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### **Supplementary information**

# Effect of nucleobase change on cytosine deamination through DNA photo-cross-linking reaction via 3-cyanovinylcarbazole nucleoside

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# 1. Mass spectral data of ODNs

| ODN(XK), X= | Calculated Mass<br>(M+H) <sup>+</sup> | Experimental Mass<br>(M+H) <sup>+</sup> |
|-------------|---------------------------------------|---|
| G           | 4625.84                               | 4625.90                                 |
| Ι           | 4610.97                               | 4608.23                                 |
| Р           | 4609.94                               | 4609.55                                 |
| R           | 4594.83                               | 4607.69                                 |
| Ν           | 4639.12                               | 4629.48                                 |

#### Table S1: MALDI-TOF-MS analysis of ODNs containing $^{\mbox{CNV}}\mbox{K}$



## 2. UPLC chromatograms of photo-cross-linking

Figure S1: UPLC chromatograms of photo-reaction between ODN(XK) and cODN(C) for the mentioned time of 366nm irradiation. Asterisks indicate the cross-linked duplex.

## 3. Hydrogen bond length and stacking distance

Table S2: Hydrogen bond length between target cytosine and counter base, and stacking distance between cytosine and <sup>CNV</sup>K. Distances are calculated based on molecular modelling experiments.

| Entry            | Hydrogen bond length (Å)<br>(before/after cross-linking) | Stacking distance (Å)<br>(average) |
|------------------|--|------------------------------------|
| ODN(GK)/c(ODN(C) | a. 1.845/2.143   | 3.432                              |
|                  | b. 1.828/2.424   |                                    |
|                  | c. 1.768/2.470   |                                    |
| ODN(IK)/c(ODN(C) | a. 1.878/2.208   | 3.443                              |
|                  | b. 1.835/2.489   |                                    |
|                  |  |                                    |
| ODN(PK)/c(ODN(C) | (no H-bond)/1.979  | 3.546                              |
|                  |  |                                    |
| ODN(NK)/c(ODN(C) | a. 1.865/1.973   | 4.427                              |
|                  |  |                                    |
|                  |  |                                    |
| ODN(RK)/c(ODN(C) | (no H-bond)/(no H-bond)                                  | 3.554                              |
|                  |  |                                    |
|                  |  |                                    |

## 4. Rate constant of photo-cross-linking reaction

| ODN(XK) | k (s <sup>-1</sup> ) | Acceleration<br>ratio ( <i>k<sub>x</sub>/k<sub>G</sub></i> ) |
|---------|----------------------|--|
| ODN(GK) | 0.0683 ±0.0075       | 1  |
| ODN(IK) | 0.2376 ±0.0087       | 2.7  |
| ODN(PK) | 0.5304 ±0.0287       | 5.8  |
| ODN(NK) | 0.0441 ±0.0028       | 0.6  |
| ODN(RK) | 0.2779 ±0.0181       | 3.5  |
|         |                      |  |

Table S3: Photo-reaction rate constants of duplex consisting of ODN(XK)/ODN(C)

# 5. Molecular modeling and hydrogen bonding pattern



Figure S2: Molecular modeling structures of ODN(XK)/cODN(C) showing hydrogen bonding patterns before and after cross-linking.

6. Experimental details of molecular-modeling

Macromodel v8.1 Maestro v5.106 ©Schrodinger LLC Dynamics method: Stochastic, no shaking Simulation temperature: 300 K Time step: 1.500 fs Equilibriation time: 1.0 ps Simulation time: 10.0 ps Minimization method: PRCG Max # of iterations: 500 Converge on: Gradient Convergence threshold: 0.0500 Force field: AMBER\* Solvent: Water Electrostatic treatment: constant dielectric Dielectric constant: 1.0 Charges from: force field; extended cut off Vanderwaals: 8.0 Electrostatic: 20.0 H-bond: 4.0

#### 7. UPLC chromatograms of deamination reaction



Figure S3: UPLC chromatograms of deamination reaction of ODN(XK<>C) for the mentioned time of 37°C incubation.

#### 8. Rate constant of deamination reaction

| ODN(XK) | Rate constant, <i>k</i> (h <sup>-1</sup> ) | Acceleration<br>ratio ( <i>k<sub>x</sub>/k<sub>G</sub></i> ) |
|---------|--|--|
| ODN(GK) | $5.17 \ge 10^{-4} \pm 7.50 \ge 10^{-5}$    | 1  |
| ODN(IK) | $6.02 \ge 10^{-3} \pm 1.47 \ge 10^{-4}$    | 11.6   |
| ODN(PK) | 0  | 0  |
| ODN(NK) | 0  | 0  |
| ODN(RK) | 0  | 0  |

Table S4: Reaction rate constants of deamination reaction

## 9. UV melting curves at 260nm



Figure S4. UV melting curves at 260nm of ODN(XK)/cODN(C)

# 10. Melting temperature of ODNs

| ODN(XK) | Т <sub>м</sub> (°С) |
|---------|---------------------|
| ODN(GK) | 56.5                |
| ODN(IK) | 49.5                |
| ODN(PK) | 45.4                |
| ODN(NK) | 41.3                |
| ODN(RK) | 37.0                |

Table S5: Melting temperature of ODNs