

Supplementary information

Acceleration of deamination of cytosine through photo-crosslinking

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1. MALDI-TOF-MS analysis

Table S1: MALDI-TOF-MS analysis of synthesized ODNs with modified cytosine.

Entry	Sequence(5'-3')	Found	Calcd [M+H] ⁺
ODN(K)	TGCG ^{CNV} KCCGT	2796.99	2797.52
cODN(C)	ACGGACGCA	2733.02	2732.52
cODN(^m C)	ACGGA ^m CGCA	2746.80	2746.53
cODN(^{hm} C)	ACGGA ^{hm} CGCA	2753.42	2752.53
cODN(^{tf} C)	ACGGA ^{tf} CGCA	2758.83	2758.53

Table S2: MALDI-TOF-MS analysis of synthesized ODNs

Entry	Sequence	Found	Calcd [M+H] ⁺
ODN(GCNVK)	AAATGCGCNVKACGTCCC	4628.11	4627.84
ODN(GOHVK)	AAATGCGOHVKACGTCCC	4632.98	4632.08
ODN(GOMeVK)	AAATGCGOMeVKACGTCCC	4661.39	4661.3
ODN(GNH2VK)	AAATGCGNH2VKACGTCCC	4645.02	4645.33
ODN(ICNVK)	AAATGCICNVKACGTCCC	4611.53	4610.97
ODN(IOHVK)	AAATGCIOHVKACGTCCC	4617.04	4617.17
ODN(IOMeVK)	AAATGCIOMeVKACGTCCC	4646.05	4645.62
ODN(INH2VK)	AAATGCINH2VKACGTCCC	4630	4629.65
ODN(CCNVK)	AAATGCCCNVKACGTCCC	4588.23	4587.84
ODN(COHVK)	AAATGCCCOHVKACGTCCC	4592.99	4592.87
ODN(COMeVK)	AAATGCCCOMeVKACGTCCC	4621.74	4621.19
ODN(CNH2VK)	AAATGCCNH2VKACGTCCC	4605.28	4605.22

Table S3: MALDI-TOF-MS analysis of cross-linked ODN/ORN

Entry	Found	Calcd [M+H] ⁺
ODN(GCNVK)/cORN(C)	9435.49	9433.49
ODN(GOHVK)/cORN(C)	9438.38	9437.73
ODN(GOMeVK)/cORN(C)	9468.02	9466.95
ODN(GNH2VK)/cORN(C)	9452.3	9450.98
ODN(ICNVK)/cORN(C)	9417.99	9416.62
ODN(IOHVK)/cORN(C)	9424.07	9422.82
ODN(IOMeVK)/cORN(C)	9452.58	9451.27
ODN(INH2VK)/cORN(C)	9438.02	9435.3
ODN(CCNVK)/cORN(C)	9395.92	9393.49
ODN(COHVK)/cORN(C)	9400.31	9398.52
ODN(COMeVK)/cORN(C)	9427.33	9426.84
ODN(CNH2VK)/cORN(C)	9429.44	9410.87

Table S4: MALDI-TOF-MS analysis of cross-linked ODN/ORN

Entry	Found	Calcd [M+H] ⁺
ODN(GCNVK)/cORN(C)	9435.49	9433.49
ODN(GOHVK)/cORN(C)	9438.38	9437.73
ODN(GOMeVK)/cORN(C)	9468.02	9466.95
ODN(GNH2VK)/cORN(C)	9452.3	9450.98
ODN(ICNVK)/cORN(C)	9417.99	9416.62
ODN(IOHVK)/cORN(C)	9424.07	9422.82
ODN(IOMeVK)/cORN(C)	9452.58	9451.27
ODN(INH2VK)/cORN(C)	9438.02	9435.3
ODN(CCNVK)/cORN(C)	9395.92	9393.49
ODN(COHVK)/cORN(C)	9400.31	9398.52
ODN(COMeVK)/cORN(C)	9427.33	9426.84
ODN(CNH2VK)/cORN(C)	9429.44	9410.87

2. Log P analysis

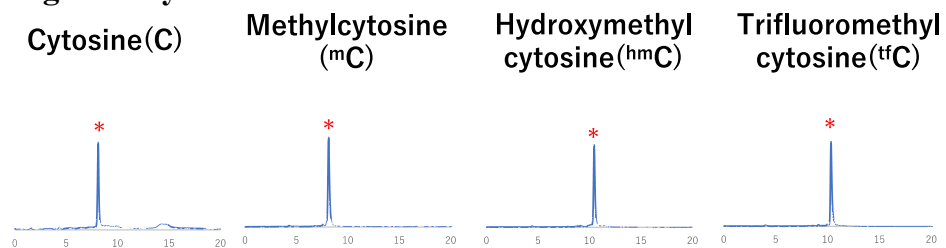


Figure S1. LogP analysis of photo-cross-linked duplex containing cytosine derivatives by water-octanol method. * Shows peak of photo-cross-linked duplex. The plots are result of HPLC analysis.

3. UPLC analysis of deamination by using varying photo-crosslinkers and counter bases

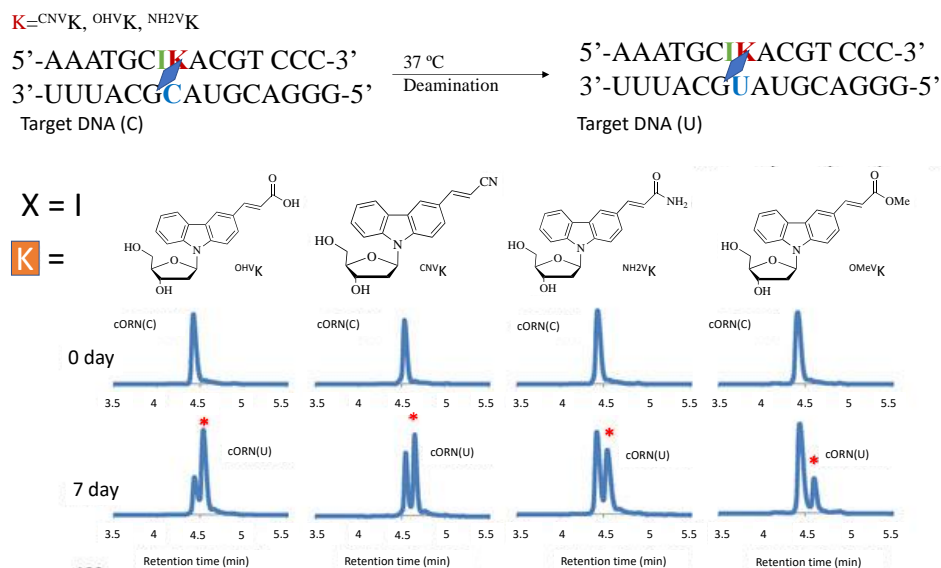


Figure S2. UPLC analysis of deamination product after photo-splitting of ODN with inosine as counter base; * indicates new peaks corresponding to cORN(U).

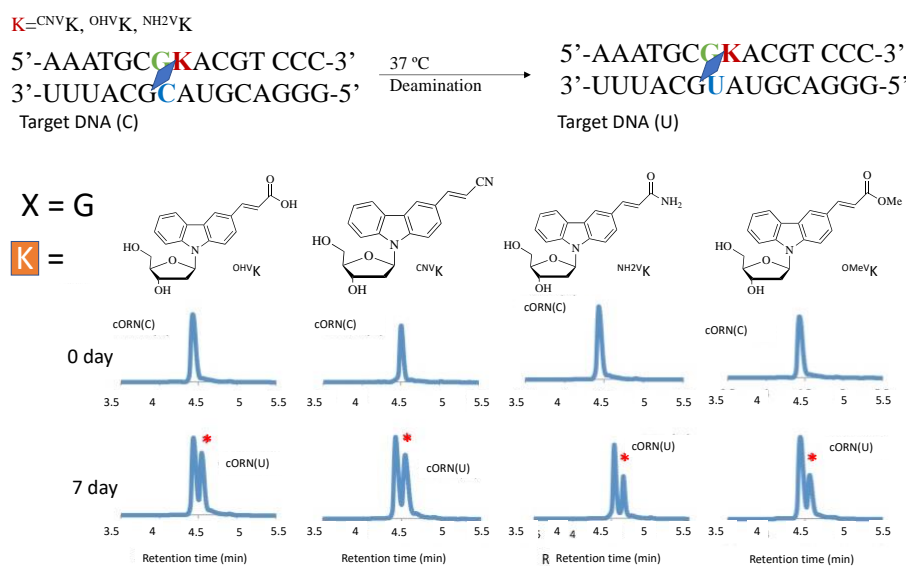


Figure S3. UPLC analysis of deamination product after photo-splitting of ODN with guanine as counter base; * indicates new peaks corresponding to cORN(U).

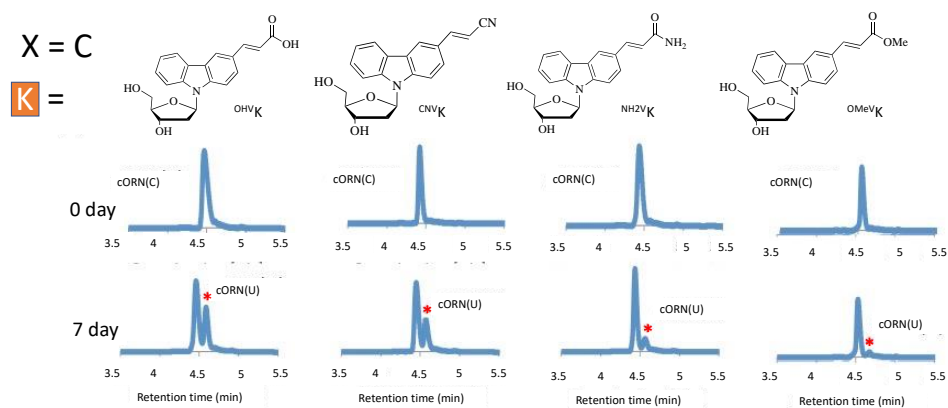
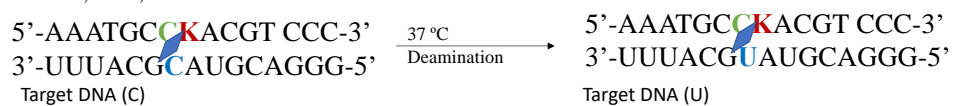


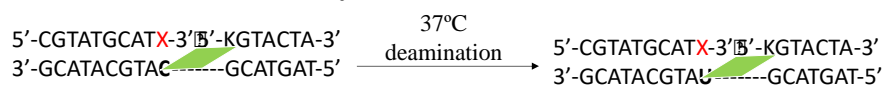
Figure S4. UPLC analysis of deamination product after photo-splitting of ODN with cytosine as counter base; * indicates new peaks corresponding to cORN(U).

4. Log P values of crosslinked ODN with varying crosslinker and counter base

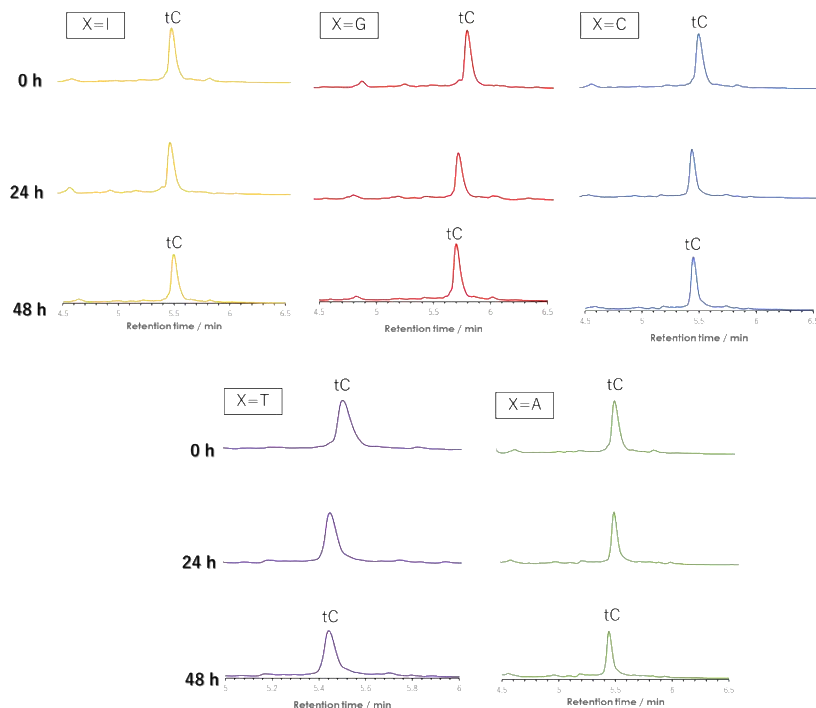
Table S5: Log P values corresponding to figure 5A of main text

		Crosslinker			
		OHvK	NH2vK	CNVK	OMevK
Counter base	Inosine	0.558513	0.713106	0.8208	0.76
	Guanine	0.640152	0.761742	0.827748	0.77
	Cytosine	0.700947	1.129986	0.902439	0.79

5. UPLC chromatograms with phosphate group modified ODN for deamination analysis



A) No Phosphate group



B) With Phosphate group

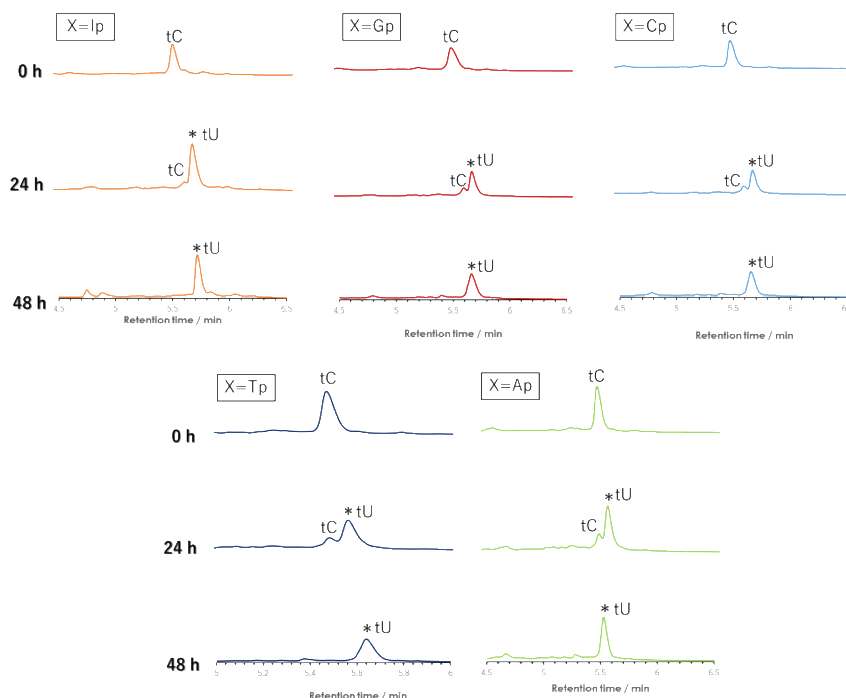


Figure S5. UPLC analysis of the deamination reaction of the photo-cross-linked duplex consisting of ODN(K), A) ODN(X); B) ODN(Xp) and cODN(C). [ODN(XK<>C)] = 5 μ M in 50 mM Na-cacodylate buffer (pH 7.4) containing 100 mM NaCl. incubated at 37 $^\circ$ C, photo splitting was performed with transilluminator (312 nm) at 37 $^\circ$ C.

6. Melting temperature analysis

Table S4: Melting temperature of duplex with modified cytosine

Entry	Melting temperature
ODN(CNVK)/ODN(C)	29.8 °C
ODN(CNVK)/ODN(mC)	33.8 °C
ODN(CNVK)/ODN(hmC)	31.6 °C
ODN(CNVK)/ODN(tfC)	28.8 °C

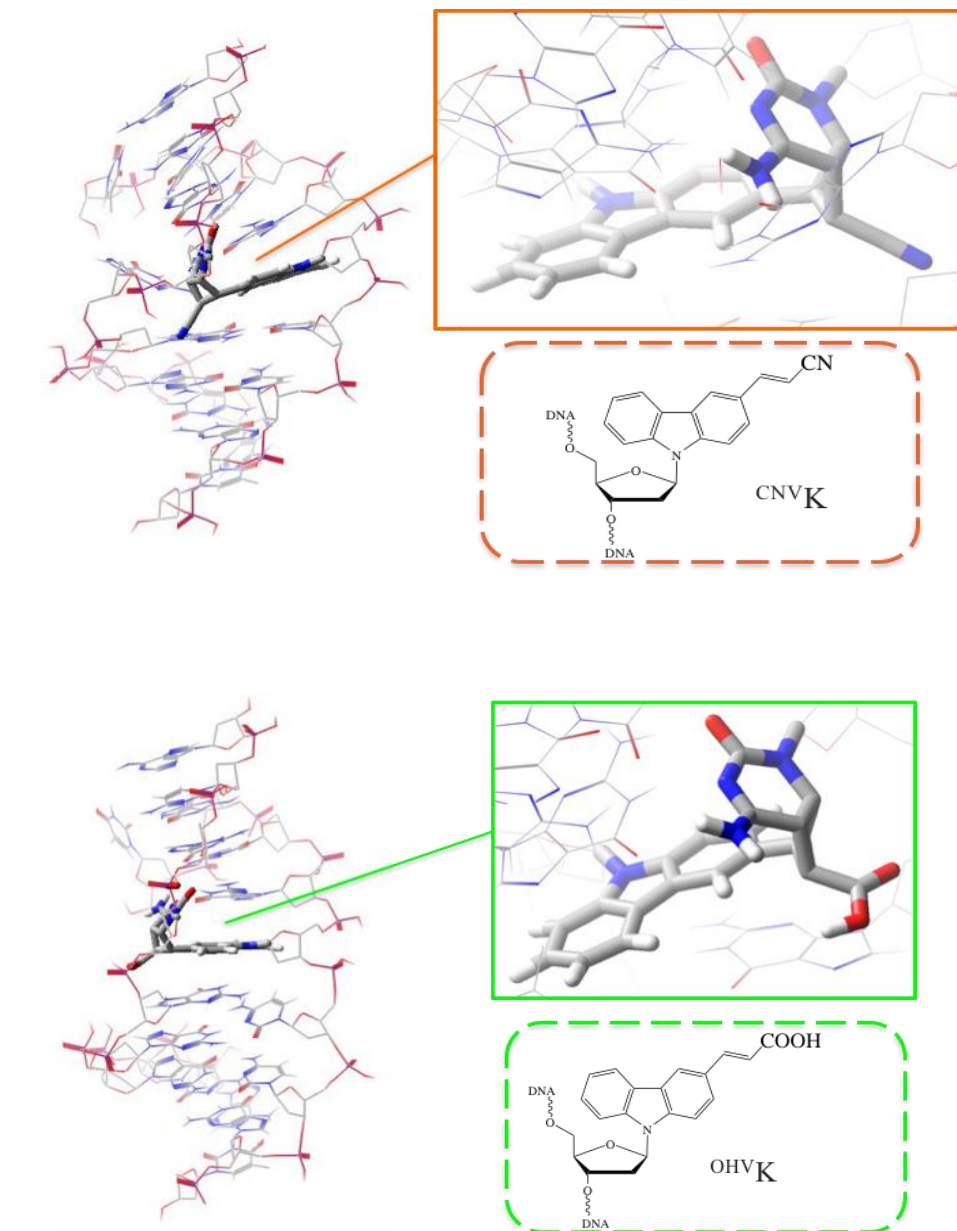
Table S5: Melting temperature of ODN/ORN duplex with CNVK

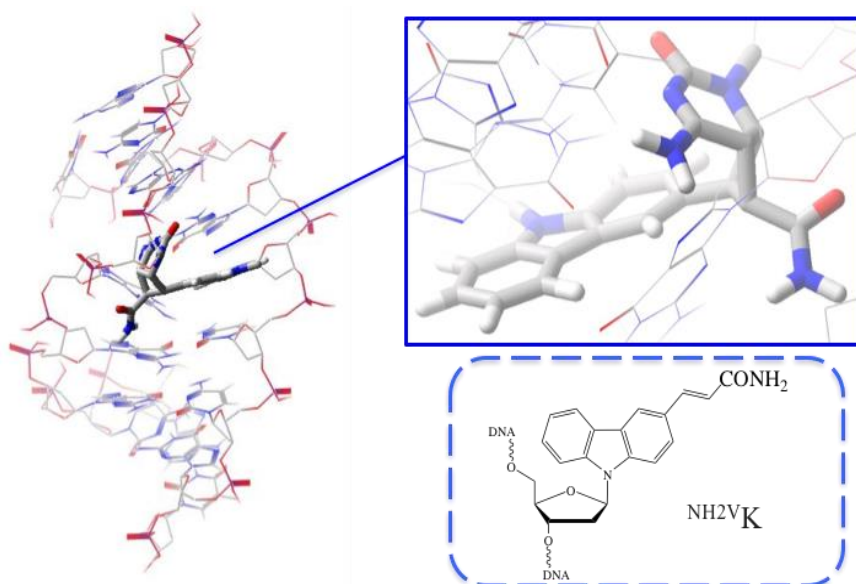
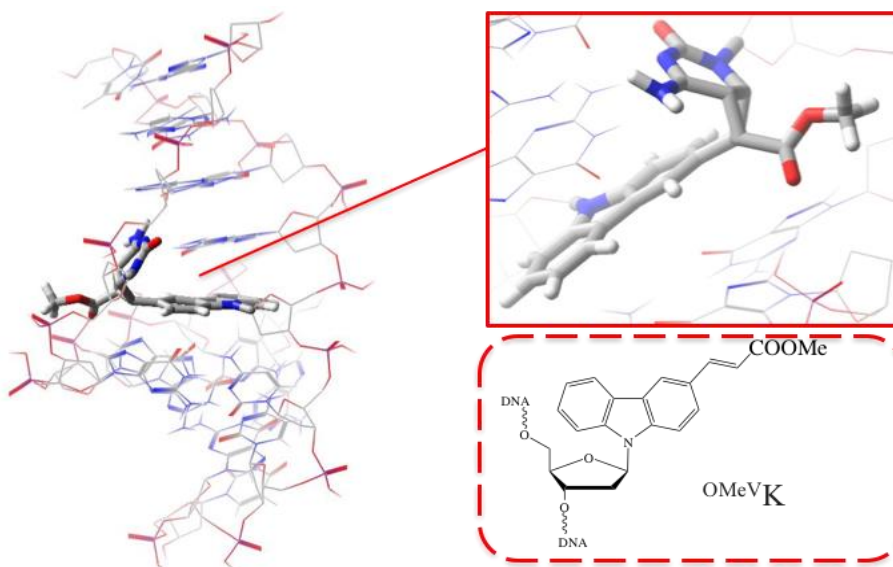
Entry	Tm
ODN(GCNVK)/cORN(C)	55.4°C
ODN(ICNVK)/cORN(C)	50.5°C
ODN(CCNVK)/cORN(C)	46.1°C

Table S6: Melting temperature of ODNs with phosphate modification

Entry	Tm (°C)
ODN(K)+ODN(C)	32.3
ODN(pK)+ODN(C)	35.4
ODN(K \blacktriangleright C)	49.9
ODN(pK \blacktriangleright C)	43.6

7. Molecular modeling





Molecular modeling experiment details

Macromodel v8.1 Maestro v5.106 ©Schrodinger LLC

Dynamics method: Stochastic, no shaking

Simulation temperature: 300 K

Time step: 1.500 fs

Equilibration 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