

Supporting Information

Target-Induced Strand Release (TISR) from Aptamer-DNA Duplex: A General Strategy for Electronic Detection of Biomolecules Ranging from A Small Molecule to A Large Protein

Jyun Yoshizumi, Satoshi Kumamoto, Mitsunobu Nakamura and Kazushige Yamana*

Materials. Deoxyribonucleoside phosphoramidites and 1-O-dimethoxytrityl-propyl-disulfide-modified CPG were purchased from Transgenomics and Glen Research Incs, respectively. 5'-Bis-anthraquinone-modified oligonucleotides and oligonucleotides containing a disulfide anchor at the 3'-terminus were synthesized on ABI 394 DNA/RNA synthesizer, purified using a reversed phase h.p.l.c.. Au[111] surfaces onto slide-glass were prepared by Osaka Vacuum Chemical (Osaka, Japan) with a vapor deposition method. Before DNA modification, the Au surface was soaked at room temperature in piranha solution ($\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4 = 1:3$, v/v) for 15 min x 2, washed with deionized water, and dried with blow of nitrogen gas. The clean Au-glass was attached to a window (geometrical area: 0.5 cm^2) of a glassware cell that is designed for electrochemical measurements.

Electrochemical Measurements. Electrochemical measurements were carried out in the cell consisting of the modified Au electrode (0.5 cm^2), a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode, using an electrochemical analyzer (ALS/H CHI Model 612B). All cyclic voltammetry and differential pulse voltammetry measurements (Incr E: 0.004 V; Amplitude: 0.1 V; Pulse width: 0.01 s; Sample width: 0.005 s; Pulse period 0.2 s) were performed at room temperature in the buffer described in each Figure legend. The buffer was thoroughly degassed with nitrogen before measurements.

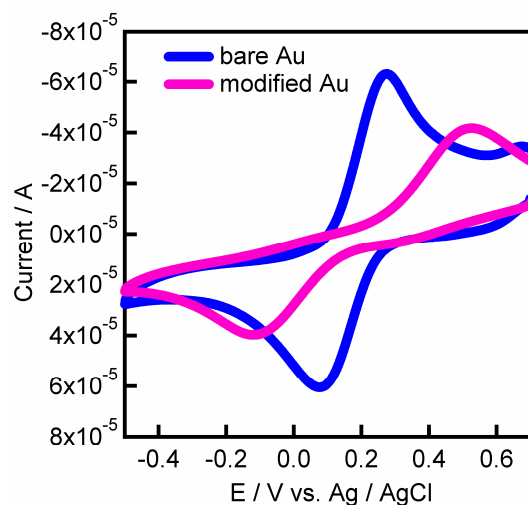


Figure S1. Cyclic voltammograms of bare gold electrode and the anti-ATP aptamer-DNA modified electrode (Sensor for ATP) in 50 mM NaCl and 10 mM sodium phosphate containing 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]^{3-}$ at a scan rate of 100 mV/s. The DNA modification resulted in the reduced peak current and large split of anodic and cathodic peaks compared with those for bare electrode.

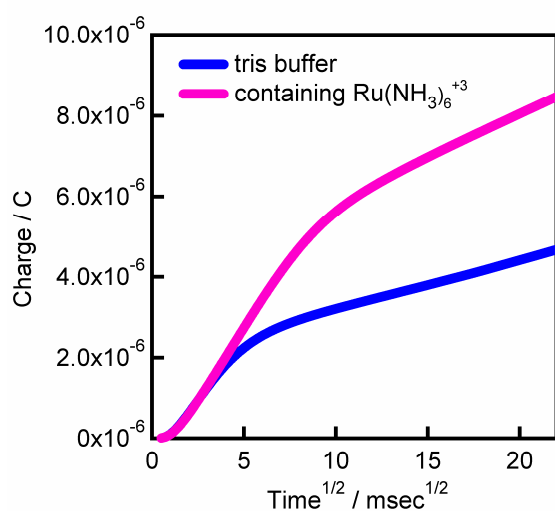


Figure S2. Quantification of the ATP-aptamer-DNA bound to the gold electrode by chronocoulometry using 0.05 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 10 mM Tris buffer (pH 7.4). Reference: Steel, A. A.; Herne, T. M.; Tarlov, M. J. *Anal. Chem.* **1998**, *70*, 4670-4677.

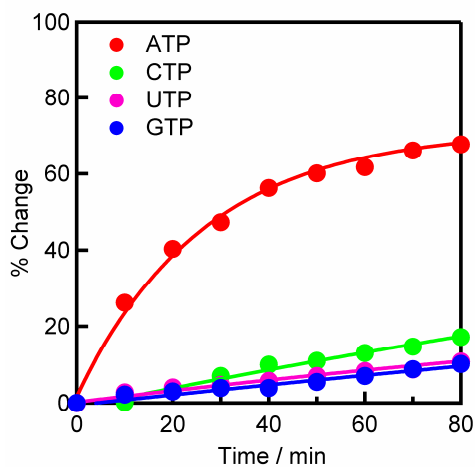


Figure S3. Selectivity in the sensor for ATP. Measurements were carried out at room temperature for 0.1 mM of nucleoside triphosphates in 20 mM Tris buffer (pH 7.6) containing 300 mM NaCl and 5 mM MgCl₂.

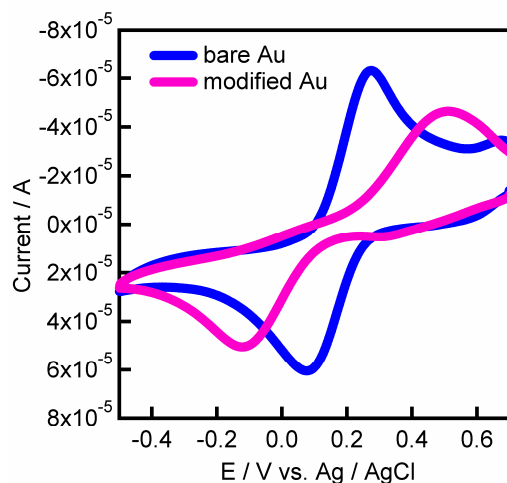


Figure S4. Cyclic voltammograms of bare gold electrode and the anti-thrombin aptamer-DNA modified electrode (Sensor for thrombin) in 50 mM NaCl and 10 mM sodium phosphate containing 1 mM K₃[Fe(CN)₆]³⁻ at a scan rate of 100 mV/s. The DNA modification resulted in the reduced peak current and large split of anodic and cathodic peaks compared with those for bare electrode.

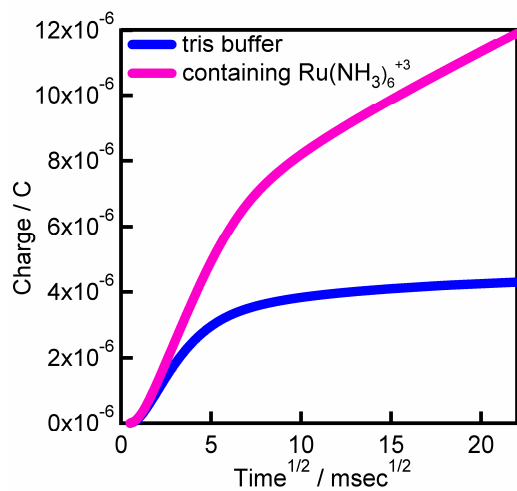


Figure S5. Quantification of the thrombin-aptamer-DNA bound to the gold electrode by chronocoulometry using 0.05 mM Ru(NH₃)₆³⁺ in 10 mM Tris buffer (pH 7.4). Reference: Steel, A. A.; Herne, T. M.; Tarlov, M. J. *Anal. Chem.* **1998**, *70*, 4670-4677.