Supporting Information

A Ruthenium(II) Complex as a Luminescent Probe for

DNA Mismatches and Abasic Sites

Adam N. Boynton, Lionel Marcélis, Anna J. McConnell, and Jacqueline K. Barton*

Division of Chemistry and Chemical Engineering

California Institute of Technology, Pasadena, California, 91125

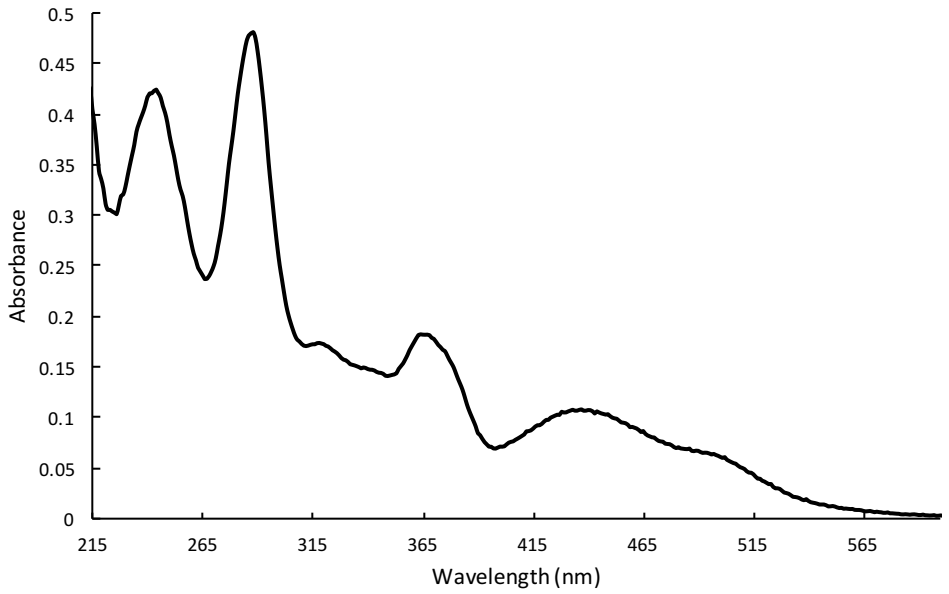

Figure S1: UV-Visible spectrum of $[Ru(bpy)_2(BNIQ)]^{2+}$ (6 μM in H_2O).

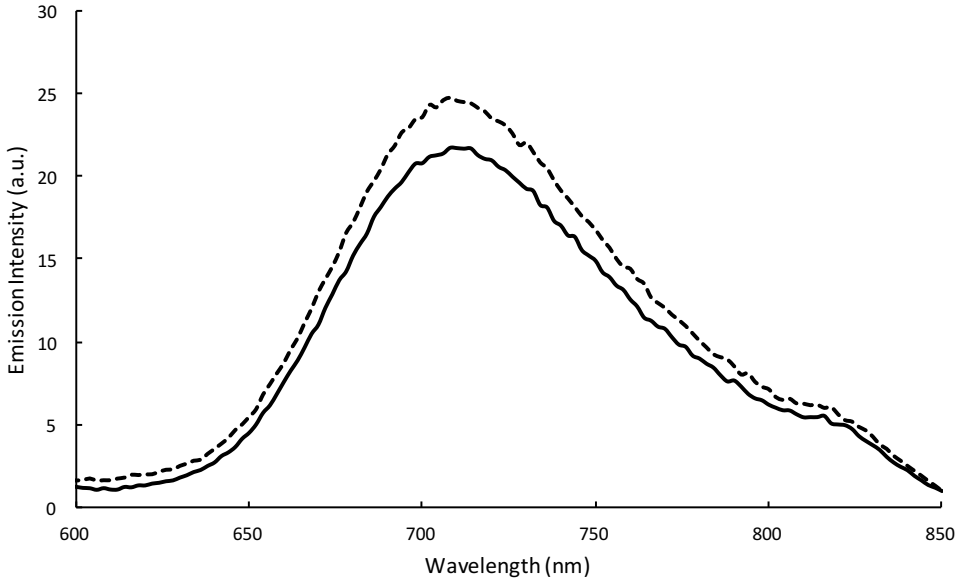

Figure S2: Steady-state emission spectra of $[Ru(bpy)_2(BNIQ)]^{2+}$ in aerated (solid line) and deoxygenated (*via* argon bubbling, dotted line) solutions (6 μM in H_2O, λ_{ex} = 440 nm).

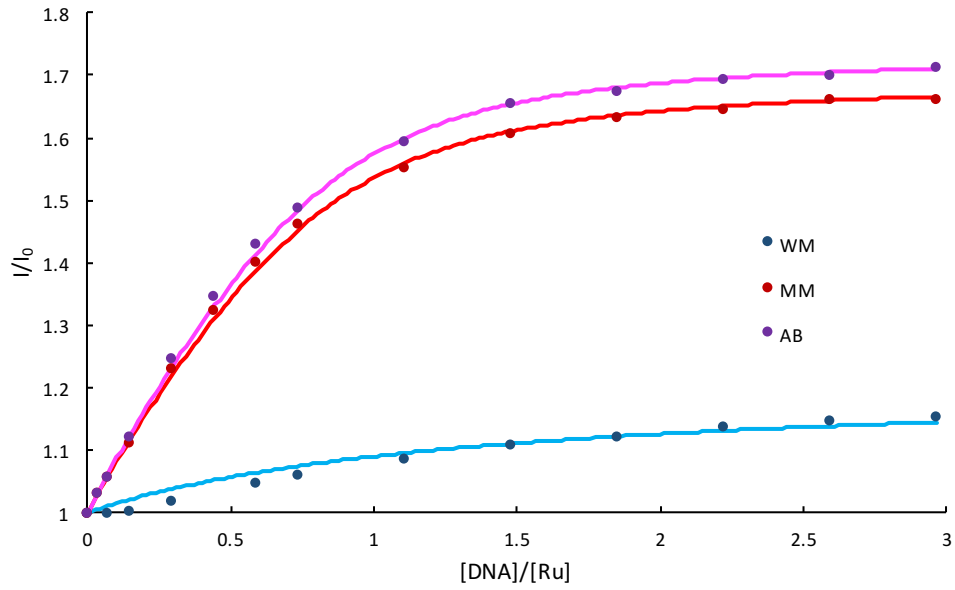

Figure S3: Steady-state luminescence titrations of $[Ru(bpy)_2(BNIQ)]^{2+}$ with well-matched (blue), mismatched (red), and abasic (pink) DNA. Samples were prepared in 5 mM Tris, 200 mM NaCl, pH 7.5. [Ru] = 4 μM, λ_{ex} = 440 nm. [DNA] reflects the concentration of full sequence. Emission spectra were integrated from 590-850 nm.

Binding affinities of the complex for well-matched, mismatched, and abasic sites were evaluated by a global fitting process using a modified McGhee-Von Hippel method.[1] Briefly, we consider the equilibrium binding (K_{ass}) of the complex (*C*) to well-matched base pair sites (BP) and the equilibrium binding (K_{MM}) to a mismatch (or abasic) site (MM):

$$C + BP \rightleftharpoons [C\_BP] \qquad K_{ass} = \frac{[C\_BP]}{[C]\,[BP]}$$

$$C + MM \rightleftharpoons [C\_MM] \qquad K_{MM} = \frac{[C\_MM]}{[C]\,[MM]}$$

As described previously,[2] we can express the luminescence intensity (*I*) as a function of these equilibria along with other parameters, defined below.

$$I = \alpha \frac{K_{ass}\, C_C\, n\, (1-x)\, R\, f}{1 + K_{ass}\, C_C\, p\, f} + \beta \frac{K_{MM}\, C_C\, n\, x\, R\, f}{1 + K_{ass}\, C_C\, f}$$

In this equation for *I,* C_c is the total concentration of complex; *R* is the ratio of total DNA duplex concentration to C_c*; f* is the molar fraction of free complex; *n* is the number of base pairs per DNA duplex; *x* is the ratio of mismatched to well-matched sites in the duplex; and *p* is the occupational factor. Important to note are α and β, which represent the the emissivities of the complex when bound to a well-matched or mismatched site, respectively, relative to free complex.

The global fitting on the three data sets is performed (occupational factor set to 2) and yields the values of K_a = 7.3 10^3 M^{-1} per well-matched base pair, K_a = 3.5 10^6 M^{-1} per CC mismatch site, and K_a = 3.8 10^6 M^{-1} per abasic site. The emissivities for the complex associated with these sites, relative to the luminescence of the free complex, are estimated to be 1.36, 1.42 and 1.46 for well-matched, mismatched, and abasic sites, respectively. The errors are evaluated to be equal to 10%.

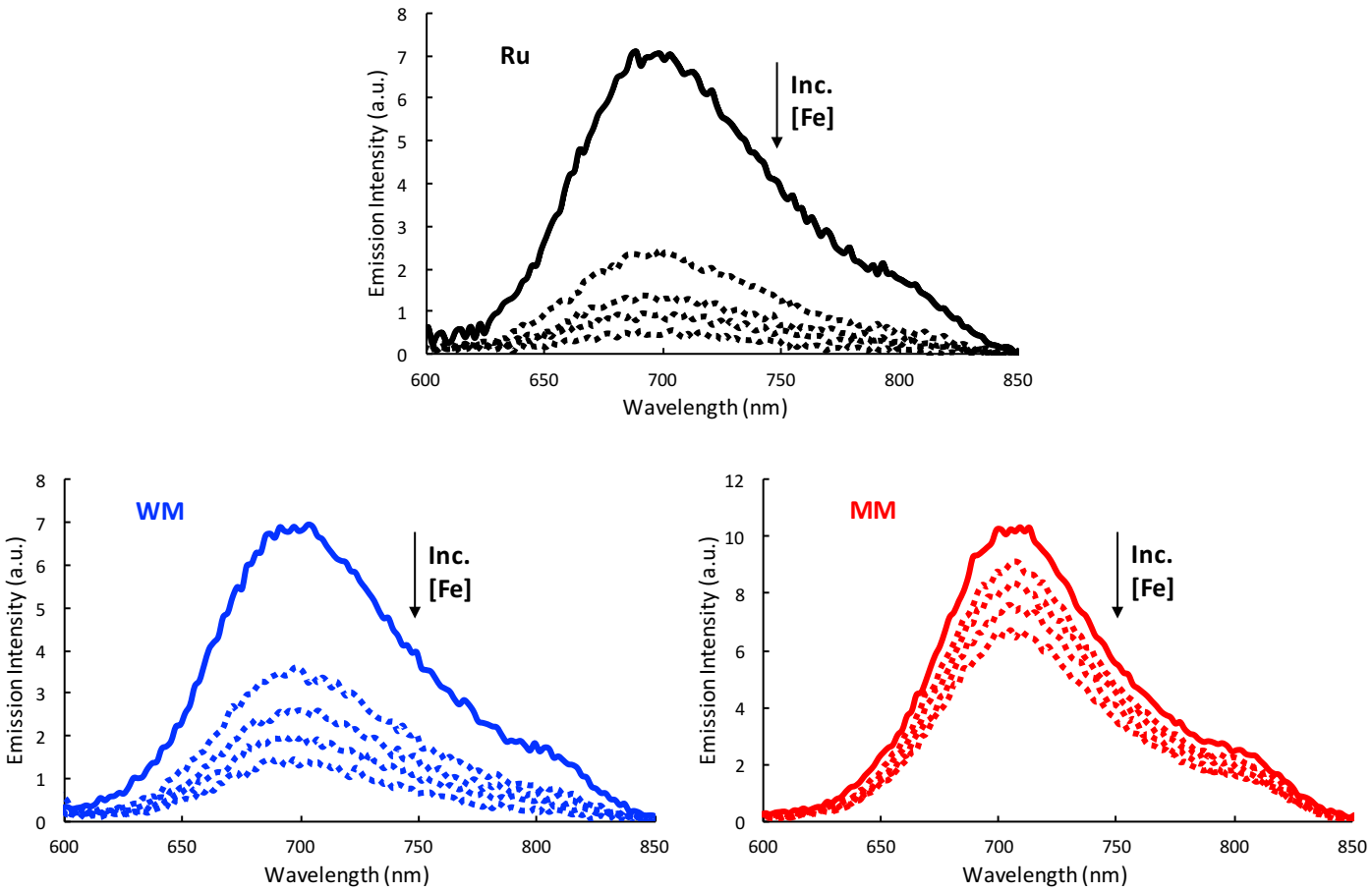

Figure S4: Ferricyanide quenching of free $[Ru(bpy)_2(BNIQ)]^{2+}$ (black) and in the presence of well-matched DNA (blue) and mismatched DNA (red). Ferricyanide was added (dotted lines) to concentrations of 1.2, 2.3, 3.5, and 5.6 mM. [Ru] = 2 μM, [DNA] = 4 μM, λ_{ex} = 440 nm. Samples were prepared in 5 mM Tris, 200 mM NaCl, pH 7.5 at 25 °C.

Supporting References

1. McGhee, J.D.; von Hippel, P.H. Theoretical Aspects of DNA-Protein Interactions: Co-operative and Non-co-operative Binding of Large Ligands to a One-dimensional Homogeneous Lattice. *J. Mol. Biol*. **1974**, *86*, 469-489.

2. Boynton, A.N.; Marcelis, L.; Barton, J.K. $[Ru(Me_4phen)_2(dppz)]^{2+}$, A Light Switch for DNA Mismatches. *J. Am. Chem. Soc.* **2016**, *138*, 5020-5023.