

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 $\mu\text{g}/1 \mu\text{L}$). Samples were prepared by first dissolving the DNA in 13 μL buffer and then adding the GSH in 3 μL and finally by adding $[\text{P}]\text{Cl}_4$ in 2 μL . Final concentrations are indicated in the figure legends. In case of Figure 2, the same concentration of 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°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 $\mu\text{L}/1 \text{ mL}$) 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 $[(\text{phen})_2\text{Ru}(\text{tatpp}^-)\text{Ru}(\text{phen})_2][\text{Cl}]_3$ ($[\text{P}]\text{Cl}_3$)

Complex $[\text{P}](\text{PF}_6)_4^1$ (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 $\sim 200\text{mL}$ of diethylether precipitated the product. The solid was filtered, washed with ether and dried under nitrogen. Yield 110 mg (60 %). The complex, $[\text{P}](\text{PF}_6)_3$, 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 $[\text{P}](\text{PF}_6)_3$ 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 $[(\text{phen})_2\text{Ru}(\text{H}_2\text{tatpp})\text{Ru}(\text{phen})_2][\text{Cl}]_4$ ($[\text{H}_2\text{P}]\text{Cl}_4$)

Complex $[\text{P}]\text{Cl}_4^1$ (0.2 g, 0.13 mmol) was dissolved in 100 mL of degassed water under nitrogen inside the glove box. 0.198 g of glutathione (0.645 mmol) was dissolved separately in 50 mL of degassed water. Both were mixed and stirred for 2 hours under nitrogen. Yield 0.18 g (90%). The identity of the complex was established by obtaining the absorption spectrum of $[\text{H}_2\text{P}](\text{PF}_6)_4$ (26 μM) in degassed acetonitrile. The spectra shown in Figure S1 is the same as previously reported for $[\text{H}_2\text{P}](\text{PF}_6)_4$ generated in situ.² The complex was converted to chloride salt with tetrabutylammonium chloride in acetone as described for $[\text{P}]\text{Cl}_3$.

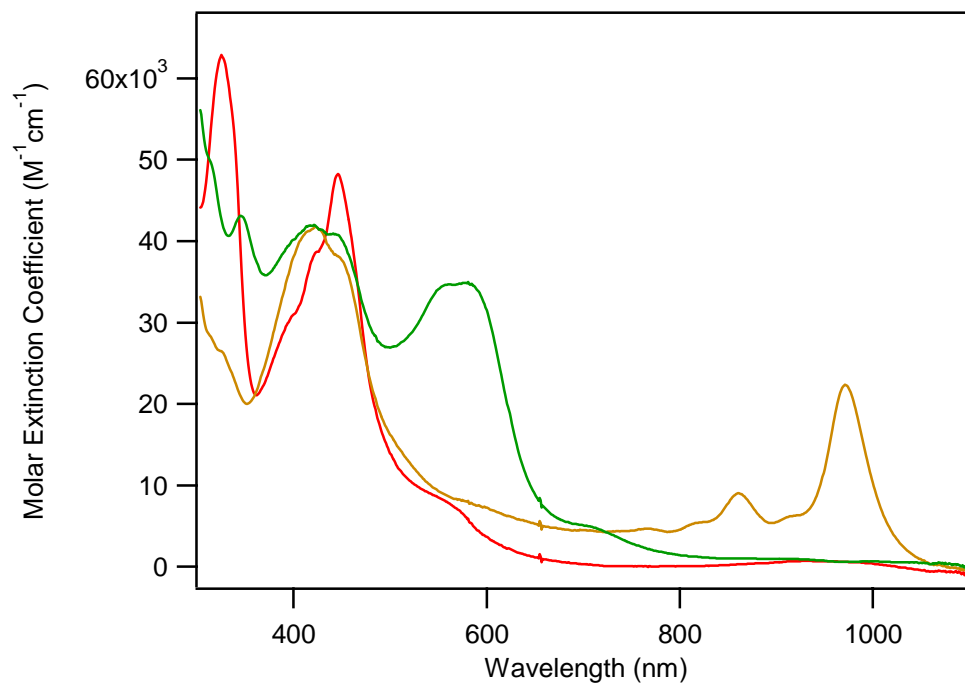


Figure S1: Absorption Spectra of complex P^{4+} , P^{3+} and H_2P^{4+} in MeCN (PF_6^- salts). Concentration for all species is 26 μM .

REFERENCES

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