Electronic Supplementary Information

for

Synthesis and Photooxidation of Oligodeoxynucleotides Containing 5-Dimethylaminocytosine that Functions as an Efficient Hole-Trapping Site in the Positive-Charge Transfer through DNA Duplex

Hisatsugu Yamada,[a] Masayuki Kurata,[b] Kazuhito Tanabe,[b] Takeo Ito,[b] and Sei-ichi Nishimoto*[b]*

[a] *Advanced Biomedical Engineering Research Unit, Kyoto University, Katsura, Kyoto 615-8510, Japan*

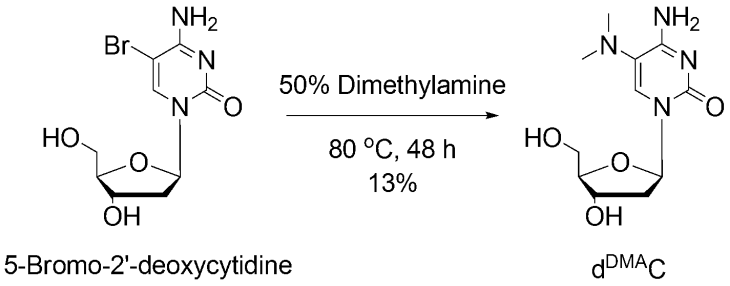
[b] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan*

*To whom correspondence should be addressed

E-mail: hisatsugu@t03.mbox.media.kyoto-u.ac.jp (H.Y) or nishimot@scl.kyoto-u.ac.jp (S. N)

1. Synthesis

5-Dimethylamino-2´-deoxycytidine ($d^{DMA}C$).



5-Bromo-2'-deoxycytidine $d^{DMA}C$

A solution of 5-bromo-2'-deoxycytidine (200 mg, 0.65 mmol) in 3 mL of 50% aqueous dimethylamine was sealed in 3 mL vial and heated at 80 °C for 40 hours. The residue was evaporated under reduced pressure and purified by reversed phase HPLC (elution with 5% acetonitrile/water, 3.0 mL/min) to give $d^{DMA}C$ (23 mg, 13%) as a white solid: mp 224-231 °C; ^{1}H NMR (D_2O, 300 MHz) δ 7.62 (s, 1H), 6.14 (t, 1H, J = 6.4 Hz), 4.34 (dd, 1H, J = 4.6, 10.8 Hz), 3.92 (t, 1H, J = 4.0), 3.73 (dd, H, J = 3.2, 15.6), 3.64 (dd, 1H, J = 4.2, 12.6), 2.45 (s, 6H), 2.30 (1H), 2.19 (1H); ^{13}C NMR (D_2O, 400 MHz) δ 163.7, 156.7, 131.2, 124.8, 87.2, 86.9, 70.7, 61.3, 43.9, 40.2; FABMS m/z 271 [$(M+H)^+$]; HRMS calcd. for $C_{11}H_{19}N_4O_4$ 271.1206, found 271.1414.

2. Stern–Volmer analysis of the fluorescence quenching

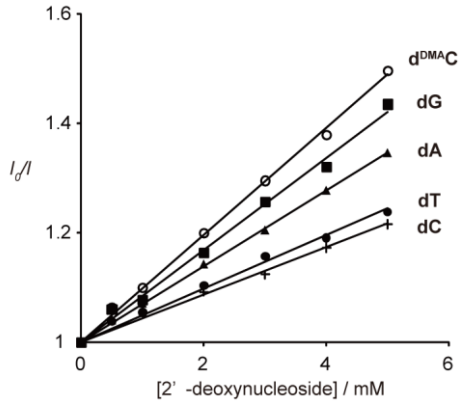


Fig. S1. Stern–Volmer plots for the fluorescence quenching of ^{1}DCA* by dC (cross), dT (closed circle), dA (triangle), dG (square), or $d^{DMA}C$ (open circle). Relative intensity of the fluorescence emission of 25 μM DCA at 487 nm was measured with varying concentrations of 2'-deoxyribonucleoside quenchers in deoxygenated solution of 10 mM phosphate buffer (pH 7.0).

3. PAGE analysis

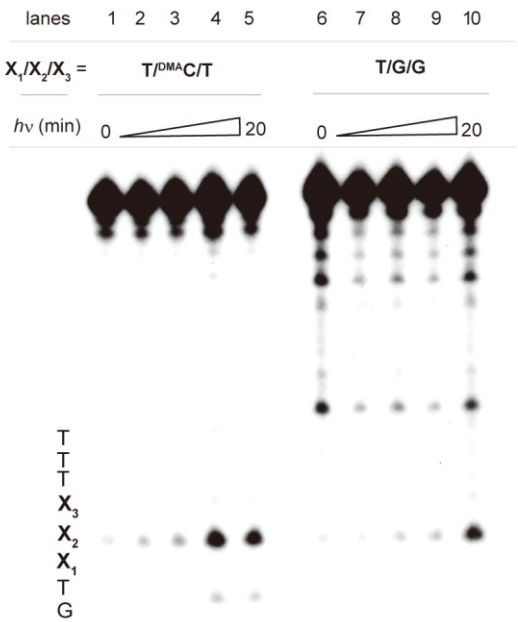


Fig. S2. PAGE image of photoirradiated ODN2($X_1/X_2/X_3$)/AQ-ODN2($Y_1/Y_2/Y_3$) [$X_1/X_2/X_3$ = $T/^{DMA}C/T$, $Y_1/Y_2/Y_3$ = A/G/A (lanes 1–5) and $X_1/X_2/X_3$ = T/G/G, $Y_1/Y_2/Y_3$ = C/C/A (lanes 6–10)]. ODN duplexes in 10 mM sodium cacodylate buffer (pH 7.0) containing 100 mM NaCl were photoirradiated (365 nm, 0–20 min) at 20 °C, followed by piperidine treatment (90 °C, 20 min).

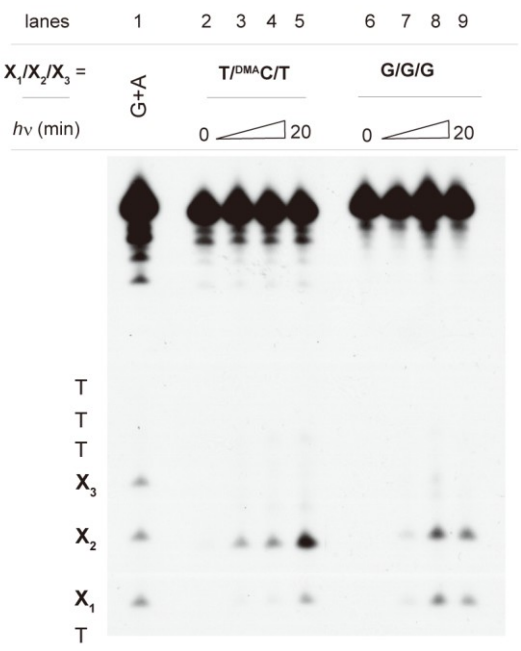


Fig. S3. PAGE image of photoirradiated ODN2($X_1/X_2/X_3$)/AQ-ODN2($Y_1/Y_2/Y_3$) [$X_1/X_2/X_3$ = T/^{DMA}C/T, $Y_1/Y_2/Y_3$ = A/G/A (lanes 2–5) and $X_1/X_2/X_3$ = G/G/G, $Y_1/Y_2/Y_3$ = C/C/C (lanes 6–9)]. G+A indicates Maxam–Gilbert sequencing lane (lane 1). ODN duplexes in 10 mM sodium cacodylate buffer (pH 7.0) containing 100 mM NaCl were photoirradiated (365 nm, 0–20 min) at 20 °C, followed by piperidine treatment (90 °C, 20 min).

4. ESI-TOF mass analysis

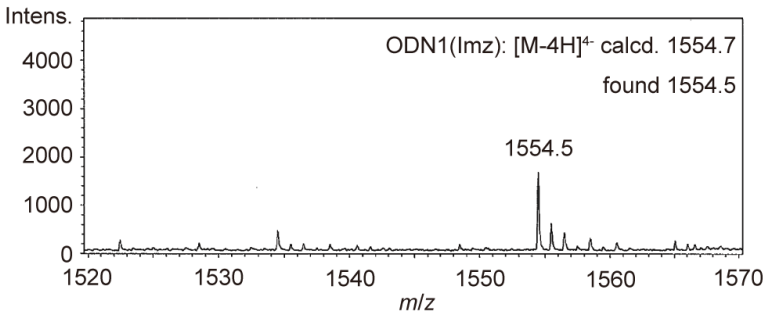


Fig. S4. ESI–TOF mass (negative mode) profiles of the photoirradiated ODN1(^{DMA}C)/AQ-ODN1(G). The duplex (10 μM) in 5 mM sodium cacodylate buffer (pH 7.0) was photoirradiated (365 nm, 20 min) at 20 °C. The reaction mixture was subjected to ESI-TOF mass analysis.