Supporting Information

Hydrogen Bond Formation between the Naturally Modified Nucleobase and Phosphate Backbone

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Table S1. Numbers of Types of Modified Natural RNAs[a]

Modified Nucleosides and Nucleobases	No. in tRNA	No. in rRNA	No. in mRNA	No. in tmRNA	No. in snRNA	No. in chromosomal RNA	No. in other small RNA	Total No. in all RNA modifications (%)[b-d]
Uridine	**35**	11	2	2	4	2	1	41 (37.6)
Uracil	34	10	1	2	3	2	1	40 (36.7)
Uracil Position-5	*26*	*2*	*0*	*1*	*0*	*1*	*0*	*28 (25.7)*
Adenosine	**18**	5	4	0	3	0	0	21 (19.3)
Adenine	16	5	3	0	2	0	0	20 (18.3)
Cytidine	**11**	8	2	0	1	0	0	14 (12.8)
Cytosine	11	7	1	0	0	0	0	14 (12.8)
Guanidine	**18**	5	4	0	3	0	0	20 (18.3)
Guanine	16	4	3	0	2	0	0	18 (16.5)
Inosine	**3**	1	1	0	0	0	0	4 (3.7)
7-deazaguanine	**7**	0	0	0	0	0	0	7 (6.4)

a: based on the RNA modification database (http://rna-mdb.cas.albany.edu/RNAmods/)
b: no modification has been found on the phosphate backbones.
c: the total number of nucleoside modification types is 109
d: the total number of nucleobase modification types is 103

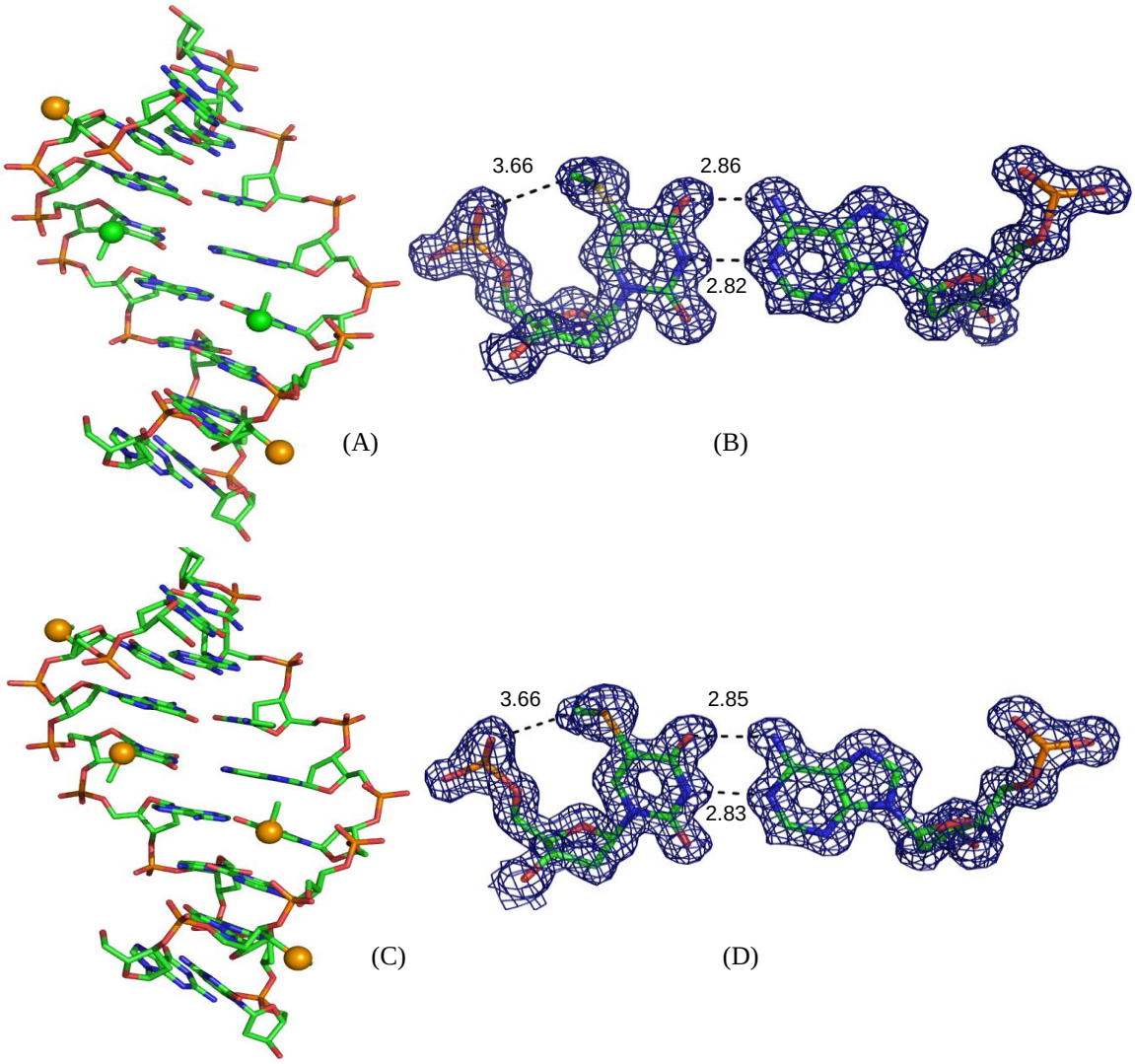

Figure S1. (A) X-ray crystal structure of A-form DNA **3b** [5'-G(dU_{Se})G(ms^5dU)ACAC-3']$_2$ at 1.38 Å resolution (PDB ID: 3IKI). (B) Electron density map of ms^5dU/A base pair, δ =1.0. (C) X-ray crystal structure of A-form DNA **3c** [5'-G(dU_{Se})G(mSe^5dU)ACAC-3']$_2$ at 1.40 Å resolution (PDB ID: 3LTU). (D) Electron density map of mSe^5dU/A base pair, δ =1.0. Yellow and green balls represent selenium and sulfur atoms of the modified moieties, respectively.

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Table S2. UV melting temperatures of the DNA duplexes containing 5-O-Me, 5-S-Me and 5-Se-Me

Entry	Oligonucleotides	Base Pair	Tm (^{o}C)
1	5'-ATGGTGCTC-3' 3'-TACCACGAG-5'	T/A	40.3
2	5'-ATGG($^{5\text{-}O}$T)GCTC-3' 3'-TACC----A-CGAG-5'	$^{5\text{-}O}$T/A	40.1
3	5'-ATGG($^{5\text{-}S}$T)GCTC-3' 3'-TACC----A-CGAG-5'	$^{5\text{-}S}$T/A	39.8
4	5'-ATGG($^{5\text{-}Se}$T)GCTC-3' 3'-TACC----A-CGAG-5'	$^{5\text{-}Se}$T/A	39.3

The melting temperatures of the 5-modified DNA duplexes were measured. Denaturation curves were acquired at 260 nm and with 1 cm path length at heating or cooling rates of 0.5 °C/min, using a UV-Vis spectrophotometer equipped with a six-sample thermo-stated cell block and a temperature controller. The experiments were performed using the DNA samples (duplexes, 1.0 μM) dissolved in the buffer of 50 mM NaCl, 10 mM NaH_2PO_4-Na_2HPO_4 (pH 6.5), 0.1 mM EDTA, and 10 mM $MgCl_2$.