Electronic Supplementary Information for

Deformable nature of various damaged DNA duplexes estimated by an electrochemical analysis on electrodes

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Experimental Section

Materials. DNA probes (**Fc1** and **Fc2**)[s1] and CPD or 6–4PP containing oligomers[s2] were synthesized according to the procedure previously reported. Fully-matched and AP^{THF} containing complements were all commercially available.

Preparation of probe-modified gold electrodes. Commercially available gold electrodes (Tanaka Kikinzoku, Tokyo, Japan) were cleaned as a reported procedure[3] and dried under argon stream before use. For immobilization of DNA probes, 1 μL of a probe DNA (100 μM) in a buffer solution (10 mM sodium cacodylate that contained 0.5 M NaCl, pH 7.0) 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, 5 μL of a target DNA (10 μM) in the buffer solution was placed on the probe-modified gold electrode and kept in a closed container under high humidity for 90 min at room temperature, then it was rinsed with the buffer solution (300 μL).

Electrochemical measurements. CV measurements were carried out in a buffer solution (10 mM sodium cacodylate that contained 0.5 M NaCl, pH 7.0) at 15 °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.

MALDI-TOF Mass Measurements. MALDI-TOF mass spectra were recorded on a Bruker-Daltonics-Autoflex mass spectrometer operating in the negative ion mode with 3-hydroxypicolinic acid as a matrix. **Fc1** : calcd for $[M–H]^-$, $C_{162}H_{195}FeN_{57}O_{88}P_{15}S$: 4900.77; found 4900.46, **Fc2** : calcd for $[M–H]^-$, $C_{179}H_{215}FeN_{67}O_{99}P_{17}S$: 5502.85; found 5500.41.

***T*$_m$ Measurements.** T_m melting curves (1.0 ºC/1.0 min) were obtained by JASCO V-560 UV/VIS spectrophotometer with a peltier and a temperature controller in a temperature range from 20 to 90 °C (10 mm pathlength). The T_m values were determined from the maxima of the first derivatives of the melting curves measured in a buffer solution: 10 mM sodium cacodylate (pH 7.0), 0.5 M NaCl. Errors were estimated at ± 1.0 ºC.

References for ESI

S1 (*a*) M. Inouye, R. Ikeda, M. Takase, T. Tsuri and J. Chiba, *Proc. Natl. Acad. Soci. U. S. A.*, 2005, **102**, 11606; (*b*) R. Ikeda, J. Chiba and M. Inouye, *e-J. Surf. Sci. Nanotecnol.*, 2005, **3**, 393; (*c*) R. Ikeda, A. Akaishi, J. Chiba and M. Inouye, *ChemBioChem*, 2007, **8**, 2219.

S2 (*a*) T. Murata, S, Iwai and E. Ohtsuka, *Nucleic Acids Res.*, 1990, **18**, 7279; (*b*) S. Iwai, M. Shimizu, H. Kamiya and E. Ohtsuka, *J. Am. Chem. Soc.*, 1996, **118**, 7642.

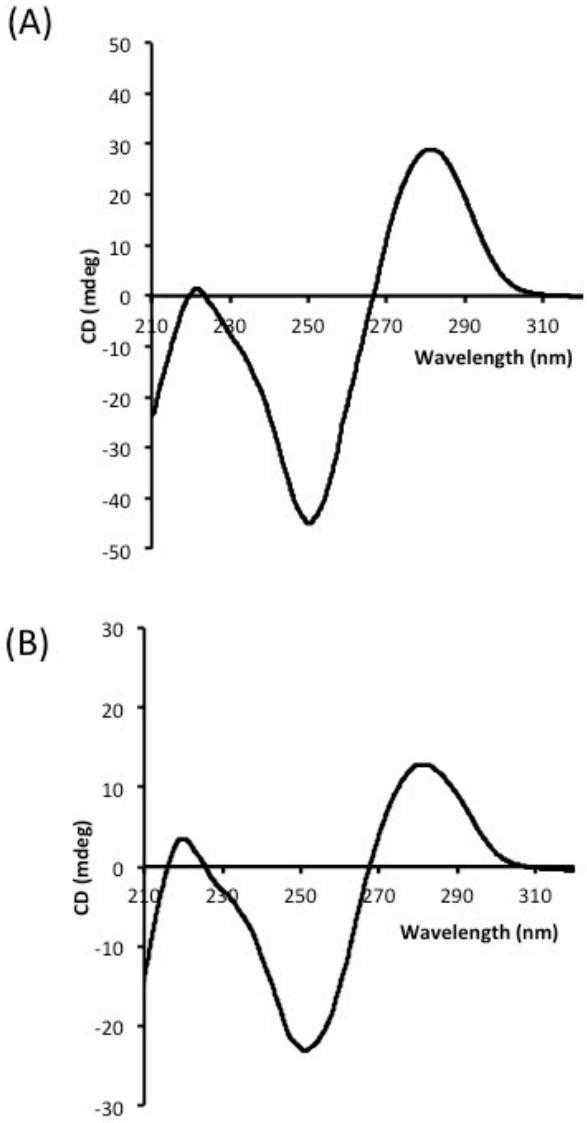

Figure S1. Typical CD spectra at 25 ºC of ds-DNAs for (A) native **1•Wild$_{14}$** and (B) photo-damaged **1•6–4PP$_{14}$**. CD spectra were recorded on a JASCO-J-720WI spectropolarimeter. Each CD spectrum of **1** (1 μM) with 1 equiv of **Wild$_{14}$** or **6–4PP$_{14}$** (1 μM) was measured in 10 mM sodium cacodylate that contained 0.5 M NaCl (pH = 7.0).

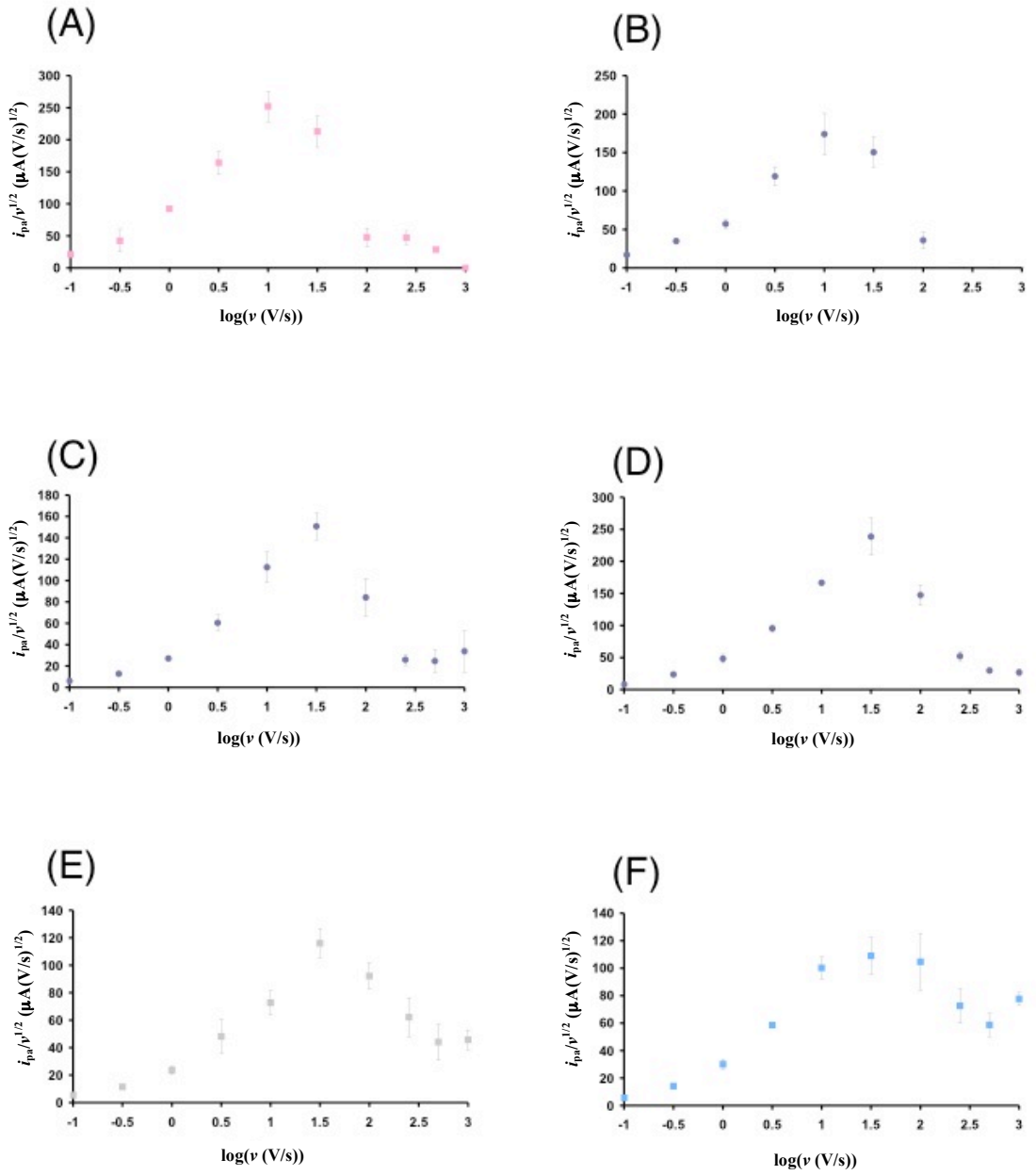

Figure S2. Scan rate v dependence of the anodic peak current i_{pa} ($i_{pa}/ v^{1/2}$ vs log(v)) of the cyclic voltammograms recorded at the **Fc1**-modified gold electrodes with (A) **Wild$_{14}$**, (B) **CPD$_{14}$**, (C) **AP$_{14}$**, (D) a single-base mismatched complement **AT$_{14}$**, (E) **6–4PP$_{14}$**, and (F) a two-base mismatched complement **AA$_{14}$**.

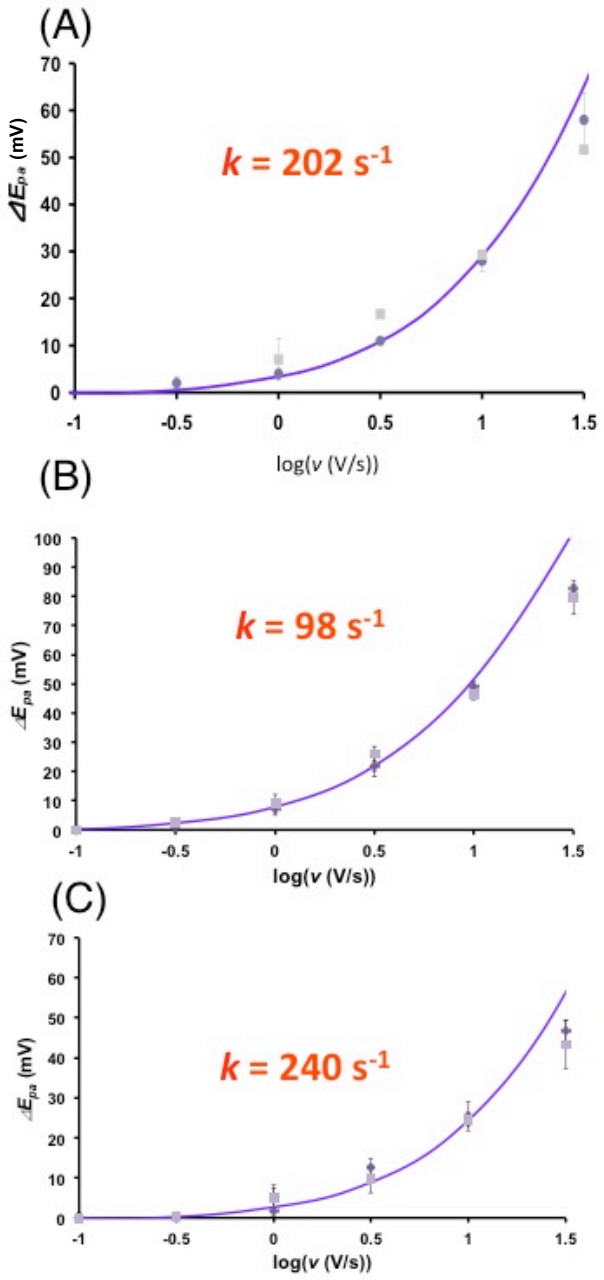

Figure S3. Scan rate v dependence of the anodic peak potential E_{pa} (ΔE_{pa} vs log(v)) of the cyclic voltammograms recorded at the **Fc1**-modified gold electrodes with (A) $\mathbf{AP_{14}}$, (B) $\mathbf{CPD_{14}}$, and (C) $\mathbf{6–4PP_{14}}$.