Supporting Information for

Preferential DNA Cleavage under Anaerobic Conditions by a DNA Binding Ruthenium Dimer

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Plasmid DNA Cleavage Assay

Cleavage reactions were carried out in a total volume of 20 μL in 0.5 mL Eppendorf tubes in a 7 mM Na_3PO_4 buffer medium (pH 7) containing 2 μL of supercoiled pUC18 DNA (1 μg/1 μL). Samples were prepared by first dissolving the DNA in 13 μL buffer and then adding the GSH in 3 μL and finally by adding [**P**]Cl_4 in 2 μL. Final concentrations are indicated in the figure legends. In case of Figure 2, the same concentration of $\mathbf{P}^{4+}$(0.0128 mM) and Fe-Blm (0.0128 mM) were used with respect to the [DNA]. After incubation (times given in the figure captions), the DNA was precipitated by adding 2 μL sodium acetate (pH 5.2) and 80 μL ethanol followed by cooling overnight at –20 ^{o}C. The precipitated DNA was then dried for about 30 minutes and resuspended in 40 μL of a storage buffer (e.g., 40 mM Tris-Cl, 1 mM EDTA at pH 8.0), 65 μL deionized water and 12 μL of a loading buffer (e.g., 30% glycerol in water with 0.1% w/v bromophenol blue). Samples were loaded on 1% agarose gel containing ethidium bromide (0.2 μL/1 mL) and electrophoresed at 80 V for 90 minutes using TAE buffer (40 mM Tris-acetate, 1 mM EDTA, pH 8).

Anaerobic experiments were conducted in a glove box under a nitrogen atmosphere. All reagents and solutions, including pUC18 DNA, were subject to five freeze-pump-thaw cycles under N_2 prior to introduction to the glove box. Incubations were stopped by precipitating the DNA using 2 μL of degassed sodium acetate at pH 5.2 and 80 μL degassed ethanol under N_2 after which the samples were removed from the glove box and treated as the aerobic samples for further work-up. Control experiments established that no aerobic cleavage reactions are observed after the ethanol precipitation step.

Synthesis of [(phen)$_2$Ru(tatpp^{-})Ru(phen)$_2$][Cl]$_3$ ([P]Cl$_3$)

Complex [**P**]$(PF_6)_4$[1] (200 mg, 0.1 mmol) was dissolved in 100 mL of degassed acetonitrile under nitrogen inside the glove box. 19 mg (0.1 mmol) of cobaltocene (Alfa) dissolved in 3 mL of degassed acetonitrile was added and the solution stirred for 30 minutes. Slow addition of ~ 200mL of diethylether precipitated the product. The solid was filtered, washed with ether and dried under nitrogen. Yield 110 mg (60 %). The complex, [**P**]$(PF_6)_3$, was converted to the chloride salt by dissolving in a minimum amount of acetone and then slow addition of a saturated solution of tetrabutylammonium chloride in acetone. The chloride salt cleanly precipitates and is filtered, washed with acetone and dried. The complex [**P**]$(PF_6)_3$ was characterized by preparing a dilute solution (26 μM) in degassed acetonitrile in an airtight 1 cm glass cuvette. The absorption spectrum was identical to that reported previously.[2](See Supporting figure S1)

Synthesis of [(phen)$_2$Ru(H$_2$tatpp)Ru(phen)$_2$][Cl]$_4$ ([H$_2$P]Cl$_4$)

Complex [**P**]$[PF_6]_4$[1] (100 mg, 0.05 mmol) was dissolved in 5 mL of degassed MeCN inside the glove box. Ascorbic acid (0.5 mmol) was dissolved in a minimum amount of water and added to the MeCN solution and the resulting mixture stirred for 1 h at RT. Addition of a aqueous solution of NH_4PF_6 (10 mg/mL) caused the product to precipitate. The solution was filtered and the solid washed with water (~2 mL - 4 times) and then ether and dried in vacuo. Yield 80 mg (80%). ^{1}H NMR (δ, 500 MHz, MeCN-d_6). The sample required that a small amount of ascorbic acid be included in the NMR solution or the spectrum noticeably broadened presumably due to the formation of paramagnetic $\mathbf{P}^{3+}$: 9.39 (d, *J* = 7.0 Hz, 2H), 8.58-8.63 (m, *J* = 9.0 Hz, 5.9 Hz, 8H), 8.45 (d, *J* = 8.7 Hz, 2H), 8.26 (d, *J* = 4.1Hz, 8H), 8.17 (d, *J* = 5.1 Hz, 2H), 8.06 (d, *J* = 4.6, Hz, 2H), 8.02 (d, *J* = 5.0 Hz, 2H), 7.99 (d, *J* = 4.1 Hz, 4H), 7.85 (d, *J* = 5.1 Hz, 2H), 7.69-7.60 (m, 10H), 7.56 (dd, *J* = 8.7Hz, 5.5Hz, 2H), 6.94 (s, 2H). The identity of the complex was further established by obtaining the absorption spectrum of [**H$_2$P**]$(PF_6)_4$ (26 μM) in degassed acetonitrile. The spectra shown in Figure S1 is the same as previously reported for [**H$_2$P**]$(PF_6)_4$ generated in situ.[2] The complex was converted to chloride salt with tetrabutylammonium chloride in acetone as described for [**P**]Cl_3.

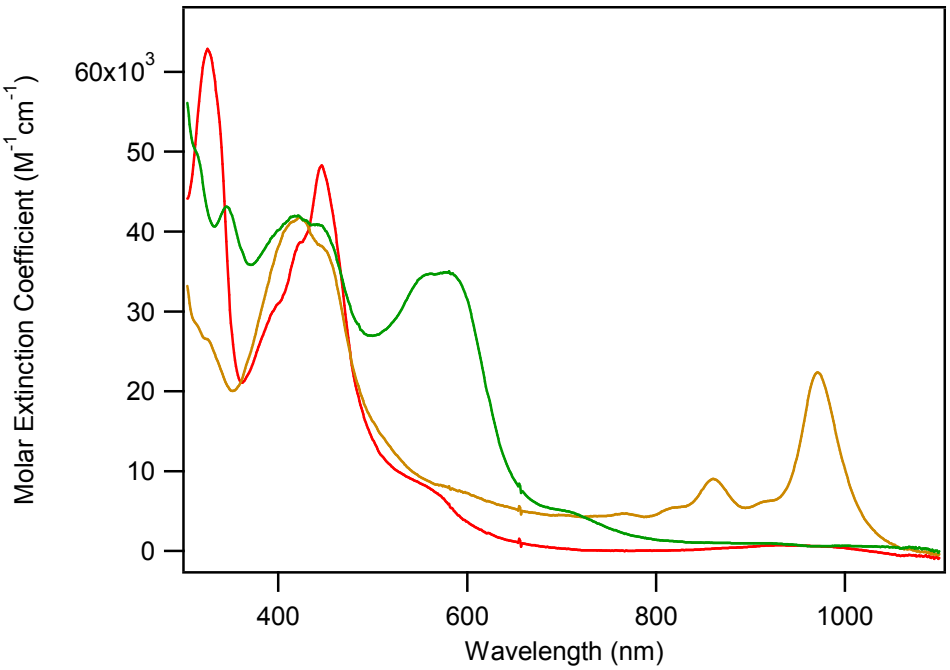

Figure S1: Absorption Spectra of complex $\mathbf{P^{4+}}$, $\mathbf{P^{3+}}$ and $\mathbf{H_2P^{4+}}$ in MeCN (PF_6^- salts). Concentration for all species is 26 μM.

REFERENCES

1) Kim, M.-J.; Konduri, R.; Ye, H.; MacDonnell, F. M.; Puntoriero, F.; Serroni, S.; Campagna, S.; Holder, T.; Kinsel, G.; Rajeshwar, R. *Inorg. Chem.* **2002**, *41*, 2471-2476.

2) Konduri, R.; de Tacconi, N. R.; Rajeshwar, K.; MacDonnell, F. M. *J. Am. Chem. Soc.* **2004**, *126*, 11621-11629.