SUPPORTING INFORMATION

A single nuclease-resistant linkage in DNA as a versatile method for the characterization of DNA lesions: application to the guanine oxidative lesion "G+34" generated by metalloporphyrin/$KHSO_5$ reagent

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LC/ESI-MS analysis of the oxidation of 5'-d(CAGCTG) by Mn-TMPyP/$KHSO_5$

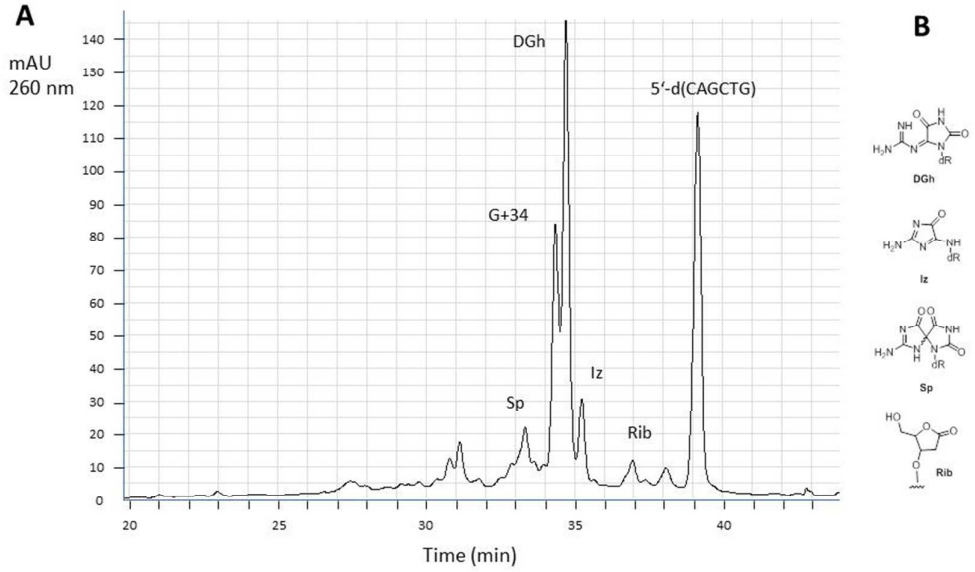

Figure S1. (A) HPLC trace of the oxidation of natural 5'-d(CAGCTG) oligonucleotide by Mn-TMPyP/$KHSO_5$. The single-stranded 6-mer elutes at 39 min. Oxidized oligonucleotides elute at different retention times. They carry different lesions, namely, « G+34 », spiroiminohydantoin (Sp), imidazolone (Iz), oxidized guanidinohydantoin (DGh) and ribonolactone (Rib) corresponding to the loss of cytidine base at the 5'-end of oligonucleotide. (B) Structure of the observed DNA lesions. See experimental section for details.

Table S1. LC/ESI-MS analysis of the oxidation of 5'-d(CAGCTG) by Mn-TMPyP/$KHSO_5$.

Rt (min)	*m/z* (*z*= 2) obs	lesion	Mass of oxidized oligonucleotide (amu)	*m/z* (*z*=2) calc
33.5	910.8	Sp	M+32	911.1
34.3	911.8	G+34	M+34	912.1
34.7	896.8	DGh	M+4	897.1
35.2	875.3	Iz	M-39	875.6
36.9	847.3	ribonolactone	M-95	847.6
39.2	894.8	5'-d(CAGCTG)	M	895.1

LC/ESI-MS analysis of the oxidation of 5'-d(CAGCTG) by Fe-TMPyP/$KHSO_5$

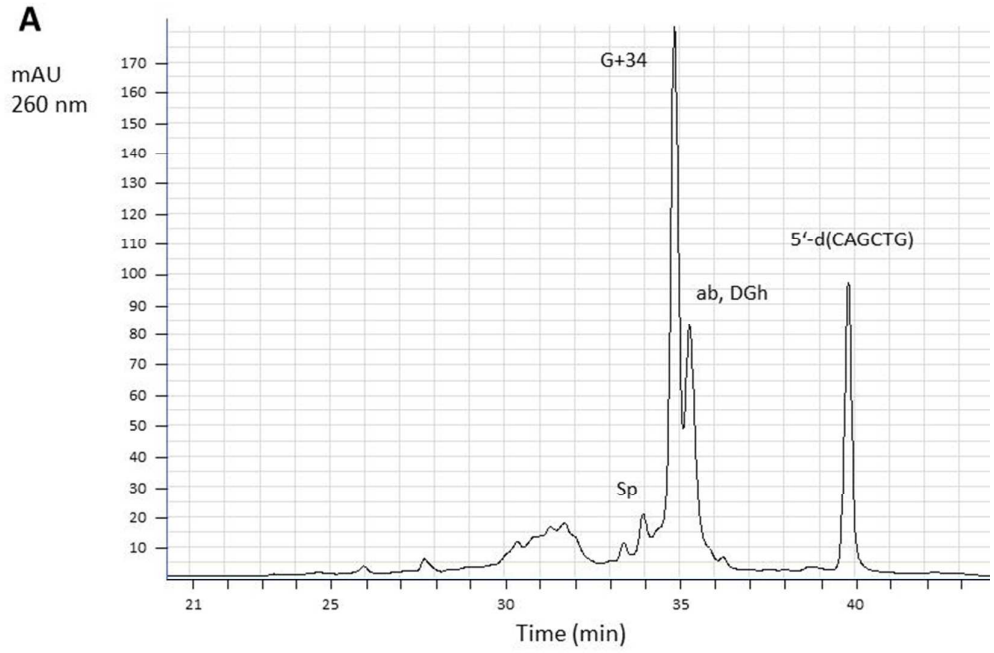

Figure S2. (A) HPLC trace of the oxidation of natural 5'-d(CAGCTG) oligonucleotide by Fe-TMPyP/$KHSO_5$. The single-stranded 6-mer elutes at 39.8 min. Oxidized oligonucleotides elute at different retention times. They carry different lesions, namely, « G+34 », spiroiminohydantoin (Sp), oxidized guanidinohydantoin (DGh) and abasic site (ab) corresponding to the loss of a guanine base. See experimental section for details.

Table S2. LC/ESI-MS analysis of the oxidation of 5'-d(CAGCTG) by Fe-TMPyP/$KHSO_5$.

Rt (min)	*m/z* (*z*= 2) obs	lesion	Mass of oxidized oligonucleotide (amu)	*m/z* (*z*=2) calc
34	910.8	Sp	M+32	911.1
34.9	911.8	G+34	M+34	912.1
35.3	896.8	DGh	M+4	897.1
35.3	828.2	abasic site	M-133	828.5
39.8	894.8	5'-d(CAGCTG)	M	895.1

LC/ESI-MS analysis of 5'-d(CAGCT$_{PMe}$G) isomer I.

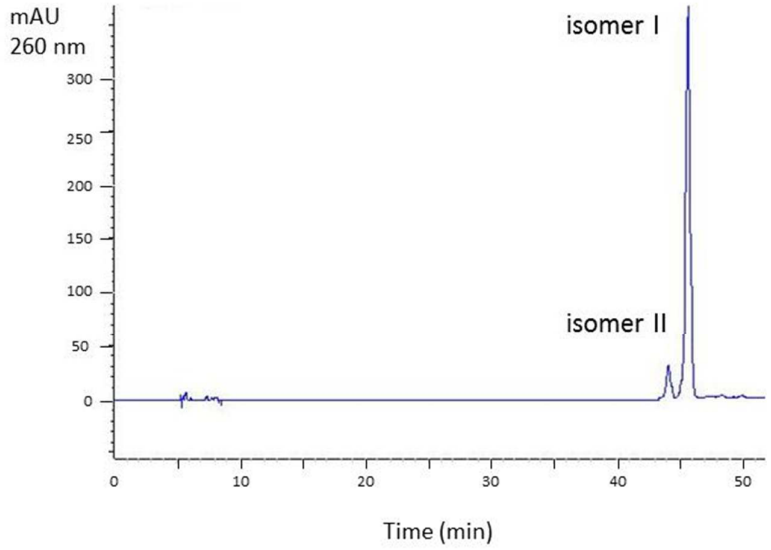

Figure S3. HPLC trace of the analysis of isomer I of 5'-d(CAGCT$_{PMe}$G) oligonucleotide (C18 reverse phase). The single-stranded modified 6-mer elutes at 45.5 min and the in-line mass spectrum shows a *m/z* signal at 894 amu for the doubly-charged species associated with a sodium adduct at *m/z* = 905 amu. See experimental section for details.

LC/ESI-MS analysis of the oxidation of 5'-d(CAGCT$_{PMe}$G) by Mn-TMPyP/KHSO$_5$

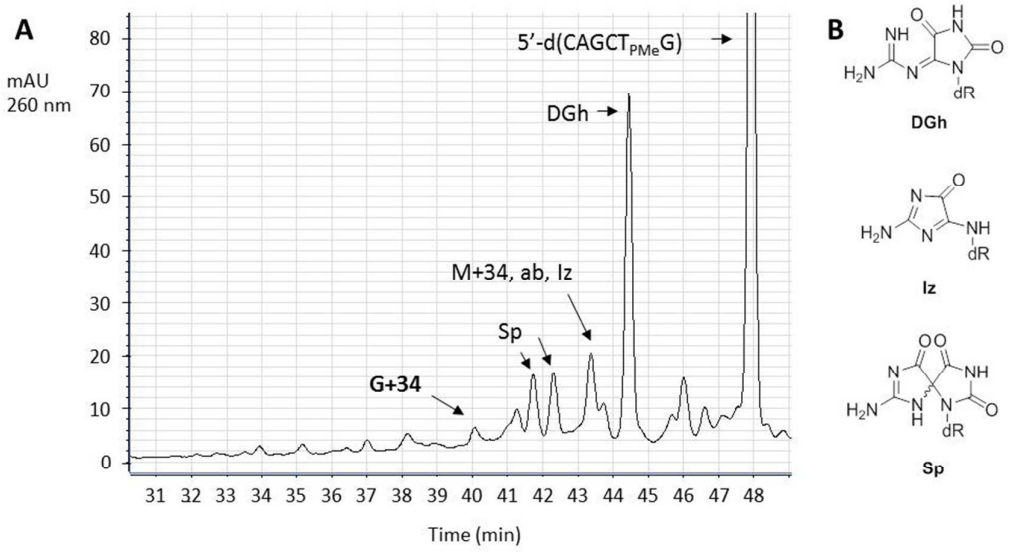

Figure S4. (A) HPLC trace of the oxidation of 5'-d(CAGCT$_{PMe}$G) oligonucleotide by Mn-TMPyP/KHSO$_5$ (C18 reverse phase). The single-stranded 6-mer elutes at 48 min. Oxidized oligonucleotides elute at different retention times. They carry different lesions, namely, « G+34 », spiroiminohydantoin (Sp), imidazolone (Iz), oxidized guanidinohydantoin (DGh), abasic site (ab) corresponding to the loss of a guanine base, and ribonolactone (rib) corresponding to the loss of cytidine base at the 5'-end of oligonucleotide. (B) Structure of the observed DNA lesions. "M+34" refers to a non-identified lesion corresponding to an increase of 34 amu with respect to the non-damaged oligonucleotide.

See experimental section for details.

Table S3. LC/ESI-MS analysis of the oxidation of 5'-d(CAGCT$_{PMe}$G) by Mn-TMPyP/KHSO$_5$.

Rt (min)	*m/z* (*z*= 2) obs	lesion	Mass of oxidized oligonucleotide (amu)	*m/z* (*z*=2) calc
40.1	910.8	G+34	M+34	911.1
41.8	909.8	Sp	M+32	910.1
42.4	909.8	Sp	M+32	910.1
43.5	910.8	M+34	M+34	911.1
	827.3	ab	M-133	827.6
	874.3	Iz	M-39	874.6
44.5	895.8	DGh	M+4	896.1
46	846.3	ribonolactone	M-95	846.6
48	893.8	5'-d(CAGCT$_{PMe}$G)	M	894.1