoes the greatest change in absorbance with time (Figure S6). This is an A → B process, where A is $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and B is $[Ru(bpy)_2(H_2O)_2)]^{2+}$; the free ligand, $(66'bpy(OH)_2)$, does not absorb in this region. The rate constant of reaction was calculated by plotting [A] vs. time. $[A]_t$ was calculated as shown in equations 1, 2, and 3. Some uncertainty in the rate constant is introduced because the ε coefficients are not known exactly for $[Ru(bpy)_2(H_2O)_2)]^{2+}$ at 461 nm since this has not been synthesized independently. We estimated that ε_{461} is 2940 - 3520 $M^{-1}cm^{-1}$ for this complex, based upon the extinction coefficients of the similar complex, $[Ru(bpy)_2(CH_3CN)_2)]^{2+}$, at similar wavelengths. The zero order initial rate constant, k_{obs} = 1.7(2) × 10^{-8} M/s, is an average value that takes into account this uncertainty in the estimated standard deviation.

a)



b)

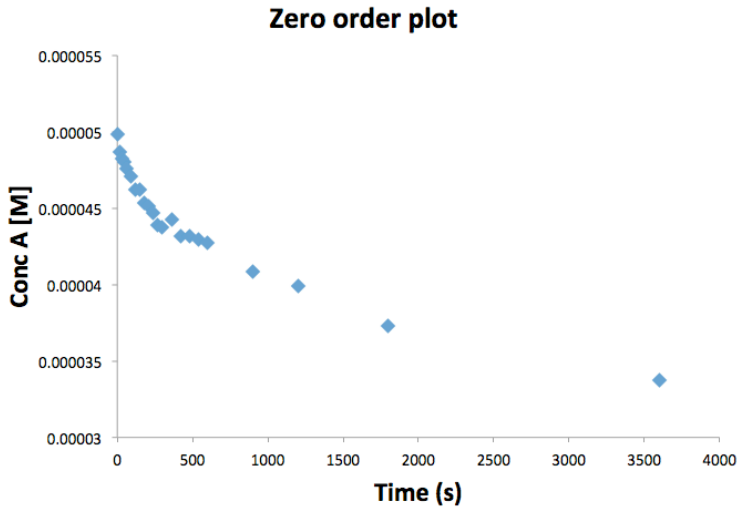


Figure S30 – a) A plot of [A] (A = $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$) vs. time for blue light induced photo-disassociation in water at pH 5. This plot used ε_{461} = 3520 $M^{-1}cm^{-1}$ for the product, $[Ru(bpy)_2(H_2O)_2)]^{2+}$. An initial rate of 1.61 × 10^{-8} M/s results when ε_{461} = 2940 $M^{-1}cm^{-1}$ is used. The value reported in the manuscript (1.7(2) × 10^{-8} M/s) represents an average initial rate. b) The long term disappearance of the reactant. Presumably, the reaction slows down at longer times due to approaching equilibrium and an appreciable extent of back reaction as free ligand concentration increases (see discussion in main text).

Aqueous studies at pH 7.5. The peak at 377 nm undergoes slight changes in absorbance upon irradiation with blue light for one hour. But upon closer inspection, the plot of absorbance vs. time or concentration (of A or B in A→B process) vs. time (Figure S31) shows no linear behavior (R^2 = 0.301 for a zero order process). Other attempts to fit the data to first or second order rate laws were unsuccessful. The fluctuation in the absorbance values appears to be mostly noise, and at this pH the rate of photodecomposition is at, or slightly above, zero.

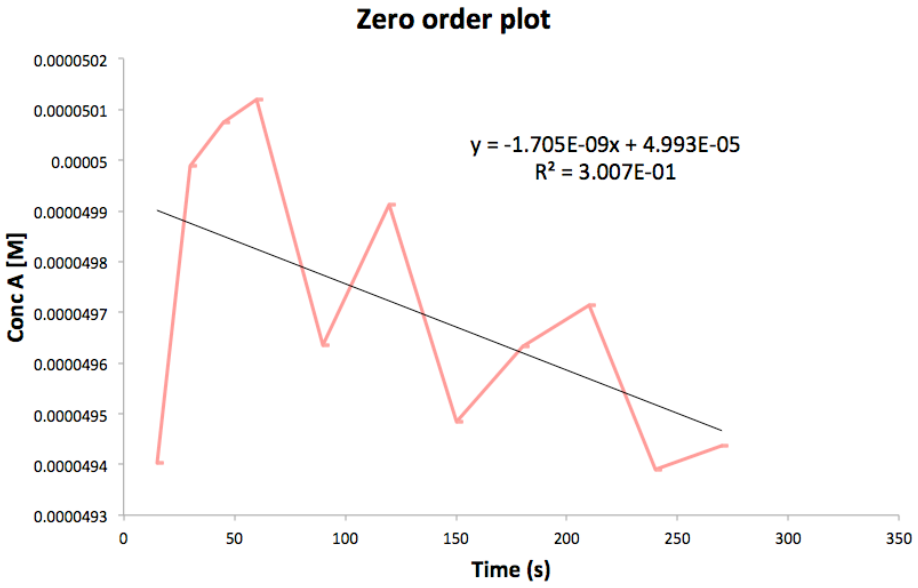


Figure S31 – An attempt to determine the initial rate of photodecomposition of $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ (A) at pH 7.5 in aqueous solution by plotting [A] vs. time. The result appears to be noise in the spectra overlapping with a slight downward slope. This initial rate is assigned to be approximately zero, as it is not big enough to be clearly determined.

Luminescence Spectroscopy

Quantum yields were determined by using the comparative method utilized by Williams et al.[4] All samples were degassed for 30 minutes. The standard used for the comparative method was $[Ru(bpy)_3]^{2+}$ with $\phi = 0.063$ in water and $\phi = 0.095$ in acetonitrile.[5]

Attempts to collected accurate emission data and quantum yields for $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ proved to be unsuccessful as the excitation of the complex lead to photo-dissociation in water and acetonitrile. These results are not surprising because the complex is photounstable as determined in crystal growth and UV/visible absorbance spectroscopy studies. However, $[Ru(bpy)_2(44'bpy(OH)_2)]^{2+}$ does not decompose when exposed to light. Quantum yield data in a 1:1 acetonitrile:water mixture are reported in Table S5. Most notably, the complex has emission properties that are quenched by over 10-fold upon deprotonation. These properties are comparable to those of $[Ru(bpy(OH)_2)_3]^{2+}$ which has a significant decrease in quantum yield upon deprotonation.[3] This quenched emission is due to an increase in the energy of the d levels of the complex upon deprotonation, that results in increasing nonradiative decay processes as expected by the energy gap law.[6] Studies carried out with $[Ru(bpy)_2(44'bpy(OMe)_2)]^{2+}$ under both acidic and basic conditions reveal no change in the respective quantum yields, confirming the quenching results are from deprotonation of the ligand. Overall, the quantum yields decrease as the quantity of electron donating ligands increase from $[Ru(bpy)_3]^{2+} > [Ru(bpy)_2(44'bpy(OMe)_2)]^{2+} > [Ru(bpy)_2(44'bpy(OH)_2)]^{2+} > [Ru(bpy(OMe)_2)_3]^{2+} > [Ru(bpy(OH)_2)_3]^{2+} > [Ru(bpy)_2(bpy(O^-)_2)] > [Ru(bpy(O^-)_2)^3]^{4-}$.[3, 5]

Table S5. Luminescence data for $[Ru(bpy)_2(X)]^{2+}$ (X = $44'bpy(OH)_2$ or $44'bpy(OMe)_2$) in 1:1 acetonitrile:water mixture

X	Acid/Base	λ_{em} (nm)	ϕ
$44'bpy(OH)_2$	0.1 M HCl	634	0.041
$44'bpy(OH)_2$	0.1 M NaOH	610	0.003
$44'bpy(OMe)_2$	0.1 M HCl	626	0.060
$44'bpy(OMe)_2$	0.1 M NaOH	626	0.063

Excitation wavelength = 460 nm, λ_{em} = wavelength of maximum emission, ϕ = quantum yield

Crystallographic Data

$[Ru(bpy)_2(66'bpy(OH)_2)][PF_6]_2$ (paul017)

Table S6. Crystal data and structure refinement for paul017.

Identification code	paul017	
Empirical formula	C79.50 H90.50 F24 N12.50 O8 P4 Ru2	
Formula weight	2131.16	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.6613(14) Å	⟨= 107.424(4)°.
	b = 16.8213(16) Å	®= 100.597(4)°.
	c = 19.0713(17) Å	© = 105.364(4)°.
Volume	4429.1(7) $Å^3$	
Z	2	
Density (calculated)	1.598 Mg/m^3	
Absorption coefficient	0.525 mm^{-1}	
F(000)	2166	
Crystal size	0.13 x 0.12 x 0.08 mm^3	
Theta range for data collection	1.41 to 33.19°.	
Index ranges	-23<=h<=24, -25<=k<=25, -29<=l<=29	
Reflections collected	94387	
Independent reflections	33738 [R(int) = 0.0534]	
Completeness to theta = 33.19°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9592 and 0.9349	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33738 / 282 / 1303	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1231	
R indices (all data)	R1 = 0.1111, wR2 = 0.1482	
Largest diff. peak and hole	1.694 and -1.147 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for paul017. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	-2405(1)	7554(1)	8566(1)	17(1)
Ru(2)	7638(1)	7399(1)	3620(1)	15(1)
N(1)	-2749(2)	8705(2)	8758(1)	19(1)
N(2)	-1276(1)	8500(2)	9473(1)	19(1)
N(3)	-1716(1)	7727(2)	7780(1)	18(1)
N(4)	-1940(1)	6505(2)	8369(1)	20(1)
N(5)	-3154(2)	7283(2)	9303(1)	19(1)
N(6)	-3655(1)	6694(1)	7809(1)	18(1)
N(7)	8812(1)	8315(1)	4503(1)	17(1)
N(8)	7308(1)	8567(1)	3887(1)	17(1)
N(9)	6894(1)	7143(1)	4366(1)	17(1)
N(10)	6380(1)	6561(1)	2868(1)	16(1)
N(11)	8283(1)	7556(2)	2803(1)	18(1)
N(12)	8048(1)	6317(2)	3369(1)	18(1)
O(1)	-3819(1)	8201(1)	7612(1)	28(1)
O(2)	-296(1)	7732(1)	9324(1)	29(1)
O(3)	9700(1)	7456(1)	4305(1)	31(1)
O(4)	6075(1)	8069(1)	2847(1)	25(1)
P(1)	2896(1)	5206(1)	4493(1)	27(1)
F(1)	3901(1)	5188(1)	4818(1)	35(1)
F(2)	3098(1)	5117(2)	3680(1)	46(1)
F(3)	3313(1)	6256(1)	4759(1)	42(1)
F(4)	2712(1)	5314(2)	5302(1)	48(1)
F(5)	2492(2)	4154(1)	4223(1)	59(1)
F(6)	1890(1)	5217(2)	4164(1)	55(1)
P(2)	2160(1)	9568(1)	7665(1)	28(1)
F(7)	1156(1)	9641(1)	7624(1)	37(1)
F(8)	2171(2)	9900(2)	6957(1)	64(1)
F(9)	1708(2)	8579(1)	7074(1)	57(1)
F(10)	2146(2)	9254(2)	8362(1)	71(1)
F(11)	2600(2)	10572(2)	8242(2)	74(1)

F(12)	3161(1)	9506(2)	7697(1)	53(1)
P(3)	2905(1)	5275(1)	9696(1)	31(1)
F(13)	3941(1)	5267(2)	9945(1)	57(1)
F(14)	2920(2)	4951(2)	8838(1)	67(1)
F(15)	3323(1)	6275(1)	9778(1)	46(1)
F(16)	2913(2)	5613(2)	10570(1)	87(1)
F(17)	2499(2)	4282(2)	9643(2)	84(1)
F(18)	1884(1)	5274(2)	9428(1)	56(1)
P(4)	1822(1)	9038(1)	2740(1)	48(1)
F(19)	2558(2)	8919(2)	3375(1)	70(1)
F(20)	2142(2)	10061(2)	3269(1)	57(1)
F(21)	1081(2)	8790(2)	3184(1)	59(1)
F(22)	1499(2)	8005(2)	2228(1)	82(1)
F(23)	2592(2)	9221(2)	2333(2)	96(1)
F(24)	1086(2)	9138(2)	2136(2)	104(1)
C(1)	-3400(2)	8855(2)	8298(2)	23(1)
C(2)	-3607(2)	9629(2)	8512(2)	32(1)
C(3)	-3117(2)	10281(2)	9218(2)	39(1)
C(4)	-2421(2)	10159(2)	9692(2)	34(1)
C(5)	-2252(2)	9372(2)	9449(2)	22(1)
C(6)	-1460(2)	9225(2)	9873(2)	20(1)
C(7)	-914(2)	9798(2)	10601(2)	25(1)
C(8)	-138(2)	9637(2)	10923(2)	26(1)
C(9)	98(2)	8955(2)	10509(2)	24(1)
C(10)	-481(2)	8400(2)	9773(2)	21(1)
C(11)	-1601(2)	8400(2)	7523(1)	21(1)
C(12)	-1062(2)	8514(2)	7038(2)	25(1)
C(13)	-625(2)	7911(2)	6799(2)	30(1)
C(14)	-754(2)	7204(2)	7042(2)	27(1)
C(15)	-1300(2)	7124(2)	7533(2)	21(1)
C(16)	-1449(2)	6419(2)	7848(2)	22(1)
C(17)	-1098(2)	5738(2)	7668(2)	30(1)
C(18)	-1220(2)	5144(2)	8039(2)	38(1)
C(19)	-1705(2)	5240(2)	8577(2)	35(1)
C(20)	-2059(2)	5916(2)	8724(2)	26(1)
C(21)	-2841(2)	7535(2)	10071(2)	23(1)

C(22)	-3409(2)	7375(2)	10526(2)	28(1)
C(23)	-4341(2)	6918(2)	10181(2)	28(1)
C(24)	-4678(2)	6640(2)	9392(2)	25(1)
C(25)	-4076(2)	6829(2)	8967(2)	19(1)
C(26)	-4359(2)	6525(2)	8125(2)	20(1)
C(27)	-5265(2)	6080(2)	7668(2)	26(1)
C(28)	-5445(2)	5761(2)	6876(2)	26(1)
C(29)	-4718(2)	5872(2)	6562(2)	24(1)
C(30)	-3835(2)	6349(2)	7043(1)	21(1)
C(31)	9615(2)	8192(2)	4748(2)	21(1)
C(32)	10290(2)	8783(2)	5424(2)	24(1)
C(33)	10148(2)	9522(2)	5851(2)	25(1)
C(34)	9347(2)	9684(2)	5588(2)	22(1)
C(35)	8703(2)	9078(2)	4911(1)	18(1)
C(36)	7856(2)	9219(2)	4574(1)	18(1)
C(37)	7651(2)	9962(2)	4915(2)	26(1)
C(38)	6860(2)	10063(2)	4540(2)	29(1)
C(39)	6320(2)	9435(2)	3844(2)	26(1)
C(40)	6565(2)	8699(2)	3530(2)	20(1)
C(41)	7195(2)	7450(2)	5136(2)	22(1)
C(42)	6616(2)	7384(2)	5592(2)	26(1)
C(43)	5676(2)	6959(2)	5253(2)	26(1)
C(44)	5351(2)	6609(2)	4461(2)	24(1)
C(45)	5962(2)	6704(2)	4027(1)	18(1)
C(46)	5686(2)	6367(2)	3188(2)	18(1)
C(47)	4783(2)	5884(2)	2735(2)	23(1)
C(48)	4588(2)	5583(2)	1942(2)	25(1)
C(49)	5309(2)	5746(2)	1620(2)	23(1)
C(50)	6190(2)	6239(2)	2099(2)	21(1)
C(51)	8382(2)	8236(2)	2553(2)	21(1)
C(52)	8828(2)	8300(2)	2000(2)	26(1)
C(53)	9174(2)	7648(2)	1686(2)	29(1)
C(54)	9064(2)	6944(2)	1931(2)	26(1)
C(55)	8622(2)	6908(2)	2495(2)	20(1)
C(56)	8476(2)	6204(2)	2805(2)	20(1)
C(57)	8767(2)	5482(2)	2567(2)	29(1)

C(58)	8638(2)	4876(2)	2922(2)	36(1)
C(59)	8215(2)	4993(2)	3502(2)	35(1)
C(60)	7930(2)	5714(2)	3706(2)	25(1)
O(5)	4386(1)	8118(1)	2432(1)	30(1)
C(61)	4811(3)	8577(3)	1437(2)	50(1)
C(62)	4065(2)	8002(3)	1637(2)	45(1)
C(63)	3708(2)	7573(2)	2661(2)	37(1)
C(64)	4048(3)	7810(3)	3509(2)	50(1)
O(6)	1120(5)	7060(5)	4769(4)	52(2)
C(65)	1372(15)	6956(9)	3529(8)	85(4)
C(66)	1838(10)	7348(11)	4378(7)	53(2)
C(67)	1070(5)	6496(5)	5046(4)	58(2)
C(68)	490(8)	6438(9)	5553(6)	74(3)
O(6')	1303(9)	7331(7)	4862(7)	44(2)
C(65')	1380(20)	6721(12)	3525(11)	51(3)
C(66')	1824(17)	7427(18)	4291(10)	49(3)
C(67')	1567(8)	7097(8)	5408(6)	56(2)
C(68')	835(12)	6638(12)	5667(10)	54(3)
O(7)	5052(2)	8510(2)	6622(1)	37(1)
C(69)	5283(3)	9119(3)	5621(2)	59(1)
C(70)	5545(3)	9264(3)	6458(2)	48(1)
C(71)	4126(3)	8412(3)	6575(3)	56(1)
C(72)	3708(3)	7662(3)	6823(2)	53(1)
O(8)	1268(11)	7521(12)	9790(8)	39(1)
C(73)	1494(5)	7440(4)	8569(4)	53(2)
C(74)	1502(9)	7020(9)	9153(6)	53(2)
C(75)	1370(8)	7208(11)	10412(7)	51(2)
C(76)	559(10)	6393(10)	10273(8)	59(3)
O(8')	1310(20)	7530(20)	9710(15)	47(2)
C(73')	2398(7)	7482(7)	8989(6)	52(3)
C(74')	1435(13)	7077(16)	8997(10)	51(3)
C(75')	1559(14)	7293(18)	10347(12)	45(3)
C(76')	791(16)	6570(16)	10412(13)	45(3)
C(77)	4783(4)	8548(3)	9223(3)	43(4)
C(78)	4230(3)	9014(3)	9019(3)	40(2)
C(79)	4403(4)	9884(3)	9487(3)	39(2)

C(80)	5128(4)	10289(3)	10160(3)	40(2)
C(81)	5681(3)	9823(3)	10365(3)	36(2)
C(82)	5509(3)	8953(3)	9896(3)	40(2)
C(83)	5296(10)	11196(10)	10660(8)	52(3)
N(13)	5449(9)	11902(6)	11040(6)	89(4)

Table S8. Bond lengths [Å] and angles [°] for paul017.

Ru(1)-N(4)	2.043(2)
Ru(1)-N(3)	2.046(2)
Ru(1)-N(6)	2.053(2)
Ru(1)-N(5)	2.066(2)
Ru(1)-N(1)	2.091(2)
Ru(1)-N(2)	2.094(2)
Ru(2)-N(12)	2.040(2)
Ru(2)-N(10)	2.050(2)
Ru(2)-N(11)	2.050(2)
Ru(2)-N(9)	2.068(2)
Ru(2)-N(7)	2.098(2)
Ru(2)-N(8)	2.103(2)
N(1)-C(1)	1.345(3)
N(1)-C(5)	1.370(3)
N(2)-C(10)	1.347(3)
N(2)-C(6)	1.365(3)
N(3)-C(11)	1.345(3)
N(3)-C(15)	1.360(3)
N(4)-C(20)	1.352(4)
N(4)-C(16)	1.361(3)
N(5)-C(21)	1.349(3)
N(5)-C(25)	1.364(3)
N(6)-C(30)	1.343(3)
N(6)-C(26)	1.357(3)
N(7)-C(31)	1.350(3)
N(7)-C(35)	1.360(3)
N(8)-C(40)	1.343(3)
N(8)-C(36)	1.372(3)
N(9)-C(41)	1.345(3)
N(9)-C(45)	1.375(3)
N(10)-C(50)	1.347(3)
N(10)-C(46)	1.354(3)
N(11)-C(51)	1.348(3)
N(11)-C(55)	1.360(3)

N(12)-C(60)	1.345(3)
N(12)-C(56)	1.362(3)
O(1)-C(1)	1.340(3)
O(1)-H(1)	0.6737
O(2)-C(10)	1.329(3)
O(2)-H(2)	0.7660
O(3)-C(31)	1.327(3)
O(3)-H(3)	0.7631
O(4)-C(40)	1.335(3)
O(4)-H(4)	0.6624
P(1)-F(4)	1.588(2)
P(1)-F(6)	1.591(2)
P(1)-F(3)	1.592(2)
P(1)-F(5)	1.592(2)
P(1)-F(1)	1.5942(18)
P(1)-F(2)	1.611(2)
P(2)-F(10)	1.572(2)
P(2)-F(9)	1.580(2)
P(2)-F(11)	1.590(2)
P(2)-F(12)	1.590(2)
P(2)-F(7)	1.5980(19)
P(2)-F(8)	1.609(2)
P(3)-F(14)	1.570(2)
P(3)-F(15)	1.583(2)
P(3)-F(18)	1.585(2)
P(3)-F(17)	1.586(2)
P(3)-F(16)	1.587(2)
P(3)-F(13)	1.609(2)
P(4)-F(24)	1.554(3)
P(4)-F(23)	1.562(3)
P(4)-F(20)	1.597(2)
P(4)-F(21)	1.599(3)
P(4)-F(22)	1.602(3)
P(4)-F(19)	1.609(2)
C(1)-C(2)	1.387(4)
C(2)-C(3)	1.375(4)

C(2)-H(2A)	0.9500
C(3)-C(4)	1.384(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.378(4)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.472(4)
C(6)-C(7)	1.382(4)
C(7)-C(8)	1.388(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.366(4)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.401(4)
C(9)-H(9A)	0.9500
C(11)-C(12)	1.383(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.382(4)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.381(4)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.391(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.467(4)
C(16)-C(17)	1.378(4)
C(17)-C(18)	1.381(5)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.380(5)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.371(4)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500
C(21)-C(22)	1.382(4)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.379(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.383(4)
C(23)-H(23A)	0.9500

C(24)-C(25)	1.388(4)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.471(4)
C(26)-C(27)	1.387(4)
C(27)-C(28)	1.389(4)
C(27)-H(27A)	0.9500
C(28)-C(29)	1.377(4)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.379(4)
C(29)-H(29A)	0.9500
C(30)-H(30A)	0.9500
C(31)-C(32)	1.394(4)
C(32)-C(33)	1.366(4)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.389(4)
C(33)-H(33A)	0.9500
C(34)-C(35)	1.383(3)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.474(3)
C(36)-C(37)	1.375(4)
C(37)-C(38)	1.390(4)
C(37)-H(37A)	0.9500
C(38)-C(39)	1.366(4)
C(38)-H(38A)	0.9500
C(39)-C(40)	1.391(4)
C(39)-H(39A)	0.9500
C(41)-C(42)	1.374(4)
C(41)-H(41A)	0.9500
C(42)-C(43)	1.382(4)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.385(4)
C(43)-H(43A)	0.9500
C(44)-C(45)	1.383(4)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.463(3)
C(46)-C(47)	1.389(3)

C(47)-C(48)	1.389(4)
C(47)-H(47A)	0.9500
C(48)-C(49)	1.384(4)
C(48)-H(48A)	0.9500
C(49)-C(50)	1.379(4)
C(49)-H(49A)	0.9500
C(50)-H(50A)	0.9500
C(51)-C(52)	1.383(4)
C(51)-H(51A)	0.9500
C(52)-C(53)	1.376(4)
C(52)-H(52A)	0.9500
C(53)-C(54)	1.380(4)
C(53)-H(53A)	0.9500
C(54)-C(55)	1.391(4)
C(54)-H(54A)	0.9500
C(55)-C(56)	1.460(4)
C(56)-C(57)	1.388(4)
C(57)-C(58)	1.375(4)
C(57)-H(57A)	0.9500
C(58)-C(59)	1.382(4)
C(58)-H(58A)	0.9500
C(59)-C(60)	1.374(4)
C(59)-H(59A)	0.9500
C(60)-H(60A)	0.9500
O(5)-C(63)	1.432(4)
O(5)-C(62)	1.443(4)
C(61)-C(62)	1.495(5)
C(61)-H(61A)	0.9800
C(61)-H(61B)	0.9800
C(61)-H(61C)	0.9800
C(62)-H(62A)	0.9900
C(62)-H(62B)	0.9900
C(63)-C(64)	1.498(5)
C(63)-H(63A)	0.9900
C(63)-H(63B)	0.9900
C(64)-H(64A)	0.9800

C(64)-H(64B)	0.9800
C(64)-H(64C)	0.9800
O(6)-C(67)	1.208(8)
O(6)-C(66)	1.514(9)
C(65)-C(66)	1.503(11)
C(65)-H(65A)	0.9800
C(65)-H(65B)	0.9800
C(65)-H(65C)	0.9800
C(66)-H(66A)	0.9900
C(66)-H(66B)	0.9900
C(67)-C(68)	1.450(10)
C(67)-H(67A)	0.9900
C(67)-H(67B)	0.9900
C(68)-H(68A)	0.9800
C(68)-H(68B)	0.9800
C(68)-H(68C)	0.9800
O(6')-C(67')	1.259(12)
O(6')-C(66')	1.495(12)
C(65')-C(66')	1.476(15)
C(65')-H(65D)	0.9800
C(65')-H(65E)	0.9800
C(65')-H(65F)	0.9800
C(66')-H(66C)	0.9900
C(66')-H(66D)	0.9900
C(67')-C(68')	1.457(13)
C(67')-H(67C)	0.9900
C(67')-H(67D)	0.9900
C(68')-H(68D)	0.9800
C(68')-H(68E)	0.9800
C(68')-H(68F)	0.9800
O(7)-C(71)	1.398(4)
O(7)-C(70)	1.452(4)
C(69)-C(70)	1.499(5)
C(69)-H(69A)	0.9800
C(69)-H(69B)	0.9800
C(69)-H(69C)	0.9800

C(70)-H(70A)	0.9900
C(70)-H(70B)	0.9900
C(71)-C(72)	1.508(6)
C(71)-H(71A)	0.9900
C(71)-H(71B)	0.9900
C(72)-H(72A)	0.9800
C(72)-H(72B)	0.9800
C(72)-H(72C)	0.9800
O(8)-C(74)	1.427(8)
O(8)-C(75)	1.435(8)
C(73)-C(74)	1.485(11)
C(73)-H(73A)	0.9800
C(73)-H(73B)	0.9800
C(73)-H(73C)	0.9800
C(74)-H(74A)	0.9900
C(74)-H(74B)	0.9900
C(75)-C(76)	1.516(10)
C(75)-H(75A)	0.9900
C(75)-H(75B)	0.9900
C(76)-H(76A)	0.9800
C(76)-H(76B)	0.9800
C(76)-H(76C)	0.9800
O(8')-C(75')	1.415(13)
O(8')-C(74')	1.427(13)
C(73')-C(74')	1.487(17)
C(73')-H(73D)	0.9800
C(73')-H(73E)	0.9800
C(73')-H(73F)	0.9800
C(74')-H(74C)	0.9900
C(74')-H(74D)	0.9900
C(75')-C(76')	1.522(14)
C(75')-H(75C)	0.9900
C(75')-H(75D)	0.9900
C(76')-H(76D)	0.9800
C(76')-H(76E)	0.9800
C(76')-H(76F)	0.9800

C(77)-C(78)	1.3900
C(77)-C(82)	1.3900
C(77)-H(77)	0.9500
C(78)-C(79)	1.3900
C(78)-H(78)	0.9500
C(79)-C(80)	1.3900
C(79)-H(79)	0.9500
C(80)-C(81)	1.3900
C(80)-C(83)	1.460(15)
C(81)-C(82)	1.3900
C(81)-H(81)	0.9500
C(82)-H(82)	0.9500
C(83)-N(13)	1.124(16)

N(4)-Ru(1)-N(3)	78.91(9)
N(4)-Ru(1)-N(6)	87.71(8)
N(3)-Ru(1)-N(6)	97.99(8)
N(4)-Ru(1)-N(5)	98.40(9)
N(3)-Ru(1)-N(5)	175.71(8)
N(6)-Ru(1)-N(5)	78.48(9)
N(4)-Ru(1)-N(1)	173.93(9)
N(3)-Ru(1)-N(1)	96.25(9)
N(6)-Ru(1)-N(1)	96.64(8)
N(5)-Ru(1)-N(1)	86.64(9)
N(4)-Ru(1)-N(2)	98.95(9)
N(3)-Ru(1)-N(2)	91.39(8)
N(6)-Ru(1)-N(2)	169.41(8)
N(5)-Ru(1)-N(2)	92.34(8)
N(1)-Ru(1)-N(2)	77.37(9)
N(12)-Ru(2)-N(10)	86.02(8)
N(12)-Ru(2)-N(11)	78.77(9)
N(10)-Ru(2)-N(11)	96.25(8)
N(12)-Ru(2)-N(9)	99.39(9)
N(10)-Ru(2)-N(9)	78.75(8)
N(11)-Ru(2)-N(9)	174.82(8)
N(12)-Ru(2)-N(7)	99.44(8)

N(10)-Ru(2)-N(7)	171.42(8)
N(11)-Ru(2)-N(7)	91.33(8)
N(9)-Ru(2)-N(7)	93.76(8)
N(12)-Ru(2)-N(8)	176.10(8)
N(10)-Ru(2)-N(8)	97.27(8)
N(11)-Ru(2)-N(8)	98.73(9)
N(9)-Ru(2)-N(8)	83.36(8)
N(7)-Ru(2)-N(8)	77.54(8)
C(1)-N(1)-C(5)	117.4(2)
C(1)-N(1)-Ru(1)	128.10(18)
C(5)-N(1)-Ru(1)	114.50(17)
C(10)-N(2)-C(6)	117.8(2)
C(10)-N(2)-Ru(1)	127.32(18)
C(6)-N(2)-Ru(1)	113.72(17)
C(11)-N(3)-C(15)	118.1(2)
C(11)-N(3)-Ru(1)	125.94(18)
C(15)-N(3)-Ru(1)	115.86(18)
C(20)-N(4)-C(16)	118.4(2)
C(20)-N(4)-Ru(1)	125.57(19)
C(16)-N(4)-Ru(1)	116.04(18)
C(21)-N(5)-C(25)	117.3(2)
C(21)-N(5)-Ru(1)	127.45(18)
C(25)-N(5)-Ru(1)	115.15(17)
C(30)-N(6)-C(26)	118.8(2)
C(30)-N(6)-Ru(1)	125.62(18)
C(26)-N(6)-Ru(1)	115.37(17)
C(31)-N(7)-C(35)	117.6(2)
C(31)-N(7)-Ru(2)	127.15(18)
C(35)-N(7)-Ru(2)	114.90(16)
C(40)-N(8)-C(36)	117.0(2)
C(40)-N(8)-Ru(2)	127.94(18)
C(36)-N(8)-Ru(2)	114.36(16)
C(41)-N(9)-C(45)	117.5(2)
C(41)-N(9)-Ru(2)	127.45(18)
C(45)-N(9)-Ru(2)	114.50(16)
C(50)-N(10)-C(46)	118.9(2)

C(50)-N(10)-Ru(2)	125.32(18)
C(46)-N(10)-Ru(2)	115.67(16)
C(51)-N(11)-C(55)	119.1(2)
C(51)-N(11)-Ru(2)	125.08(18)
C(55)-N(11)-Ru(2)	115.81(18)
C(60)-N(12)-C(56)	117.8(2)
C(60)-N(12)-Ru(2)	126.14(18)
C(56)-N(12)-Ru(2)	116.06(18)
C(1)-O(1)-H(1)	109.5
C(10)-O(2)-H(2)	109.5
C(31)-O(3)-H(3)	109.5
C(40)-O(4)-H(4)	109.5
F(4)-P(1)-F(6)	89.90(12)
F(4)-P(1)-F(3)	89.61(12)
F(6)-P(1)-F(3)	90.65(12)
F(4)-P(1)-F(5)	90.96(13)
F(6)-P(1)-F(5)	90.05(13)
F(3)-P(1)-F(5)	179.10(13)
F(4)-P(1)-F(1)	90.30(11)
F(6)-P(1)-F(1)	179.61(15)
F(3)-P(1)-F(1)	89.68(11)
F(5)-P(1)-F(1)	89.62(11)
F(4)-P(1)-F(2)	178.78(14)
F(6)-P(1)-F(2)	90.54(11)
F(3)-P(1)-F(2)	89.25(12)
F(5)-P(1)-F(2)	90.18(13)
F(1)-P(1)-F(2)	89.26(10)
F(10)-P(2)-F(9)	91.42(15)
F(10)-P(2)-F(11)	89.93(16)
F(9)-P(2)-F(11)	178.42(15)
F(10)-P(2)-F(12)	90.24(13)
F(9)-P(2)-F(12)	90.15(12)
F(11)-P(2)-F(12)	90.66(12)
F(10)-P(2)-F(7)	90.70(12)
F(9)-P(2)-F(7)	90.18(11)
F(11)-P(2)-F(7)	88.99(11)

F(12)-P(2)-F(7)	178.99(14)
F(10)-P(2)-F(8)	179.22(14)
F(9)-P(2)-F(8)	89.21(14)
F(11)-P(2)-F(8)	89.43(16)
F(12)-P(2)-F(8)	90.21(12)
F(7)-P(2)-F(8)	88.84(11)
F(14)-P(3)-F(15)	90.62(14)
F(14)-P(3)-F(18)	89.77(13)
F(15)-P(3)-F(18)	91.16(12)
F(14)-P(3)-F(17)	91.08(17)
F(15)-P(3)-F(17)	178.15(15)
F(18)-P(3)-F(17)	89.58(14)
F(14)-P(3)-F(16)	178.79(15)
F(15)-P(3)-F(16)	88.74(14)
F(18)-P(3)-F(16)	91.27(15)
F(17)-P(3)-F(16)	89.55(17)
F(14)-P(3)-F(13)	88.66(13)
F(15)-P(3)-F(13)	88.83(12)
F(18)-P(3)-F(13)	178.43(14)
F(17)-P(3)-F(13)	90.48(13)
F(16)-P(3)-F(13)	90.30(15)
F(24)-P(4)-F(23)	93.95(19)
F(24)-P(4)-F(20)	91.90(16)
F(23)-P(4)-F(20)	91.94(15)
F(24)-P(4)-F(21)	90.79(17)
F(23)-P(4)-F(21)	174.50(18)
F(20)-P(4)-F(21)	90.69(13)
F(24)-P(4)-F(22)	89.00(17)
F(23)-P(4)-F(22)	89.14(15)
F(20)-P(4)-F(22)	178.54(16)
F(21)-P(4)-F(22)	88.15(14)
F(24)-P(4)-F(19)	178.16(19)
F(23)-P(4)-F(19)	87.83(17)
F(20)-P(4)-F(19)	88.51(13)
F(21)-P(4)-F(19)	87.42(14)
F(22)-P(4)-F(19)	90.56(16)

O(1)-C(1)-N(1)	114.4(2)
O(1)-C(1)-C(2)	122.8(3)
N(1)-C(1)-C(2)	122.8(3)
C(3)-C(2)-C(1)	118.9(3)
C(3)-C(2)-H(2A)	120.6
C(1)-C(2)-H(2A)	120.6
C(2)-C(3)-C(4)	119.7(3)
C(2)-C(3)-H(3A)	120.2
C(4)-C(3)-H(3A)	120.2
C(5)-C(4)-C(3)	118.7(3)
C(5)-C(4)-H(4A)	120.7
C(3)-C(4)-H(4A)	120.7
N(1)-C(5)-C(4)	122.6(3)
N(1)-C(5)-C(6)	114.8(2)
C(4)-C(5)-C(6)	122.3(3)
N(2)-C(6)-C(7)	122.4(3)
N(2)-C(6)-C(5)	114.4(2)
C(7)-C(6)-C(5)	123.1(3)
C(6)-C(7)-C(8)	118.4(3)
C(6)-C(7)-H(7A)	120.8
C(8)-C(7)-H(7A)	120.8
C(9)-C(8)-C(7)	120.1(3)
C(9)-C(8)-H(8A)	119.9
C(7)-C(8)-H(8A)	119.9
C(8)-C(9)-C(10)	118.8(3)
C(8)-C(9)-H(9A)	120.6
C(10)-C(9)-H(9A)	120.6
O(2)-C(10)-N(2)	115.1(2)
O(2)-C(10)-C(9)	122.8(2)
N(2)-C(10)-C(9)	122.1(3)
N(3)-C(11)-C(12)	122.8(3)
N(3)-C(11)-H(11A)	118.6
C(12)-C(11)-H(11A)	118.6
C(11)-C(12)-C(13)	119.1(3)
C(11)-C(12)-H(12A)	120.5
C(13)-C(12)-H(12A)	120.5

C(14)-C(13)-C(12)	118.9(3)
C(14)-C(13)-H(13A)	120.6
C(12)-C(13)-H(13A)	120.6
C(13)-C(14)-C(15)	119.6(3)
C(13)-C(14)-H(14A)	120.2
C(15)-C(14)-H(14A)	120.2
N(3)-C(15)-C(14)	121.5(3)
N(3)-C(15)-C(16)	114.6(2)
C(14)-C(15)-C(16)	123.8(3)
N(4)-C(16)-C(17)	121.3(3)
N(4)-C(16)-C(15)	114.5(2)
C(17)-C(16)-C(15)	124.2(3)
C(16)-C(17)-C(18)	119.7(3)
C(16)-C(17)-H(17A)	120.2
C(18)-C(17)-H(17A)	120.2
C(17)-C(18)-C(19)	119.0(3)
C(17)-C(18)-H(18A)	120.5
C(19)-C(18)-H(18A)	120.5
C(20)-C(19)-C(18)	119.3(3)
C(20)-C(19)-H(19A)	120.3
C(18)-C(19)-H(19A)	120.3
N(4)-C(20)-C(19)	122.3(3)
N(4)-C(20)-H(20A)	118.8
C(19)-C(20)-H(20A)	118.8
N(5)-C(21)-C(22)	123.3(3)
N(5)-C(21)-H(21A)	118.3
C(22)-C(21)-H(21A)	118.3
C(23)-C(22)-C(21)	118.9(3)
C(23)-C(22)-H(22A)	120.5
C(21)-C(22)-H(22A)	120.5
C(22)-C(23)-C(24)	119.0(3)
C(22)-C(23)-H(23A)	120.5
C(24)-C(23)-H(23A)	120.5
C(23)-C(24)-C(25)	119.5(3)
C(23)-C(24)-H(24A)	120.3
C(25)-C(24)-H(24A)	120.3

N(5)-C(25)-C(24)	121.9(2)
N(5)-C(25)-C(26)	114.5(2)
C(24)-C(25)-C(26)	123.5(2)
N(6)-C(26)-C(27)	121.0(2)
N(6)-C(26)-C(25)	114.7(2)
C(27)-C(26)-C(25)	124.2(2)
C(26)-C(27)-C(28)	119.2(3)
C(26)-C(27)-H(27A)	120.4
C(28)-C(27)-H(27A)	120.4
C(29)-C(28)-C(27)	119.3(2)
C(29)-C(28)-H(28A)	120.4
C(27)-C(28)-H(28A)	120.4
C(28)-C(29)-C(30)	118.9(3)
C(28)-C(29)-H(29A)	120.6
C(30)-C(29)-H(29A)	120.6
N(6)-C(30)-C(29)	122.5(3)
N(6)-C(30)-H(30A)	118.8
C(29)-C(30)-H(30A)	118.8
O(3)-C(31)-N(7)	114.8(2)
O(3)-C(31)-C(32)	123.0(2)
N(7)-C(31)-C(32)	122.2(3)
C(33)-C(32)-C(31)	119.3(3)
C(33)-C(32)-H(32A)	120.3
C(31)-C(32)-H(32A)	120.3
C(32)-C(33)-C(34)	119.3(3)
C(32)-C(33)-H(33A)	120.4
C(34)-C(33)-H(33A)	120.4
C(35)-C(34)-C(33)	118.9(3)
C(35)-C(34)-H(34A)	120.5
C(33)-C(34)-H(34A)	120.5
N(7)-C(35)-C(34)	122.4(2)
N(7)-C(35)-C(36)	115.3(2)
C(34)-C(35)-C(36)	122.4(2)
N(8)-C(36)-C(37)	123.0(2)
N(8)-C(36)-C(35)	114.8(2)
C(37)-C(36)-C(35)	122.2(2)

C(36)-C(37)-C(38)	118.5(3)
C(36)-C(37)-H(37A)	120.8
C(38)-C(37)-H(37A)	120.8
C(39)-C(38)-C(37)	119.5(3)
C(39)-C(38)-H(38A)	120.2
C(37)-C(38)-H(38A)	120.2
C(38)-C(39)-C(40)	119.3(3)
C(38)-C(39)-H(39A)	120.4
C(40)-C(39)-H(39A)	120.4
O(4)-C(40)-N(8)	115.1(2)
O(4)-C(40)-C(39)	122.2(2)
N(8)-C(40)-C(39)	122.7(2)
N(9)-C(41)-C(42)	123.3(3)
N(9)-C(41)-H(41A)	118.4
C(42)-C(41)-H(41A)	118.4
C(41)-C(42)-C(43)	119.4(3)
C(41)-C(42)-H(42A)	120.3
C(43)-C(42)-H(42A)	120.3
C(42)-C(43)-C(44)	118.5(3)
C(42)-C(43)-H(43A)	120.8
C(44)-C(43)-H(43A)	120.8
C(45)-C(44)-C(43)	120.0(3)
C(45)-C(44)-H(44A)	120.0
C(43)-C(44)-H(44A)	120.0
N(9)-C(45)-C(44)	121.4(2)
N(9)-C(45)-C(46)	114.5(2)
C(44)-C(45)-C(46)	124.1(2)
N(10)-C(46)-C(47)	121.1(2)
N(10)-C(46)-C(45)	115.3(2)
C(47)-C(46)-C(45)	123.6(2)
C(48)-C(47)-C(46)	119.5(3)
C(48)-C(47)-H(47A)	120.2
C(46)-C(47)-H(47A)	120.2
C(49)-C(48)-C(47)	118.9(2)
C(49)-C(48)-H(48A)	120.5
C(47)-C(48)-H(48A)	120.5

C(50)-C(49)-C(48)	118.9(3)
C(50)-C(49)-H(49A)	120.6
C(48)-C(49)-H(49A)	120.6
N(10)-C(50)-C(49)	122.5(3)
N(10)-C(50)-H(50A)	118.7
C(49)-C(50)-H(50A)	118.7
N(11)-C(51)-C(52)	121.9(3)
N(11)-C(51)-H(51A)	119.1
C(52)-C(51)-H(51A)	119.1
C(53)-C(52)-C(51)	119.5(3)
C(53)-C(52)-H(52A)	120.3
C(51)-C(52)-H(52A)	120.3
C(52)-C(53)-C(54)	119.0(3)
C(52)-C(53)-H(53A)	120.5
C(54)-C(53)-H(53A)	120.5
C(53)-C(54)-C(55)	119.9(3)
C(53)-C(54)-H(54A)	120.1
C(55)-C(54)-H(54A)	120.1
N(11)-C(55)-C(54)	120.7(3)
N(11)-C(55)-C(56)	114.7(2)
C(54)-C(55)-C(56)	124.7(2)
N(12)-C(56)-C(57)	121.7(3)
N(12)-C(56)-C(55)	114.6(2)
C(57)-C(56)-C(55)	123.6(2)
C(58)-C(57)-C(56)	119.1(3)
C(58)-C(57)-H(57A)	120.5
C(56)-C(57)-H(57A)	120.5
C(57)-C(58)-C(59)	119.5(3)
C(57)-C(58)-H(58A)	120.2
C(59)-C(58)-H(58A)	120.2
C(60)-C(59)-C(58)	118.7(3)
C(60)-C(59)-H(59A)	120.6
C(58)-C(59)-H(59A)	120.6
N(12)-C(60)-C(59)	123.1(3)
N(12)-C(60)-H(60A)	118.4
C(59)-C(60)-H(60A)	118.4

C(63)-O(5)-C(62)	111.9(2)
C(62)-C(61)-H(61A)	109.5
C(62)-C(61)-H(61B)	109.5
H(61A)-C(61)-H(61B)	109.5
C(62)-C(61)-H(61C)	109.5
H(61A)-C(61)-H(61C)	109.5
H(61B)-C(61)-H(61C)	109.5
O(5)-C(62)-C(61)	108.9(3)
O(5)-C(62)-H(62A)	109.9
C(61)-C(62)-H(62A)	109.9
O(5)-C(62)-H(62B)	109.9
C(61)-C(62)-H(62B)	109.9
H(62A)-C(62)-H(62B)	108.3
O(5)-C(63)-C(64)	108.5(3)
O(5)-C(63)-H(63A)	110.0
C(64)-C(63)-H(63A)	110.0
O(5)-C(63)-H(63B)	110.0
C(64)-C(63)-H(63B)	110.0
H(63A)-C(63)-H(63B)	108.4
C(63)-C(64)-H(64A)	109.5
C(63)-C(64)-H(64B)	109.5
H(64A)-C(64)-H(64B)	109.5
C(63)-C(64)-H(64C)	109.5
H(64A)-C(64)-H(64C)	109.5
H(64B)-C(64)-H(64C)	109.5
C(67)-O(6)-C(66)	125.3(9)
C(65)-C(66)-O(6)	107.3(11)
C(65)-C(66)-H(66A)	110.2
O(6)-C(66)-H(66A)	110.2
C(65)-C(66)-H(66B)	110.2
O(6)-C(66)-H(66B)	110.2
H(66A)-C(66)-H(66B)	108.5
O(6)-C(67)-C(68)	118.6(8)
O(6)-C(67)-H(67A)	107.7
C(68)-C(67)-H(67A)	107.7
O(6)-C(67)-H(67B)	107.7

C(68)-C(67)-H(67B)	107.7
H(67A)-C(67)-H(67B)	107.1
C(67')-O(6')-C(66')	123.8(15)
C(66')-C(65')-H(65D)	109.5
C(66')-C(65')-H(65E)	109.5
H(65D)-C(65')-H(65E)	109.5
C(66')-C(65')-H(65F)	109.5
H(65D)-C(65')-H(65F)	109.5
H(65E)-C(65')-H(65F)	109.5
C(65')-C(66')-O(6')	113.6(16)
C(65')-C(66')-H(66C)	108.8
O(6')-C(66')-H(66C)	108.8
C(65')-C(66')-H(66D)	108.8
O(6')-C(66')-H(66D)	108.8
H(66C)-C(66')-H(66D)	107.7
O(6')-C(67')-C(68')	115.5(11)
O(6')-C(67')-H(67C)	108.4
C(68')-C(67')-H(67C)	108.4
O(6')-C(67')-H(67D)	108.4
C(68')-C(67')-H(67D)	108.4
H(67C)-C(67')-H(67D)	107.5
C(67')-C(68')-H(68D)	109.5
C(67')-C(68')-H(68E)	109.5
H(68D)-C(68')-H(68E)	109.5
C(67')-C(68')-H(68F)	109.5
H(68D)-C(68')-H(68F)	109.5
H(68E)-C(68')-H(68F)	109.5
C(71)-O(7)-C(70)	114.2(3)
C(70)-C(69)-H(69A)	109.5
C(70)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(70)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
O(7)-C(70)-C(69)	112.9(3)
O(7)-C(70)-H(70A)	109.0

C(69)-C(70)-H(70A)	109.0
O(7)-C(70)-H(70B)	109.0
C(69)-C(70)-H(70B)	109.0
H(70A)-C(70)-H(70B)	107.8
O(7)-C(71)-C(72)	109.6(3)
O(7)-C(71)-H(71A)	109.8
C(72)-C(71)-H(71A)	109.8
O(7)-C(71)-H(71B)	109.8
C(72)-C(71)-H(71B)	109.8
H(71A)-C(71)-H(71B)	108.2
C(71)-C(72)-H(72A)	109.5
C(71)-C(72)-H(72B)	109.5
H(72A)-C(72)-H(72B)	109.5
C(71)-C(72)-H(72C)	109.5
H(72A)-C(72)-H(72C)	109.5
H(72B)-C(72)-H(72C)	109.5
C(74)-O(8)-C(75)	112.7(8)
O(8)-C(74)-C(73)	110.1(10)
O(8)-C(74)-H(74A)	109.6
C(73)-C(74)-H(74A)	109.6
O(8)-C(74)-H(74B)	109.6
C(73)-C(74)-H(74B)	109.6
H(74A)-C(74)-H(74B)	108.1
O(8)-C(75)-C(76)	112.0(9)
O(8)-C(75)-H(75A)	109.2
C(76)-C(75)-H(75A)	109.2
O(8)-C(75)-H(75B)	109.2
C(76)-C(75)-H(75B)	109.2
H(75A)-C(75)-H(75B)	107.9
C(75')-O(8')-C(74')	119.3(16)
C(74')-C(73')-H(73D)	109.5
C(74')-C(73')-H(73E)	109.5
H(73D)-C(73')-H(73E)	109.5
C(74')-C(73')-H(73F)	109.5
H(73D)-C(73')-H(73F)	109.5
H(73E)-C(73')-H(73F)	109.5

O(8')-C(74')-C(73')	110.0(16)
O(8')-C(74')-H(74C)	109.7
C(73')-C(74')-H(74C)	109.7
O(8')-C(74')-H(74D)	109.7
C(73')-C(74')-H(74D)	109.7
H(74C)-C(74')-H(74D)	108.2
O(8')-C(75')-C(76')	114.2(15)
O(8')-C(75')-H(75C)	108.7
C(76')-C(75')-H(75C)	108.7
O(8')-C(75')-H(75D)	108.7
C(76')-C(75')-H(75D)	108.7
H(75C)-C(75')-H(75D)	107.6
C(75')-C(76')-H(76D)	109.5
C(75')-C(76')-H(76E)	109.5
H(76D)-C(76')-H(76E)	109.5
C(75')-C(76')-H(76F)	109.5
H(76D)-C(76')-H(76F)	109.5
H(76E)-C(76')-H(76F)	109.5
C(78)-C(77)-C(82)	120.0
C(78)-C(77)-H(77)	120.0
C(82)-C(77)-H(77)	120.0
C(77)-C(78)-C(79)	120.0
C(77)-C(78)-H(78)	120.0
C(79)-C(78)-H(78)	120.0
C(78)-C(79)-C(80)	120.0
C(78)-C(79)-H(79)	120.0
C(80)-C(79)-H(79)	120.0
C(79)-C(80)-C(81)	120.0
C(79)-C(80)-C(83)	119.9(6)
C(81)-C(80)-C(83)	120.0(7)
C(82)-C(81)-C(80)	120.0
C(82)-C(81)-H(81)	120.0
C(80)-C(81)-H(81)	120.0
C(81)-C(82)-C(77)	120.0
C(81)-C(82)-H(82)	120.0
C(77)-C(82)-H(82)	120.0

N(13)-C(83)-C(80)	178(2)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for paul017. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	20(1)	14(1)	6(1)	2(1)	5(1)
Ru(2)	13(1)	20(1)	14(1)	7(1)	2(1)	6(1)
N(1)	19(1)	22(1)	15(1)	6(1)	4(1)	6(1)
N(2)	16(1)	22(1)	16(1)	6(1)	3(1)	3(1)
N(3)	15(1)	21(1)	16(1)	5(1)	2(1)	4(1)
N(4)	16(1)	23(1)	18(1)	9(1)	2(1)	4(1)
N(5)	21(1)	21(1)	15(1)	7(1)	2(1)	9(1)
N(6)	18(1)	18(1)	17(1)	7(1)	2(1)	7(1)
N(7)	14(1)	23(1)	14(1)	8(1)	3(1)	6(1)
N(8)	14(1)	20(1)	17(1)	7(1)	3(1)	6(1)
N(9)	17(1)	19(1)	17(1)	9(1)	3(1)	6(1)
N(10)	15(1)	19(1)	15(1)	6(1)	2(1)	7(1)
N(11)	15(1)	23(1)	16(1)	8(1)	3(1)	7(1)
N(12)	17(1)	21(1)	18(1)	10(1)	5(1)	8(1)
O(1)	32(1)	28(1)	21(1)	7(1)	-3(1)	15(1)
O(2)	20(1)	36(1)	25(1)	3(1)	-3(1)	14(1)
O(3)	21(1)	40(1)	26(1)	4(1)	-1(1)	18(1)
O(4)	23(1)	27(1)	22(1)	6(1)	-3(1)	13(1)
P(1)	20(1)	33(1)	26(1)	13(1)	4(1)	8(1)
F(1)	26(1)	40(1)	37(1)	13(1)	0(1)	15(1)
F(2)	43(1)	75(2)	25(1)	18(1)	11(1)	28(1)
F(3)	50(1)	35(1)	56(1)	22(1)	27(1)	23(1)
F(4)	45(1)	75(2)	37(1)	32(1)	22(1)	20(1)
F(5)	47(1)	34(1)	74(2)	11(1)	5(1)	-2(1)
F(6)	26(1)	95(2)	54(1)	36(1)	9(1)	27(1)
P(2)	26(1)	32(1)	23(1)	7(1)	2(1)	12(1)
F(7)	25(1)	46(1)	37(1)	12(1)	6(1)	13(1)
F(8)	52(1)	102(2)	72(2)	62(2)	32(1)	35(1)
F(9)	49(1)	37(1)	60(2)	-8(1)	9(1)	11(1)
F(10)	95(2)	120(2)	52(1)	59(2)	40(1)	76(2)
F(11)	37(1)	47(1)	91(2)	-18(1)	-10(1)	10(1)

F(12)	33(1)	76(2)	48(1)	11(1)	7(1)	31(1)
P(3)	32(1)	30(1)	25(1)	8(1)	0(1)	8(1)
F(13)	35(1)	58(1)	67(2)	26(1)	-13(1)	13(1)
F(14)	62(2)	100(2)	28(1)	-5(1)	4(1)	47(2)
F(15)	43(1)	36(1)	64(1)	21(1)	19(1)	13(1)
F(16)	86(2)	109(2)	35(1)	22(1)	26(1)	-16(2)
F(17)	68(2)	39(1)	115(2)	34(2)	-21(2)	-2(1)
F(18)	34(1)	51(1)	77(2)	13(1)	14(1)	18(1)
P(4)	41(1)	67(1)	25(1)	2(1)	2(1)	21(1)
F(19)	60(2)	81(2)	58(2)	9(1)	-6(1)	43(1)
F(20)	56(1)	54(1)	56(1)	13(1)	4(1)	28(1)
F(21)	63(2)	62(2)	42(1)	3(1)	19(1)	20(1)
F(22)	67(2)	82(2)	54(2)	-24(1)	21(1)	15(1)
F(23)	81(2)	100(2)	64(2)	1(2)	30(2)	-9(2)
F(24)	86(2)	111(3)	87(2)	55(2)	-37(2)	11(2)
C(1)	24(1)	27(1)	21(1)	11(1)	7(1)	10(1)
C(2)	38(2)	40(2)	25(1)	12(1)	7(1)	23(2)
C(3)	55(2)	38(2)	29(2)	8(1)	11(2)	30(2)
C(4)	42(2)	30(2)	24(1)	5(1)	4(1)	18(2)
C(5)	26(1)	22(1)	17(1)	7(1)	7(1)	8(1)
C(6)	21(1)	22(1)	17(1)	9(1)	7(1)	5(1)
C(7)	31(2)	24(1)	15(1)	5(1)	6(1)	5(1)
C(8)	27(1)	26(2)	17(1)	8(1)	2(1)	2(1)
C(9)	21(1)	28(2)	21(1)	12(1)	0(1)	4(1)
C(10)	16(1)	24(1)	21(1)	9(1)	4(1)	4(1)
C(11)	21(1)	22(1)	17(1)	8(1)	3(1)	4(1)
C(12)	24(1)	29(2)	18(1)	8(1)	6(1)	3(1)
C(13)	26(2)	39(2)	23(1)	10(1)	10(1)	7(1)
C(14)	29(2)	32(2)	24(1)	10(1)	14(1)	13(1)
C(15)	17(1)	24(1)	18(1)	5(1)	2(1)	5(1)
C(16)	18(1)	26(1)	20(1)	8(1)	4(1)	7(1)
C(17)	28(2)	33(2)	33(2)	11(1)	11(1)	13(1)
C(18)	40(2)	35(2)	50(2)	19(2)	18(2)	24(2)
C(19)	32(2)	33(2)	51(2)	24(2)	15(2)	15(1)
C(20)	23(1)	28(2)	30(2)	14(1)	7(1)	10(1)
C(21)	24(1)	27(1)	18(1)	10(1)	5(1)	6(1)

C(22)	32(2)	32(2)	20(1)	12(1)	9(1)	8(1)
C(23)	30(2)	29(2)	26(1)	10(1)	14(1)	7(1)
C(24)	23(1)	27(2)	28(1)	10(1)	9(1)	8(1)
C(25)	19(1)	20(1)	20(1)	7(1)	6(1)	7(1)
C(26)	17(1)	20(1)	20(1)	6(1)	4(1)	6(1)
C(27)	18(1)	27(2)	28(1)	10(1)	4(1)	5(1)
C(28)	18(1)	26(2)	24(1)	7(1)	-4(1)	4(1)
C(29)	24(1)	24(1)	18(1)	6(1)	-1(1)	7(1)
C(30)	23(1)	22(1)	15(1)	5(1)	2(1)	7(1)
C(31)	17(1)	28(1)	18(1)	10(1)	5(1)	8(1)
C(32)	15(1)	33(2)	22(1)	14(1)	1(1)	5(1)
C(33)	22(1)	28(2)	19(1)	10(1)	0(1)	2(1)
C(34)	22(1)	22(1)	17(1)	7(1)	1(1)	2(1)
C(35)	15(1)	23(1)	16(1)	9(1)	4(1)	3(1)
C(36)	15(1)	21(1)	18(1)	8(1)	4(1)	5(1)
C(37)	25(1)	25(1)	23(1)	4(1)	3(1)	10(1)
C(38)	29(2)	26(2)	30(2)	3(1)	7(1)	15(1)
C(39)	22(1)	27(2)	29(1)	10(1)	4(1)	12(1)
C(40)	16(1)	24(1)	19(1)	9(1)	2(1)	7(1)
C(41)	21(1)	27(1)	18(1)	10(1)	4(1)	7(1)
C(42)	28(2)	30(2)	20(1)	11(1)	8(1)	7(1)
C(43)	24(1)	34(2)	24(1)	14(1)	13(1)	11(1)
C(44)	18(1)	27(2)	27(1)	11(1)	7(1)	7(1)
C(45)	16(1)	19(1)	20(1)	9(1)	4(1)	7(1)
C(46)	16(1)	21(1)	21(1)	9(1)	4(1)	8(1)
C(47)	16(1)	26(1)	26(1)	10(1)	3(1)	5(1)
C(48)	18(1)	24(1)	25(1)	6(1)	-2(1)	4(1)
C(49)	24(1)	22(1)	18(1)	4(1)	0(1)	8(1)
C(50)	20(1)	22(1)	18(1)	5(1)	3(1)	8(1)
C(51)	21(1)	22(1)	20(1)	8(1)	4(1)	7(1)
C(52)	29(2)	27(2)	23(1)	12(1)	9(1)	8(1)
C(53)	29(2)	32(2)	27(1)	12(1)	13(1)	8(1)
C(54)	26(1)	32(2)	25(1)	11(1)	12(1)	14(1)
C(55)	16(1)	23(1)	18(1)	7(1)	4(1)	6(1)
C(56)	18(1)	24(1)	19(1)	8(1)	4(1)	8(1)
C(57)	33(2)	32(2)	28(2)	12(1)	14(1)	18(1)

C(58)	46(2)	36(2)	43(2)	21(2)	21(2)	28(2)
C(59)	43(2)	34(2)	47(2)	26(2)	24(2)	24(2)
C(60)	25(1)	30(2)	27(1)	17(1)	10(1)	11(1)
O(5)	22(1)	38(1)	29(1)	10(1)	1(1)	14(1)
C(61)	56(2)	70(3)	41(2)	30(2)	15(2)	35(2)
C(62)	35(2)	61(2)	30(2)	12(2)	-6(1)	19(2)
C(63)	22(2)	42(2)	50(2)	21(2)	7(1)	14(1)
C(64)	43(2)	76(3)	52(2)	37(2)	20(2)	32(2)
O(6)	29(3)	60(4)	67(3)	20(3)	-5(2)	29(3)
C(65)	66(5)	77(9)	82(4)	-5(6)	32(4)	11(7)
C(66)	24(3)	40(4)	86(4)	15(3)	5(3)	14(3)
C(67)	48(3)	57(4)	65(4)	16(3)	8(3)	24(3)
C(68)	118(8)	97(9)	40(5)	28(5)	32(5)	79(7)
O(6')	41(4)	36(4)	53(3)	13(3)	8(3)	19(3)
C(65')	51(6)	30(6)	66(5)	9(4)	25(5)	7(5)
C(66')	27(4)	47(5)	65(4)	8(4)	12(4)	16(4)
C(67')	49(4)	57(5)	57(4)	13(3)	-4(3)	35(4)
C(68')	80(8)	33(6)	43(6)	17(5)	-3(5)	22(6)
O(7)	37(1)	44(1)	33(1)	14(1)	2(1)	21(1)
C(69)	73(3)	80(3)	53(2)	38(2)	26(2)	51(3)
C(70)	49(2)	55(2)	52(2)	31(2)	14(2)	23(2)
C(71)	45(2)	69(3)	65(3)	30(2)	17(2)	33(2)
C(72)	49(2)	51(2)	63(3)	22(2)	19(2)	19(2)
O(8)	30(2)	54(2)	31(3)	5(2)	3(2)	26(2)
C(73)	66(4)	42(3)	52(3)	12(3)	33(3)	18(3)
C(74)	58(3)	62(4)	42(4)	10(3)	16(3)	32(3)
C(75)	46(5)	67(4)	33(3)	11(3)	-1(3)	28(4)
C(76)	66(8)	67(7)	48(7)	23(6)	12(5)	29(5)
O(8')	43(4)	59(4)	32(4)	7(3)	5(3)	21(4)
C(73')	57(5)	53(6)	48(6)	16(5)	18(4)	24(5)
C(74')	51(4)	60(5)	35(4)	0(4)	8(4)	28(4)
C(75')	35(5)	61(5)	35(4)	7(4)	8(4)	26(4)
C(76')	46(8)	50(8)	30(6)	2(5)	5(6)	22(6)
C(77)	35(5)	52(10)	51(9)	32(8)	8(6)	15(7)
C(78)	42(4)	52(5)	33(3)	18(3)	9(3)	24(4)
C(79)	47(5)	49(5)	41(4)	26(4)	17(4)	34(4)

C(80)	48(5)	50(5)	36(4)	20(4)	18(4)	28(4)
C(81)	34(4)	50(5)	38(4)	30(4)	10(3)	23(4)
C(82)	42(4)	51(4)	45(4)	28(4)	17(3)	27(4)
C(83)	67(7)	48(6)	42(5)	17(4)	6(5)	27(5)
N(13)	122(10)	65(7)	67(7)	17(5)	-12(6)	45(7)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for paul017.

	x	y	z	U(eq)
H(1)	-4127(16)	8315(6)	7402(11)	42
H(2)	160(20)	7713(2)	9531(10)	44
H(3)	10160(20)	7422(2)	4480(9)	46
H(4)	5719(18)	8169(5)	2700(8)	38
H(2A)	-4079	9708	8177	39
H(3A)	-3256	10812	9378	47
H(4A)	-2067	10609	10176	40
H(7A)	-1067	10289	10873	30
H(8A)	229	10002	11433	31
H(9A)	644	8859	10716	29
H(11A)	-1903	8814	7682	25
H(12A)	-992	9000	6872	30
H(13A)	-243	7981	6473	36
H(14A)	-471	6775	6875	33
H(17A)	-774	5677	7291	37
H(18A)	-974	4676	7926	45
H(19A)	-1792	4842	8842	42
H(20A)	-2401	5971	9088	31
H(21A)	-2198	7838	10312	28
H(22A)	-3162	7577	11066	33
H(23A)	-4745	6796	10480	34
H(24A)	-5318	6322	9144	31
H(27A)	-5757	5995	7895	31
H(28A)	-6062	5470	6555	31
H(29A)	-4822	5623	6023	28
H(30A)	-3336	6437	6825	26
H(32A)	10844	8673	5587	29
H(33A)	10591	9922	6322	30
H(34A)	9243	10203	5869	26
H(37A)	8040	10396	5396	31

H(38A)	6696	10565	4766	35
H(39A)	5783	9501	3578	31
H(41A)	7841	7726	5377	27
H(42A)	6858	7628	6135	31
H(43A)	5262	6908	5558	31
H(44A)	4710	6303	4215	28
H(47A)	4301	5760	2967	28
H(48A)	3971	5269	1625	29
H(49A)	5198	5522	1080	28
H(50A)	6683	6357	1877	25
H(51A)	8139	8685	2764	25
H(52A)	8895	8789	1837	31
H(53A)	9484	7683	1306	34
H(54A)	9291	6484	1714	31
H(57A)	9051	5407	2164	35
H(58A)	8838	4381	2769	43
H(59A)	8123	4583	3755	42
H(60A)	7637	5790	4103	30
H(61A)	4602	8497	896	76
H(61B)	5365	8412	1526	76
H(61C)	4957	9199	1758	76
H(62A)	3503	8167	1550	54
H(62B)	3906	7374	1308	54
H(63A)	3609	6940	2388	44
H(63B)	3113	7672	2530	44
H(64A)	3606	7420	3670	76
H(64B)	4107	8428	3776	76
H(64C)	4651	7739	3637	76
H(65A)	1835	7062	3254	127
H(65B)	917	7234	3408	127
H(65C)	1060	6317	3372	127
H(66A)	2085	8003	4555	64
H(66B)	2357	7134	4499	64
H(67A)	1704	6587	5333	70
H(67B)	848	5915	4619	70
H(68A)	437	5899	5667	111

H(68B)	-125	6418	5305	111
H(68C)	767	6958	6032	111
H(65D)	1764	6817	3184	77
H(65E)	769	6733	3315	77
H(65F)	1325	6144	3568	77
H(66C)	1883	8008	4242	59
H(66D)	2454	7428	4488	59
H(67C)	1991	7632	5848	67
H(67D)	1926	6705	5250	67
H(68D)	1031	6838	6228	81
H(68E)	707	5998	5445	81
H(68F)	274	6769	5502	81
H(69A)	5627	9649	5545	88
H(69B)	4619	9003	5439	88
H(69C)	5432	8610	5333	88
H(70A)	6217	9385	6639	58
H(70B)	5415	9793	6748	58
H(71A)	3781	8285	6042	67
H(71B)	4084	8969	6910	67
H(72A)	3056	7587	6780	80
H(72B)	4040	7799	7356	80
H(72C)	3757	7114	6493	80
H(73A)	1549	7041	8099	79
H(73B)	2015	7999	8768	79
H(73C)	914	7557	8457	79
H(74A)	1052	6408	8921	64
H(74B)	2124	6989	9329	64
H(75A)	1425	7684	10891	61
H(75B)	1946	7064	10481	61
H(76A)	637	6220	10721	88
H(76B)	531	5905	9821	88
H(76C)	-15	6525	10185	88
H(73D)	2466	7202	8482	78
H(73E)	2828	7394	9378	78
H(73F)	2536	8119	9102	78
H(74C)	996	7110	8570	62

H(74D)	1310	6445	8924	62
H(75C)	1762	7826	10821	53
H(75D)	2093	7089	10312	53
H(76D)	955	6549	10926	67
H(76E)	709	5997	10028	67
H(76F)	214	6698	10326	67
H(77)	4665	7954	8903	52
H(78)	3735	8737	8559	49
H(79)	4025	10202	9347	47
H(81)	6177	10100	10825	43
H(82)	5887	8635	10036	48

Table S11. Hydrogen bonds for paul017 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(7)#1	0.67	1.95	2.609(3)	168.4
O(2)-H(2)...O(8)	0.77	1.85	2.601(14)	166.0
O(2)-H(2)...O(8')	0.77	1.88	2.62(3)	161.3
O(3)-H(3)...O(6)#2	0.76	1.82	2.567(7)	166.4
O(3)-H(3)...O(6')#2	0.76	1.87	2.629(14)	177.1
O(4)-H(4)...O(5)	0.66	2.03	2.649(3)	156.5

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

$[Ru(bpy)_2(66'bpy(O^-)_2)]$ (paul020s)

Table S12. Crystal data and structure refinement for paul020s.

Identification code	paul020s	
Empirical formula	C33 H28.50 N6.50 O2.50 Ru	
Formula weight	657.19	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4108(7) Å	⟨= 84.343(4)°.
	b = 12.2807(9) Å	®= 88.748(4)°.
	c = 13.0032(10) Å	© = 73.877(4)°.
Volume	1436.63(19) $Å^3$	
Z	2	
Density (calculated)	1.519 Mg/m^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	672	
Crystal size	0.18 x 0.18 x 0.10 mm^3	
Theta range for data collection	1.57 to 31.79°.	
Index ranges	-13<=h<=13, -18<=k<=18, -19<=l<=16	
Reflections collected	26434	
Independent reflections	9615 [R(int) = 0.0293]	
Completeness to theta = 31.79°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9433 and 0.9011	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9615 / 0 / 352	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0854	
R indices (all data)	R1 = 0.0478, wR2 = 0.0889	
Largest diff. peak and hole	0.778 and -0.513 $e.Å^{-3}$	

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for paul020s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	6297(1)	6956(1)	7186(1)	20(1)
N(1)	8278(2)	7184(2)	6560(1)	29(1)
N(2)	7647(2)	5272(1)	7219(1)	23(1)
N(3)	6843(2)	6995(1)	8692(1)	22(1)
N(4)	4497(2)	6630(1)	7946(1)	20(1)
N(5)	5559(2)	7010(1)	5704(1)	22(1)
N(6)	4998(2)	8600(1)	6948(1)	26(1)
O(1)	7728(2)	9108(1)	6621(1)	44(1)
O(2)	5984(2)	4383(1)	7982(1)	28(1)
C(1)	8561(2)	8225(2)	6306(2)	37(1)
C(2)	9844(3)	8217(3)	5649(2)	49(1)
C(3)	10741(3)	7244(3)	5347(2)	50(1)
C(4)	10497(2)	6209(2)	5692(2)	42(1)
C(5)	9283(2)	6211(2)	6312(1)	31(1)
C(6)	9012(2)	5145(2)	6784(1)	30(1)
C(7)	10078(2)	4104(2)	6829(2)	40(1)
C(8)	9745(2)	3147(2)	7333(2)	42(1)
C(9)	8389(2)	3248(2)	7743(2)	36(1)
C(10)	7264(2)	4314(2)	7659(1)	26(1)
C(11)	8062(2)	7239(2)	9021(2)	30(1)
C(12)	8375(2)	7228(2)	10054(2)	31(1)
C(13)	7406(2)	6942(2)	10794(1)	29(1)
C(14)	6149(2)	6706(2)	10472(1)	25(1)
C(15)	5884(2)	6740(2)	9418(1)	20(1)
C(16)	4563(2)	6537(1)	8992(1)	20(1)
C(17)	3463(2)	6259(2)	9608(1)	24(1)
C(18)	2248(2)	6080(2)	9140(2)	27(1)
C(19)	2158(2)	6210(2)	8068(2)	29(1)
C(20)	3292(2)	6483(2)	7499(1)	24(1)
C(21)	5918(2)	6148(2)	5096(1)	26(1)
C(22)	5411(2)	6264(2)	4088(1)	30(1)

C(23)	4496(2)	7288(2)	3680(2)	33(1)
C(24)	4107(2)	8183(2)	4290(1)	30(1)
C(25)	4647(2)	8025(2)	5302(1)	23(1)
C(26)	4316(2)	8913(2)	6012(1)	26(1)
C(27)	3381(2)	9995(2)	5758(2)	34(1)
C(28)	3143(3)	10771(2)	6480(2)	42(1)
C(29)	3831(3)	10448(2)	7437(2)	44(1)
C(30)	4739(3)	9372(2)	7644(2)	38(1)

Table S14. Bond lengths [Å] and angles [°] for paul020s.

Ru(1)-N(3)	2.0439(14)
Ru(1)-N(6)	2.0467(16)
Ru(1)-N(5)	2.0511(14)
Ru(1)-N(4)	2.0567(15)
Ru(1)-N(1)	2.0969(15)
Ru(1)-N(2)	2.1020(16)
N(1)-C(5)	1.364(3)
N(1)-C(1)	1.384(3)
N(2)-C(6)	1.367(2)
N(2)-C(10)	1.391(3)
N(3)-C(11)	1.351(2)
N(3)-C(15)	1.365(2)
N(4)-C(20)	1.348(2)
N(4)-C(16)	1.356(2)
N(5)-C(21)	1.347(2)
N(5)-C(25)	1.364(2)
N(6)-C(30)	1.345(3)
N(6)-C(26)	1.359(2)
O(1)-C(1)	1.249(3)
O(2)-C(10)	1.251(2)
C(1)-C(2)	1.462(3)
C(2)-C(3)	1.346(4)
C(3)-C(4)	1.384(4)
C(4)-C(5)	1.383(3)
C(5)-C(6)	1.475(3)
C(6)-C(7)	1.385(3)
C(7)-C(8)	1.398(3)
C(8)-C(9)	1.350(3)
C(9)-C(10)	1.433(3)
C(11)-C(12)	1.379(3)
C(12)-C(13)	1.397(3)
C(13)-C(14)	1.378(2)
C(14)-C(15)	1.391(2)
C(15)-C(16)	1.465(2)

C(16)-C(17)	1.391(2)
C(17)-C(18)	1.387(2)
C(18)-C(19)	1.389(3)
C(19)-C(20)	1.383(3)
C(21)-C(22)	1.385(3)
C(22)-C(23)	1.376(3)
C(23)-C(24)	1.381(3)
C(24)-C(25)	1.397(2)
C(25)-C(26)	1.461(3)
C(26)-C(27)	1.387(3)
C(27)-C(28)	1.374(3)
C(28)-C(29)	1.385(3)
C(29)-C(30)	1.364(3)

N(3)-Ru(1)-N(6)	97.35(6)
N(3)-Ru(1)-N(5)	174.74(6)
N(6)-Ru(1)-N(5)	78.47(6)
N(3)-Ru(1)-N(4)	78.63(6)
N(6)-Ru(1)-N(4)	85.43(6)
N(5)-Ru(1)-N(4)	97.75(6)
N(3)-Ru(1)-N(1)	95.85(6)
N(6)-Ru(1)-N(1)	99.00(7)
N(5)-Ru(1)-N(1)	88.00(6)
N(4)-Ru(1)-N(1)	173.38(6)
N(3)-Ru(1)-N(2)	89.79(6)
N(6)-Ru(1)-N(2)	172.49(6)
N(5)-Ru(1)-N(2)	94.53(6)
N(4)-Ru(1)-N(2)	98.34(6)
N(1)-Ru(1)-N(2)	77.83(7)
C(5)-N(1)-C(1)	119.57(17)
C(5)-N(1)-Ru(1)	114.88(13)
C(1)-N(1)-Ru(1)	125.28(15)
C(6)-N(2)-C(10)	119.27(16)
C(6)-N(2)-Ru(1)	115.51(13)
C(10)-N(2)-Ru(1)	125.21(12)
C(11)-N(3)-C(15)	118.14(15)

C(11)-N(3)-Ru(1)	125.71(12)
C(15)-N(3)-Ru(1)	116.15(11)
C(20)-N(4)-C(16)	118.03(15)
C(20)-N(4)-Ru(1)	126.09(12)
C(16)-N(4)-Ru(1)	115.86(11)
C(21)-N(5)-C(25)	117.83(15)
C(21)-N(5)-Ru(1)	125.98(13)
C(25)-N(5)-Ru(1)	116.17(12)
C(30)-N(6)-C(26)	118.11(18)
C(30)-N(6)-Ru(1)	125.58(14)
C(26)-N(6)-Ru(1)	116.28(13)
O(1)-C(1)-N(1)	120.16(19)
O(1)-C(1)-C(2)	123.5(2)
N(1)-C(1)-C(2)	116.4(2)
C(3)-C(2)-C(1)	121.8(2)
C(2)-C(3)-C(4)	120.1(2)
C(5)-C(4)-C(3)	118.3(2)
N(1)-C(5)-C(4)	123.2(2)
N(1)-C(5)-C(6)	114.98(16)
C(4)-C(5)-C(6)	121.8(2)
N(2)-C(6)-C(7)	122.4(2)
N(2)-C(6)-C(5)	114.71(18)
C(7)-C(6)-C(5)	122.81(18)
C(6)-C(7)-C(8)	118.9(2)
C(9)-C(8)-C(7)	119.6(2)
C(8)-C(9)-C(10)	121.6(2)
O(2)-C(10)-N(2)	121.08(17)
O(2)-C(10)-C(9)	121.01(19)
N(2)-C(10)-C(9)	117.90(18)
N(3)-C(11)-C(12)	122.52(18)
C(11)-C(12)-C(13)	119.09(17)
C(14)-C(13)-C(12)	119.09(17)
C(13)-C(14)-C(15)	119.27(17)
N(3)-C(15)-C(14)	121.87(15)
N(3)-C(15)-C(16)	114.40(14)
C(14)-C(15)-C(16)	123.71(16)

N(4)-C(16)-C(17)	122.24(15)
N(4)-C(16)-C(15)	114.80(15)
C(17)-C(16)-C(15)	122.96(15)
C(18)-C(17)-C(16)	119.17(16)
C(17)-C(18)-C(19)	118.58(17)
C(20)-C(19)-C(18)	119.45(17)
N(4)-C(20)-C(19)	122.47(16)
N(5)-C(21)-C(22)	122.50(18)
C(23)-C(22)-C(21)	119.74(19)
C(22)-C(23)-C(24)	118.81(17)
C(23)-C(24)-C(25)	119.33(19)
N(5)-C(25)-C(24)	121.78(17)
N(5)-C(25)-C(26)	114.29(15)
C(24)-C(25)-C(26)	123.93(18)
N(6)-C(26)-C(27)	122.12(18)
N(6)-C(26)-C(25)	114.77(17)
C(27)-C(26)-C(25)	123.12(18)
C(28)-C(27)-C(26)	118.7(2)
C(27)-C(28)-C(29)	119.1(2)
C(30)-C(29)-C(28)	119.7(2)
N(6)-C(30)-C(29)	122.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for paul020s. The anisotropic displacement factor exponent takes the form: $-2\rho^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	18(1)	32(1)	13(1)	-5(1)	0(1)	-10(1)
N(1)	24(1)	52(1)	16(1)	-1(1)	-1(1)	-20(1)
N(2)	17(1)	38(1)	15(1)	-7(1)	-2(1)	-6(1)
N(3)	20(1)	32(1)	16(1)	-6(1)	0(1)	-9(1)
N(4)	17(1)	25(1)	17(1)	-5(1)	-1(1)	-5(1)
N(5)	19(1)	33(1)	15(1)	-3(1)	1(1)	-11(1)
N(6)	29(1)	29(1)	21(1)	-4(1)	2(1)	-11(1)
O(1)	45(1)	48(1)	46(1)	14(1)	-12(1)	-29(1)
O(2)	30(1)	32(1)	20(1)	-4(1)	4(1)	-8(1)
C(1)	32(1)	54(1)	28(1)	12(1)	-10(1)	-23(1)
C(2)	43(1)	77(2)	35(1)	23(1)	-12(1)	-38(1)
C(3)	28(1)	96(2)	27(1)	6(1)	-2(1)	-25(1)
C(4)	24(1)	84(2)	21(1)	-9(1)	2(1)	-20(1)
C(5)	18(1)	65(1)	15(1)	-10(1)	-2(1)	-15(1)
C(6)	18(1)	54(1)	19(1)	-16(1)	-1(1)	-10(1)
C(7)	19(1)	63(2)	37(1)	-21(1)	0(1)	-4(1)
C(8)	29(1)	45(1)	50(1)	-19(1)	-8(1)	0(1)
C(9)	33(1)	36(1)	37(1)	-9(1)	-11(1)	-4(1)
C(10)	26(1)	36(1)	14(1)	-8(1)	-6(1)	-4(1)
C(11)	25(1)	48(1)	22(1)	-8(1)	0(1)	-17(1)
C(12)	27(1)	49(1)	24(1)	-12(1)	-4(1)	-16(1)
C(13)	30(1)	41(1)	17(1)	-8(1)	-5(1)	-9(1)
C(14)	26(1)	31(1)	18(1)	-4(1)	-1(1)	-8(1)
C(15)	19(1)	25(1)	16(1)	-4(1)	-1(1)	-6(1)
C(16)	18(1)	23(1)	16(1)	-5(1)	-1(1)	-4(1)
C(17)	21(1)	32(1)	17(1)	-3(1)	2(1)	-7(1)
C(18)	19(1)	38(1)	26(1)	-3(1)	3(1)	-10(1)
C(19)	18(1)	45(1)	25(1)	-6(1)	-1(1)	-10(1)
C(20)	19(1)	35(1)	18(1)	-4(1)	-2(1)	-8(1)
C(21)	25(1)	36(1)	20(1)	-6(1)	0(1)	-11(1)
C(22)	32(1)	42(1)	19(1)	-8(1)	0(1)	-15(1)

C(23)	36(1)	51(1)	18(1)	0(1)	-6(1)	-23(1)
C(24)	30(1)	40(1)	22(1)	4(1)	-6(1)	-17(1)
C(25)	20(1)	33(1)	20(1)	0(1)	0(1)	-13(1)
C(26)	24(1)	32(1)	24(1)	-1(1)	3(1)	-13(1)
C(27)	34(1)	35(1)	32(1)	3(1)	3(1)	-9(1)
C(28)	45(1)	30(1)	47(1)	-1(1)	10(1)	-6(1)
C(29)	57(2)	35(1)	38(1)	-12(1)	12(1)	-11(1)
C(30)	52(1)	38(1)	27(1)	-10(1)	4(1)	-14(1)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for paul020s.

	x	y	z	U(eq)
H(2A)	10050	8918	5429	59
H(3A)	11542	7268	4896	60
H(4A)	11146	5515	5507	50
H(7A)	11019	4042	6522	48
H(8A)	10469	2429	7387	51
H(9A)	8175	2597	8095	43
H(11A)	8729	7426	8521	36
H(12A)	9236	7411	10259	38
H(13A)	7613	6912	11510	35
H(14A)	5469	6521	10963	30
H(17A)	3544	6191	10340	28
H(18A)	1493	5874	9544	33
H(19A)	1325	6112	7729	35
H(20A)	3219	6570	6767	29
H(21A)	6541	5433	5369	31
H(22A)	5695	5639	3681	36
H(23A)	4138	7379	2991	39
H(24A)	3479	8899	4025	36
H(27A)	2915	10195	5099	41
H(28A)	2514	11520	6325	51
H(29A)	3671	10972	7946	52
H(30A)	5204	9161	8302	46

Computational Methods

Structure

The structures of both $[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$ and $[Ru(bpy)_2(66'bpy(O^-)_2)]$ were also studied through computational methods in the gas phase. Selected bond lengths and angles are reported in Table 1. All of the Ru-N bond lengths are overestimated by approximately 0.04 to 0.06 Å compared to the crystal structure data, similar to other ruthenium polypyridyl complexes.[7] The structure is a distorted octahedron with Ru-N bond lengths for the 6,6'-hydroxy-substituted ligand that are longer than the Ru-N bond lengths for the unsubstituted ligands in all cases and in accordance with the crystal structure. The theoretical data predicts that the Ru-N bond lengths for the 6,6'-hydroxy-substituted ligand will decrease by ~ 0.07 Å upon deprotonation of the complex. The decrease in bond length upon deprotonation is not observed in the experimental crystal structure. In addition, from simple bond order analysis, there is a slight increase in the bond order between the metal and $66'bpy(O^-)_2$ ligand that occurs upon deprotonation of the complex (0.4 to 0.5), which helps to explain why photo-dissociation is much slower once deprotonated (see below). The theoretical C-O bond lengths decrease upon deprotonation from 1.347 Å and 1.346 Å to 1.247 Å and 1.248 Å, which is in accordance with the crystal structure data.

$[Ru(bpy)_2(66'bpy(OH)_2)]^{2+}$

Nuclear Repulsion Energy (a.u.) = -1705.510299

Total Energy (a.u.) = 4816.556905

Max. Gradient = 0.000361 hartree/bohr RMS Gradient = 0.000116 hartree/bohr

Number of Imaginary Frequencies = 0

C_1 symmetry

Nuclear Coordinates (Ångstroms)

RU	44.0	7.3030648272	9.5549795520	6.3566713761
N	7.0	8.4832210289	10.4330406972	7.9334011349
N	7.0	6.2049342362	11.3646296113	6.8409602622
N	7.0	5.9705967948	8.5333705726	7.6146312118
N	7.0	5.9815811218	8.7130757477	4.9804146146
N	7.0	8.6219630584	10.3783320278	4.9586449306
N	7.0	8.4767567859	7.9046983876	5.8704996550
O	8.0	10.1578880641	8.8946880390	7.7992710299
O	8.0	4.7133779496	11.1725871262	5.1363211596
C	6.0	9.6679966748	9.9955753653	8.4002837142
C	6.0	10.3615608497	10.6235454138	9.4452228181
C	6.0	9.8118062472	11.7564254245	10.0195751022
C	6.0	8.5916488193	12.2332970163	9.5407261405
C	6.0	7.9489338027	11.5571073593	8.5041648243
C	6.0	6.6625613408	12.0279790992	7.9460297352
C	6.0	5.9679792338	13.1030600210	8.4988990265
C	6.0	4.7886078974	13.5422457446	7.8966305269
C	6.0	4.3439366555	12.9060032967	6.7509817750
C	6.0	5.0850147519	11.8229651170	6.2548883178
C	6.0	6.0196188470	8.5124039310	8.9599081482
C	6.0	5.0879490593	7.8359169496	9.7399542062
C	6.0	4.0547164947	7.1498812333	9.1014187016
C	6.0	3.9963683467	7.1662604575	7.7098214523
C	6.0	4.9646818617	7.8654210155	6.9814965084
C	6.0	4.9920217979	7.9400724409	5.5069341318
C	6.0	4.0755720384	7.2799120526	4.6811281012
C	6.0	4.1727960024	7.4119072476	3.2983245038
C	6.0	5.1884040090	8.2093555353	2.7701458398
C	6.0	6.0670308867	8.8400682602	3.6456261524
C	6.0	8.6574282828	11.6688199825	4.5785055123
C	6.0	9.5762700255	12.1576492994	3.6556206235
C	6.0	10.5027688130	11.2737660201	3.1023678553

C	6.0	10.4747944102	9.9375369962	3.4935859083
C	6.0	9.5256120698	9.5072088122	4.4264995765
C	6.0	9.4175283035	8.1165247442	4.9097373098
C	6.0	10.2194648579	7.0698140966	4.4463554751
C	6.0	10.0629795329	5.7917244207	4.9771547519
C	6.0	9.1032541730	5.5886972275	5.9673402646
C	6.0	8.3337497852	6.6704975594	6.3809561772
H	1.0	11.0106257053	8.6556640035	8.2003997368
H	1.0	3.9073858052	11.5793017944	4.7750816471
H	1.0	11.3124090628	10.2236896360	9.7855824711
H	1.0	10.3253392746	12.2695434786	10.8265556571
H	1.0	8.1651897494	13.1298021777	9.9690182678
H	1.0	6.3265366267	13.6002504124	9.3899365727
H	1.0	4.2337565788	14.3758581276	8.3156943872
H	1.0	3.4405001164	13.2267227910	6.2401355619
H	1.0	6.8416687488	9.0551932192	9.4109038463
H	1.0	5.1760720319	7.8502176766	10.8212445525
H	1.0	3.3070816552	6.6102033243	9.6741674112
H	1.0	3.1981336017	6.6397608216	7.1999154589
H	1.0	3.2941173777	6.6626127045	5.1097499357
H	1.0	3.4688958589	6.9011022810	2.6480749914
H	1.0	5.3040034251	8.3448118053	1.6998038996
H	1.0	6.8605126612	9.4796205401	3.2779939713
H	1.0	7.9155597288	12.3131199838	5.0351976636
H	1.0	9.5611549599	13.2070280462	3.3819384860
H	1.0	11.2358147141	11.6169979046	2.3790532705
H	1.0	11.1926828480	9.2397221428	3.0790264036
H	1.0	10.9600119711	7.2441750827	3.6748233684
H	1.0	10.6790912013	4.9722497682	4.6222991114
H	1.0	8.9456265162	4.6125937994	6.4137660548
H	1.0	7.5789900436	6.5598345766	7.1494287175

[Ru(bpy)$_2$(66'bpy(O$^-$)$_2$)]

Nuclear Repulsion Energy (a.u.) = -1704.211323

Total Energy (a.u.) = 4761.500132

Max. Gradient = 0.000100 hartree/bohr RMS Gradient = 0.000021 hartree/bohr

Number of Imaginary Frequencies = 0

C_1 symmetry

Nuclear Coordinates (Ångstroms)

RU	44.0	8.5001620788	9.0595792488	9.2189350226
N	7.0	10.3773400059	9.2561019274	8.3776583080
N	7.0	9.2104941138	7.1038400582	9.2983234386
N	7.0	9.1424310325	9.2729197506	11.2213174470
N	7.0	6.7020693283	8.7931231890	10.2936941434
N	7.0	7.6789897907	9.0057396603	7.3117279697
N	7.0	7.8102696374	11.0363036600	9.0040925969
O	8.0	10.1238103916	11.3569731046	7.4618319931
O	8.0	7.2391398838	6.0442817725	9.8204565538
C	6.0	10.8627228153	10.4072672765	7.7047049834
C	6.0	12.2706725102	10.4209691057	7.2883706351
C	6.0	13.0619875681	9.3172229147	7.4374465245
C	6.0	12.5004063876	8.1570340758	8.0178643414
C	6.0	11.1694664819	8.1619392977	8.4643729524
C	6.0	10.5210929617	6.9623002150	9.0136672734
C	6.0	11.2086519391	5.7484938674	9.2010600665
C	6.0	10.5253772736	4.6230415096	9.7070166359
C	6.0	9.1873842675	4.7317146703	9.9782844252
C	6.0	8.4626892207	5.9782498030	9.7163164937
C	6.0	10.4003418827	9.5519761586	11.6128731863
C	6.0	10.7588241171	9.6919246799	12.9488437468
C	6.0	9.7733502434	9.5323938667	13.9233278313
C	6.0	8.4695970407	9.2479537213	13.5242804493
C	6.0	8.1684166674	9.1234009943	12.1639526804
C	6.0	6.8116305399	8.8505240462	11.6466268582
C	6.0	5.6945138090	8.6643909132	12.4662073058
C	6.0	4.4498634959	8.4246358889	11.8886780601
C	6.0	4.3499949814	8.3770534574	10.4997086547
C	6.0	5.5014811777	8.5626158191	9.7410901941
C	6.0	7.6698615652	7.9254173322	6.5060070369
C	6.0	7.1213036588	7.9505224033	5.2297237900
C	6.0	6.5678233310	9.1441235743	4.7641683891

C	6.0	6.5779461704	10.2641172770	5.5923161173
C	6.0	7.1390616800	10.1789753093	6.8699218820
C	6.0	7.1904313570	11.3032108767	7.8238784804
C	6.0	6.6576703669	12.5668668701	7.5616408336
C	6.0	6.7728011675	13.5746790629	8.5170725382
C	6.0	7.4160556002	13.2913360259	9.7197746951
C	6.0	7.9157310246	12.0079944584	9.9228588455
H	1.0	12.6203957360	11.3390625762	6.8275962092
H	1.0	14.0959634302	9.3132411217	7.1063096894
H	1.0	13.1076616527	7.2646793507	8.1040012043
H	1.0	12.2656864853	5.6728965130	8.9810285748
H	1.0	11.0594377574	3.6923561058	9.8732025303
H	1.0	8.5962274847	3.9058948120	10.3600880616
H	1.0	11.1295975527	9.6775074866	10.8218621265
H	1.0	11.7852699638	9.9236455222	13.2123778044
H	1.0	10.0124063501	9.6330146773	14.9776052741
H	1.0	7.6940887370	9.1279750474	14.2710730601
H	1.0	5.7877599339	8.7040378819	13.5447815647
H	1.0	3.5759944008	8.2760183383	12.5152541352
H	1.0	3.4030500598	8.1897958886	10.0050115739
H	1.0	5.4734608590	8.5092632978	8.6600196283
H	1.0	8.1091477187	7.0247539494	6.9160657883
H	1.0	7.1289069337	7.0529782719	4.6204938597
H	1.0	6.1326692190	9.2040027401	3.7714380162
H	1.0	6.1552493978	11.1972229974	5.2400183543
H	1.0	6.1605741680	12.7716273366	6.6210903831
H	1.0	6.3671389042	14.5623354151	8.3212449070
H	1.0	7.5330913491	14.0442777173	10.4918175465
H	1.0	8.4230050176	11.7453271647	10.8432229552

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