Transient photocyclization in Ruthenium (II) polypyridine Complexes of indolamines

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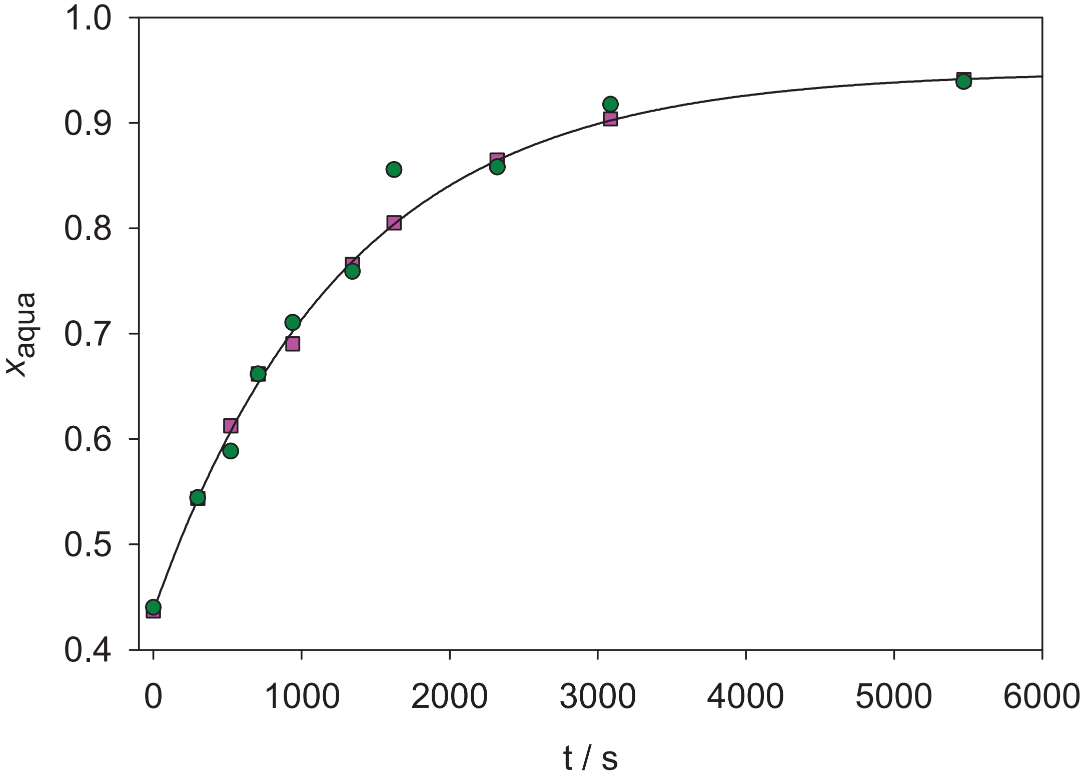


Figure S1. Dark decay of a sample of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ UV-Vis (circles, green) and NMR (squares, pink) immediately after irradiation in D_2O and after 300,520,710,940,1620,2320 and 5470 seconds. Factor analysis performed independently over the ^{1}H-NMR and UV-vis spectra reveal the presence of at most two "colored" species. Integration of the ^{1}H-NMR peaks allows establishing the relative amounts of $Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ and $Ru(55dmb)_2(5MT)]^{2+}$. The molar absorbance for the colored complexes was than deconvoluted by least square fitting employing the UV-Vis data and the concentration profiles. The full line represents the best both experimental sets. UV-Vis data are depicted in Figure 3a. RMN data are depicted in Figure S2.

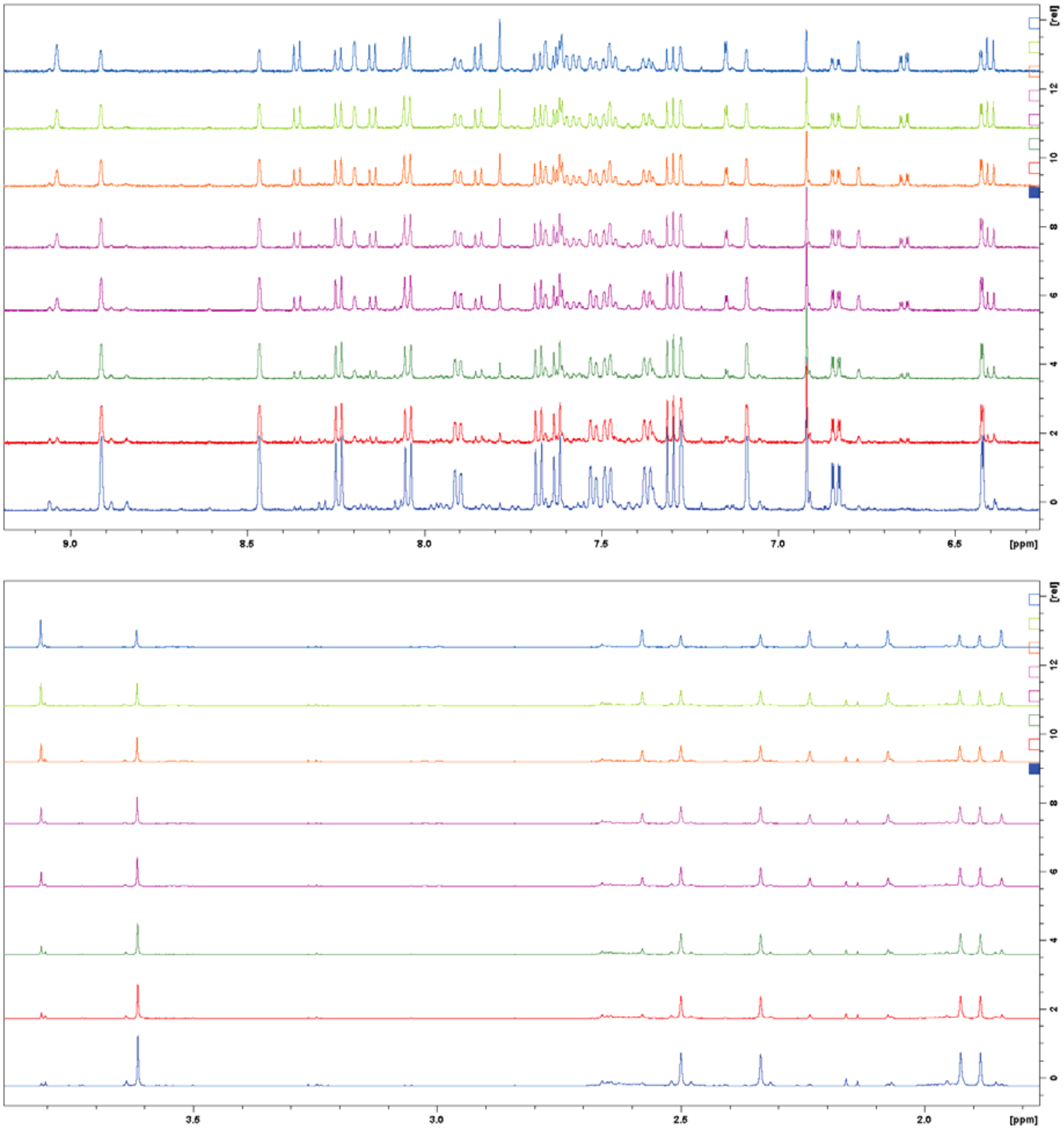


Figure S2. ^{1}H-RMN spectra of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ immediately after irradiation in D_2O (top) and at 300,520,710,940,1620,2320 and 5470 seconds. Initial photoconversion (x_0=0.56) into the bidentate complex $[Ru(55dmb)_2(5MT)]^{2+}$ was calculated by integration of the signals at 1.89, 3.61 and 6.77 ppm.

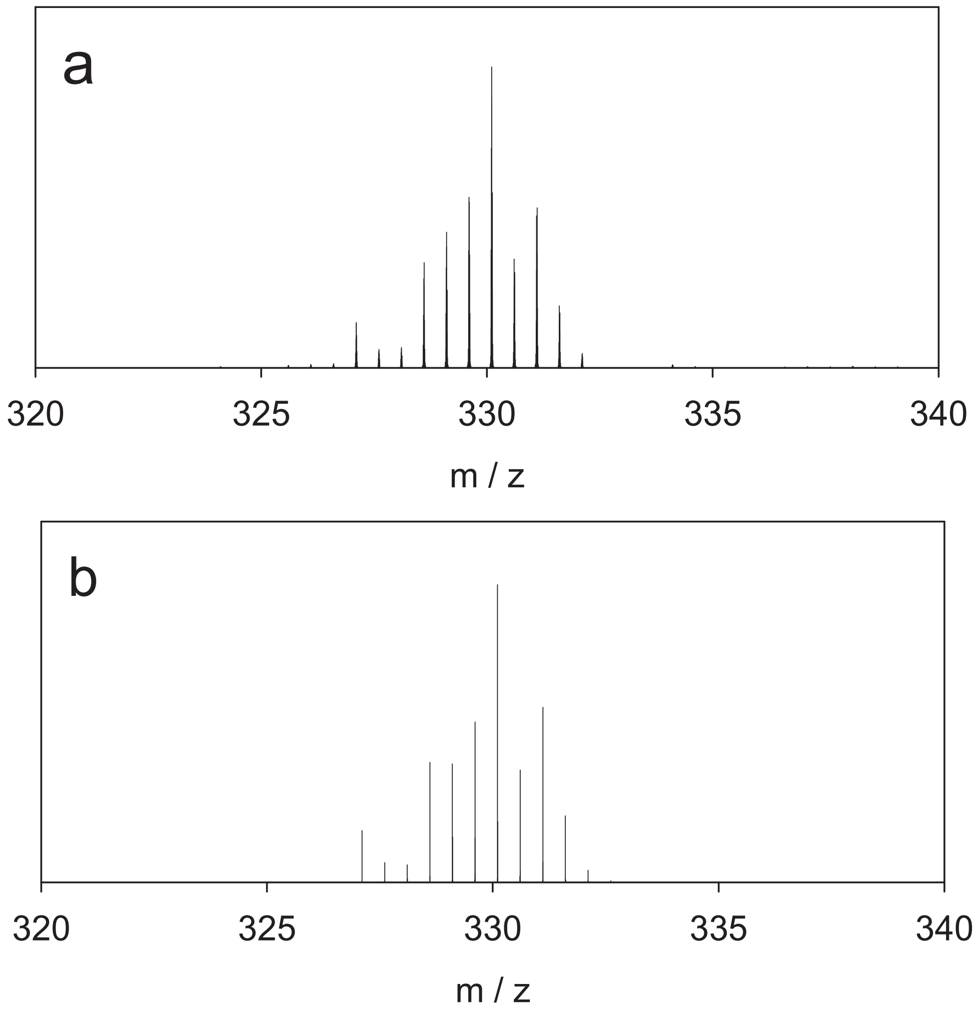


Figure S3. a) Experimental mass spectrum of [Ru(55dmb)$_2$(5MT)(H$_2$O)]$^{2+}$. b) simulated mass spectrum for [Ru(55dmb)$_2$(5MT)]$^{2+}$.

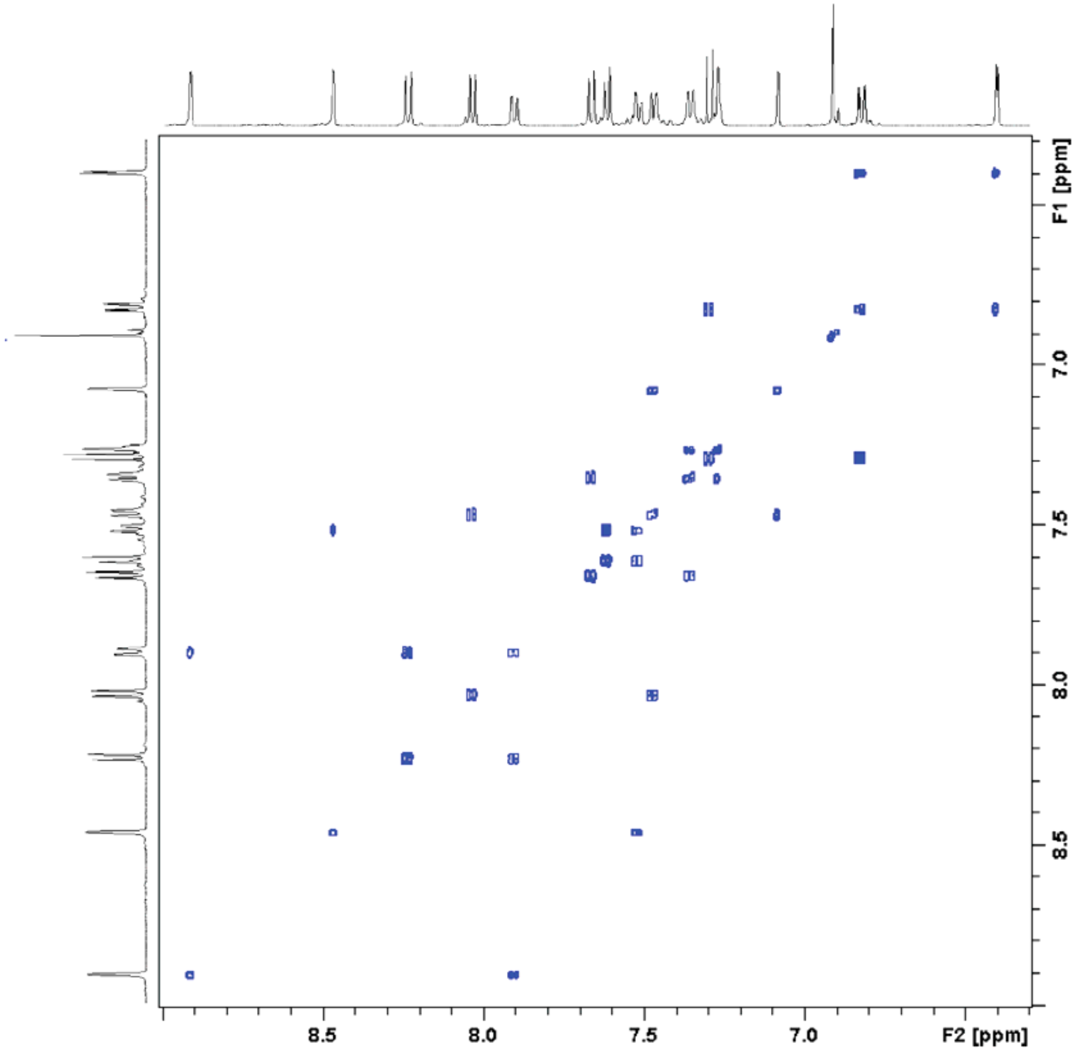


Figure S4. COSY spectrum of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ in D_2O.

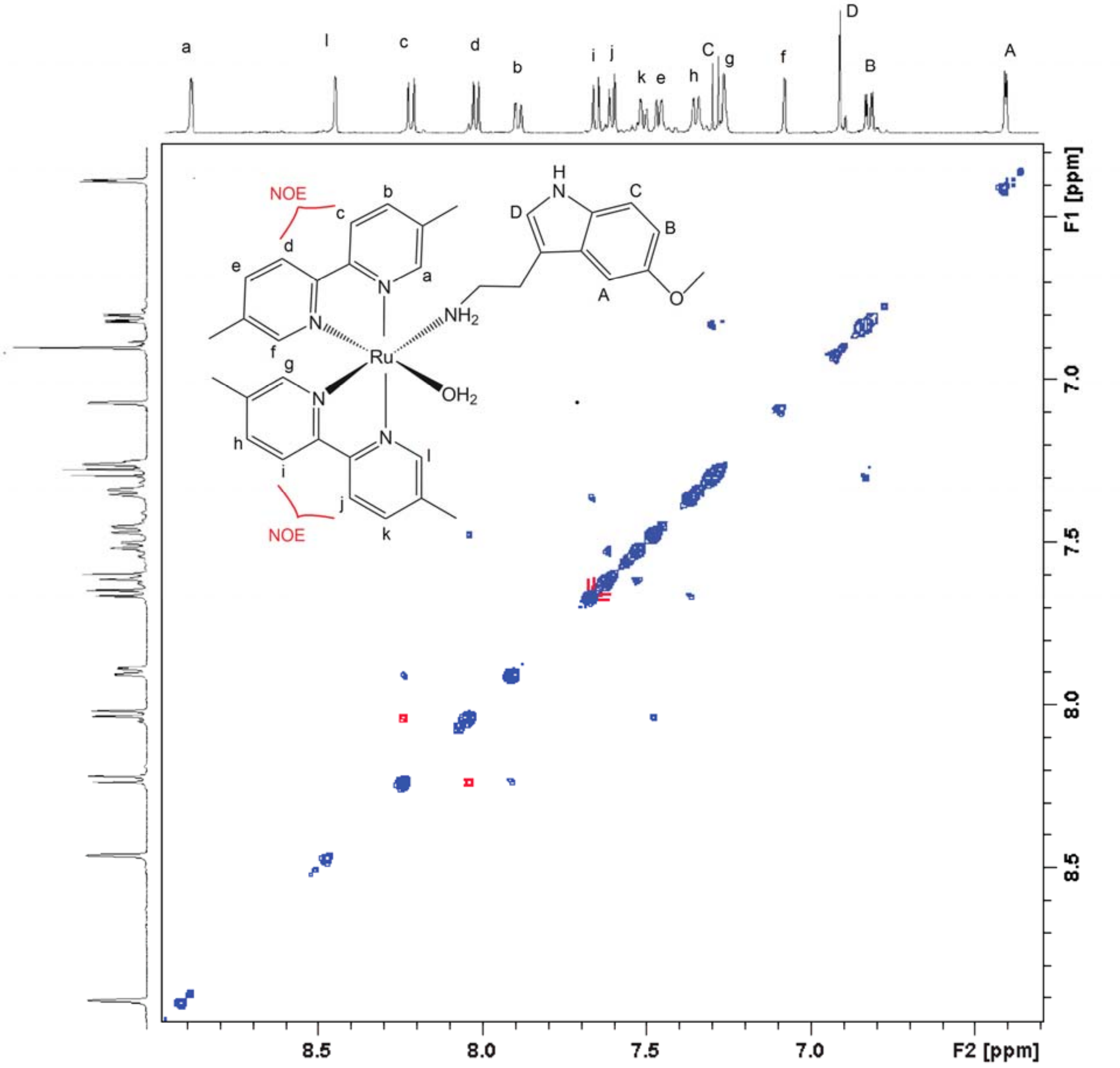


Figure S5. NOESY spectrum of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ in D_2O. NOE correlation is seen between spatially close hydrogens pairs c/d and j/i, but no NOE is apparent between bpy protons and any indolic hydrogen.

Derivation of Equation 2 (see main text).

$$\begin{tikzcd} A \arrow[r, shift left=2, "\varphi_{A\to B}"] & B \arrow[l, "\varphi_{B\to A}"] \arrow[l, shift left=2, "k"] \end{tikzcd}$$

$$\frac{dB}{dt} = I_{IRR}\varphi_{A\to B}\left(1-10^{-Abs_T}\right)\frac{Abs_A}{Abs_T} - I_{IRR}\varphi_{B\to A}\left(1-10^{-Abs_T}\right)\frac{Abs_B}{Abs_T} - k[B]$$

$$\lim_{Abs\to 0}(1-10^{-Abs}) = 2.3Abs = 2.3\varepsilon lc$$

$$\frac{dB}{dt} = I_{IRR}\varphi_{A\to B}2.3\varepsilon_A l[A] - I_{IRR}\varphi_{B\to A}2.3\varepsilon_B l[B] - k[B]$$

$$\frac{dB}{dt} = I_{IRR}2.3\left(\varphi_{A\to B}\varepsilon_A l[A] - \varphi_{B\to A}\varepsilon_B l[B]\right) - k[B]$$

In steady state

$$\frac{dB}{dt} = 0$$

$$[B]\left(I_{IRR}2.3\varphi_{B\to A}\varepsilon_B l + k\right) = [A]\left(I_{IRR}2.3\varphi_{A\to B}\varepsilon_A l\right)$$

$$\frac{[A]}{[B]} = \frac{I_{IRR}2.3\varphi_{B\to A}\varepsilon_B l}{I_{IRR}2.3\varphi_{A\to B}\varepsilon_A l} + \frac{k}{I_{IRR}2.3\varphi_{A\to B}\varepsilon_A l}$$

$$\frac{[A]}{[B]} = \frac{\varphi_{B\to A}\varepsilon_B}{\varphi_{A\to B}\varepsilon_A} + \frac{k}{2.3\varphi_{A\to B}\varepsilon_A l}\frac{1}{I_{IRR}}$$

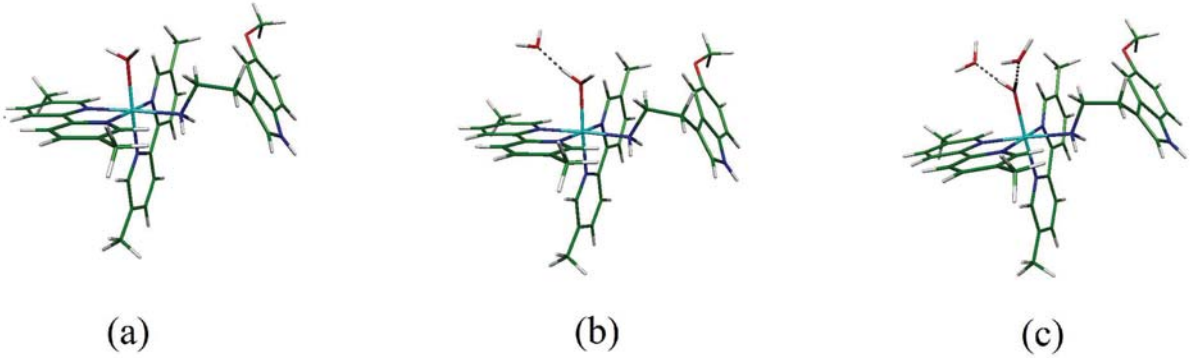
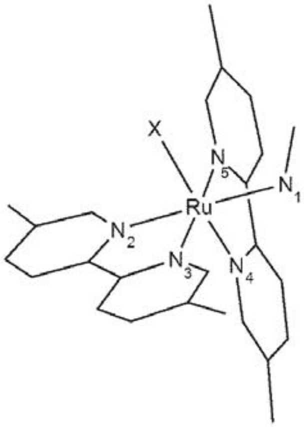


Figure S6. Comparative computed structures for $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ in the presence of explicit water molecules. a) no additional H_2O. b) one H_2O. c) two H_2O.

Table S1. Selected bondlengths (Å) (top) and Mayer Bond Order (bottom) for the DFT optimized structures of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ and $[Ru(55dmb)_2(5MT)]^{2+}$.



	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$ + H_2O	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$ + $2H_2O$	$Ru(Me_2bpy)_2(5MT)]^{2+}$
Ru-N_1	2.194	2.201	2.196	2.200
Ru-N_2	2.090	2.084	2.080	2.090
Ru-N_3	2.112	2.105	2.101	2.099
Ru-N_4	2.055	2.063	2.067	2.071
Ru-N_5	2.084	2.083	2.084	2.142
Ru-X	2.229 (X = O)	2.195 (X = O)	2.169 (X = O)	2.663 (X = C) 2.635 (X = C)

	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$ + H_2O	$Ru(Me_2bpy)_2(5MT)(H_2O)]^{2+}$ + $2H_2O$	$Ru(Me_2bpy)_2(5MT)]^{2+}$
Ru-N_1	0.381	0.371	0.378	0.398
Ru-N_2	0.456	0.460	0.460	0.435
Ru-N_3	0.386	0.388	0.388	0.388
Ru-N_4	0.542	0.515	0.496	0.498
Ru-N_5	0.402	0.398	0.392	0.367
Ru-X	0.286 (X = O)	0.333 (X = O)	0.388 (X = O)	0.271 (X = C) 0.261 (X = C)
C=C(η^2)	1.460	1.462	1.465	1.303

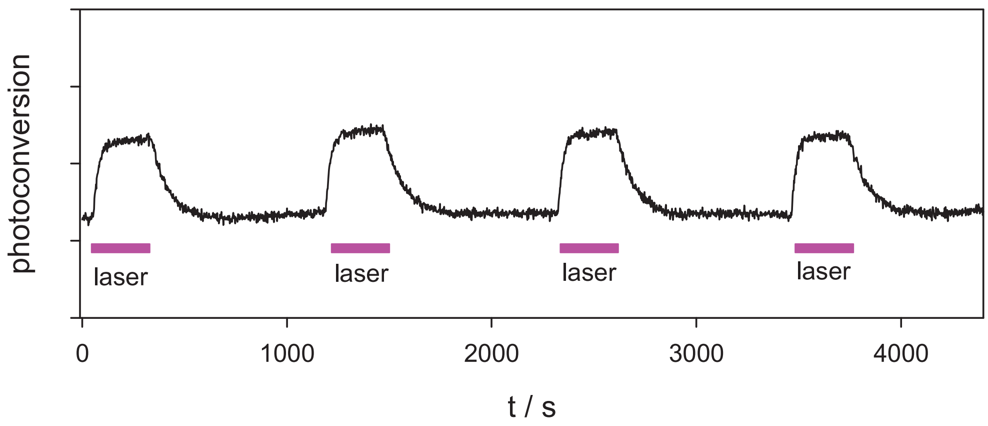


Figure S7. Photoconversion of $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ into $[Ru(55dmb)_2(5MT)(H_2O)]^{2+}$ followed by UV-Vis spectrometry. T ≅ 40 ºC, λ_{irr} = 405 nm, I_{irr} = 80 mW.