Supporting Information

New Cyclometallated Ru(II) Complex for Potential Application in Photochemotherapy

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Table S1. Crystal Structural Data and Refinement Parameters for $[Ru(biq)_2(phpy)][PF_6]\bullet 2CH_2Cl_2$ (**1**)

Formula	$C_{49}H_{36}N_5F_6Cl_4PRu$
Formula weight	1082.67
Crystal size/mm^3	0.37 x 0.14 x 0.10
Temperature/K	291(2)
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a/Å	13.314(3)
b/Å	22.497(5)
c/Å	15.709(3)
β/deg	100.67(3)
V/Å^3	4623.8(16)
Z	4
ρ_{calc}/g•cm^{-3}	1.555
F_{000}	2184
μ/cm^{-1}	0.671
Theta range for data collection/°	1.60 to 27.40
Reflexions collected	49647
Independent reflexions	10375 [R_{int} = 0.0609]
Data/parameters/restraints	10375/595/0
Completeness to theta max/%	98.8
Final R indexes [$I > 2\sigma(I)$]	R1[a] = 0.0637, wR2[b] = 0.1918
Final R indexes [all data]	R1[a] = 0.0828, wR2[b] = 0.2107
Goodness-of-fit on F^2	1.075

[a] $R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$. [b] $wR2 = [\, \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \,]^{1/2}$

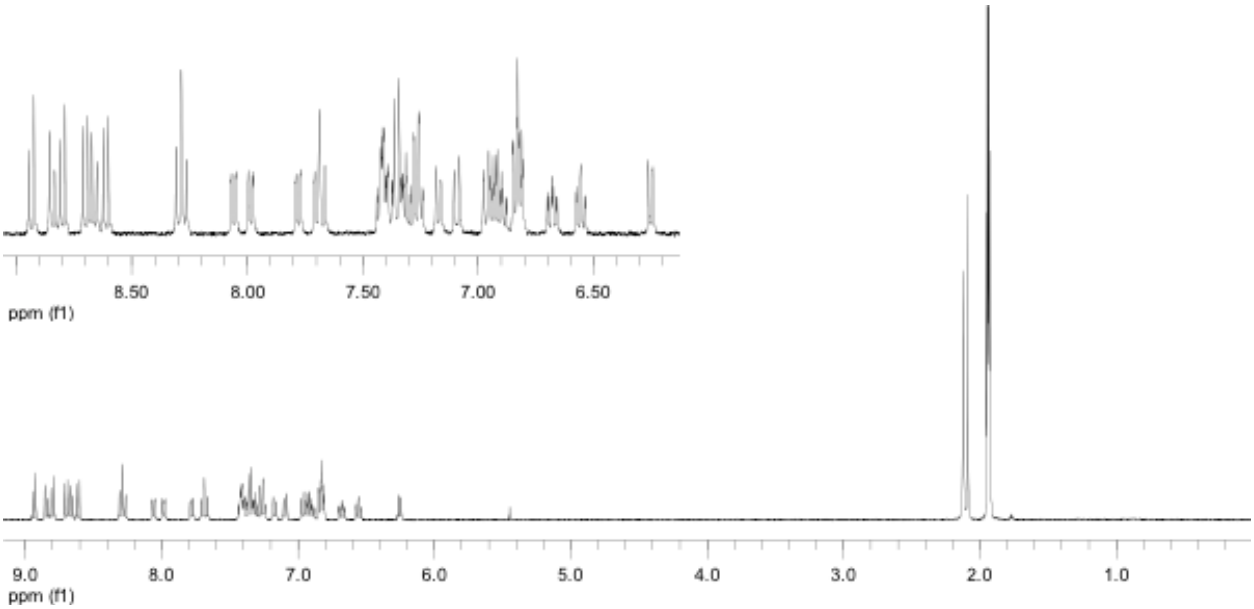


Figure S1. ^{1}H NMR of **1** in CD_3CN. There are 25 aromatic resonances that correspond to 32 protons.

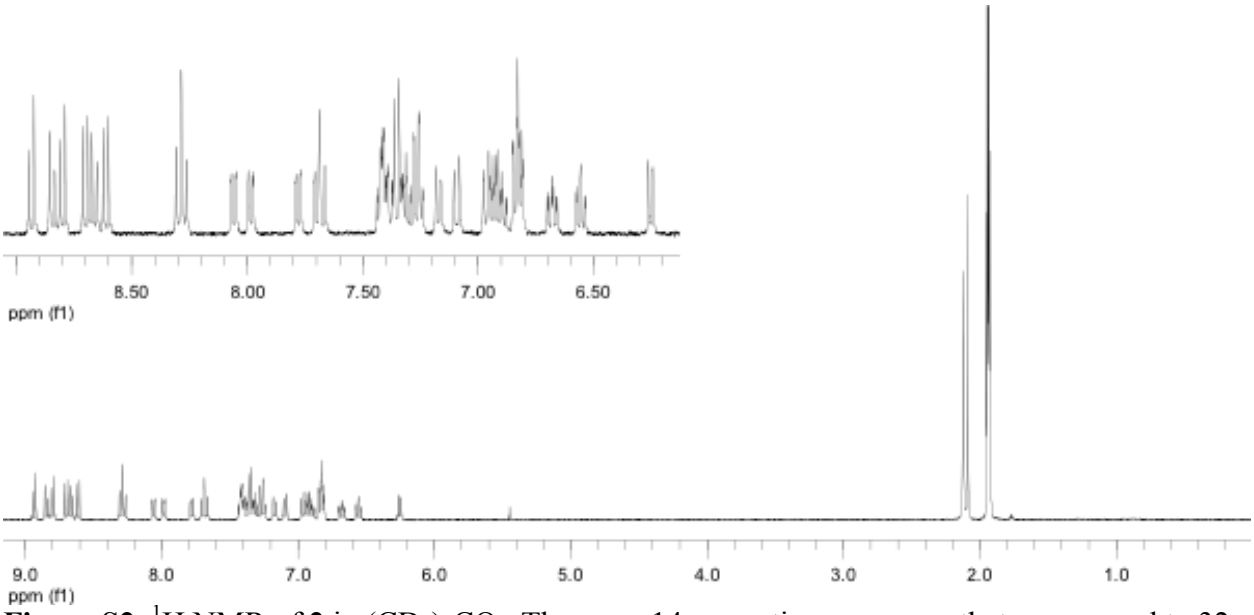


Figure S2. ^{1}H NMR of **2** in $(CD_3)_2CO$. There are 14 aromatic resonances that correspond to 32 protons.

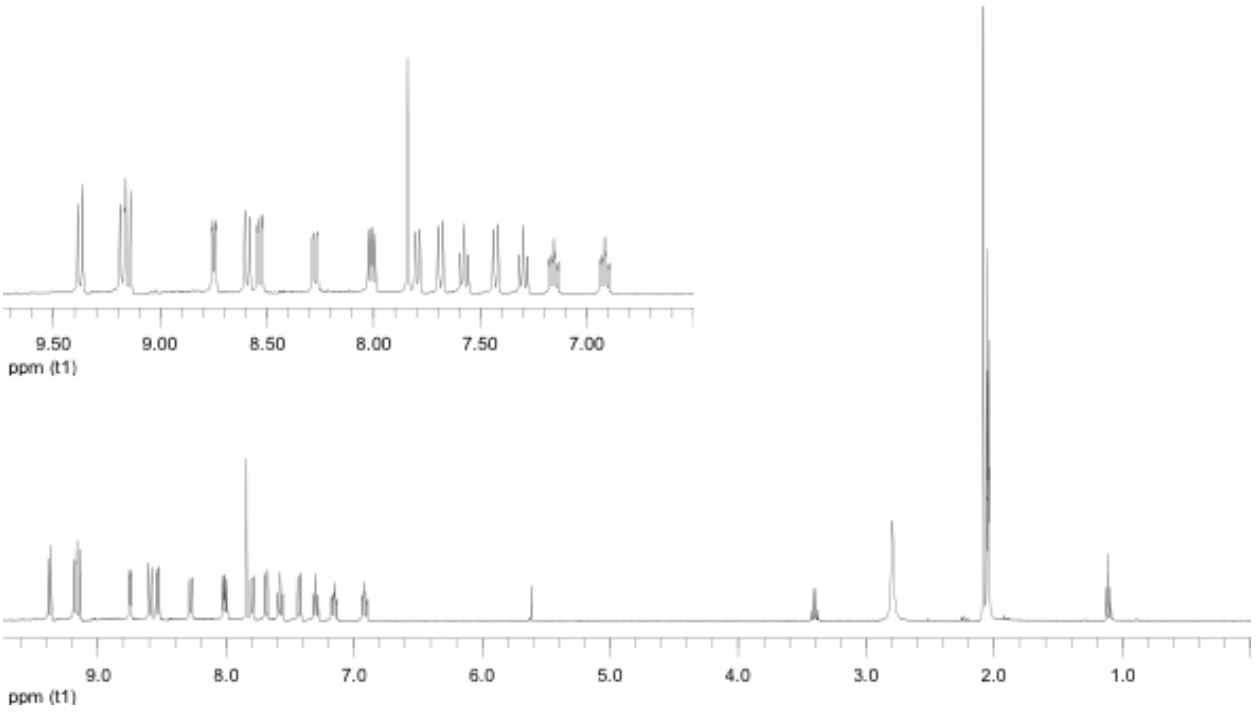


Figure S3. ^{1}H NMR of **3** in $(CD_3)_2CO$. There are 15 aromatic resonances that correspond to 32 protons.

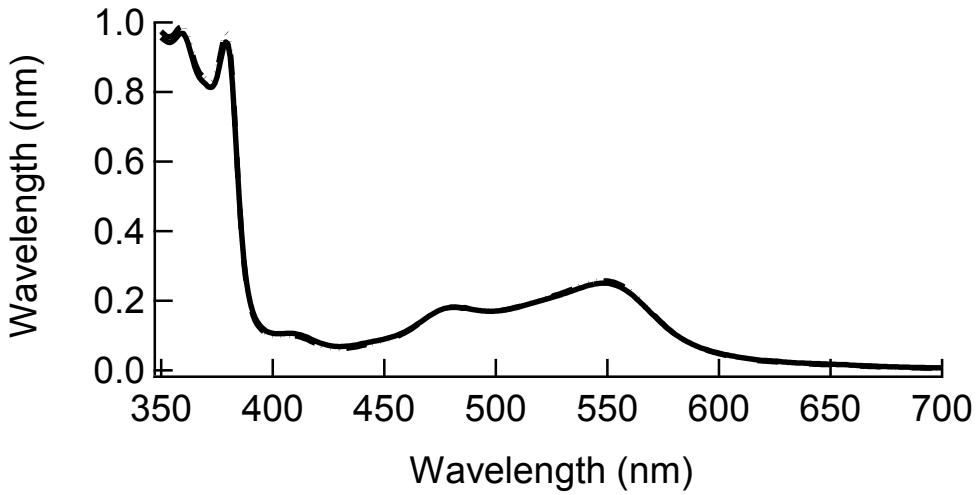


Figure S4. Changes to the electronic absorption spectrum of **2** (20 μM) incubated in H_2O for 3 hours at room temperature.

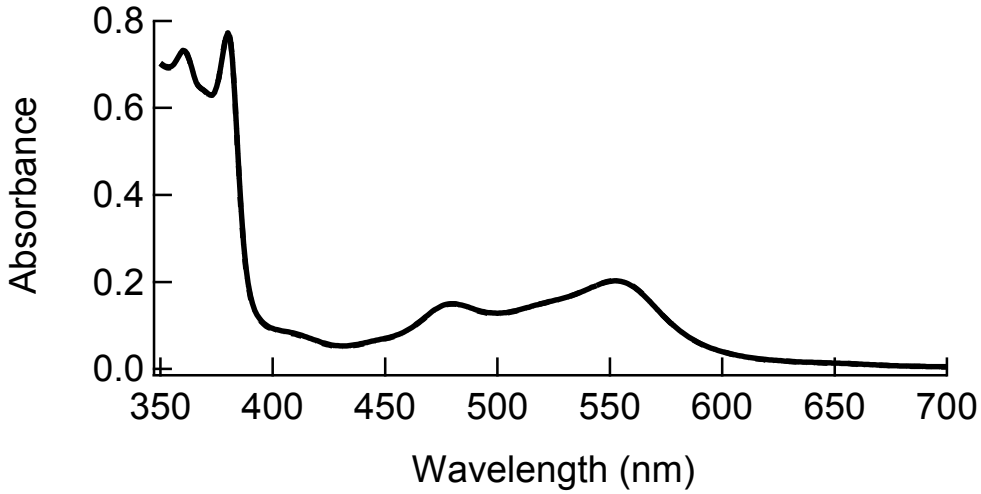


Figure S5. Changes to the electronic absorption spectrum of **3** (20 μM) incubated in H_2O for 3 hours at room temperature.

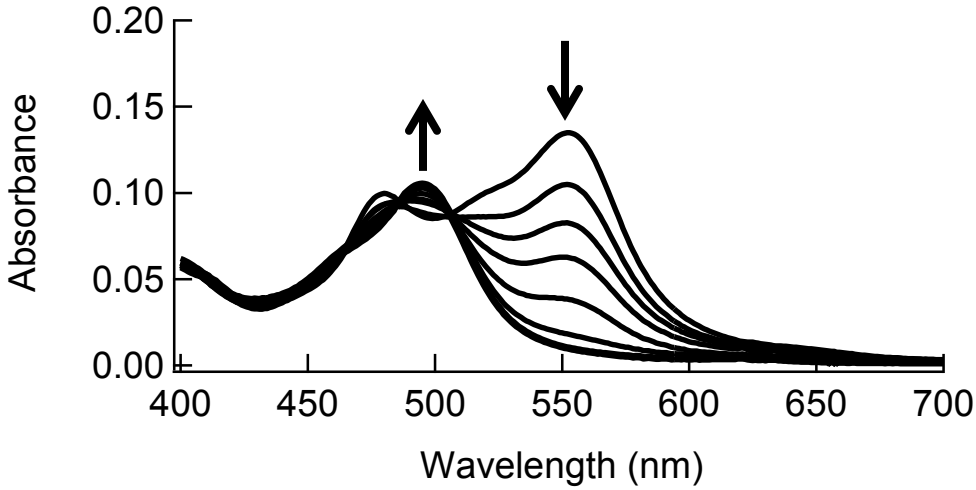


Figure S6. Changes to the electronic absorption spectrum of **3** (15 μM) in CH_3CN with increasing irradiation times: 0, 1, 2, 3, 5, 10, 20, and 30 min ($\lambda_{irr} \geq 530$ nm).

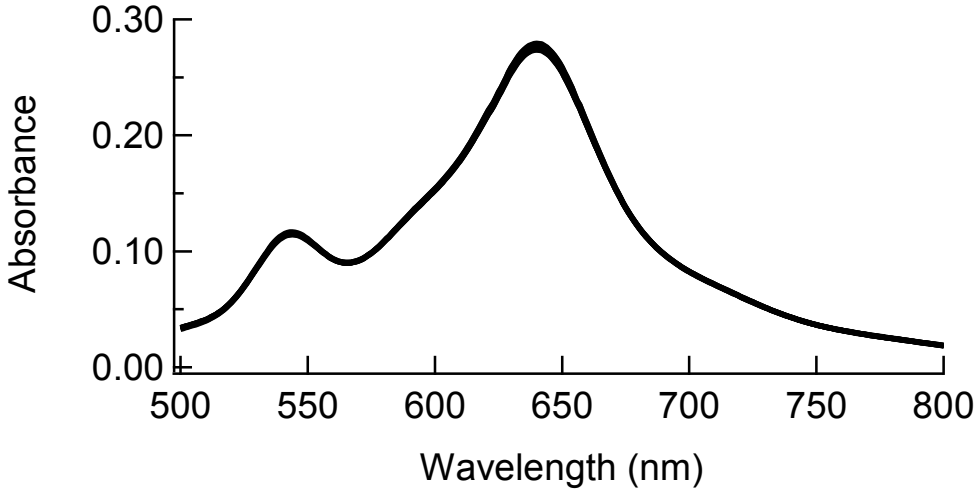


Figure S7. Changes to the electronic absorption spectrum of **1** (50 μM) in CH_3CN with increasing irradiation times: 0, 1, 5, 10, 20, and 30 min ($\lambda_{irr} \geq 530$ nm).

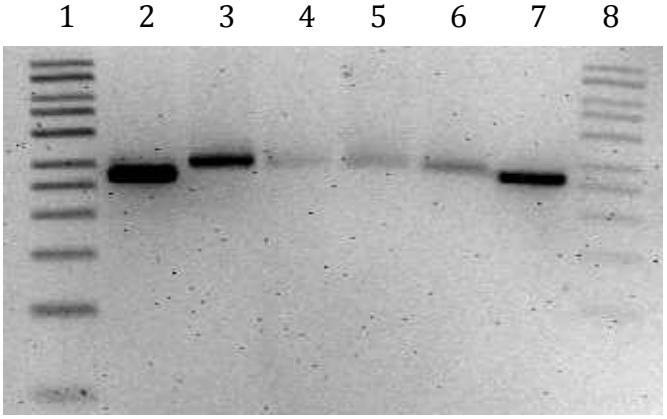


Figure S8. Imaged ethidium bromide stained agarose gels in 1xTBE buffer of 50 μM linearized pUC18 plasmid (10mM phosphate buffer, pH = 7.8) in the presence of various concentrations of **3**: lanes 1 and 8, 1 kb DNA molecular weight standard; lanes 2 and 7, linearized plasmid alone; lanes 3-6, 25, 50, 75, 100 μM complex irradiated with $\lambda_{irr} \geq 630$ nm (t_{irr} = 30 min).

Table S2. 10 lowest energy singlet excited states obtained from DFT calculations, and the transitions associated with these states in CH_3CN (H = HOMO, L = LUMO) for complex **1.**

Wavelength (nm)	*f*	Calculated Transitions and Orbital Contributions[a]
839.53	0.0013	H→L(88%), H→L+1(8%)
765.85	0.0004	H→L+1(86%), H→L(9%), H-1→L+1(2%)
686.27	0.0266	H-1→L(83%), H-2→L(13%)
636.97	0.0288	H-2→L(46%), H-2→L+1(23%), H-1→L+1(18%), H-1→L(10%)
606.78	0.0397	H-2→L(39%), H-1→L+1(29%), H-2→L+1(26%)
537.81	0.0336	H-2→L+1(42%), H-1→L+1(41%), H→L+3(7%)
461.97	0.0068	H→L+2(52%), H→L+4(43%)
455.84	0.0122	H→L+4(46%), H→L+2(39%), H→L+3(10%)
438.86	0.0396	H→L+3(76%), H→L+2(5%)
418.32	0.0302	H-1→L+2(85%), H-1→L+4(5%)

[a]Only contribution ≥5% are listed.

Table S3. 10 lowest energy singlet excited states obtained from DFT calculations, and the transitions associated with these states in CH_3CN (H = HOMO, L = LUMO) for complex **2.**

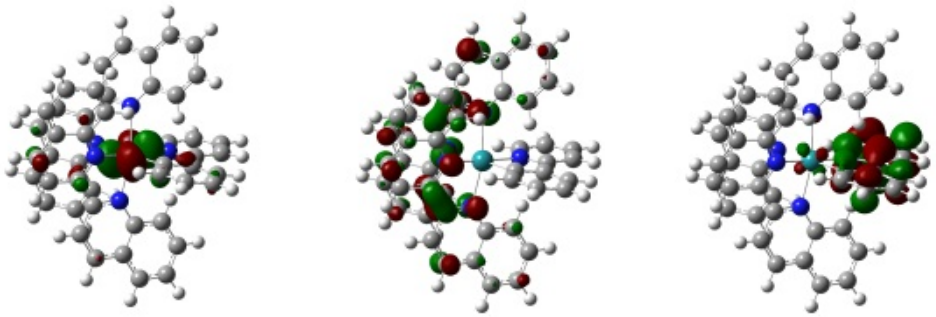
Wavelength (nm)	*f*	Calculated Transitions and Orbital Contributions[a]
586.3	0.0003	H→L(97%)
560.87	0.00004	H→L+1(90%), H-1→L+1(4%)
522.69	0.0762	H-1→L(93%)
514.61	0.0041	H-2→L(96%)
491.68	0.0126	H-2→L+1(90%), H-1→L(5%)
476.43	0.0013	H→L+2(97%)
467.09	0.0527	H-1→L+1(76%), H-2→L+2(6%), H→L+1(6%)
439.47	0.0015	H-1→L+2(96%)
404.76	0.0388	H-2→L+2(85%)
389.55	0.005	H-3→L(95%)

[a]Only contribution ≥5% are listed.

Table S4. 10 lowest energy singlet excited states obtained from DFT calculations, and the transitions associated with these states in CH_3CN (H = HOMO, L = LUMO) for complex **3.**

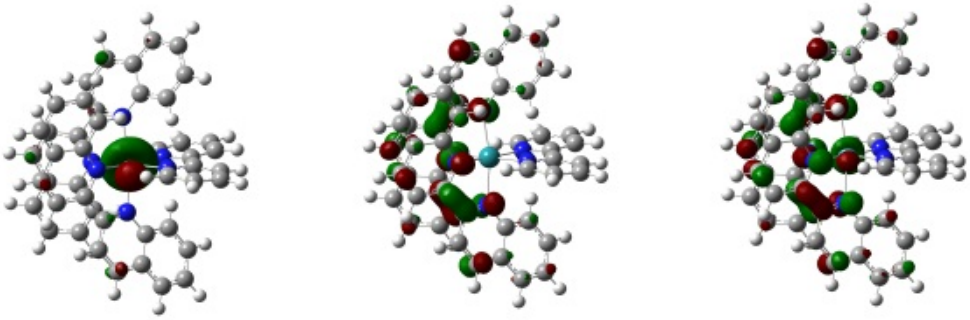
Wavelength (nm)	*f*	Calculated Transitions and Orbital Contributions[a]
587.43	0.0004	H→L(98%)
550.42	0.0002	H→L+1(89%)
527.23	0.0026	H-2→L(96%)
526.72	0.0862	H-1→L(96%)
493.16	0.0037	H-2→L+1(93%)
467.2	0.0008	H→L+2 (97%)
464.34	0.0657	H-1→L+1(75%), H-2→L+2(7%), H→L+1(6%)
435.34	0.0006	H-2→L+2(97%)
420.11	0.0005	H→L+3(72%), H-2→L+2(22%)
399.83	0.0208	H-1→L+3(37%), H-3→L+2(33%), H→L+3(19%)

[a]Only contribution ≥5% are listed.



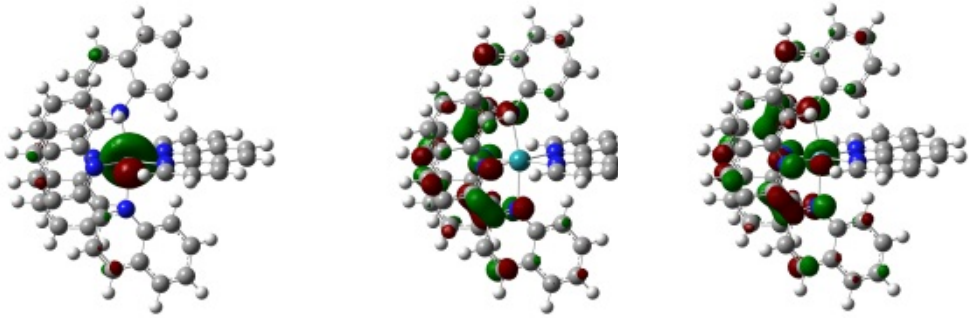
HOMO-1 LUMO LUMO+4

Figure S9. Surface images of select molecular orbitals in **1**.



HOMO-1 LUMO LUMO+1

Figure S10. Surface images of select molecular orbitals in **2**.



HOMO-1 LUMO LUMO+1

Figure S11. Surface images of select molecular orbitals in **3**.