Electrochemical DNA sensors based on polymeric indicator: Use of poly(4-vinylpyridine) derivative bearing $[Os(5,6\text{-dmphen})_2Cl]^{2+}$(5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline)

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Abstract

DNA hybridization biosensors are of increasingly significance in disease diagnostics, pharmacological screening, and forensic applications. It is reported that the redox labels which are bound to DNA duplexes by non-covalent interactions such as electrostatic attraction, hydrophobic interaction, or intercalation have proven to be particularly important in DNA hybridization recognition processes. Currently, it is gradually attracted interest to develop indicators bearing high affinity to ds-DNA by designing molecular structure of redox indicators.

A poly(4-vinylpyridine) (PVP) derivative bearing redox-active osmium complexes, PVP-$[Os(5,6\text{-dmphen})_2Cl]^{2+}$ (5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline), was employed as a hybridization indicator for electrochemical DNA sensors. PVP-$[Os(5,6\text{-dmphen})_2Cl]^{2+}$ exhibited ~1000 times higher sensitivity than the corresponding monomeric analogue, $[Os(5,6\text{-dmphen})_3]^{2+}$, in DNA determination due to polymeric effects. The detection limit of the present sensor was 0.1 pM. Another merit of the polymeric indicator is that the redox potential was found to be +360 mV (vs Ag/AgCl), which is significantly lower than that reported for the monomeric analogue (+672 mV). The polymeric indicator was applicable to the discrimination of single- and double-base-mismatched DNAs from fully matched target DNA. The polymeric indicator can be removed from the electrode surface by rinsing the electrode in a high-temperature buffer for 6 min, and thus, the polymeric indicator-based DNA sensor can be used repeatedly.

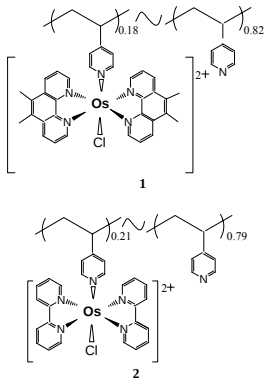

Figure 1. Chemical structures of indicators **1** and **2**.

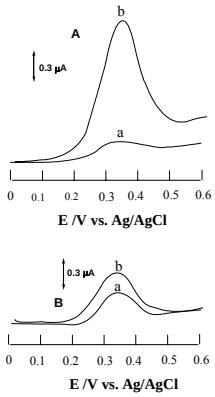

Figure 2. DPVs of **1** (A) and **2** (B) adsorbed on the sensor before (a) and after hybridization (b). The Au electrode was modified with 0.1 μM $HS(CH_2)_6$-5'-d(TAA GGG AAT GGT TAG GAA GGC)-3' and hybridized with 1.0 nM target DNA. Differential pulse voltammetry conditions: scan rate, 50 mV s^{-1}; pulse height, 50 mV; pulse width, 100 ms; pulse period, 200 ms. The voltammograms were obtained in 10 mM Tris-HCl buffer containing 0.1 M $NaClO_4$ (pH 7.4).

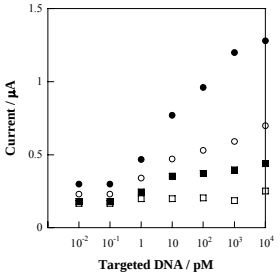

Figure 3. Typical calibration graphs of the sensor modified with $HS(CH_2)_6$-5'-d(TAA GGG AAT GGT TAG GAA GGC)-3' to fully matched (●), one-base-mismatched (○), two-base-mismatched (■), and fully mismatched DNA (□). DPV was carried out under the same conditions as in Figure 2.

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