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New Ru(II) Complex for Dual Photochemotherapy: Release of Cathepsin K Inhibitor and $^1O_2$ Production

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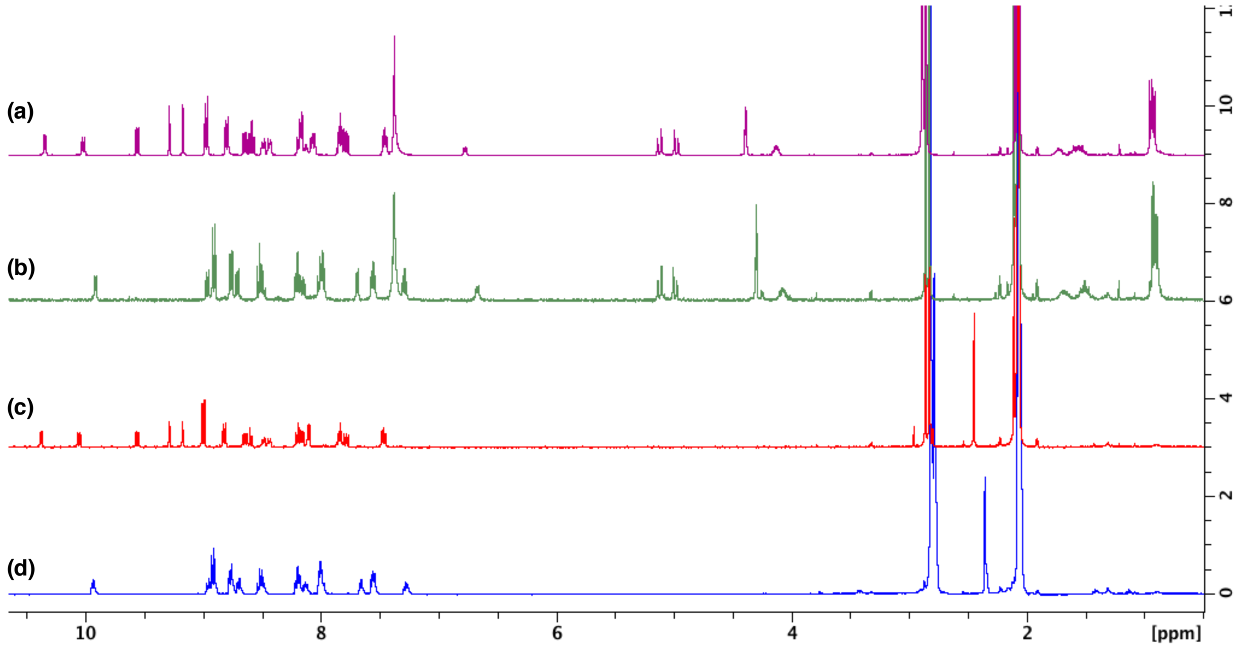

Figure S1. ^{1}H NMR spectra of [Ru(tpy)(dppn)(Cbz-Leu-NHCH$_2$CN)](PF$_6$)$_2$ (a), [Ru(tpy)(bpy)(Cbz-Leu-NHCH$_2$CN)](PF$_6$)$_2$ (b), [Ru(tpy)(dppn)(CH$_3$CN)](PF$_6$)$_2$ (c), and [Ru(tpy)(bpy)(CH$_3$CN)](PF$_6$)$_2$ (d) in d_6-acetone.

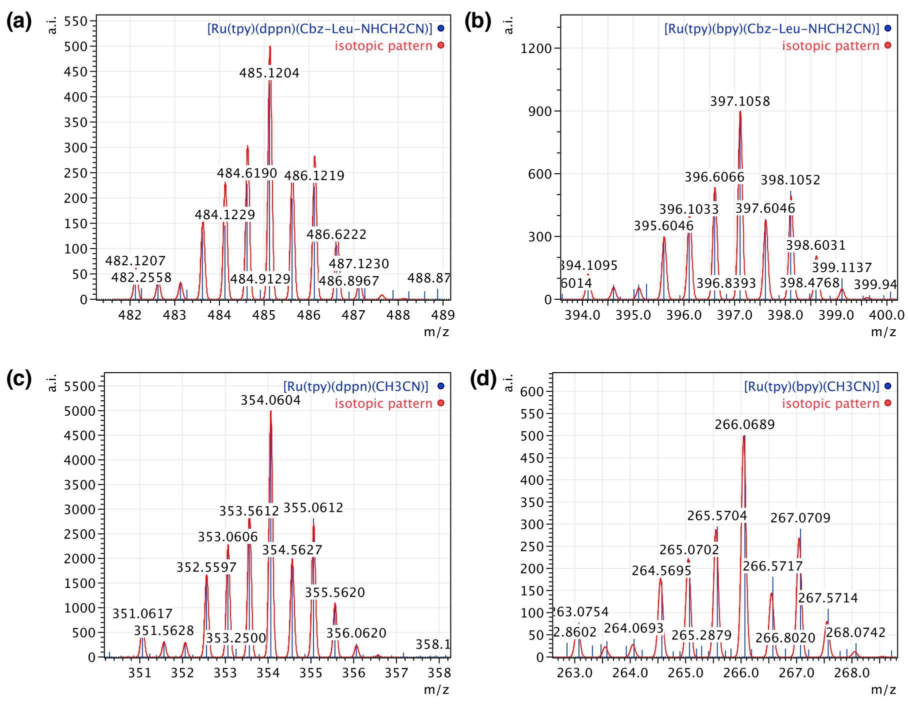

Figure S2. The ESI-MS spectra experimental (—) and calculated (—) of [Ru(tpy)(dppn)(Cbz-Leu-NHCH$_2$CN)](PF$_6$)$_2$ (a), [Ru(tpy)(bpy)(Cbz-Leu-NHCH$_2$CN)](PF$_6$)$_2$ (b), [Ru(tpy)(dppn)(CH$_3$CN)](PF$_6$)$_2$ (c), and [Ru(tpy)(bpy)(CH$_3$CN)](PF$_6$)$_2$ (d)

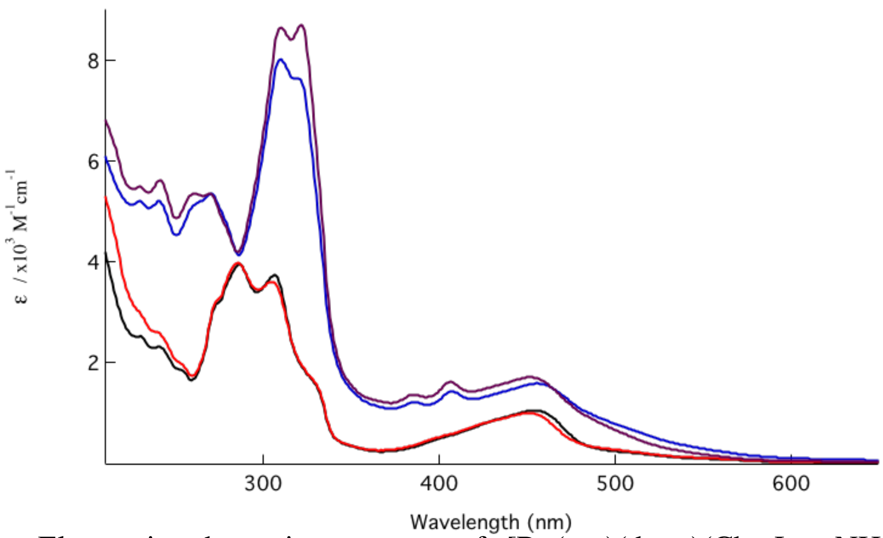

Figure S3. Electronic absorption spectra of $[Ru(tpy)(dppn)(Cbz\text{-}Leu\text{-}NHCH_2CN)]^{2+}$ (—), $[Ru(tpy)(bpy)(Cbz\text{-}Leu\text{-}NHCH_2CN)]^{2+}$ (—), $[Ru(tpy)(dppn)(CH_3CN)]^{2+}$ (—), $[Ru(tpy)(bpy)(CH_3CN)]^{2+}$ (—) in Acetonitrile.

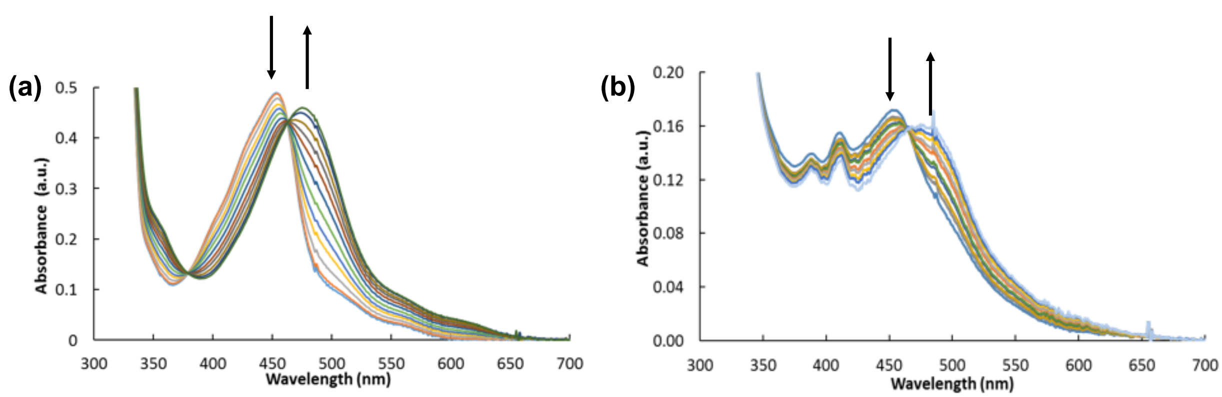

Figure S4. Electronic absorption spectra of $[Ru(tpy)(bpy)(CH_3CN)]^{2+}$ (a) and $[Ru(tpy)(dppn)(CH_3CN)]^{2+}$ (b) in aqueous solution (< 5% acetone; sparged with N_2 for 10 min) irradiated with λ_{irr} ≥ 395 nm for 0-50 min and 0-140 min, respectively.

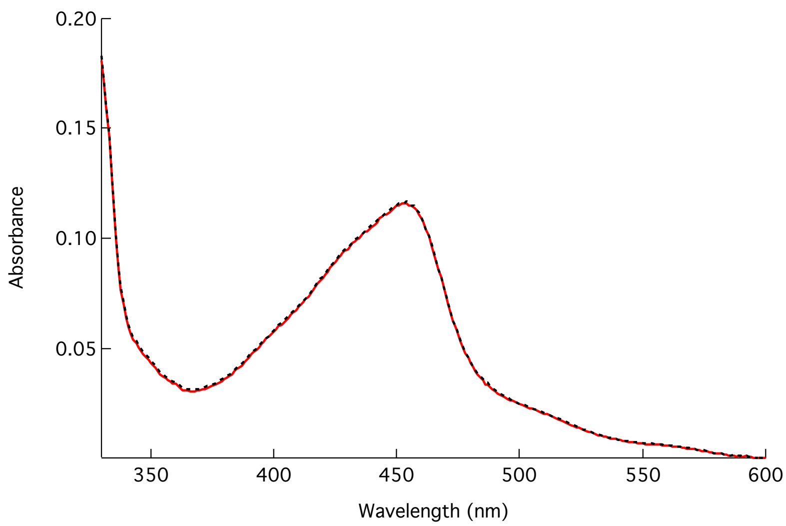

Figure S5. Electronic absorption spectra of $[Ru(tpy)(bpy)(CH_3CN)]^{2+}$ in water (<5% acetone) (—) and after 2 hours in the dark (---).

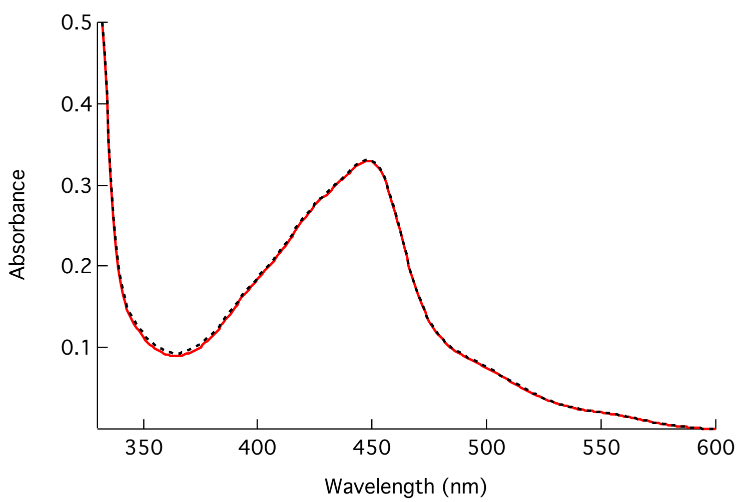

Figure S6. Electronic absorption spectra of $[Ru(tpy)(bpy)(Cbz\text{-}Leu\text{-}NHCH_2CN)]^{2+}$ in water (<5% acetone) (—) and after 30 mins in the dark (---).

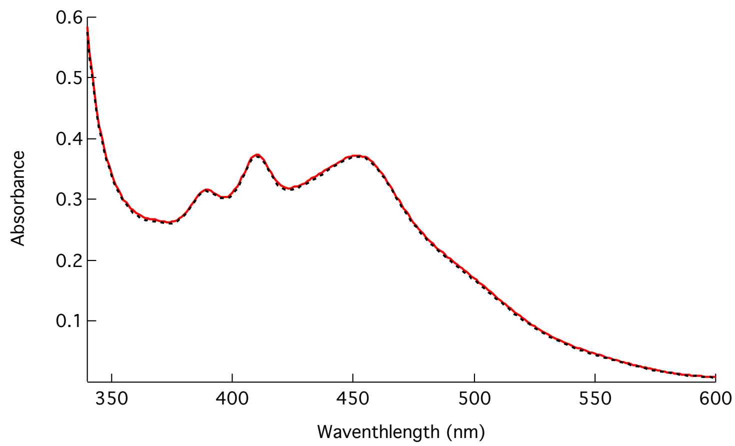

Figure S7. Electronic absorption spectra of [Ru(tpy)(dppn)(CH_3CN)]$^{2+}$ in water (<5% acetone) (—) and after 1.5 hours in the dark (---).

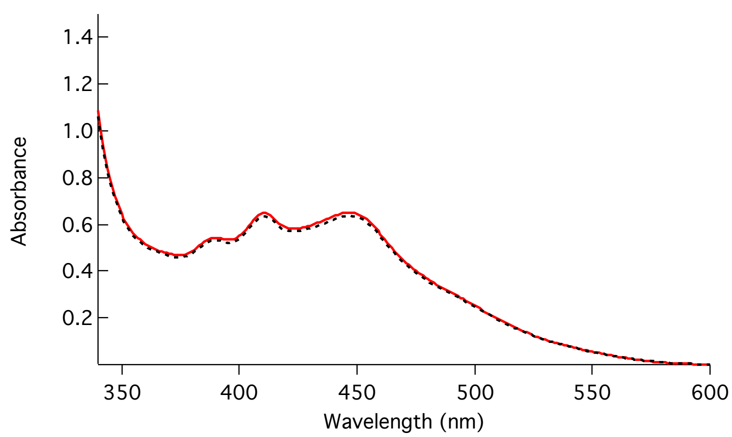

Figure S8. Electronic absorption spectra of [Ru(tpy)(dppn)(Cbz-Leu-NHCH_2CN)]$^{2+}$ in water (<5% acetone) (—) and after 30 mins in the dark (---).

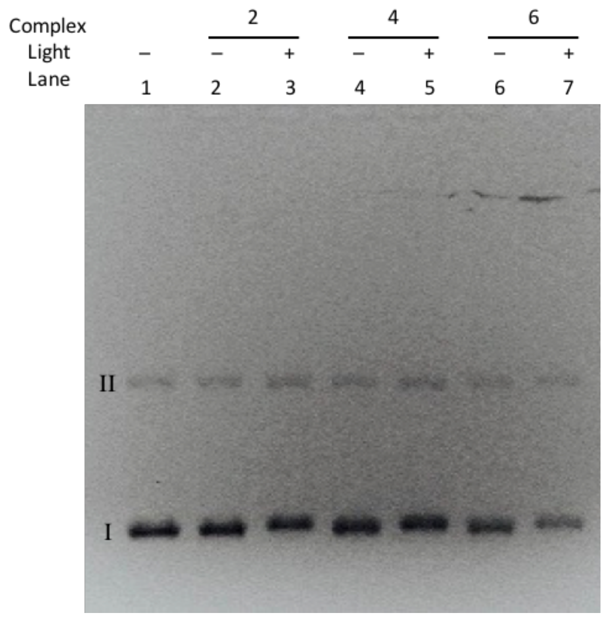

Figure S9. Ethidium bromide-imaged agarose gel (1%) of 100 μM pUC19 (5 μM Tris buffer, pH = 7.5, 50 μM NaCl) and 10 μM of comp1exes **2**, **4**, **6** in air ($\lambda_{irr} \geq 395$ nm, 5 min). Where lanes 1, 2, 4, 6 are dark controls and lanes 3, 5, and 7 are irradiated: lane 1, plasmid only; lanes 2 and 3, **2**; lanes 4 and 5, **4**; lanes 6 and 7, **6.**

$$\Phi_L = \left(\frac{rate\ of\ consumption\ of\ reactant}{photon\ flux}\right)\left(\frac{1}{f_m}\right)$$

Equation S1. Equation used to calculate the ligand exchange quantum yield (Φ_L), where f_m is the mean fraction of light absorbed by the sample.[S1]

$$f_m = \frac{(1 - 10^{-A_0}) + (1 - 10^{-A_f})}{2}$$

Equation S2. Equation used to calculate the mean fraction of light absorbed by the sample, where A_0 is the initial absorbance at the irradiation wavelength (450 nm) before irradiation and A_f is the final absorbance at the irradiation wavelength at the end of the experiment.[1]

REFERENCES

(S1) V. Balzani, P. Ceroni and A. Juris, *Photochemistry and Photophysics Concepts, Research, Applications*, Wiley-VCH, Weinheim, Bergstr, 2014.