

Electronic Supplemental Information for:

Ligand-based Photooxidations of Dithiomaltolato Complexes of Ru(II) and Zn(II): Photolytic CH Activation and Evidence of Singlet Oxygen Generation and Quenching

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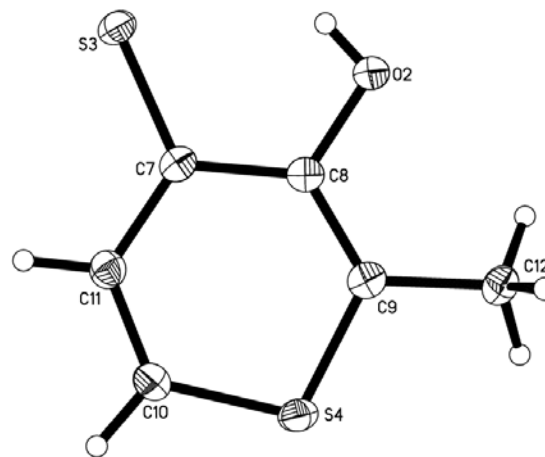
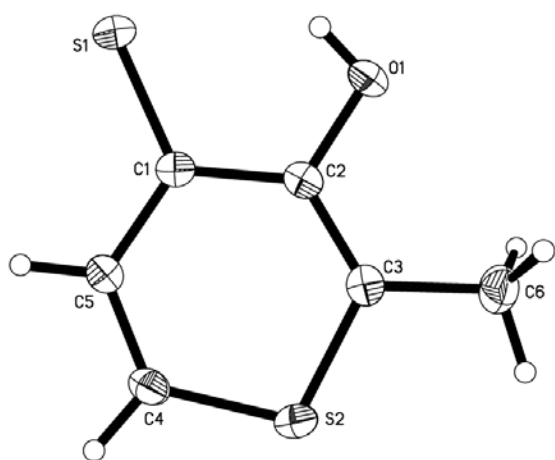
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SM1. Crystallographic Data for Httma

Table S1. Structural data for Httma, numbered as indicated in figure below, with two molecules re within the unit cell.

Bond	(Å)		
S(1)-C(1)	1.6900(16)	S(3)-C(7)	1.6901(16)
S(2)-C(4)	1.6903(19)	S(4)-C(10)	1.6892(18)
S(2)-C(3)	1.7110(17)	S(4)-C(9)	1.7094(17)
O(1)-C(2)	1.3544(19)	O(2)-C(8)	1.3550(19)
C(1)-C(5)	1.421(2)	C(7)-C(11)	1.422(2)
C(1)-C(2)	1.439(2)	C(7)-C(8)	1.441(2)
C(2)-C(3)	1.372(2)	C(8)-C(9)	1.371(2)
C(4)-C(5)	1.360(2)	C(10)-	1.356(2)
C(3)-C(6)	1.499(2)	C(11)	1.356(2)
		C(9)-C(12)	1.505(2)



SM2.Comparison of crystallographic data for ttma moiety

Scheme S2. ttma numbering

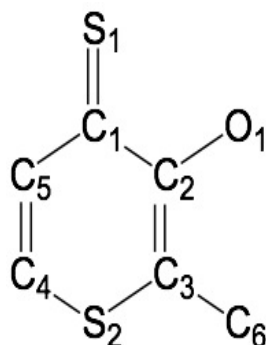


Table S2A. Comparison of ttma bond lengths

Bond	Httma		4		1
S(1)-C(1)	1.6900(16)	1.6901(16)	1.732(3)	1.720(3)	1.70832
S(2)-C(4)	1.6903(19)	1.6892(18)	1.679(3)	1.679(3)	1.68526
S(2)-C(3)	1.7110(17)	1.7094(17)	1.686(3)	1.695(3)	1.69077
O(1)-C(2)	1.3544(19)	1.3550(19)	1.309(3)	1.301(3)	1.29534
C(1)-C(5)	1.421(2)	1.422(2)	1.410(4)	1.411(4)	1.42183
C(1)-C(2)	1.439(2)	1.441(2)	1.440(4)	1.452(4)	1.44574
C(2)-C(3)	1.372(2)	1.371(2)	1.409(4)	1.398(4)	1.40207
C(3)-C(6)	1.499(2)	1.505(2)	1.503(4)	1.500(4)	1.51495
C(4)-C(5)	1.360(2)	1.356(2)	1.374(4)	1.360(5)	1.33729

Table S2B. Statistical comparison of ring C-C bond lengths in ttma moieties.

	Httma	1	4
Total Values	8	4	8
Mean	1.39775	1.40173	1.40675
Standard deviation	0.03635	0.04652	0.03052
Variance	0.00132	0.00216	0.00093

Mean (M) = sum of X values / n (number of values); standard deviation (SD) = $(\sum(X-M)^2/n-1)^{1/2}$;
variance = (SD)²

SM3. Photolytic dissociation of compound 1 at room temperature

Photolysis of $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ in H_2O . Photolysis of $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ in H_2O but in the absence of an electron transfer agent at room temperature leads to displacement of the ttma ligand to form the $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^+$ complex, detected by UV-vis and ESI-MS analysis. This is not an unusual behavior for $\text{Ru}(\text{diimine})_2$ complexes and there are several reports in the literature where these complexes form similar $\text{Ru}(\text{II})$ -aqua species in the presence of water (Figure S3).^{1,2,3}

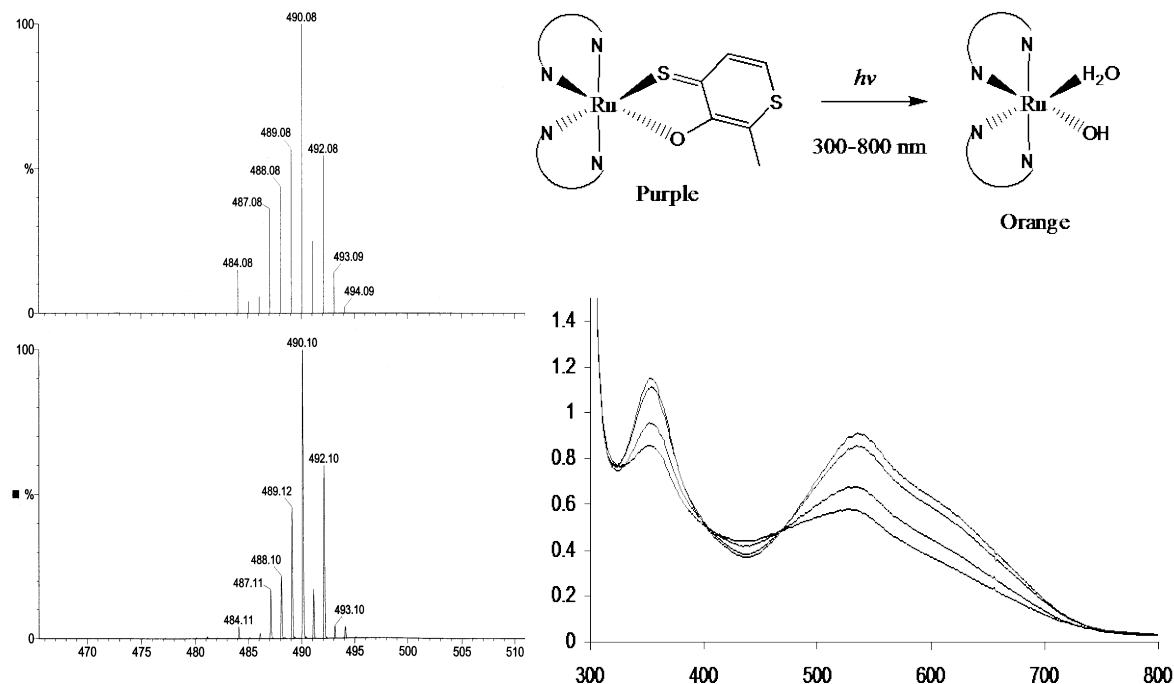


Figure S3. (Right) Sequential electronic spectrum of $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ during photolysis in CH_3CN and in the presence of H_2O . (Left) ESI-MS studies of $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ after photolysis (in the presence of H_2O) shows the formation of $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})]^+$ $m/z = 490$.

¹ Petroni, A.; Slep, L. D.; Etchenique, R. *Inorg. Chem.* **2008**, *47*, 951-956.

² Hurst, J. K. *Coord. Chem. Rev.* **2005**, *249*, 313-328.

³ Zhang, H.; Rajesh, C. S.; Dutta, P. K. *J. Phys. Chem. A.* **2008**, *112*, 808-817

SM4. ^1H NMR comparison of compounds **1**, **3** and **4**.

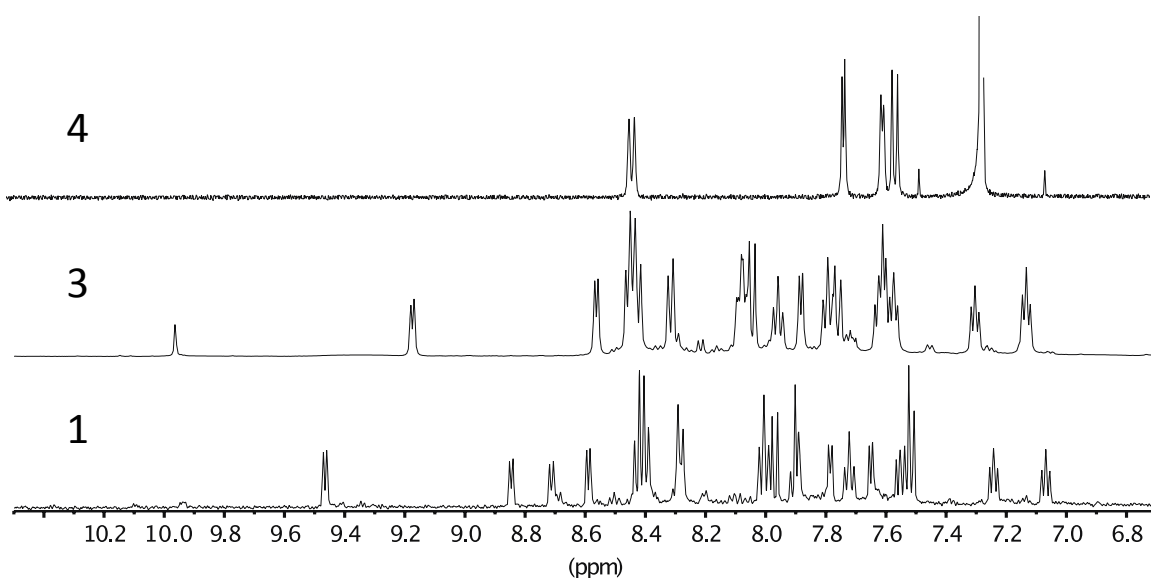


Figure S4. ^1H NMR of complex **1**, **3** and **4** recorded in CD_3CN at room temp. Spectrum of **3** is as isolated from flash-quench oxidation of **1** using $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, and is identical to that determined for **3** isolated from dark oxidations of **1** using DDQ and IBX.

Table S4. NMR Peak Assignments

Complex	H1	H2	H avg
Ru*tma	7.65	7.29	7.47
1	7.97	7.52	7.745
2	-	-	-
3	8.05	7.76	7.905
4	7.71	7.59	7.65
4	8.41	7.55	7.98

SM5. MS analysis of soluble products obtained after photo-oxidations of 4.

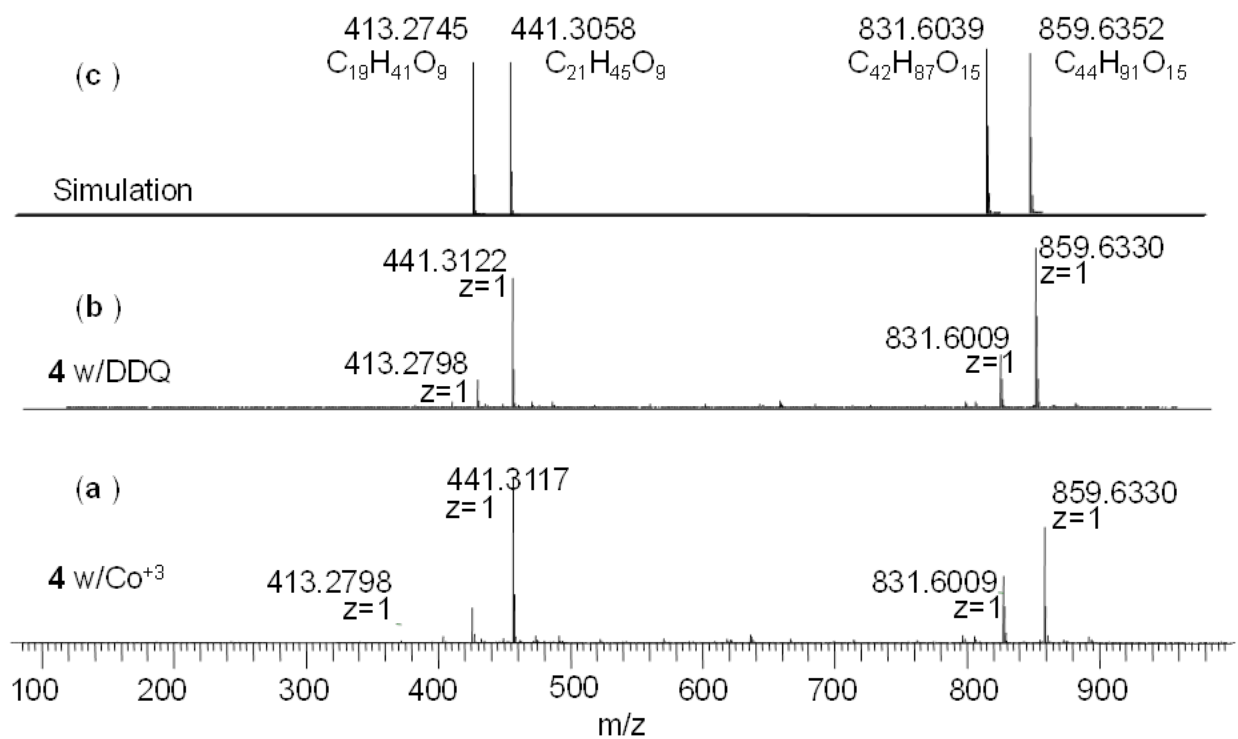


Figure S5. Direct infusion mass spectra of **4** photolyzed in presence of Co(NH₃)₅Cl₃ (a), DDQ (b), and simulated spectra with mass tolerance < 15ppm (c) of elemental composition identified by Thermo Xcalibur Qual Browser

SM6. Steady State Quenching Experiments of 1.

Quenching of the 410 nm fluorescence of $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ by methylviologen (MV^{2+}) was investigated by steady state measurements. Five samples of the complex were prepared as MeOH/EtOH solutions with MV^{2+} concentrations between 0 and 11 mM. Stern-Volmer plots of the observed decrease in emission intensity with an increase in the quencher concentration showed a good linear relationship with an intercept of 1. The oxidative-quenching rate constant k_q could be calculated using eq. 1, eq. 2 and the emission lifetime of the complex in the absence of quencher, τ_{em} .

$$F^0/F = 1 + K_{\text{sv}}[\text{Q}] \quad (1)$$

$$K_{\text{sv}} = k_q \tau_{\text{em}} \quad (2)$$

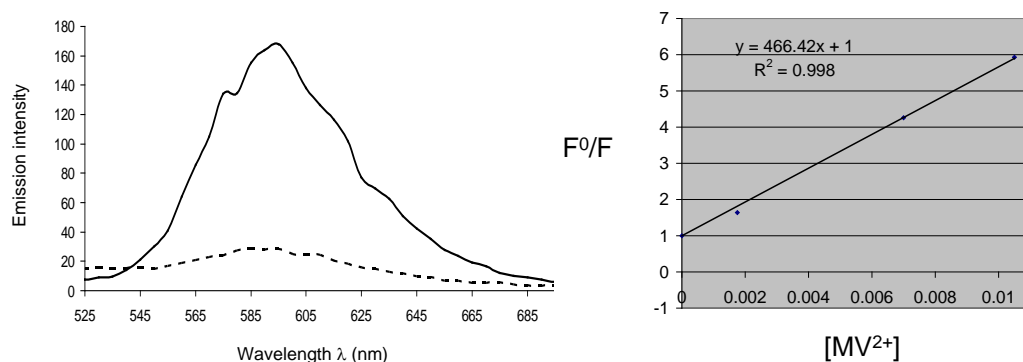


Figure S6A Left) Quenching of luminescent emission for $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ at 595 nm: solid line, emission intensity without addition of MV^{2+} ; dotted line, after addition of excess of MV^{2+} . Right) Stern-Volmer plot of quenching data.

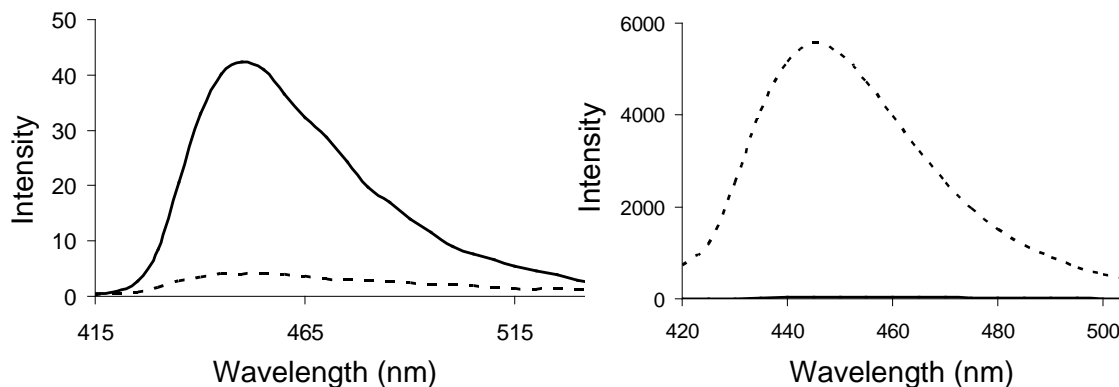


Figure S6B Left: spectra showing quenching of $\text{Zn}(\text{ttma})_2$ (0.132 mM), $\lambda_{\text{em}} = 450$ nm with $[\text{MV}^{2+}]$ (26.3 μM , dotted line in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$). Right: spectra showing increase in intensity of $\text{Zn}(\text{ttma})_2$, $\lambda_{\text{em}} = 450$ nm at 77 °K (dotted line, 26.3 μM in EtOH/MeOH).

SM7. Singlet oxygen quenching by compound 1.

Quenching of Singlet Oxygen by $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$ Excitation wavelength: 532 nm. External sensitizer: Rose Bengal. For quenching of singlet oxygen in solution, we can use the modified Stern-Vollmer equation

$$k(\text{obsd}) = k_d + k_t [[\text{Ru}(\text{bpy})_2(\text{ttma})]^+]$$

where k_d = decay rate of singlet oxygen in the solvent (CD_3OD), and k_t = total rate of singlet oxygen removal by $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$. The intercept of the plots of $k(\text{obsd})$ vs. $[[\text{Ru}(\text{bpy})_2(\text{ttma})]^+]$ are therefore the decay rate of singlet oxygen in CD_3OD , and the slope is the value of k_t , i.e. the quenching rate of singlet oxygen by $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$. The average value of k_t obtained from the three plots below is $k_t = 5.0 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$.

Quenching of Singlet Oxygen by $[\text{Ru}(\text{bpy})_2(\text{ttma})]^+$

