Electronic Supplementary Information for

Electrochemical Detection of Insertion/Deletion Mutations Based on Enhanced Flexibility of Bulge-Containing Duplexes on Electrodes

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Experimental section

Materials. DNA probes were synthesized as a procedure previously reported.[1–3]

DNA probe characterization. DNA probes were characterized by using MALDI-TOF mass spectrometry measurements recorded on a Bruker-Daltonics-Autoflex mass spectrometer with 3-hydroxypicolinic acid as the matrix (Figure S4): m/z for **CYP3A4**: (calcd: 5170.83 $[M-H]^-$; found: 5171.62), **CYP2D6** (calcd: 5043.80 $[M-H]^-$; found: 5046.76), **C6-CYP3A4** (calcd: 5212.89 $[M-H]^-$; found: 5216.51), **C6-CYP2D6** (calcd: 5085.85 $[M-H]^-$; found: 5085.65), **p53** (calcd: 5091.82 $[M-H]^-$; found: 5092.14), **ABCA** (calcd: 5096.81 $[M-H]^-$; found: 5099.59), **PCM1** (calcd: 5078.79 $[M-H]^-$; found: 5082.36), **PDK4** (calcd: 5202.85 $[M-H]^-$; found: 5203.15).

Immobilization of DNA probes onto gold electrodes. Commercially available gold electrodes (Tanaka Kikinzoku, Tokyo, Japan) were cleaned as previously reported[1–5] and dried under argon stream before use. For immobilization of DNA probes, a probe DNA (100 μM) in a buffer solution (1 μL, 10 mM phosphate buffer that contained 1 M $NaClO_4$, pH 7) was placed on the gold electrode and kept in a closed container under high humidity for 90 min at room temperature. After having been rinsed with the buffer solution (300 μL), the probe DNA-modified gold electrode was soaked in a solution of 1 mM 6-mercaptohexan-1-ol in the buffer solution contained 1% Tween 20 (300 μL) for 90 min at room temperature. Then, it was thoroughly washed with Milli-Q water and the buffer solution successively. For hybridization of target DNAs, the modified gold electrode was soaked into a solution of 100 μM (down to 1 μM) target DNAs in the buffer solution (50 μL) for 90 min at room temperature, then it was rinsed with the buffer solution (300 μL).

Electrochemical Measurements. CV and SWV measurements were carried out as previously reported.[4,5] The buffer solution (10 mM phosphate buffer that contained 1 M $NaClO_4$, pH 7) was used as the electrolyte solution for all electrochemical studies. CV and SWV measurements were carried out at 25 °C on the probe-modified electrodes by means of a normal three-electrode configuration consisting of the gold working electrode, a saturated Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The working compartment of the electrochemical cell was separated from the reference compartment by a glass frit.

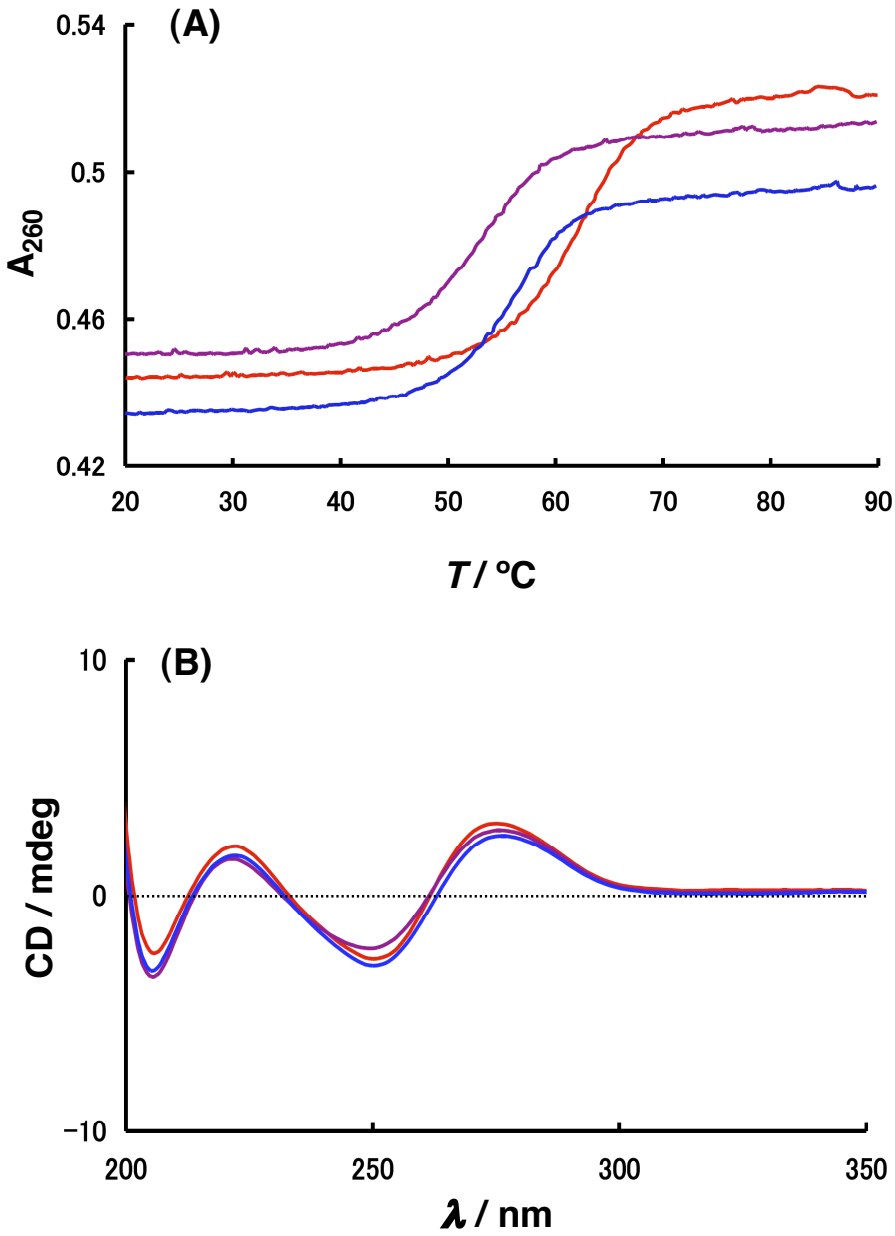

Figure S1. (A) UV-melting curves at 260 nm and (B) CD spectra at 25 °C of fully-matched **Iq1'·wild** (red line), insertion-type **Iq1'·insC** (purple line), and deletion-type **Iq1'·delT** (blue line). The solution for the measurements by 1 mm path-length contained **Iq1'** (1 μM) and 1 equiv of **wild**, **insC**, or **delT** (1 μM) in 10 mM phosphate buffer (pH 7) with 1 M $NaClO_4$. Absorbance vs. temperature profiles of the duplexes were measured by using a JASCO-V-560 spectrophotometer with a peltier and a temperature controller in a range from 20 to 90 °C. CD spectra were recorded on a JASCO-J-720WI spectropolarimeter.

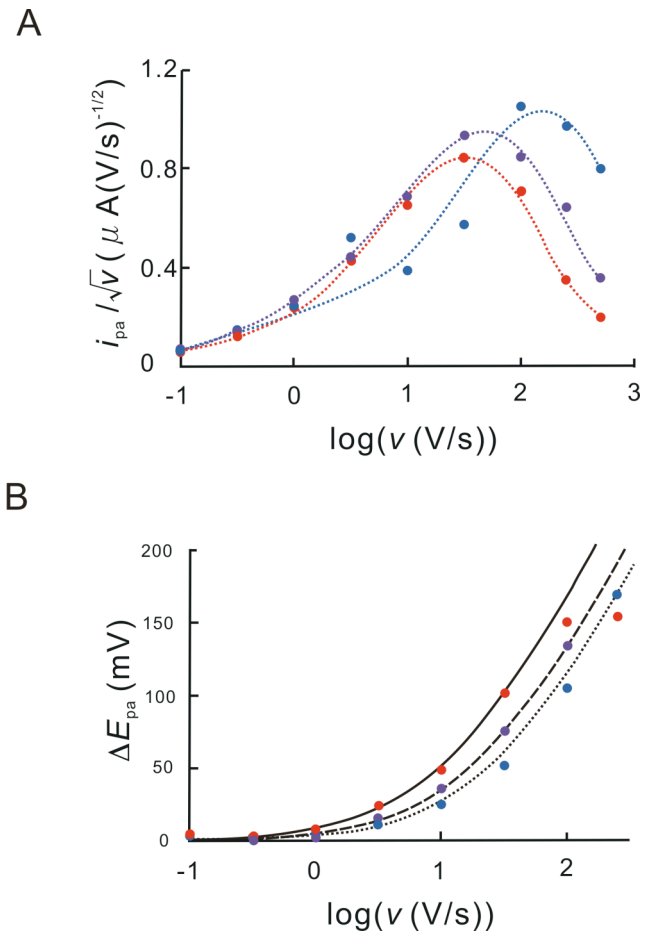

Figure S2. Scan rate v dependence of the anodic peak current i_{pa} and of the anodic peak potential E_{pa} of the cyclic voltammograms recorded at the **Iq1**-modified gold electrodes with **wild** (red symbols), **insC** (purple symbols), and **delA** (blue symbols). (A) Bell shaped variation of the anodic peak-current function $i_{pa}/\sqrt{v}$ vs log(v). (B) Variation of ΔE_{pa} vs log(v). Simulated curves are shown in the case for k = 90 s^{-1} (continuous line), 160 s^{-1} (dashed line), and 180 s^{-1} (dotted line).

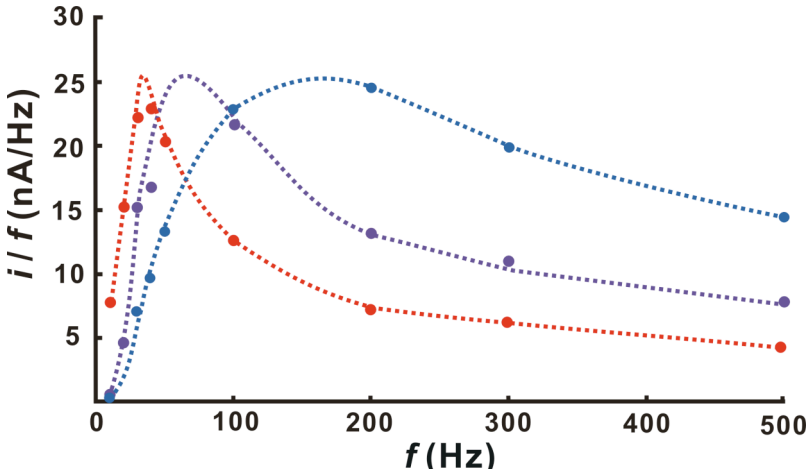

Figure S3. Frequency *f* dependence of SWV peak current at the electrodes modified with the duplexes of wild-type **Iq1•wild** (red symbols), the insertion-type **Iq1•insC** (purple symbols), and the deletion-type **Iq1•delA** (blue symbols). SWV peak current is normalized versus *f*.

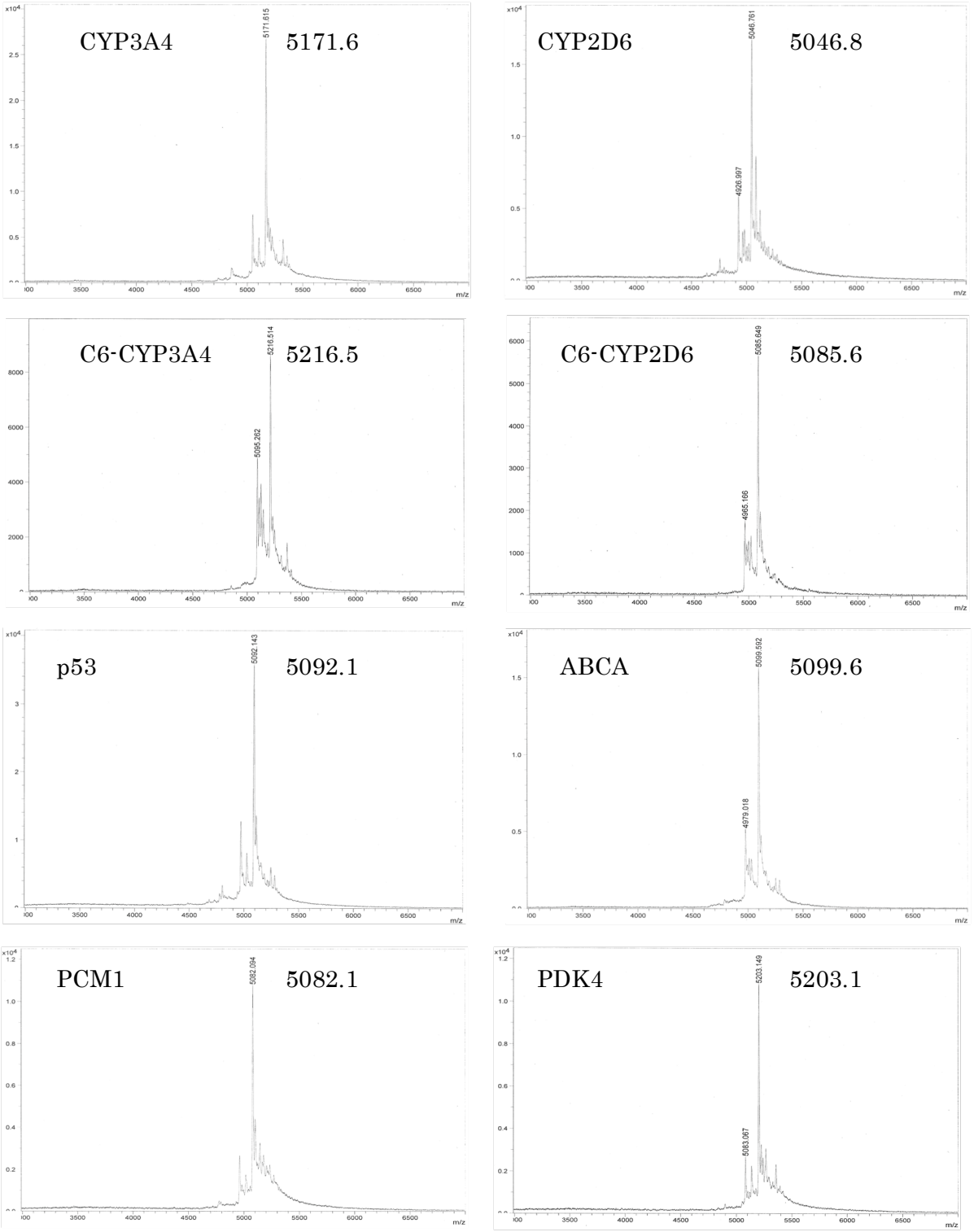

Figure S4. MALDI-TOF mass spectra of the newly synthesized DNA probes.

Supporting References

1. M. Inouye, R. Ikeda, M. Takase, T. Tsuri and J. Chiba, *Proc. Natl. Acad. Soc. USA*, 2005, **102**, 11606.

2. R. Ikeda, J. Chiba and M. Inouye, *e-J. Surf. Sci. Nanotechnol*., 2005, **3**, 393.

3. R. Ikeda, A. Akaishi, J. Chiba and M. Inouye, *ChemBioChem*, 2007, **8**, 2219.

4. R. Ikeda, S. Kobayashi, J. Chiba and M. Inouye, *Chem. Eur. J*., 2009, **15**, 4822.

5. R. Ikeda, S. Kitagawa, J. Chiba and M. Inouye, *Chem. Eur. J*., 2009, **15**, 7048.