Supporting information

Adenosine-1,3-diazaphenoxazine Derivative (Adap) for Selective Base Pair Formation with 8-Oxo-2'-deoxyguanosine in DNA

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Synthesis of Adap (adenosine-1,3,-diazaphenoxazine)

General: The ^1H NMR (400 MHz, 500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded by a Varian UNITY-400 and INOVA-500 spectrometers. The ^{31}P -NMR (161 MHz) spectrum was recorded using 10% phosphoric acid in D_2O as the internal standard at 0 ppm. The UV-vis spectra and T_m measurement were measured by BECKMAN COULTER DU-800, and thermodynamic parameters were analyzed by the melt curve processing program, MeltWin (V3.5). The high-resolution mass spectra were recorded by Applied Biosystems Mariner System 5299 spectrometer using bradykinin and angiotensin as the internal standard. The MALD-TOF/MS spectra were recorded by BRUKER DALTONICS Microflex.

N1-Methyl-5-bromouracil (2): A solution of 5-bromouracil (**1**) (11 g, 58.3 mmol) in HMDS (40 mL, 192 mmol) was refluxed at 130°C for 12 h. HMDS was evaporated, and the residue was dissolved in CH_3CN (80 mL). Methyl iodide (15 mL, 241 mmol) was added into the above solution and the mixture was refluxed at 60°C for 12 h. The reaction mixture was quenched with 20% aqueous sodium thiosulfate, and CH_3CN was evaporated. The residue was extracted with EtOAc, and the organic layers were dried over Na_2SO_4 . The solvents were evaporated to give white solids, which were recrystallized from ethanol to afford **2** as white crystals (8.11 g, 39.5 mmol, 68 %). mp 216-218°C. IR (cm^{-1}): 1674, 1620. ^1H -NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 11.69 (1H, s), 8.18 (1H, s), 3.23 (3H, s). ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$) δ (ppm): 159.7, 150.6, 146.1, 94.0, 35.4. HRESI-MS (m/z): calcd. for $\text{C}_5\text{H}_5\text{BrN}_2\text{O}_2 (\text{M}+\text{H})^+$, 204.9607, 206.9587; found, 204.9653, 206.9622

5-Bromo-N-(2,6-dihydroxyphenyl)-1-methyl-cytosine (3): A solution of **2** (1.91 g, 9.32 mmol) and triphenylphosphine (3.67 g, 14.0 mmol) in CH_2Cl_2 - CCl_4 (35 mL-35 mL) was refluxed at 70°C for 4 h. The reaction mixture was cooled to room temperature, followed by the addition of 2,6-dihydroxyaniline (1.4 g, 11.1 mmol) and DBU (2.53 mL, 20.5 mmol). After stirring for 24 h at room temperature, 5% aqueous citric acid (10 mL) and methanol (20 mL) were added to the reaction mixture, and the whole was vigorously stirred. The resulting precipitates were collected by filtration to give **3** as yellow solids (940 mg). **3** was recovered from the filtrate by silica-gel column chromatography (Fuji Silysia FL60D, chloroform /methanol = 80:1) to afford **3** (381.6 mg). Total yield **3** (1.32 g, 4.23 mmol, 45%). mp 268°C (dec.). IR (cm^{-1}): 3072, 1627, 1564, 1477, 1348, 1329, 1273. ^1H -NMR (400 MHz, CD_3OD) δ (ppm): 8.09 (1H, s), 6.92 (1H, t, $J = 8.0$ Hz), 6.42 (2H, d, $J = 8.0$ Hz), 3.42 (3H, s). ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$) δ (ppm): 158.0, 153.8, 151.9, 147.8, 126.9, 114.0, 107.5, 85.9, 36.7. HR-ESIMS (m/z), calcd for $\text{C}_{11}\text{H}_{10}\text{BrN}_3\text{O}_3 (\text{M}+\text{H})^+$, 311.9978, 313.9959; found, 312.0039, 313.9980.

5-Bromo-N-{2-(N-Fmoc-aminoethoxy)-6-hydroxyphenyl}-1-methyl-cytosine (4): Triphenylphosphine (433 mg, 1.65 mmol) was added to a solution of **3** (304 mg, 0.97 mmol) and N-Fmoc-aminoethanol (414 mg, 1.46 mmol) in CH_2Cl_2 (12 mL), and the whole was stirred for 10 min, and cooled to 0°C. Diisopropylazodicarboxylate (DIAD, 40% in toluene, 0.77 mL, 1.46 mmol) was added dropwise to the above mixture, and the whole was stirred for 12 h at room temperature. This solution was diluted with EtOAc, and whole was washed with saturated ammonium chloride solution, and dried over sodium sulfate. After evaporation, the resulting yellow oil was purified by

column chromatography (Fuji Silysia NH, chloroform/methanol = 100:1) to yield **4** (538 mg, 0.93 mmol, 96%) as yellow solids. mp 152-153 °C. IR (cm⁻¹): 1687, 1662, 1629, 1576, 1258. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.75-7.71 (2H, m), 7.58-7.54 (2H, m), 7.48 (1H, s), 7.40-7.34 (2H, m), 7.32-7.26 (2H, m), 7.05 (1H, dd, *J* = 8.9, 7.3 Hz), 6.73 (1H, d, *J* = 8.9 Hz), 6.42 (1H, d, *J* = 7.3 Hz), 5.14 (1H, s), 4.42 (2H, m), 4.21 (2H, m), 3.64 (2H, m), 3.42 (3H, s). ¹³C-NMR (125 MHz, DMSO-d₆) δ (ppm): 158.5, 157.4, 154.0, 153.3, 152.5, 147.7, 142.5, 139.4, 137.4, 128.9, 127.2, 121.3, 112.0, 115.1, 110.4, 109.6, 103.4, 85.8, 67.3, 36.7. HR-ESIMS (*m/z*): calcd for C₂₈H₂₅BrN₄O₅ (M+H)⁺, 577.1081, 579.1065; found 577.1126, 579.1115.

9-(2-Aminoethoxy)-1,3-diaza-3-methylphenoxazine-2-one (5): **4** (538 mg, 0.93 mmol) was dissolved in 7 M ammonia in methanol (35 mL), and the mixture was stirred for 72 h. The organic solvent was evaporated, and the residue was purified by silica-gel column chromatography (Fuji Silysia NH, dichloromethane/methanol/triethylamine = 150:1:1, 100:1:1, 100:2:1) to give **5** (255 mg, 0.93 mmol, 100%) as yellow powders. mp 207-220 °C (sublimation). IR (cm⁻¹): 2675, 1673, 1564, 1510, 1475, 1432. ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm): 7.49 (1H, s), 6.79 (1H, dd, *J* = 8.6, 8.2 Hz), 6.62 (1H, d, *J* = 8.6 Hz), 6.45 (1H, d, *J* = 8.2 Hz), 4.16 (2H, t, *J* = 4.5 Hz), 3.22 (2H, t, *J* = 4.5 Hz), 3.16 (3H, s). ¹³C-NMR (125 MHz, DMSO-d₆) δ (ppm): 154.3, 153.7, 145.5, 142.3, 129.0, 125.7, 122.9, 116.1, 108.3, 107.1, 62.7, 38.3, 36.5. HR-ESIMS (*m/z*), calcd for C₁₃H₁₄N₄O₃ (M+H)⁺, 275.1139; found, 275.1149.

TBDMS-Adap (6): A solution of **5** (130 mg, 0.47 mmol), diisopropylethylamine (0.12 mL, 0.71 mmol) and 2'-*O*-,5'-*O*-diTBDMS-6-chloroadenosine (300 mg, 0.60 mmol) in propanol (5.0 mL) was refluxed for 12 h at 100 °C, then cooled to room temperature. A saturated aqueous NaHCO₃ solution was added into the above mixture and the organic solvents were evaporated. The residue was extracted with EtOAc, and organic layers were washed successively with water and brine, dried over sodium sulfate, then evaporated. The residue was purified by column chromatography (Fuji Silysia FL60D, hexane/dichloromethane/triethylamine = 1:2:0.03) to produce **6** (155 mg, 0.21 mmol, 44%) as yellow powders. mp 117-119 °C. IR (cm⁻¹): 1462, 1471, 1621, 1698, 2929, 3296. ¹H-NMR (400MHz, CDCl₃) δ (ppm): 8.43 (1H, bs), 8.33 (1H, s), 8.24 (1H, s), 6.75 (1H, dd, *J* = 7.8, 7.5 Hz), 6.63 (1H, d, *J* = 7.8 Hz), 6.40 (1H, d, *J* = 7.5 Hz), 6.38 (1H, dd, *J* = 7.3, 5.7 Hz), 6.31 (1H, s), 4.60-4.58 (1H, m), 4.18 (2H, t, *J* = 4.7 Hz), 4.02-3.99 (1H, m), 3.86 (2H, bs), 3.80-3.71 (2H, m), 3.17 (3H, s), 2.76 (1H, ddd, *J* = 13.1, 7.3, 5.5 Hz), 2.37 (1H, ddd, *J* = 13.1, 5.7, 2.8 Hz), 0.88 (18H, s), 0.09 (6H, s), 0.03 (6H, s). ¹³C-NMR (125 MHz, CDCl₃) δ (ppm): 154.4, 153.2, 152.7, 151.8, 151.3, 148.4, 144.8, 139.0, 129.1, 124.0, 119.8, 119.3, 115.3, 110.1, 88.1, 84.7, 72.6, 72.1, 63.1, 41.5, 40.1, 35.7, 29.7, 27.0, 26.8, 25.9, 25.8, 24.9, 24.7, 18.3, 18.0, -4.7, -4.8, -5.5, -5.5. HR-ESIMS (*m/z*), calcd for C₃₅H₅₂N₈O₆Si₂ (M+H)⁺, 737.3621; found, 737.3639.

Adap (7): A solution of **6** (145 mg, 0.20 mmol) and 1 M TBAF solution (0.43 mL in THF, 0.43 mmol) in THF (2 mL) was stirred for 40 minutes at room temperature, and the solvents were evaporated. The residue was purified by column chromatography (Fuji Silysia FL60D, dichloromethane/methanol/triethylamine = 100:1:1, 20:1:0.2) to give **7** (115 mg containing TBA) as yellow powders. Adap: mp 227-229 °C. IR (cm⁻¹): 3215, 2325, 1671, 1629, 1562, 1509, 1475, 1428,

1359, 1281, 1092. ¹H-NMR (500MHz, DMSO-d₆) δ (ppm): 9.89 (1H, bs), 8.41 (1H, bs), 8.36 (1H, s), 8.23 (1H, s), 7.47 (1H, bs), 6.74 (1H, t, *J* = 8.2 Hz), 6.56 (1H, d, *J* = 8.2 Hz), 6.40 (1H, d, *J* = 8.2 Hz), 6.34 (1H, t, *J* = 6.8 Hz), 5.29 (1H, s), 5.17 (1H, t, *J* = 5.4 Hz), 4.40-4.39 (1H, m), 4.05 (2H, s), 3.88 (1H, bs), 3.87-3.86 (1H, m), 3.63-3.60 (1H, m), 3.53-3.50 (1H, m), 3.18 (3H, s), 2.70 (1H, ddd, *J* = 13.3, 6.8, 5.7 Hz), 2.27-2.24 (1H, m). ¹³C-NMR (125MHz, DMSO-d₆) δ (ppm): 154.2, 152.3, 148.2, 146.0, 142.3, 139.5, 128.9, 125.9, 122.8, 119.6, 115.8, 107.8, 88.0, 84.0, 70.9, 67.6, 61.8, 36.4, 18.5. HR-ESIMS (m/z), calcd for C₂₃H₂₄N₈O₆ (M+H)⁺, 509.1892; found: 509.1933. UV-visible (water) E₂₆₀ = 2970 M⁻¹cm⁻¹.

The β-phosphoroamidite precursor of Adap (8): DMTrCl (133 mg, 0.39 mmol) was added to a solution of **7** (100 mg, 0.20 mmol) in pyridine (3.0 mL), and the mixture was stirred for 1 h. The reaction mixture was diluted with AcOEt, and whole was successively washed with saturated aqueous NaHCO₃ solution and brine. The organic layers were dried over sodium sulfate, evaporated to give a crude yellow oil, which was purified by column chromatography (Fuji Silysia FL60D, chloroform/methanol/triethylamine = 200:1:1, 100:1:1) to give yellow powders (123 mg, 0.15 mmol, 77%). Diisopropylethylamine (0.16 mL, 0.91 mmol) and 2-cyanoethyl-*N,N'*-diisopropylchlorophosphorodiamidite (0.10 mL, 0.46 mmol) were added into a solution of the above material in dichloromethane (2.0 mL), the reaction mixture was stirred for 1 h at 0 °C. The mixture was diluted with AcOEt, and successively washed with saturated NaHCO₃ aqueous solution and brine. The organic layers were dried over sodium sulfate, and evaporated to give a crude yellow oil, which was purified by column chromatography (Fuji Silysia FL60D, Hexane/AcOEt = 1:1, 1:5) to give a yellow foam (145 mg, 0.14 mmol, 95%). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.29 (1H, s), 7.73 (1H, s), 7.39-7.13 (9H, m), 6.80-6.66 (4H, m), 6.50-6.24 (3H, m), 6.17-6.11 (1H, m), 5.65-5.52 (1H, m), 4.79-4.68 (1H, m), 4.28-4.08 (4H, m), 3.89-3.81 (1H, m), 3.77-3.65 (2H, m), 3.74 (6H, s), 3.60-3.46 (2H, m), 3.17 (3H, s), 2.81-2.70 (4H, m), 2.66-2.59 (1H, m), 2.49-2.42 (1H, m), 1.34-1.04 (12H, m). ³¹P-NMR (161MHz, CDCl₃) δ (ppm): 148.8, 148.6. ESI-MASS (m/z): 1011.4 (M+H)⁺.

DNA synthesis and MALDI-TOF mass measurements

Oligonucleotides (ODNs) were synthesized by the standard DNA synthesis procedures with a NTS-H6 DNA/RNA synthesizer (NIHON TECHNO SERVICE CO., LTD.). The synthesized ODN was cleaved from the resin. The protecting groups were removed by heating in 28% ammonium solution at 55°C for 5 h. The DMTr-ODN was purified by HPLC (nacalai tesque COSMOSIL C18-ARII) using a linear gradient (A: 0.1 M TEAA buffer, B: CH₃CN, B conc. 10 to 40%/20 min). The DMTr-group was cleaved in 10% aqueous acetic acid at room temperature, the resulting DMTr-OH was removed by washing with ether. The purities and structures of synthesized ODNs were confirmed by the MALDI-TOF Mass measurement. The natural and 8-oxodG-containing ODNs were purchased from Gene Design Inc. or Genenet.

ODN1: 5' d(CTTTCT Adap CTCCTT), calcd 4081.67, found 4080.30.

ODN2: 5' d(AAGGAG Adap AGAAAG), calcd 4344.86, found 4343.40.

ODN3: 5' d(Adap CGCGCG), calcd 2362.46, found 2361.53.

ODN4: 5' d(TAACCCCTAA Adap TACTA), calcd 4759.78, found: 4761.90.

ODN5: 5' d(CCCTAACC Adap TAACTA), calcd 4720.76, found: 4718.82.

ODN6: 5' d(CCCTAAC Adap CTAATA), calcd 4720.76, found: 4718.86.

ODN7: 5'd(GGCCTT Adap GGTTCAGT), calcd 4854.73, found: 4754.89.

***T_m* measurements**

The duplex DNA (1-12 μ M) was heated to 90°C for 5 min and annealed by slow cooling in the buffer containing 100 mM NaCl and 10 mM sodium phosphate at pH 7.0. UV melting behavior was monitored at 260 nm from 20°C to 70°C with a rate of 1.0°C/min with a DU 800 spectrometer (Beckman Coulter) and the data were analyzed by the program MeltWin(v3.5).

Fluorescence measurements

Fluorescence quenching study was carried out in 1 cm path length quartz cells with a JASCO FP-6500 fluorescence spectrometer. The fluorescence spectra were measured using 50 nM or 10 nM each of the ODNs with excitation at 365 nm in the buffer containing 100 mM NaCl, 10 mM sodium phosphate buffer, pH 7.0 at 30°C.

Circular dichroism (CD) measurements

CD spectra were measured using 5.0 μ M each ODN in the 10 mM sodium phosphate buffer (pH 7.0) containing 100 mM NaCl at 25°C with a JASCO J-720W spectrometer in a cylindrical quartz cell with a path length of 0.1 cm.

(A) **ODN1-ODN2** (X = Adap, Y = 8-oxodG, dG, dC, T, dA)

(B) **ODN1-ODN2** (X = 8-oxodG, dG, dC, T, dA, Y = Adap)

Figure S1. Normalized melting curves for the sequence of **ODN1** and **ODN2** using 2 μ M each strand in 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0. (A) **ODN1** having Adap and **ODN2** having 8-oxodG, dG, dC, T or dA. (B) **ODN1** having 8-oxodG, dG, dC, T or dA and **ODN2** having Adap.

ODN1: 5' d (CTTTCT~~X~~CTCCTT) 3'

ODN2: 3' d (GAAAGAYGAGGAA) 5'

Figure S2. The results of van't Hoff plots of **ODN1** and **ODN2** using five data points (1-12 μ M, in 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0.).

Figure S3. CD spectra of duplex DNA containing Adap-8-oxodG base pairs and A-T base pairs. These spectra were measured using 5.0 μ M each of the **ODN1** (X = Adap, 8-oxodG, dA or T.) and **ODN2** (Y = 8-oxodG, Adap, T or dA) in the buffer containing 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0 at 25°C.

Table S1. Thermodynamic parameters of **ODN3**, 5'-d(ZCGCGCG)₂^a

ODN3 Z =	T_m^b (°C)	ΔH° (kcal/mol)	ΔS° (cal/Kmol)	ΔG°_{310K} (kcal/mol)	$\Delta\Delta G^\circ^c$ (kcal/mol)
non	49.8	-79.60	-228.21	-8.82	0
A	60.7	-80.00	-221.32	-11.36	-1.27
Adap	59.6	-83.58	-232.86	-11.35	-1.27

^a Conditions: 1M NaCl and 10 mM phosphate buffer pH 7.0. The parameters were determined by van't Hoff plots of $1/T_m$ versus $\ln[C]$. ^b T_m value is calculated at 0.1 mM. ^c $\Delta\Delta G^\circ = (\Delta G^\circ_{310K} - \Delta G^\circ_{310K(\text{core duplex})})/2$

ODN1: 5' d (CTTTCT**X**CTCCTT) 3'
ODN2: 3' d (GAAAGAYGAGGAA) 5'

X = Adap
Y = 8-oxodG or dG

Figure S4. Fluorescence quenching of **ODN1** containing Adap. The fluorescent spectra were measured using 1 μM each of the **ODN1** (X = Adap) and **ODN2** (A: Y = 8-oxodG, B: Y = dG) with excitation at 365 nm in the buffer containing 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0 at 25°C. The black curve represents the spectrum of **ODN1** and the red curve shows that after the addition of **ODN2**. T_m value at 2 μM is summarized in Table 1 in this

Figure S5. Fluorescence quenching of Adap-containing **ODN1**. The fluorescent spectra were measured using 50 nM each of the **ODNc1-ODNc5** (the nucleotide at the opposite site of Adap of the ODN1 is shown in bold) with excitation at 365 nm in the buffer containing 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0 at 30°C. The black curve represents the spectrum of **ODN1** (Adap) and the red curve shows that after the addition of **ODNc1-ODNc5** or **ODN1** (oxodG).

ODN1: 5' d (CTTTCT**X**CTCCTT) 3' X = 8-oxodG, dG, dC, T, dA or AP

ODN2: 3' d (GAAAGAYGAGGAA) 5' Y = Adap

Figure S6. Fluorescence quenching of Adap-containing **ODN2**. The fluorescent spectra were measured using 50 nM each of the **ODN1** (X = 8-oxodG, B: X = dG, C: X = dC, D: X = T, E: X = dA and F: X = AP, AP = dAP) and **ODN2** (Y = Adap) with excitation at 365 nm in the buffer containing 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0 at 30°C. The black curve represents the spectrum of **ODN2** and the red curve shows that after the addition of **ODN1**.

Figure S7. Fluorescence properties of TBDMS-protected Adap (**6**). The fluorescent spectra were measured using 1.0 μ M of the TBDMS-protected Adap and TBDMS-protected 8-oxodG (left) and TBDMS-protected dG with excitation at 365 nm in CHCl_3 at 25°C. The black, the pink and the red curves represent **6**, **6** in the presence of 0.1 μ M 8-oxodG derivative, and **6** in the presence of 1.0 μ M of 8-oxodG derivative, respectively.

A: ODN4: 3' ATC AT **Adap** AAT CCC AAT 5'
 5' TAG TA **X** TTA GGG TTA GGG TTA GGG TTA GGG

B: ODN5: 3' ATC AAT **Adap** CC AAT CCC 5'
 5' TAG TAG TTA **X** GG TTA GGG TTA GGG TTA GGG

C: ODN6: 3' ATC AAT C **Adap** C AAT CCC 5'
 5' TAG TAG TTA G **X** G TTA GGG TTA GGG TTA GGG

D: ODN7: 3' TGA CTT GG **Adap** TTC CGG 5'
 5' ATA ATG ACT GAA CC **X** AAG GCC GGT TC 3'

Figure S8. Fluorescence quenching of ODN4-7 containing Adap. The fluorescent spectra were measured using 50 nM each ODN in the buffer containing 100 mM NaCl and 10 mM sodium phosphate buffer at pH 7.0 and 30°C with excitation at 365 nm. The black curve represents the spectrum of ODN4-7 alone and the red curve shows that after the addition of the substrate ODN.

ODN1: 5' d (CTTTCT**Adap**CTCCTT) 3'

ODN10 (80mer):

3' d (TACCTCGTTAAGCGTCGGCCGCTACGGGTATGACAACTTC-
-GAAAGA^{oxo}**GGAGGAA**CGGAGAACTTAACCTAATTGCCGCTAT)

ODN11 (80mer):

3' d (TACCTCGTTAAGCGTCGGCCGCTACGGGTATGACAACTTC-
-GAAAGAG**GGAGGAA**CGGAGAACTTAACCTAATTGCCGCTAT)

Figure S9. Fluorescence quenching of **ODN1** containing Adap. The conditions were described in Figure 2, except for the length of the target ODN. The black curve represents the spectrum of **ODN1** and the red curve shows that after the addition of **ODN10** or **ODN11**.

(A) The optimized complex between Adap and 8-oxodG

(B) Side view

(C) Top view

Figure S10. Molecular modeling of the complex of Adap and 8-oxodG in DNA. The Adap-8-oxodG complex structure was optimized by MOPAC (PM3) (A). Molecular modeling was performed in Amber force field, and the Adap-8-oxodG complex was showed by CPK model, side view (B) and top view (C).

ODN1:

5' d (CTTTCT **Adap** CTCCTT) 3'
calcd 4081.67, found 4080.30.

ODN2:

5' d (AAGGAG **Adap** AGAAAG) 3'
calcd 4344.86, found 4343.40.

ODN3:

5' d (**Adap** CGCGCG)
calcd 2362.46; found 2361.53.

ODN4: 5' d(TAACCCTAA Adap TACTA)
calcd, 4759.78; found: 4761.90.

ODN5: 5' d(CCCTAACC Adap TAACTA)
calcd 4720.76, found: 4718.82.

ODN6: 5' d(CCCTAAC Adap CTA ACTA)
calcd 4720.76, found 4718.86.

ODN7: 5'd(GGCCTT Adap GGTTCAGT)
calcd 4854.73, found: 4754.89.