17:55 – 18:20

Electrochemical Analysis of Sequence-Specific Binding of Methylene Blue to Gold-Tethered DNA

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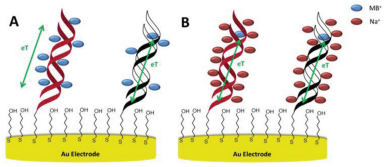

Electron transfer (ET) in DNA depends on the ET pathways predetermined by interactions of redox active species with DNA molecules [1–3]. Here, interactions between double stranded (ds)DNA tethered to gold electrodes through the alkanethiol linker and the positively charged Methylene Blue (MB) redox indicator capable of intercalating, groove and electrostatic binding to dsDNA were studied at different ionic strengths and MB concentrations (Figure) [4]. The gold surface electrodes were modified with dsDNA composed of G-C 20 base pairs (bp) and A-T 25 bp. Cyclic voltammetry was used for analysis and the ionic strength of the solutions was adjusted by NaCl.

At low MB concentrations the ET between the electrode and G-C DNA-intercalated MB is shown to be mediated by DNA and is characterized by the ET rate constant k_s approaching 40 s^{-1}. Interactions of MB with A-T DNA were restricted solely to the minor and major groove binding; with the apparent DNA-mediated ET rates increased to ca. 70 s^{-1}. This increase was associated with the varying mechanism of the ET reaction and easier protonation of the groove-bound MB as compared to the intercalated MB. At high MB concentrations, MB binding to G-C DNA was no longer restricted to intercalation but also groove and electrostatic binding, which resulted in the higher ET, k_s values approaching those obtained with A-T DNA. By screening the charges, electrostatic interactions and groove binding of MB to DNA were diminished, and the whole ET reaction was governed by diffusion of MB to the electrode surface.

The results show that modes of interaction between MB redox indicator and dsDNA tethered to gold surface electrodes is sequence-specific, and depend on the concentration of MB and the solution ionic strength.The results are particularly important for understanding the ET properties of DNA and for the development of new concepts of biosensors based DNA-mediated ET reactions.

References

[1] Slinker, J. D.; Muren, N. B.; Renfrew, S. E.; Barton, J. K. *Nature Chem*. 2011, 3, 228–233
[2] Anne, A.; Demaille, C. *J. Am. Chem*. Soc. 2006, 128, 542–557.
[3] Ferapontova E. E., *Curr. Anal. Chem*., 7 2011 51–62.
[4] Kekedy-Nagy, L., Campos, R., Ferapontova, E. **2014**, in preparation.