Supporting information

Antioxidant Redox Sensors Based on DNA Modified Carbon Screen Printed Electrode

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S.1 Chemicals and materials

Salmon testes DNA sodium salt (Sigma) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Aldrich) were dissolved in water used as stock solution at concentrations of 5 mM (nucleotide phosphate concentration) and 1 mM, respectively. The PBS buffer was made of sodium phosphate (Na_2HPO_4: NaH_2PO_4 = 81:19, molar ratio) and NaCl dissolved in water at a final concentration of 50 and 10 mM, respectively (pH 7.4). Screen printed electrodes (SPEs, 12.5 mm^2) were used as working electrodes. An Ag/AgCl/saturated KCl reference electrode and a platinum counter electrode were used.

S.2 Simulations

PGSTAT 30 potentiostat was used for electrochemical study. Cyclic voltammograms were simulated using the DigiSim 3.03 software (BAS Inc.). Equations 1 to 12 from the scheme illustrated below [1] were used for simulation when $Ru(bpy)_3^{3+/2+}$ is bound to DNA. The forward rate constants for all binding steps were assumed to be diffusion limited and were fixed at 1.0×10^9 M^{-1} s^{-1}. The default transfer coefficient (α) is 0.5. For simulations that returned homogeneous guanine-metal electron-transfer rate constants, the input DNA nucleotide phosphate concentrations was in terms of guanine concentration, and here we assume that salmon testes DNA is 25% guanine. Second order guanine oxidation rate constants were determined by fitting of cyclic

voltammetric data using the listed mechanisms.

At lower salt concentrations (50 mM NaCl plus 10 mM sodium phosphate, pH 7.4), the electrostatic binding of $Ru(bpy)_3^{3+/2+}$ to the DNA becomes important and digital simulation requires more extensive mechanisms to fit the data. We use equations 1 to 12 to describe the mechanism under this condition.

$$Ru(bpy)_3^{3+} + DNA \rightarrow Ru(bpy)_3^{3+}/\ DNA \quad (1)$$

$$Ru(bpy)_3^{2+} + DNA \rightarrow Ru(bpy)_3^{2+}/\ DNA \quad (2)$$

$$Ru(bpy)_3^{3+}/\ DNA + e \rightarrow Ru(bpy)_3^{2+}/\ DNA \quad (3)$$

$$Ru(bpy)_3^{3+}/\ DNA \rightarrow Ru(bpy)_3^{2+}/\ DNAox' \quad (4)$$

$$Ru(bpy)_3^{2+} + DNAox' \rightarrow Ru(bpy)_3^{2+}/\ DNAox' \quad (5)$$

$$Ru(bpy)_3^{3+} + DNA \rightarrow Ru(bpy)_3^{2+} + DNAox' \quad (6)$$

$$Ru(bpy)_3^{3+} + DNAox' \rightarrow Ru(bpy)_3^{3+}/\ DNAox' \quad (7)$$

$$Ru(bpy)_3^{2+} + DNAox' \rightarrow Ru(bpy)_3^{2+}/\ DNAox' \quad (8)$$

$$Ru(bpy)_3^{3+}/\ DNAox' + e \rightarrow Ru(bpy)_3^{2+}/\ DNAox' \quad (9)$$

$$Ru(bpy)_3^{3+}/\ DNAox' \rightarrow Ru(bpy)_3^{2+}/\ DNAox'' \quad (10)$$

$$Ru(bpy)_3^{2+} + DNAox' \rightarrow Ru(bpy)_3^{2+}/\ DNAox'' \quad (11)$$

$$Ru(bpy)_3^{3+} + DNAox' \rightarrow Ru(bpy)_3^{2+} + DNAox'' \quad (12)$$

Simulation results under low salt conditions are shown in Fig. S.1. For these simulations, the best fit for scan rate 50 mV s^{-1} was obtained, and the second order rate constant for DNA oxidation (equation 6) obtained by simulation is 1.3×10^5 M^{-1} s^{-1}.

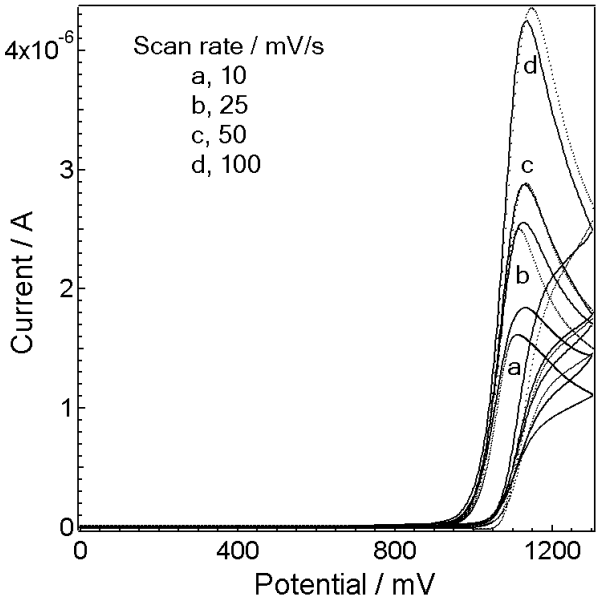

Fig. S.1. Cyclic voltammograms (solid line) and digital simulations (dot line) using equations 1 to 12 for 5.0×10^{-5} M $Ru(bpy)_3^{2+}$ plus 1.25 mM salmon testes DNA in 50 mM NaCl and 10 mM sodium phosphate, pH 7.4, area (planar) = 12.5 mm^2, $E°$ (bound) 1.07 V, k_s(free) and k_s(bound))= 0.02 cm/s, α (free) and α (bound) = 0.5, $K_{Ru(bpy)_3^{2+}}$ = 2000 M^{-1}, $K_{Ru(bpy)_3^{3+}}$ = 10^4 M^{-1}, $k_f(1) = k_f(2) = k_f'(7) = k_f'(8) = k_f''(11) = 10^9$ M^{-1} s^{-1}, [guanine] = 3.1×10^{-4} M, $D_{Ru(bpy)_3^{2+}} = D_{Ru(bpy)_3^{3+}} = 1.0\times10^{-5}$ cm^2 s^{-1}, D_{DNA} (all forms) = 5.0×10^{-7} cm^2 s^{-1}. k_4 = 10 s^{-1}, k_{10} = 0.75s^{-1}, $k_6 = 1.3\times10^5$ M^{-1} s^{-1}, k_{12} = 200 M^{-1} s^{-1}.

Reference

[1] Johnston, D. H.; Thorp, H. H. *J. Phys. Chem.* **1996**, *100*,13837