Differentiated oxidation modes of guanine between CpG and ^{5m}CpG by a photoactivatable Pt(IV) anticancer prodrug

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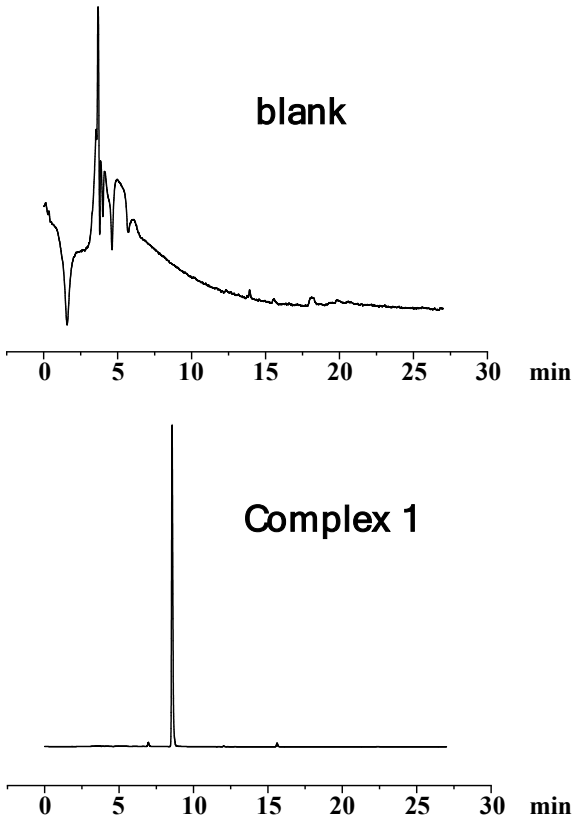
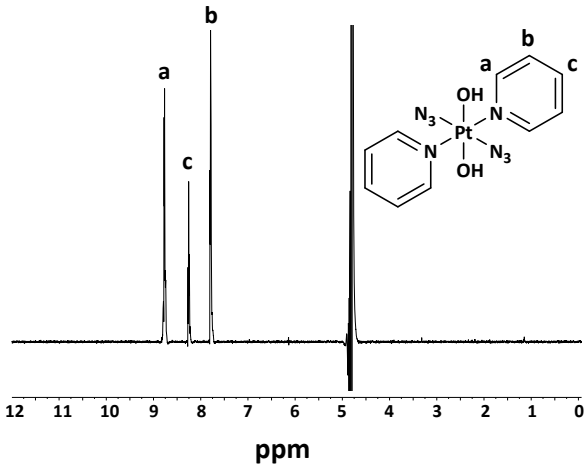
Electronic Supplementary Information

Purity of the synthesized complex 1

HPLC, ^{1}H NMR and ESI-MS were applied to verify the structure of synthesized complex **1**. For HPLC assay, an Agilent 1200 system using a C18 reversed-phase column (4.6 × 150 mm, 5 μm, Agilent Technologies Co. Ltd.). The mobile phases were water containing 0.1% TFA (Solvent A) and acetonitrile containing 0.1% TFA (Solvent B). The gradient was: (B%) 5% from 0 to 3 min, increasing to 55% at 18 min, then maintaining 55% until 25 min, and finally resetting to 5% at 26 min. The eluent at a flow rate of 1 mL/min.



^{1}H NMR (D_2O, Agilent DD2 600 MHz spectrometer): δ = 8.76 (d, J_{1H1H} = 6 Hz, 4H, py-Ha), 8.26 (t, J_{1H1H} = 8 Hz, 2H, py-Hc), 7.79 (t, J_{1H1H} = 7 Hz, 4H, py-Hb).



The obtained ESI-MS data was as follows: ESI-MS: *m/z* (the most abundant isotopomer) 494.068 ($M + Na^+$, $C_{10}H_{12}N_8O_2PtNa$ requires 494.067); *m/z* 943.168 ($M_2 + H^+$, $C_{20}H_{24}N_{16}O_4Pt_2$ requires 943.162); *m/z* 965.145 ($M_2 + Na^+$, $C_{20}H_{24}N_{16}O_4Pt_2Na$ requires 965.135).

Table S1. Mass data for the reaction mixture between Pt(IV) complex **1** and 5′-CpG at a molar ratio of Pt/CpG = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleotides and the protons for balancing the charges of the ions are omitted for clarity). All the platinated products were numbered as their appearances in the main text and the corresponding numbers are shown in bold.

Fragment ions	Molecular formula	Observed *m/z*	Theoretical *m/z*
$\{[CpG]_2 + [Pt(N_3)(py)_2]\}^+$	$C_{48}H_{59}N_{21}O_{20}P_2Pt$	1507.318	1507.344
$\{[CpG] + [Pt(N_3)(py)_2]_2\}^+$ **3**$^+$	$C_{39}H_{43}N_{18}O_{10}PPt_2$	1345.233	1345.251
$\{[CpG]_4 + [Pt(N_3)(py)_2]\}^{2+}$	$C_{86}H_{109}N_{37}O_{40}P_4Pt$	1310.803	1310.820
$\{[CpG - C] + [Pt(N_3)(py)_2]_2\}^+$ **6**	$C_{35}H_{38}N_{15}O_9PPt_2$	1234.191	1234.208
$[CpG]_2^+$	$C_{38}H_{50}N_{16}O_{20}P_2$	1113.280	1113.292
$\{[(ImidCyt)p(RedSp)] + [Pt(N_3)(py)_2]\}^+$ **15**	$C_{29}H_{38}N_{13}O_{15}PPt$	1035.195	1035.207
$\{[(CytGly)p(RedSp)] + [Pt(N_3)(py)_2]\}^+$ **14**	$C_{29}H_{38}N_{13}O_{14}PPt$	1019.184	1019.212
$\{[(ImidCyt)p(^{ox}G)] + [Pt(N_3)(py)_2]\}^+$ **13**	$C_{29}H_{36}N_{13}O_{14}PPt$	1017.184	1017.196
$\{[CpG] + [Pt(NH_3)(py)_2] + MeCN + 2Na\}^+$	$C_{31}H_{37}N_{12}O_{10}PNa_2Pt$	1010.194	1010.201
$\{[(UraGly)pG] + [Pt(N_3)(py)_2] + Na\}^+$ **11a+Na** or $\{[(5\text{-}OH\text{-}U)p(FapyG)] + [Pt(N_3)(py)_2] + Na\}^+$ **11b+Na**	$C_{29}H_{34}N_{12}O_{13}PNaPt$	1008.183	1008.173
$\{[CpG] + [Pt(N_3)(py)_2] + Na\}^+$ **2**+Na	$C_{29}H_{33}N_{13}O_{10}PNaPt$	973.173	973.183
$\{[CpG] + [Pt(N_3)(py)_2]\}^+$ **2**	$C_{29}H_{34}N_{13}O_{10}PPt$	951.191	951.201
$\{[Cp(DGh)] + [Pt(py)_2]\}^+$ **10**	$C_{28}H_{33}N_{10}O_{11}PPt$	912.189	912.179
$\{[Cp(Gh)] + [Pt(N)(py)_2] - H_2O\}^+$ **9**	$C_{28}H_{34}N_{11}O_{10}PPt$	911.191	911.195
$\{[CpG - C] + [Pt(N_3)(py)_2]\}^+$ **4**	$C_{25}H_{29}N_{10}O_9PPt$	840.150	840.158
$\{[Cp^{ox}G - C] + [Pt(N_3)(py)] + MeCN]\}^+$ **8**+MeCN	$C_{22}H_{27}N_{10}O_{10}PPt$	818.147	818.137
$\{[CpG - G] + [Pt(N_3)(py)_2]\}^+$ **5**	$C_{24}H_{29}N_8O_9PPt$	800.144	800.152
$\{[CpG]_2 + [Pt(N_3)(py)_2] + K\}^{2+}$	$C_{48}H_{58}N_{21}O_{20}P_2KPt$	773.141	773.154
$\{w + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.119	742.121
$\{d + [Pt(N_3)(py)_2]\}^+$	$C_{19}H_{23}N_8O_7PPt$	702.115	702.115
$\{[CpG] + [Pt(N_3)(py)_2]_2\}^{2+}$ **3**$^{2+}$	$C_{39}H_{43}N_{18}O_{10}PPt_2$	673.125	673.129
$\{[Cp^{ox}G] + [Pt(N)(py)_2]_2\}^{2+}$ **7a** or $\{[Cp(DIz)] + [Pt(N_3)(py)_2]_2\}^{2+}$ **7b**	$C_{39}H_{43}N_{14}O_{11}PPt_2$ or $C_{37}H_{43}N_{18}O_9PPt_2$	653.126	653.120 653.132
$\{w + [Pt(N)(py)]\}^+$	$C_{15}H_{18}N_7O_7PPt$	635.079	635.073
$\{[CpG] + [Pt(py)_2] + [Pt(N_3)(py)] + MeCN\}^{2+}$	$C_{36}H_{40}N_{15}O_{10}PPt_2$	632.609	632.613
$\{[CpG] + K\}^+$	$C_{19}H_{24}N_8O_{10}PK$	595.098	595.106
$\{[CpG] + Na\}^+$	$C_{19}H_{24}N_8O_{10}PNa$	579.133	579.132
$[CpG]^+$	$C_{19}H_{25}N_8O_{10}P$	557.151	557.150

$\{G + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}OPt$	546.106	546.107
$\{G + [Pt(py)_2] + MeCN\}^+$	$C_{17}H_{16}N_8OPt$	544.117	544.117
$\{C + G + [Pt(py)]\}^+$	$C_{14}H_{13}N_9O_2Pt$	535.092	535.091
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.102	506.101
$\{G + [Pt(py)_2]\}^+$	$C_{15}H_{13}N_7OPt$	503.093	503.090
$\{[CpG] + [Pt(N_3)(py)_2] + K\}^{2+}$	$C_{29}H_{33}N_{13}O_{10}PPtK$	495.078	495.082
$[Pt(N_3)_2(H_2O)_2(py)_2]^+$	$C_{10}H_{14}N_8O_2Pt$	474.101	474.096
$\{[(5\text{-OH-C})p(DGh)] + [Pt^{III}(N)(py)_2]\}^{2+}$ **12**	$C_{28}H_{33}N_{11}O_{12}PPt$	471.583	471.592
$\{G + [Pt(py)] + MeCN\}^+$	$C_{12}H_{11}N_7OPt$	465.077	465.075
$[CpG - C]^+$	$C_{15}H_{20}N_5O_9P$	446.110	446.107
$[CpG - G]^+$	$C_{14}H_{20}N_3O_9P$	406.099	406.101
$[Pt(N_3)(py)_2]^+$	$C_{10}H_9N_5Pt$	395.061	395.058
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.057	387.054
$[Pt^{III}(N)(OH)(py)_2]^+$	$C_{10}H_{10}N_3OPt$	384.053	384.054
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.049	367.052
$[w]^+$	$C_{10}H_{14}N_5O_7P$	348.074	348.070
$\{G + [Pt(py)_2] + MeCN\}^{2+}$	$C_{17}H_{16}N_8OPt$	272.568	272.562
$[G]^+$	$C_5H_5N_5O$	152.061	152.057
$[C]^+$	$C_4H_5N_3O$	112.055	112.053

Table S2. Fragment ions observed by MS/MS analysis under positive ion mode of the mono- and di-platinated adducts $\{[CpG] + [Pt(N_3)(py)_2]_2\}^+$, $\{[CpG] + [Pt(N_3)(py)_2] + Na\}^+$, $\{[CpG] + [Pt(N_3)(py)_2]\}^+$, and $\{[CpG] + [Pt(N_3)(py)_2]_2\}^{2+}$ produced by the reaction of complex **1** with CpG at 373 K after irradiation under blue light for 1 h. (Charges for Pt moiety in platinated nucleotide and the protons for balancing the charges of the ions are omitted for clarity). The scheme shows the fragmentation pathways of 5′-CpG as a representative during the CID fragmentation.

Fragment ions	Molecular formula	Observed m/z	Theoretical m/z
Parent ion $\{[CpG] + [Pt(N_3)(py)_2]_2\}^+$ (3^+)			
$\{[CpG] + [Pt(N_3)(py)_2]_2\}^+$	$C_{39}H_{43}N_{18}O_{10}PPt_2$	1345.241	1345.251
$\{[CpG] + [Pt(N_3)(py)] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{38}N_{17}O_{10}PPt_2$	1266.201	1266.209
$\{[CpG - C] + [Pt(N_3)(py)_2]_2\}^+$	$C_{35}H_{38}N_{15}O_9PPt_2$	1234.206	1234.208
$\{[CpG - C] + G + [Pt(py)] + [Pt(N_3)(py)] + MeCN\}^+$	$C_{32}H_{35}N_{16}O_{10}PPt_2$	1225.186	1225.182
$\{[CpG] + [Pt(N_3)(py)]_2\}^+$	$C_{29}H_{33}N_{16}O_{10}PPt_2$	1187.159	1187.166
$\{[CpG] + [Pt(N)(py)] + [Pt(N_3)(py)]\}^+$	$C_{29}H_{33}N_{14}O_{10}PPt_2$	1159.141	1159.160
$\{w + [Pt(N_3)(py)_2]_2\}^+$	$C_{30}H_{32}N_{15}O_7PPt_2$	1136.161	1136.171
$\{w + [Pt(N_3)(py)] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{27}N_{14}O_7PPt_2$	1057.136	1057.129
$\{[CpG] + [Pt(N)] + [Pt(py)]\}^+$	$C_{24}H_{27}N_{10}O_{10}PPt_2$	1037.094	1037.101
$\{[CpG] + [Pt(N_3)(py)_2] + Na\}^+$	$C_{29}H_{33}N_{13}O_{10}PNaPt$	973.180	973.183
$\{[CpG] + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{34}N_{13}O_{10}PPt$	951.198	951.201
$\{G + [Pt(N_3)(py)_2]_2\}^+$	$C_{25}H_{23}N_{15}OPt_2$	940.151	940.157
$\{w + [Pt(N)(py)] + [Pt(N_3)]\}^+$ or $\{w + [Pt(N_3)(py)] + [Pt(N)]\}^+$	$C_{15}H_{17}N_{10}O_7PPt_2$	871.033	871.038
$\{[CpG - C] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_{10}O_9PPt$	840.157	840.158
$\{w + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.119	742.121
$\{[CpG] + Na\}^+$	$C_{19}H_{24}N_8O_{10}PNa$	579.133	579.132
$[CpG]^+$	$C_{19}H_{25}N_8O_{10}P$	557.151	557.150
$\{G + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}OPt$	546.111	546.107
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.103	506.101
$[w]^+$	$C_{10}H_{14}N_5O_7P$	348.072	348.070
Parent ion $\{[CpG] + [Pt(N_3)(py)_2] + Na\}^+$ (2 + Na)			
$\{[CpG] + [Pt(N_3)(py)_2] + Na\}^+$	$C_{29}H_{33}N_{13}O_{10}PNaPt$	973.169	973.183
$\{[CpG] + [Pt(N_3)(py)] + Na\}^+$	$C_{24}H_{28}N_{12}O_{10}PNaPt$	894.132	894.141
$\{[CpG] + [Pt(N)(py)] + Na\}^+$	$C_{24}H_{28}N_{10}O_{10}PNaPt$	866.134	866.135
unspecified		853.133	

{[CpG] + [Pt(N)]}$^+$	$C_{19}H_{24}N_9O_{10}PPt$	765.107	765.111
{w + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.111	742.121
{w + [Pt(N$_3$)(py)] + Na}$^+$	$C_{15}H_{17}N_9O_7PNaPt$	685.058	685.061
{[CpG] + Na}$^+$	$C_{19}H_{24}N_8O_{10}PNa$	579.128	579.132
{G + C + [Pt(N)(py)] + Na}$^+$	$C_{14}H_{13}N_{10}O_2NaPt$	572.081	572.084
{G + [Pt(N$_3$)(py)$_2$] + Na}$^+$	$C_{15}H_{13}N_{10}ONaPt$	568.086	568.089
[CpG]$^+$	$C_{19}H_{25}N_8O_{10}P$	557.151	557.150
{G + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}OPt$	546.106	546.107
{C + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{14}H_{14}N_8OPt$	506.098	506.101
{G + Na}$^+$	$C_5H_4N_5ONa$	174.043	174.039
[G]$^+$	$C_5H_5N_5O$	152.061	152.057
{C + Na}$^+$	$C_4H_4N_3ONa$	134.035	134.032
[C]$^+$	$C_4H_5N_3O$	112.055	112.053
Parent ion {[CpG] + [Pt(N$_3$)(py)$_2$]}$^+$ (2)			
{[CpG] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{29}H_{34}N_{13}O_{10}PPt$	951.199	951.201
{[CpG] + [Pt(N$_3$)(py)]}$^+$	$C_{24}H_{29}N_{12}O_{10}PPt$	872.158	872.159
{[CpG − C] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{25}H_{29}N_{10}O_9PPt$	840.157	840.158
{[CpG − G] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{24}H_{29}N_8O_9PPt$	800.157	800.152
{w + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.125	742.121
{d + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{19}H_{23}N_8O_7PPt$	702.126	702.115
{w + [Pt(N)(py)]}$^+$	$C_{15}H_{18}N_7O_7PPt$	635.074	635.073
{x + [Pt(N)(py)]}$^+$	$C_{15}H_{16}N_7O_6PPt$	617.066	617.062
{G + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}OPt$	546.111	546.107
{C + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{14}H_{14}N_8OPt$	506.106	506.101
{G + [Pt(N$_3$)(py)]}$^+$	$C_{10}H_9N_9OPt$	467.066	467.065
[CpG − C]$^+$	$C_{15}H_{20}N_5O_9P$	446.112	446.107
{G + [Pt(N)(py)]}$^+$	$C_{10}H_9N_7OPt$	439.063	439.059
{C + [Pt(N$_3$)(py)]}$^+$	$C_9H_9N_7OPt$	427.061	427.059
{C + [Pt(N)(py)]}$^+$	$C_9H_9N_5OPt$	399.059	399.053
[w]$^+$	$C_{10}H_{14}N_5O_7P$	348.078	348.070
[G]$^+$	$C_5H_5N_5O$	152.062	152.057
Parent ion {[CpG] + [Pt(N$_3$)(py)$_2$]$_2$}$^{2+}$ (3^{2+})			
{[CpG] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{29}H_{34}N_{13}O_{10}PPt$	951.201	951.201
{[CpG] + [Pt(N$_3$)(py)]}$^+$	$C_{24}H_{29}N_{12}O_{10}PPt$	872.162	872.159
{[CpG − C] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{25}H_{29}N_{10}O_9PPt$	840.156	840.158
{[CpG − G] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{24}H_{29}N_8O_9PPt$	800.150	800.152
{w + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.119	742.121
{[CpG] + [Pt(N$_3$)(py)$_2$]$_2$}$^{2+}$	$C_{39}H_{43}N_{18}O_{10}PPt_2$	673.130	673.129
[CpG]$^+$	$C_{19}H_{25}N_8O_{10}P$	557.151	557.150
{G + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}OPt$	546.109	546.107
{[w]$_2$ + [Pt(py)$_2$]}$^+$	$C_{30}H_{36}N_{12}O_{14}P_2Pt$	523.589	523.587
{C + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{14}H_{14}N_8OPt$	506.101	506.101
{G + [Pt(N)(py)]}$^+$	$C_{10}H_9N_7OPt$	439.060	439.059
{C + [Pt(N)(py)]}$^+$	$C_9H_9N_5OPt$	399.053	399.053

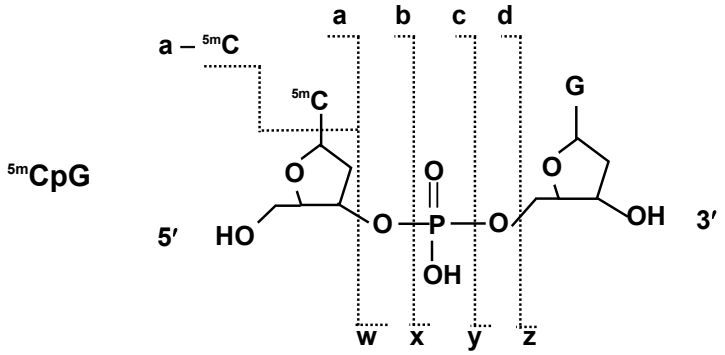
$[Pt(N_3)(py)]^+$	$C_{10}H_9N_5Pt$	395.057	395.058
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.056	367.052

Table S3. Ions identified by MS in the reaction mixture between Pt(IV) complex **1** and 5′-^{5m}CpG at a molar ratio of Pt/^{5m}CpG = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleotides and the protons for balancing the charges of the ions are omitted for clarity). All the platinated products were numbered as their appearances in the main text and the corresponding numbers are shown in the following brackets.

Fragment ions	Molecular formula	Observed *m/z*	Theoretical *m/z*
{[^{5m}CpG]$_2$ + [Pt(N$_3$)(py)$_2$]}$^+$ **27**	$C_{50}H_{63}N_{21}O_{20}P_2Pt$	1535.360	1535.376
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$]$_2$ + 2O + 2(OH)}$^+$ **39**	$C_{40}H_{47}N_{18}O_{14}PPt_2$	1425.254	1425.262
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$]$_2$}$^+$ **18**$^+$	$C_{40}H_{45}N_{18}O_{10}PPt_2$	1359.254	1359.267
{[^{5m}CpG]$_4$ + [Pt(N$_3$)(py)$_2$]}$^{2+}$ **29**	$C_{90}H_{117}N_{37}O_{40}P_4Pt$	1338.837	1338.851
{[^{5m}CpG]$_3$ + [Pt(N$_3$)(py)$_2$]$_2$}$^{2+}$ **30**	$C_{80}H_{99}N_{34}O_{30}P_3Pt_2$	1250.780	1250.797
{[^{5m}CpG − ^{5m}C] + [Pt(N$_3$)(py)$_2$]$_2$}$^+$ **31**	$C_{35}H_{38}N_{15}O_9PPt_2$	1234.205	1234.208
{[^{5m}CpG]$_2$ + K}$^+$	$C_{40}H_{53}N_{16}O_{20}P_2K$	1179.261	1179.281
[^{5m}CpG]$_2^+$	$C_{40}H_{54}N_{16}O_{20}P_2$	1141.317	1141.325
{[^{5m}CpG]$_3$ + [Pt(N$_3$)(py)$_2$]}$^{2+}$ **28**	$C_{70}H_{90}N_{29}O_{30}P_3Pt$	1053.764	1053.772
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$] + H$_2$O$_3$ + 2(OH)}$^+$ **38**	$C_{30}H_{40}N_{13}O_{15}PPt$	1049.214	1049.223
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$] + 2O + 2(OH)}$^+$ **37**	$C_{30}H_{38}N_{13}O_{14}PPt$	1031.207	1031.212
{[^{5m}CpG] + [Pt(NH$_3$)(py)$_2$] + 2Na + MeCN}$^+$ **33+MeCN+2Na**	$C_{32}H_{39}N_{12}O_{10}PNa_2Pt$	1024.215	1024.217
{[^{5m}CpG] + [Pt(N)(py)$_2$] + 2Na + MeCN}$^+$ **32+MeCN+2Na**	$C_{32}H_{37}N_{12}O_{10}PNa_2Pt$	1022.210	1022.201
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$] + H$_2$O + 2(OH)}$^+$ **36**	$C_{30}H_{40}N_{13}O_{13}PPt$	1017.226	1017.233
{[^{5m}Cp(RedSp)] + [Pt(N$_3$)(py)$_2$]}$^+$ **35**	$C_{30}H_{38}N_{13}O_{12}PPt$	999.212	999.222
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$] + 2O}$^+$ **34a** or **34b** or **34c** or **34d**	$C_{30}H_{36}N_{13}O_{12}PPt$	997.200	997.207
{[^{5m}CpG] + [Pt(N$_3$)(py)$_2$]}$^+$ **16**	$C_{30}H_{36}N_{13}O_{10}PPt$	965.213	965.217
{[^{5m}CpG] + [Pt(py)$_2$] + MeCN}$^+$ **22**+MeCN	$C_{32}H_{38}N_{11}O_{10}PPt$	963.222	963.226
[Pt(N$_3$)$_2$(OH)$_2$(py)$_2$]$_2^+$	$C_{20}H_{24}N_{16}O_4Pt_2$	943.159	943.153
{[^{5m}Cp(Iz)] + [Pt(N$_3$)(py)$_2$]}$^+$ **25**	$C_{28}H_{35}N_{12}O_{10}PPt$	926.209	926.206
{[^{5m}Cp(Iz)] + [Pt(py)$_2$] + MeCN}$^+$ **24**+MeCN	$C_{30}H_{37}N_{10}O_{10}PPt$	924.209	926.215
{RedSp + [Pt(N)(py)$_2$]$_2$}$^+$ **26**	$C_{25}H_{25}N_{11}O_3Pt_2$	918.142	918.150
{[^{5m}CpG − ^{5m}C] + [Pt(N$_3$)(py)$_2$]}$^+$ **17**	$C_{25}H_{29}N_{10}O_9PPt$	840.156	840.158
{[^{5m}CpG − G] + [Pt(N$_3$)(py)$_2$]}$^+$ **21**	$C_{25}H_{31}N_8O_9PPt$	814.162	814.167
{[^{5m}CpG]$_2$ + [Pt(N$_3$)(py)$_2$] + K}$^{2+}$ **20**+K	$C_{50}H_{62}N_{21}O_{20}P_2KPt$	787.163	787.169
{w + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.120	742.121
{d + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{25}N_8O_7PPt$	716.123	716.131

{[^{5m}CpG] + [Pt(N_3)(py)$_2$]$_2$}$^{2+}$ **18^{2+}**	$C_{40}H_{45}N_{18}O_{10}PPt_2$	680.134	680.137
{[^{5m}Cp(DIz)] + [Pt(N_3)(py)$_2$]$_2$}$^{2+}$ **23**	$C_{38}H_{45}N_{18}O_9PPt_2$	660.130	660.139
{[^{5m}CpG] + [Pt(py)] + [Pt(N_3)(py)$_2$] + MeCN}$^{2+}$	$C_{37}H_{42}N_{15}O_{10}PPt_2$	639.622	639.621
19a + MeCN			
or {[^{5m}CpG] + [Pt(N_3)(py)] + [Pt(py)$_2$] + MeCN}$^{2+}$			
19b + MeCN			
{w + [Pt(N)(py)]}$^+$	$C_{15}H_{18}N_7O_7PPt$	635.077	635.073
{[^{5m}CpG] + K}$^+$	$C_{20}H_{26}N_8O_{10}PK$	609.113	609.122
{[^{5m}CpG] + Na}$^+$	$C_{20}H_{26}N_8O_{10}PNa$	593.150	593.148
[^{5m}CpG]$^+$	$C_{20}H_{27}N_8O_{10}P$	571.170	571.166
{G + [Pt(N_3)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}OPt$	546.111	546.107
{G + [Pt(py)$_2$] + MeCN}$^+$	$C_{17}H_{16}N_8OPt$	544.117	544.117
{^{5m}C + [Pt(N_3)(py)$_2$]}$^+$	$C_{15}H_{16}N_8OPt$	520.118	520.117
{G + [Pt(py)$_2$]}$^+$	$C_{15}H_{13}N_7OPt$	503.094	503.090
{[^{5m}CpG] + [Pt(N_3)(py)$_2$]}$^{2+}$	$C_{30}H_{36}N_{13}O_{10}PPt$	483.115	483.112
{G + w + [Pt(N_3)(py)$_2$] + MeCN + Na}$^{2+}$	$C_{27}H_{30}N_{16}O_8PNaPt$	478.593	478.593
[Pt(N_3)$_2$(H_2O)$_2$(py)$_2$]$^+$	$C_{10}H_{14}N_8O_2Pt$	474.100	474.096
{G + [Pt(py)] + MeCN}$^+$	$C_{12}H_{11}N_7OPt$	465.078	465.075
{[^{5m}CpG] + [Pt(py)$_2$]}$^{2+}$ **40**	$C_{30}H_{35}N_{10}O_{10}PPt$	461.608	461.604
[^{5m}CpG − ^{5m}C]$^+$	$C_{15}H_{20}N_5O_9P$	446.110	446.107
[^{5m}CpG − G]$^+$	$C_{15}H_{22}N_3O_9P$	420.117	420.117
[Pt^{III}(OH)$_2$(py)$_2$]$^+$	$C_{10}H_{11}N_2O_2Pt$	387.056	387.054
[Pt(N)(OH)(py)$_2$]$^+$	$C_{10}H_{10}N_3OPt$	384.056	384.055
[w]$^+$	$C_{10}H_{14}N_5O_7P$	348.074	348.070
{^{5m}C + G + [Pt(py)$_2$]}$^{2+}$	$C_{20}H_{20}N_{10}O_2Pt$	314.581	314.578
{G + [Pt(py)$_2$] + MeCN}$^{2+}$	$C_{17}H_{16}N_8OPt$	272.568	272.562
[G]$^+$	$C_5H_5N_5O$	152.060	152.057
[^{5m}C]$^+$	$C_5H_7N_3O$	126.071	126.066

Table S4. Fragment ions observed by MS/MS analysis under positive ion mode of the mono- and di-platinated dideoxynucleotides $\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^+$, $\{[^{5m}CpG] + [Pt(N_3)(py)_2]\}^+$, and $\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^{2+}$ produced by the reaction of complex **1** with ^{5m}CpG at 373 K after irradiation under blue light for 1 h. (Charges for Pt moiety in platinated nucleotide and the protons for balancing the charges of the ions are omitted for clarity). The scheme shows the fragmentation pathways of 5′-^{5m}CpG as a representative during the CID fragmentation.



Fragment ions	Molecular formula	Observed *m/z*	Theoretical *m/z*
Parent ion $\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^+$ (18^+)			
$\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^+$	$C_{40}H_{45}N_{18}O_{10}PPt_2$	1359.254	1359.267
$\{[^{5m}CpG] + [Pt(N_3)(py)] + [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{40}N_{17}O_{10}PPt_2$	1280.208	1280.224
$\{[^{5m}CpG - {}^{5m}C] + [Pt(N_3)(py)_2]_2\}^+$	$C_{35}H_{38}N_{15}O_9PPt_2$	1234.198	1234.208
$\{[^{5m}CpG] + [Pt(N_3)(py)]_2\}^+$	$C_{30}H_{35}N_{16}O_{10}PPt_2$	1201.173	1201.182
unspecified		1198.725	
$\{[^{5m}CpG] + [Pt(N)(py)] + [Pt(N_3)(py)]\}^+$	$C_{30}H_{35}N_{14}O_{10}PPt_2$	1173.171	1173.176
$\{w + [Pt(N_3)(py)_2]_2\}^+$	$C_{30}H_{32}N_{15}O_7PPt_2$	1136.161	1136.171
$\{w + [Pt(N_3)(py)] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{27}N_{14}O_7PPt_2$	1057.124	1057.129
$\{[^{5m}CpG] + [Pt(N)] + [Pt(py)]\}^+$	$C_{25}H_{29}N_{10}O_{10}PPt_2$	1051.113	1051.117
$\{[^{5m}CpG] + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{13}O_{10}PPt$	965.207	965.217
$\{w + [Pt(N)] + [Pt(N_3)(py)]\}^+$ or $\{w + [Pt(N_3)] + [Pt(N)(py)]\}^+$	$C_{15}H_{17}N_{10}O_7PPt_2$	871.038	871.038
$\{[^{5m}CpG - {}^{5m}C] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_{10}O_9PPt$	840.156	840.158
$\{w + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.121	742.121
$[^{5m}CpG]^+$	$C_{20}H_{27}N_8O_{10}P$	571.170	571.166
$\{G + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}OPt$	546.111	546.107
$\{^{5m}C + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{16}N_8OPt$	520.123	520.117

$[^{5m}CpG - {}^{5m}C]^+$	$C_{15}H_{20}N_5O_9P$	446.110	446.107
$[w]^+$	$C_{10}H_{14}N_5O_7P$	348.075	348.070
$[G]^+$	$C_5H_5N_5O$	152.061	152.057
$[^{5m}C]^+$	$C_5H_7N_3O$	126.069	126.066
Parent ion $\{[^{5m}CpG] + [Pt(N_3)(py)_2]\}^+$ (16)			
$\{[^{5m}CpG] + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{13}O_{10}PPt$	965.213	965.217
$\{[^{5m}CpG] + [Pt(N)(py)_2] + O\}^+$	$C_{30}H_{36}N_{11}O_{11}PPt$	953.218	953.206
unspecified		925.218	
$\{[^{5m}CpG] + [Pt(N_3)(py)]\}^+$	$C_{25}H_{31}N_{12}O_{10}PPt$	886.172	886.175
$\{[^{5m}CpG - {}^{5m}C] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_{10}O_9PPt$	840.156	840.158
$\{[^{5m}CpG - G] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{31}N_8O_9PPt$	814.162	814.167
$\{[^{5m}CpG] + [Pt(NH_3)] + H_2O\}^+$	$C_{20}H_{30}N_9O_{11}PPt$	799.160	799.152
unspecified		788.134	
$\{[^{5m}CpG] + [Pt(N)]\}^+$	$C_{20}H_{26}N_9O_{10}PPt$	779.127	779.126
$\{w + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.120	742.121
$\{y + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{22}N_{10}O_4Pt$	662.158	662.155
$\{w + [Pt(N)(py)]\}^+$	$C_{15}H_{18}N_7O_7PPt$	635.077	635.073
$\{w + [Pt(N)(py)] - H_2O\}^+$	$C_{15}H_{16}N_7O_6PPt$	617.064	617.062
$\{G + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}OPt$	546.111	546.107
$\{^{5m}C + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{16}N_8OPt$	520.118	520.117
$\{G + [Pt(N_3)(py)] + H_2O\}^+$	$C_{10}H_{11}N_9O_2Pt$	485.080	485.076
$\{G + [Pt(N)(py)] + H_2O\}^+$	$C_{10}H_{11}N_7O_2Pt$	457.069	457.069
$\{G + [Pt(N)(py)]\}^+$	$C_{10}H_9N_7OPt$	439.061	439.059
Parent ion $\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^{2+}$ (18^{2+})			
$\{[^{5m}CpG] + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{13}O_{10}PPt$	965.211	965.217
$\{[^{5m}CpG] + [Pt(N_3)(py)]\}^+$	$C_{25}H_{31}N_{12}O_{10}PPt$	886.171	886.175
$\{[^{5m}CpG - G] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{31}N_8O_9PPt$	814.161	814.167
$\{[^{5m}CpG - G] + [Pt(N_3)(py)_2] - H_2O\}^+$	$C_{25}H_{29}N_8O_8PPt$	796.151	796.157
$\{w + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.119	742.121
$\{[^{5m}CpG] + [Pt(N_3)(py)_2]_2\}^{2+}$	$C_{40}H_{45}N_{18}O_{10}PPt_2$	680.132	680.137
$\{w + [Pt(N)(py)]\}^+$	$C_{15}H_{18}N_7O_7PPt$	635.076	635.073
$\{w + [Pt(N_3)] + H_2O\}^+$	$C_{10}H_{15}N_8O_8PPt$	602.050	602.047
$\{w + [Pt(N)]\}^+$	$C_{10}H_{13}N_6O_7PPt$	556.028	556.030
$\{G + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}OPt$	546.109	546.107
$\{^{5m}C + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{16}N_8OPt$	520.117	520.117
$\{G + [Pt(N_3)(py)]\}^+$	$C_{10}H_9N_9OPt$	467.062	467.065
$\{^{5m}C + [Pt(N)(py)]\}^+$	$C_{10}H_{11}N_5OPt$	413.068	413.068
$[Pt(N_3)(py)_2]^+$	$C_{10}H_9N_5Pt$	395.058	395.058
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.053	367.052
$[Pt(N)(py)]^+$	$C_5H_4N_2Pt$	288.013	288.010
$[G]^+$	$C_5H_5N_5O$	152.060	152.057
$[^{5m}C]^+$	$C_5H_7N_3O$	126.069	126.066