Supporting Information

$[Ru(bpy)_2(5CNU)_2]^{2+}$ as a Potential Dual Action PDT Agent

Robert N. Garner,[¥] Judith C. Gallucci,[¥] Kim R. Dunbar,[†,]* and Claudia Turro[¥,]*

[¥]*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*
[†]*Department of Chemistry, Texas A&M University, College Station, TX 77842*

Synthesis and Characterization

$[Ru(bpy)_2(5CNU)_2](PF_6)_2$ was prepared by reacting 50 mg (0.1 mmol) $Ru(bpy)_2Cl_2$ with 55 mg (0.22 mmol) of $AgSO_3CF_3$ in 10 mL of methanol which led to a color change from an intense purple color to dark red. The solution was placed in the freezer overnight and then filtered to remove AgCl. A quantity of 5-CNU (137 mg, 1.0 mmol) was added to the solution and refluxed under N_2 for 2 h which led to a color change from dark red to bright yellow. The solvent was removed and the crude product was re-dissolved in boiling water and filtered. To the filtrate was added 5 mL of saturated NH_4PF_6. The yellow precipitate was collect on a frit and washed with 3 x 5 mL portions of cold water followed by diethyl ether and dried under a vacuum. Yield 65 mg (67%). ^{1}H NMR (400 MHz) in dimethyl sulfoxide-d6 (splitting, integration): 7.44 (t, 2H) bpy, 7.68 (d, 2H) bpy, 7.97 (t, 2H) bpy , 8.11 (t, 2H) bpy, 8.42 (t, 2H)bpy, 8.51 (s, 2H) 5CNU, 8.77 (d, 2H) bpy, 8.89 (d, 2H) bpy, 9.52 (d, 2H) bpy, 11.75 (s, 2H) 5CNU, 12.22 (s, 2H) 5CNU.

^{1}H NMR (400 MHz) in dimethyl sulfoxide-d6 for the 5CNU ligand: splitting, integration): 8.43 (s, 1H), 11.72 (s, 1H), 11.95 (s, 1H).

Crystallography

The data collection crystal was an orange trapezoid-shaped prism. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a triclinic crystal system. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure a hemisphere of reciprocal space with a redundancy factor of 3.2, which means that 90% of the reflections were measured at least 3.2 times. Phi and omega scans with a frame width of 1.0° were used. Data integration were carried out with Denzo[1], and scaling and merging of the data was done with the use of the Scalepack[1] program. After merging the data and averaging the symmetry equivalent reflections a Rint value of 0.045 was obtained.

The structure was solved by the Patterson method in SHELXS-97[2] for the position of the Ru atom. Standard Fourier methods were used to obtain the rest of the structure. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97[2], as incorporated in the WinGX package.[3] The asymmetric unit consists of the Ru complex, two PF_6 anions, and two solvent molecules of acetone. There is also a region of electron density which contains a disordered solvent molecule. This was treated with the SQUEEZE procedure[4] of Platon[5]. The total volume of the solvent accessible void for this region is 260.0 Å^3, with an electron count of 73 electrons/unit cell.

Similarity restraints were used for the refinement of the $[PF_6]^-$ anions such that the P-F bonds were restrained to be equal within a standard uncertainty of 0.01 Å (SADI restraint). For each methyl group of the acetone molecules, the hydrogen atoms were added at calculated positions using a riding model with U(H) = 1.5 * Ueq(bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(bonded atom). Atoms N(2), N(3), N(5) and N(6) are involved in intermolecular hydrogen bonds (see Table 6).

The final refinement cycle was based on 10553 intensities, 30 restraints and 604 variables and resulted in agreement factors of R1(F) = 0.068 and wR2(F^2) = 0.145. For the subset of data with I > 2*sigma(I), the R1(F) value is 0.052 for 8370 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.97 and -0.81 e/$Å^3$. Neutral atom scattering factors were used and include terms for anomalous dispersion.[6]

Table S1. Crystallographic details for **1**

Formula	$C_{30}H_{22}N_{10}O_4Ru + 2(PF_6) + 2(C_3H_6O)$	
Formula weight	1093.74	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space Group	$P\bar{1}$	
Unit Cell dimensions	a = 11.5899(1) Å	α = 103.009(1)°
	b = 13.8311(1) Å	β = 109.326(1)°
	c = 16.6970(2) Å	γ = 103.741(1)°
Volume	2314.85(4) $Å^3$	
Z	2	
Density (calculated)	1.569 Mg / m^3	
Absorption coefficient	0.510 mm^{-1}	
F(000)	1100	
Crystal size	0.12 x 0.19 x 0.19 mm^3	
Θ range for data collection	2.08 to 27.48°	
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-21 \le l \le 21$	
Reflections collected	64704	
Independent reflections	10553 [R(int) = 0.045]	
Completeness to Θ = 27.48°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10553 / 30 / 604	
Goodness-of-fit on F^2	1.048	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0517, wR_2 = 0.1360	
R indices (all data)	R_1 = 0.0685, wR_2 = 0.1447	
Largest diff. peak and hole	0.969 and -0.807 e/$Å^3$	

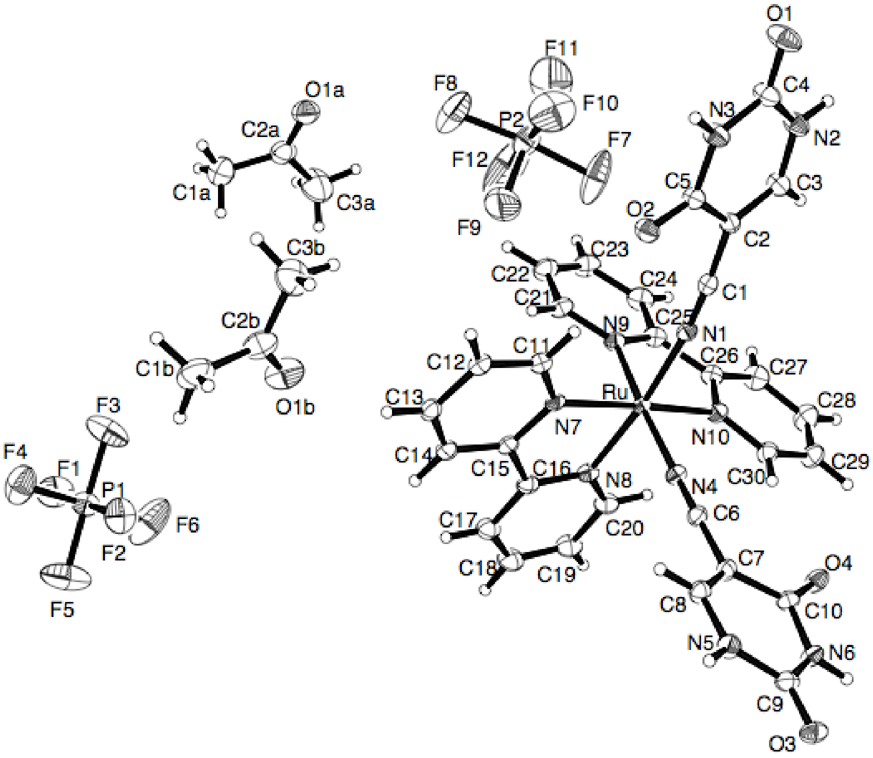

Figure S1. ORTEP diagrm of **1** drawn with 30% probability ellipsoid for the non-hydrogen atoms. The hydrogen atoms are drawn with an artificial radius.

Table S2. Selected bond lengths of **1** from crystallography and from the calculated optimized geometry.

Selected Bonds	Crystallographic lengths (Å)	Calculated lengths (Å)
Ru–N(1)	2.034(3)	2.038
Ru–N(4)	2.025(3)	2.038
Ru–N(7)	2.067(3)	2.106
Ru–N(8)	2.044(3)	2.047
Ru–N(9)	2.044(3)	2.094
Ru–N(10)	2.061(3)	2.111

DFT optimized geometry and MO diagram

Calculations were performed with density functional theory (DFT) using the Gaussian 03 program.[7] The B3LYP[8–10] functional along with the 6-31G* basis set for H, C, N, and S,[11] and the SDD energy-consistent pseudopotentials for Ru were used.[12] Geometries were fully optimized using the criteria of the respective programs. Orbital analysis was completed with GaussView.[13] Electronic transitions were calculated using the TDDFT methods implementation within Gaussian 03.

Dark reactivity of intermediate

The chloride salt of $[Ru(bpy)_2(5CNU)_2]^{2+}$ (80 μM) was irradiated in H_2O for 1.5 min then left in the dark and monitored by electronic absorption. After irradiation the MCLT shifts from 410 nm to 450 nm indicating the formation of the intermediate $[Ru(bpy)_2(5CNU)(H_2O)]^{2+}$ (**3**). The data in Fig. S2 show that, unlike the reactivity observed upon 15 min irradiation, the reaction does not proceed from **3** to the bis-aqua complex **4** in the dark at room temperature during the same time period.

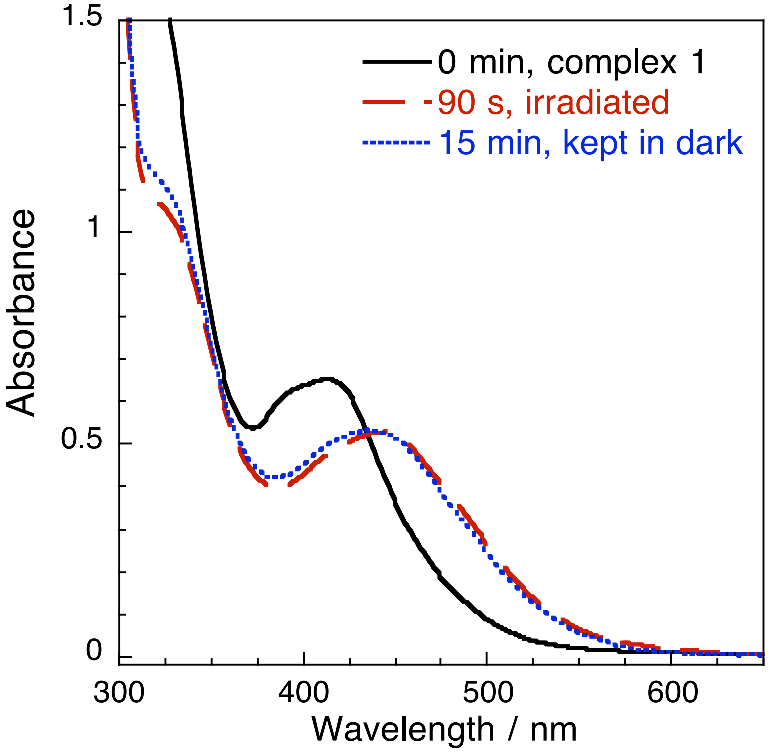

Figure S2. Changes to the absorption spectrum of 1 in water (black, solid) upon irradiation for 90 s (red, long dashed), then kept in the dark for 15 min (blue, dotted).

Ligand Exchange Quantum Yield Determination

Quantum yields were determined following the procedure outlined in *Handbook of Photochemistry*, 3rd ed.[14] The sample was irradiated with a 150 W Xe are lamp. The wavelength of light was controlled with a 400 nm band-pass filter (Newport). Quantum yields were measure relative to ferrioxalate.

References

(1) DENZO: Otwinowski, Z. & Minor, W., Methods in Enzymology, Vol 276: Macromolecular Crystallography, part A, 307-326, (1997), Carter, Jr., C. W. & Sweet, R. M., Eds., Academic Press.

(2) SHELXS-97: Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112-122.

(3) WinGX-Version 1.80.01: Farrugia, L. J. *J. Appl. Cryst*. **1999**, *32*, 837-838.

(4) Sluis, P. v. d.; Spek, A. L. *Acta Cryst*. **1990**, *A46*,194-201.

(5) (a) Spek, A. L. 1990 *Acta Cryst*. A46, C34. (b) Spek, A. L. 1998, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

(6) International Tables for Crystallography, **1992**, Volume C. Dordrecht: Kluwer Academic Publishers.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, Revision Edition; Gaussian Inc.: Wallingford CT, 2004.

(8) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789.

(11) Hehre, W. J.; Radom, L.; Schleyer, P. V.; Pople, J. A. *Ab initio Molecular Orbital Theory*. John Wiley & Sons: New York, **1986**.

(12) Andrae, D.; Haussermann, U.; Dolg M.; Stoll, H.; Preuss, H. *Theoretica Chimica Acta* **1990**, *77*, 123-141.

(13) Dennington II, R.; Keith, T.; Millam, J. *GaussView 3*; Semichem, Inc.: Shawnee Mission, KS, **2007**.

(14) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC press: Boca Raton, FL, **2006**.