

*Supporting Information*

**Drastic promotion of guanine oxidation *via* electron transfer  
in  $\Psi$ -type DNA**

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## **Materials**

HPLC-grade DNAs were purchased from Japan Bio Services Co., LTD. *Crotalus adamanteus* venom phosphodiesterase I (Worthington), and Alkaline Phosphatase, Calf Intestinal (Promega) were used for the enzymatic digestion of oligonucleotides. PEG1000 and 1540 were purchased from Wako Pure Chemical Industries, Ltd. Stock solutions of PEG were stored refrigerated under argon atmosphere for preventing degradation. Aliquots of dsDNA samples were prepared by annealing equimolar amount of desired DNA complements. The samples were heated at 90 °C for 3 minutes, then cooled slowly. Before each experiment, a concentrated aqueous buffer-salt solution of PEG was added to a DNA sample solution. All aqueous solutions utilized ultra-pure water (KOMATSU ELECTRONICS, UL-pure).

## **UV-vis and CD spectral measurements**

Absorption spectra were obtained using a JASCO V-730BIO spectrophotometer at room temperature using 1 mm path length cell. CD measurements were carried out on a JASCO J-720W spectropolarimeter (Japan Spectroscopic Co., Ltd.) using one-drop measurement unit (1 mm path length).

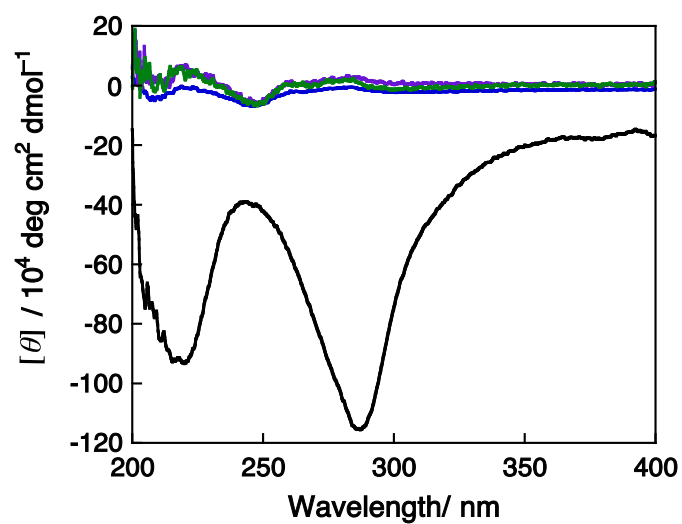
## **Melting temperature measurements**

Melting temperatures ( $T_m$ ) of all the duplexes were measured using a JASCO V-730BIO spectrophotometer with a temperature control attachment. Absorption at 260 nm (A260) of equimolar DNA complements (4.0  $\mu$ M in 100 mM NaCl, 50 mM Tris-HCl buffer pH7.4) were measured every 0.5 °C/min from 20 °C to 80 °C.

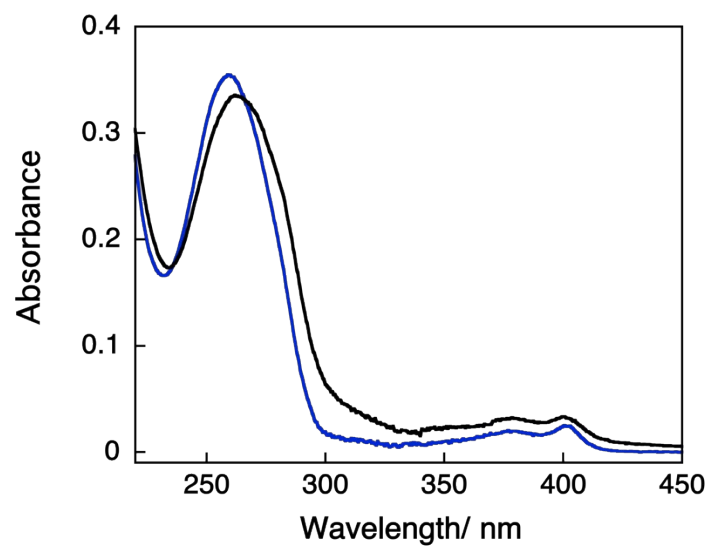
## **Photooxidation experiments**

Aliquots (4.0  $\mu$ M for PyU1-4, 16.0  $\mu$ M for N1, 100 mM NaCl, 50 mM Tris-HCl, pH 7.4, total volume 30  $\mu$ L) for irradiation were prepared. DNA solutions were irradiated with a Xe lamp (300 W; Asahi Spectra Co. Ltd.; MAX-303) through UV cut-off filter (LUX350). The irradiated solutions were filtered using amicon membrane NMWL of 3 kDa (Merck) to remove PEG. Filtrated DNA samples were digested by incubation with both alkaline phosphatase and phosphodiesterase I at 37 °C overnight in order to yield the free nucleosides, and the digested samples were analyzed by reversed phase HPLC monitored at 254 nm. HPLC analyses were performed with a JASCO Chromatograph,

EXTREMA using a CHEMCOBOND 5-ODS-H column (4.6x150 mm) eluted with 0.05 M ammonium acetate buffer containing acetonitrile (Gradient: 3-9 % over 25 min). The percentage decomposition of dG was determined using dC as an internal standard for all HPLC traces. Irradiation experiments were repeated at least three times to give average results.



**Fig. S1** CD spectra of PyU3 in aqueous buffer solution (blue line), 40 wt % PEG 1000 solution (green line), 30 wt % PEG 1540 solution (purple line) and 40 wt % PEG 1540 solution (black line). The conditions were as follows: [DNA] = 4.0  $\mu\text{M}$  in pH 7.4 Tris-HCl buffer (50 mM) and [NaCl] = 100 mM.

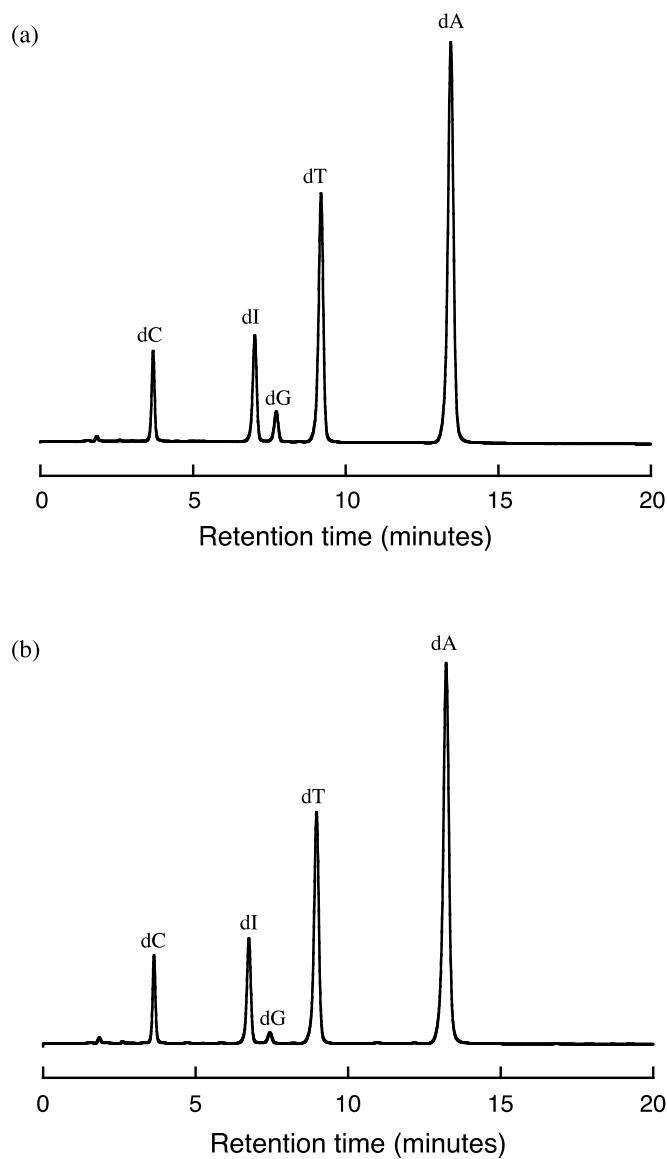


**Fig. S2** Absorption spectra of PyU1 in aqueous buffer solution (blue line) and 40 wt % PEG 1540 solution (black line). The conditions were as follows: [DNA] = 4.0  $\mu$ M in pH 7.4 Tris-HCl buffer (50 mM) and [NaCl] = 100 mM.

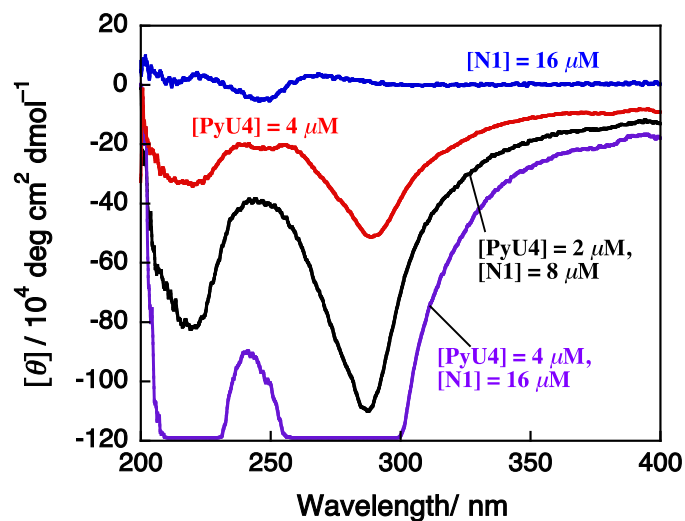
**Table S1.** Representative melting temperatures ( $T_m$ ) for dsDNA in the absence and presence of PEG1540.

Cosolute	$T_m$ , °C	$T_m$ , °C	$T_m$ , °C	$T_m$ , °C
	PyUA <sub>5</sub> GG/T	PyUA <sub>5</sub> /GG	PyUA <sub>5</sub> /II	N1
none	54.0	54.1	52.4	51.4
30 wt % PEG1540	56.0	57.3	53.8	53.4
40 wt % PEG1540	52.8	55.2	52.7	50.4

Experimental conditions: [DNA duplex] = 4.0  $\mu$ M in 50 mM Tris-HCl, pH7.4, 100 mM NaCl.  $T_m$  is determined by monitoring the UV absorption at 260 nm. The error of  $T_m$  was less than 0.5 °C.

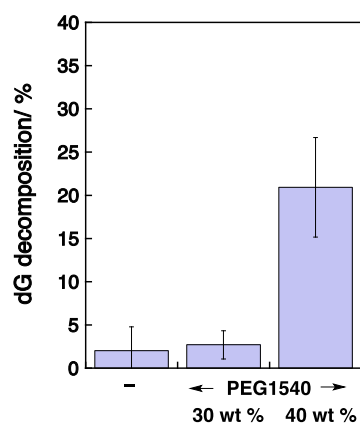


**Fig. S3** Representative HPLC chromatograms ( $\lambda_{\text{detection}} = 254 \text{ nm}$ ) of the digested PyU1 obtained after 10 min irradiation in 40 wt % PEG 1000 solution (a) and in 40 wt % PEG 1540 solution (b). HPLC analyses showed no obvious peaks of oxidized products, presumably due to the low yields. The small peak of 8-oxo-7,8-dihydro-2'-deoxyguanosine (8oxoG) may be overlapped with that of dT.



**Fig. S4** CD spectra of PyU4 in the presence of 4eq N1 obtained in 40 wt % PEG 1540 solution, together with those of PyU4 (4.0  $\mu\text{M}$ , red line) and N1 (16  $\mu\text{M}$ , blue line) measured separately. The intensity of the CD spectrum of the solution containing 4.0  $\mu\text{M}$  PyU4 and 16  $\mu\text{M}$  N1 exceeded the detection limit. Experimental conditions:  $[\text{NaCl}] = 100 \text{ mM}$  in pH 7.4 Tris-HCl buffer (50 mM).





**Fig. S5** dG decompositions of N1 obtained from photoirradiation ( $\lambda_{\text{ex}} > 350$  nm, 10 min) of PyU4 in a buffer solution and PEG mixed solutions. The conditions were as follows: [PyU4] = 2.0  $\mu\text{M}$ , [N1] = 8.0  $\mu\text{M}$ , and [NaCl] = 100 mM in pH 7.4 Tris-HCl buffer (50 mM).