Reaction of human telomeric unit TTAGGG and a photoactivatable Pt(IV) anticancer prodrug

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Electronic Supplementary Information

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Figure S1. The isotopic models and corresponding mass spectrum under positive-ion mode.

Table S1. MS data under positive-ion mode for the reaction between Pt(IV) complex **1** and ODN **I** at a molar ratio of **1** / **I** = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety and the loss of protons from **I** for balancing the charges of the ions are omitted for clarity). **1** = $[Pt(N_3)_2(OH)_2(Py)_2]$, **1′** = $[Pt(N_3)(py)_2]^+$, **1″** = $[Pt(py)_2]^{2+}$.

Ions	Formula	*m/z* observed(calculated)
$[A]^+$	$C_5H_5N_5$	136.066(136.062)
$[G]^+$	$C_5H_5N_5O$	152.061(152.057)
$[w_1]^+$	$C_{10}H_{14}N_5O_7P$	348.073(348.070)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.048(367.052)
$[Pt(N)(OH)(py)_2]^+$	$C_{10}H_{10}N_3OPt$	384.058(384.055)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.058(387.054)
$[Pt^{III}(N_3)(OH)(py)_2]^+$	$C_{10}H_{10}N_5OPt$	412.065(412.0.61)
$\{[Pt(N_3)(OH)(py)_2] + 2H_2O\}^+$	$C_{10}H_{13}N_5O_3Pt$	447.077(477.074)
{**1′** + MeCN + Na}$^+$	$C_{12}H_{10}N_6PtNa$	457.056(457.059)
$[T]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.059(483.056)
$[G_4/G_5{}^d]^+$	$C_{15}H_{19}N_5O_{11}P_2$	508.064(508.063)
$[a_2]^+$	$C_{20}H_{25}N_4O_{11}P$	529.135(529.133)
$[\mathbf{I}]^{3+}$	$C_{60}H_{75}N_{24}O_{35}P_5$	616.460(616.458)
$[T_2{:}G_5{}^d]^{2+}$	$C_{45}H_{56}N_{17}O_{29}P_5$	727.613(727.613)
{**I** + **1″**}$^{3+}$ (**4**)	$C_{70}H_{83}N_{26}O_{35}P_5Pt$	733.802(733.806)
{[**I** − C + H_2O] + **1″**}$^{3+}$ (Gh)^e (**9**)	$C_{69}H_{85}N_{26}O_{36}P_5Pt$	735.807(735.798)
{**I** + [Pt(N)(py)$_2$]}$^{3+}$ (**5**)	$C_{70}H_{84}N_{27}O_{35}P_5Pt$	738.804(738.807)
{[**I** + 2O] + **1″**}$^{3+}$ (Sp or (8-OH-G)$_2$)^e (**10a** or **10b**)	$C_{70}H_{83}N_{26}O_{37}P_5Pt$	744.465(744.466)
{[**I** − C + 4H + 3O)] + **1″**}$^{3+}$ (Gh + RedSp or DGh + 2FapyG)^e (**11a** or **11b**)	$C_{69}H_{87}N_{26}O_{38}P_5Pt$	747.144(747.142)
{**I** + **1′**}$^{3+}$ (**6**)	$C_{70}H_{84}N_{29}O_{35}P_5Pt$	748.141(748.142)
{[**I** + 2(H_2O)] + **1″** + Na}$^{3+}$ (2FapyG)^e (**12** + Na)	$C_{70}H_{86}N_{26}O_{37}P_5PtNa$	753.141(753.137)
$[T_2{:}A_3]^+$	$C_{25}H_{32}N_7O_{17}P_3$	796.117(796.114)
$[\mathbf{I} - G^b - H_2O]^{2+}$	$C_{55}H_{68}N_{19}O_{33}P_5$	839.651(839.653)
$[\mathbf{I} - G^b]^{2+}$	$C_{55}H_{70}N_{19}O_{34}P_5$	848.660(848.658)
{**I** + **1′** + **1″**}$^{3+}$ (**7**)	$C_{80}H_{92}N_{31}O_{35}P_5Pt_2$	865.153(865.153)
{**I** + **1′**$_2$}$^{3+}$ (**8**)	$C_{80}H_{93}N_{34}O_{35}P_5Pt_2$	879.489(879.492)
$[\mathbf{I}]^{2+}$	$C_{60}H_{75}N_{24}O_{35}P_5$	924.182(924.183)
{**I** + Na}$^{2+}$	$C_{60}H_{74}N_{24}O_{35}P_5Na$	935.167(935.174)
{**I** + K}$^{2+}$	$C_{60}H_{74}N_{24}O_{35}P_5K$	943.157(943.161)
{[**I** − G^b + H_2O]+ **1′** − py}$^{2+}$ (FapyG)^e (**14**)	$C_{60}H_{76}N_{23}O_{35}P_5Pt$	1015.663(1015.669)

$[a_4 - G_4]^+$	$C_{35}H_{44}N_9O_{21}P_3$	1020.192(1020.194)
$\{[\mathbf{I} - G^b] + \mathbf{1''}\}^{2+}$ (**3** − G)	$C_{65}H_{78}N_{21}O_{34}P_5Pt$	1024.671(1024.676)
$\{[\mathbf{I} - G^b - H_2O] + \mathbf{1'}\}^{2+}$ (**2** − G − H_2O)	$C_{65}H_{77}N_{24}O_{33}P_5Pt$	1037.179(1037.179)
$\{[\mathbf{I} - G^b] + \mathbf{1'}\}^{2+}$ (**2** − G)	$C_{65}H_{79}N_{24}O_{34}P_5Pt$	1046.182(1046.185)
$\{[\mathbf{I} - A^b] + \mathbf{1'}\}^{2+}$ (**2** − A)	$C_{65}H_{79}N_{24}O_{35}P_5Pt$	1054.180(1054.182)
$\{[\mathbf{I} + O] + \mathbf{1'} - py\}^{2+}$ (8-OH-G)[e] (**15**)	$C_{65}H_{79}N_{28}O_{36}P_5Pt$	1090.185(1090.186)
$\{\mathbf{I} + \mathbf{1''}\}^{2+}$ (**3**)	$C_{70}H_{83}N_{26}O_{35}P_5Pt$	1100.196(1100.201)
$\{[\mathbf{I} - C + H_2O] + \mathbf{1''}\}^{2+}$ (Gh)[e] (**16**)	$C_{69}H_{85}N_{26}O_{36}P_5Pt$	1103.201(1103.193)
$\{\mathbf{I} + [Pt(N)(py)_2]\}^{2+}$ (**13**)	$C_{70}H_{84}N_{27}O_{35}P_5Pt$	1107.695(1107.706)
$\{\mathbf{I} + \mathbf{1''} + Na\}^{2+}$ (**3** + Na)	$C_{70}H_{82}N_{26}O_{35}P_5PtNa$	1111.188(1111.192)
$\{[\mathbf{I} + 2O] + \mathbf{1''}\}^{2+}$ ((8-OH-G)$_2$ or Sp)[e] (**17a** or **17b**)	$C_{70}H_{83}N_{26}O_{37}P_5Pt$	1116.191(1116.196)
$\{[\mathbf{I} - C + 4H + 3O] + \mathbf{1''}\}^{2+}$ (Gh + RedSp or DGh + 2FapyG)[e] (**18**)	$C_{69}H_{87}N_{26}O_{38}P_5Pt$	1120.204(1120.209)
$\{\mathbf{I} + \mathbf{1'}\}^{2+}$ (**2**)	$C_{70}H_{84}N_{29}O_{35}P_5Pt$	1121.706(1121.709)
$\{[\mathbf{I} + 2(H_2O)] + \mathbf{1''} + Na\}^{3+}$ (2FapyG)[e] (**19** + Na)	$C_{70}H_{86}N_{26}O_{37}P_5PtNa$	1129.202(1129.202)
$\{\mathbf{I} + \mathbf{1''} + Na\}^{2+}$ (**2** + Na)	$C_{70}H_{83}N_{29}O_{35}P_5PtNa$	1132.694(1132.700)
$\{[\mathbf{I} - C + 2H + 3O] + \mathbf{1''} + K\}^{2+}$ (Gh + Sp or DGh + RedSp)[e] (**20** + K)	$C_{69}H_{84}N_{26}O_{38}P_5PtK$	1138.202(1138.179)
$\{[\mathbf{I} + O] + \mathbf{1'} + Na\}^{2+}$ (8-OH-G)[e] (**21** + Na)	$C_{70}H_{83}N_{29}O_{36}P_5PtNa$	1140.684(1140.698)
$\{[\mathbf{I} - C + O] + \mathbf{1'} + K\}^{2+}$ (DGh)[e] (**22** + K)	$C_{65}H_{83}N_{29}O_{36}P_5PtK$	1142.698(1142.685)
$\{[\mathbf{I} + 2(H_2O)] + \mathbf{1'} + Na\}^{2+}$ (2FapyG)[e] (**23** + Na)	$C_{70}H_{87}N_{29}O_{37}P_5PtNa$	1150.729(1150.711)
$\{[\mathbf{I}]_2 - G^b\}^{3+}$	$C_{115}H_{145}N_{43}O_{69}P_{10}$	1181.889(1181.893)
$\{[\mathbf{I}]_2 - A^b\}^{3+}$	$C_{115}H_{145}N_{43}O_{70}P_{10}$	1187.218(1187.224)
$[\mathbf{I}]_2^{3+}$	$C_{120}H_{150}N_{48}O_{70}P_{10}$	1232.237(1232.243)
$\{[\mathbf{I}]_2 + Na\}^{3+}$	$C_{120}H_{149}N_{48}O_{70}P_{10}Na$	1239.559(1239.570)
$\{[\mathbf{I}]_2 + K\}^{3+}$	$C_{120}H_{149}N_{48}O_{70}P_{10}K$	1244.887(1244.894)
$\{\mathbf{I} + \mathbf{1'} + \mathbf{1''}\}^{2+}$ (**24**)	$C_{80}H_{92}N_{31}O_{35}P_5Pt_2$	1297.216(1297.226)
$\{\mathbf{I} + \mathbf{1'}_2\}^{2+}$ (**25**)	$C_{80}H_{93}N_{34}O_{35}P_5Pt_2$	1318.727(1318.734)
$\{[\mathbf{I} + 2H + 5O] + \mathbf{1'} + \mathbf{1''}\}^{2+}$	$C_{80}H_{94}N_{31}O_{40}P_5Pt_2$	1338.218(1338.221)
$\{[\mathbf{I} - C + 2H + 3O] + \mathbf{1'} + \mathbf{1''} + 2Na\}^{2+}$	$C_{79}H_{92}N_{31}O_{38}P_5Pt_2Na_2$	1338.218(1338.208)
$\{[\mathbf{I}]_2 + \mathbf{1'}\}^{3+}$ (**26**)	$C_{130}H_{159}N_{53}O_{70}P_{10}Pt$	1363.586(1363.593)
$[\mathbf{I}]_3^{4+}$	$C_{180}H_{225}N_{72}O_{105}P_{15}$	1386.262 (1386.272)
$\{[\mathbf{I}]_3 + \mathbf{1''}\}^{4+}$ (**27**)	$C_{190}H_{233}N_{74}O_{105}P_{15}Pt$	1474.015(1474.031)
$\{[\mathbf{I}]_3 + \mathbf{1'}\}^{4+}$ (**28**)	$C_{190}H_{234}N_{77}O_{105}P_{15}Pt$	1484.768(1484.785)
$\{[\mathbf{I}]_2 + \mathbf{1'} + \mathbf{1''} + K + 2Na\}^{3+}$	$C_{140}H_{164}N_{55}O_{70}P_{10}Pt_2Na_2$	1508.251(1508.244)

	K	
$\{[\mathbf{I}]_2 - C + H_2O + \mathbf{1'} + \mathbf{1''} + 2K\}^{3+}$ (Gh)[e]	$C_{139}H_{167}N_{55}O_{71}P_{10}Pt_2K_2$	1508.251(1508.245)
$\{[\mathbf{I}]_3 + O + \mathbf{1'} + \mathbf{1''} + 3Na\}^{3+}$ (8-OH-G)[e]	$C_{140}H_{164}N_{55}O_{71}P_{10}Pt_2Na_3$	1508.251(1508.251)
$\{[a_6 - G_6{}^c] - G^b\}^+$	$C_{50}H_{63}N_{14}O_{32}P_5$	1527.241(1527.249)
$\{[\mathbf{I}]_3 + \mathbf{1'} + \mathbf{1''}\}^{4+}$ (**29**)	$C_{200}H_{242}N_{79}O_{105}P_{15}Pt_2$	1572.775(1572.794)
$\{[\mathbf{I}]_3 + \mathbf{1'}_2\}^{4+}$ (**30**)	$C_{200}H_{243}N_{82}O_{105}P_{15}Pt_2$	1583.531(1583.548)
$\{[\mathbf{I}]_3 + \mathbf{1'} + \mathbf{1''} + K + 2Na\}^{4+}$	$C_{200}H_{239}N_{79}O_{105}P_{15}Pt_2Na_2K$	1593.269(1593.273)
$\{[\mathbf{I}]_3 - C + H_2O + \mathbf{1'} + \mathbf{1''} + 2K\}^{4+}$ (Gh)[e]	$C_{199}H_{242}N_{79}O_{106}P_{15}Pt_2K_2$	1593.269(1593.274)
$\{[\mathbf{I}]_3 + O + \mathbf{1'} + \mathbf{1''} + 3Na\}^{4+}$ (8-OH-G)[e]	$C_{200}H_{239}N_{79}O_{106}P_{15}Pt_2Na_3$	1593.269(1593.279)
$[d_5]^+$	$C_{50}H_{64}N_{19}O_{32}P_5$	1598.260(1598.273)
$[a_6 - G_6{}^c]^+$	$C_{55}H_{68}N_{19}O_{33}P_5$	1678.284(1678.299)
$\{[\mathbf{I}]_2 - G^b - H_2O\}^{2+}$	$C_{115}H_{143}N_{43}O_{68}P_{10}$	1763.315(1763.330)
$\{[\mathbf{I}]_2 - G^b\}^{2+}$	$C_{115}H_{145}N_{43}O_{69}P_{10}$	1772.314(1772.335)
$\{[\mathbf{I}]_2 - A^b\}^{2+}$	$C_{115}H_{145}N_{43}O_{70}P_{10}$	1780.316(1780.333)
$\{[\mathbf{I}]_3 - G^b\}^{3+}$	$C_{175}H_{220}N_{67}O_{104}P_{15}$	1797.659(1797.677)
$\{[\mathbf{I}]_3 - A^b\}^{3+}$	$C_{175}H_{220}N_{67}O_{105}P_{15}$	1802.994(1803.009)
$[\mathbf{I}]^+$	$C_{60}H_{75}N_{24}O_{35}P_5$	1847.347(1847.356)
$\{[\mathbf{I}]_2 + 2(MeCN) + Na + K\}^{2+}$	$C_{122}H_{151}N_{49}O_{70}P_{10}NaK$	1898.401(1898.342)
$\{[\mathbf{I}]_4 + \mathbf{1'}\}^{4+}$ (**31**)	$C_{250}H_{309}N_{101}O_{140}P_{20}Pt$	1946.606(1946.623)
$\{[\mathbf{I}]_3 + \mathbf{1''}\}^{3+}$ (**32**)	$C_{190}H_{233}N_{74}O_{105}P_{15}Pt$	1965.021(1965.038)
$\{[\mathbf{I}]_3 + \mathbf{1'}\}^{3+}$ (**33**)	$C_{190}H_{234}N_{77}O_{105}P_{15}Pt$	1979.356(1979.377)

[a]The most abundant isotopic mass-to-charge ratio.

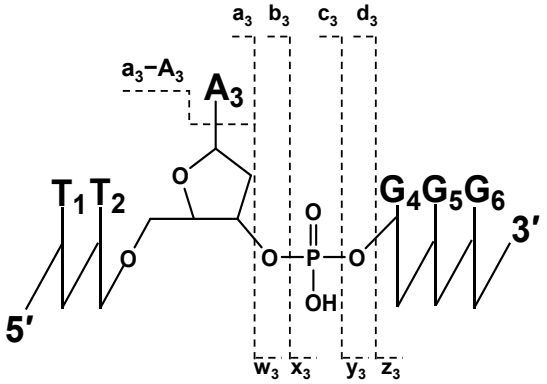
[b]A and G represent the neutral loss of an adenine and a guanine base, respectively.

[c]T_n, A_n and G_n represent the loss of a thymine, an adenine and a guanine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **I**.

[d]The internal fragment B_m:B_n results from fragmentation at both the a- and w-sites, having a phosphate group at their 5′-terminus and a furan ring at the 3′-terminus.

[e]The most likely oxidation adduct is indicated in brackets.

Table S2. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **I** ([**I** + **1′**]$^{2+}$, *m/z* 1121.706) produced by the reaction of complex **1** with ODN **I** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **I** for balancing the charges of the ions are omitted for clarity). **1′** = $[Pt(N_3)(py)_2]^+$.



Fragments	Formula(neutral)	*m/z*[a] observed(calculated)
$[w_1]^+$	$C_{10}H_{14}N_5O_7P$	348.080(348.070)
$\{w_1 + \mathbf{1'}\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.133(742.117)
$[y_2 - G_6{}^c]^+$	$C_{15}H_{18}N_5O_8P$	428.048(428.094)
$[w_2]^+$	$C_{20}H_{26}N_{10}O_{13}P_2$	677.137(677.125)
$\{w_2 + \mathbf{1'}\}^+$	$C_{30}H_{35}N_{15}O_{13}P_2Pt$	1071.182(1071.172)
$\{w_3 + \mathbf{1'} - N_3\}^{2+}$	$C_{40}H_{46}N_{17}O_{19}P_3Pt$	679.121(679.109)
$\{w_3 + \mathbf{1'}\}^{2+}$	$C_{40}H_{47}N_{20}O_{19}P_3Pt$	700.627(700.617)
$\{w_3 + \mathbf{1'}\}^+$	$C_{40}H_{47}N_{20}O_{19}P_3Pt$	1400.251(1400.226)
$\{x_5 + \mathbf{1'} - py\}^{2+}$	$C_{55}H_{67}N_{26}O_{30}P_5Pt$	962.162(962.151)
$\{w_5 + \mathbf{1'}\}^{2+}$	$C_{60}H_{72}N_{27}O_{31}P_5Pt$	1009.670(1009.669)
$\{z_5 + \mathbf{1'} - N_3 + MeCN + K\}^{2+}$	$C_{62}H_{70}N_{25}O_{27}P_4PtK$	978.661(978.664)
$\{[a_2 - T_2{}^c] - H_2O\}^+$	$C_{15}H_{17}N_2O_8P$	385.090(385.078)
$[a_2]^+$	$C_{20}H_{25}N_4O_{11}P$	529.141(529.133)
$[a_3 - A_3{}^c]^+$	$C_{25}H_{32}N_4O_{16}P_2$	707.148(707.133)
$\{[a_3 - A_3{}^c] + Na\}^+$	$C_{25}H_{31}N_4O_{16}P_2Na$	729.134(729.117)
$\{b_3 + \mathbf{1'} - N_3 + K\}^+$	$C_{40}H_{46}N_{11}O_{17}P_2PtK$	1249.188(1249.191)
$[a_4 - G_4{}^c]^+$	$C_{35}H_{44}N_9O_{21}P_3$	1020.202(1020.194)
$\{[a_4 - G_4{}^c] + \mathbf{1'}\}^+$	$C_{45}H_{53}N_{14}O_{21}P_3Pt$	1414.257(1414.245)
$\{a_4 + \mathbf{1'} - 2py\}^{2+}$	$C_{40}H_{48}N_{17}O_{22}P_3Pt$	704.123(704.109)
$\{d_4 + \mathbf{1'} - N_3\}^+$	$C_{50}H_{60}N_{16}O_{26}P_4Pt$	1621.267(1621.255)
$\{d_4 + \mathbf{1'}\}^+$	$C_{50}H_{61}N_{19}O_{26}P_4Pt$	1663.284(1663.272)

$\{d_5 + \mathbf{1'} - N_3\}^{2+}$	$C_{60}H_{72}N_{21}O_{32}P_5Pt$	975.665(975.658)
$\{[a_5 - G_5] - G^b\}$	$C_{40}H_{51}N_9O_{26}P_4$	1198.200(1198.197)
$[a_5 - G_5{}^c]^+$	$C_{45}H_{56}N_{14}O_{27}P_4$	1349.260(1349.246)
$\{[a_5 - G_5{}^c] + \mathbf{1'} - N_3\}^+$	$C_{55}H_{64}N_{16}O_{27}P_4Pt$	1701.285(1701.282)
$\{[a_5 - G_5{}^c] + \mathbf{1'}\}^+$	$C_{55}H_{65}N_{19}O_{27}P_4Pt$	1744.282(1744.297)
$\{[a_6 - G_6{}^c] + \mathbf{1'} - N_3\}^{2+}$	$C_{65}H_{76}N_{21}O_{33}P_5Pt$	1015.673(1015.671)
$\{[a_6 - G_6{}^c] + \mathbf{1'} - py + MeCN\}^{2+}$	$C_{62}H_{75}N_{24}O_{33}P_5Pt$	1018.181(1018.171)
$\{[a_6 - G_6{}^c] + \mathbf{1'}\}^{2+}$	$C_{65}H_{77}N_{24}O_{33}P_5Pt$	1037.182(1037.180)
Other fragment ions		
$[A]^+$	$C_5H_5N_5$	136.067(136.062)
$[G]^+$	$C_5H_5N_5O$	152.065(152.057)
$[T_2{}^d]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.068(483.055)
$[A_3{}^d]^+$	$C_{15}H_{19}N_5O_{10}P_2$	492.076(492.070)
$[G_4/G_5{}^d]^+$	$C_{15}H_{19}N_5O_{11}P_2$	508.074(508.063)
$\{G + \mathbf{1'} - N_3 + MeCN\}^+$	$C_{17}H_{16}N_8OPt$	544.123(544.117)
$\{G + \mathbf{1'}\}^+$	$C_{15}H_{14}N_{10}OPt$	546.122(546.109)
$[T_2{:}A_3{}^d]^+$	$C_{25}H_{32}N_7O_{17}P_3$	796.125(796.117)
$\{[G_4/G_5{}^d] + \mathbf{1'}\}^+$	$C_{25}H_{28}N_{10}O_{11}P_2Pt$	902.128(902.114)
$\{[\mathbf{I} - G^b] + \mathbf{1'} - N_3\}^{2+}$	$C_{65}H_{78}N_{21}O_{34}P_5Pt$	1024.681(1024.676)
$\{[\mathbf{I} - G^b] + \mathbf{1'}\}^{2+}$	$C_{65}H_{79}N_{24}O_{34}P_5Pt$	1046.186(1046.185)
$\{[\mathbf{I} - A^b] + \mathbf{1'}\}^{2+}$	$C_{65}H_{79}N_{24}O_{35}P_5Pt$	1054.190(1054.180)
$\{\mathbf{I} + \mathbf{1'}\}^{2+}$	$C_{70}H_{84}N_{29}O_{35}P_5Pt$	1121.710(1121.709)
$[T_2{:}G_4{}^d]^+$	$C_{35}H_{44}N_{12}O2_3P_4$	1125.177(1125.167)
$\{[G_4{:}G_5{}^d] + \mathbf{1'}\}^+$	$C_{35}H_{40}N_{15}O_{17}P_3Pt$	1231.178(1231.166)
$[\mathbf{I} + \mathbf{1'} - N_3\}^{2+}$	$C_{70}H_{83}N_{26}O_{35}P_5Pt$	1100.207(1100.201)
$\{\mathbf{I} + \mathbf{1'} - py + MeCN\}^{2+}$	$C_{67}H_{82}N_{29}O_{35}P_5Pt$	1102.708(1102.701)

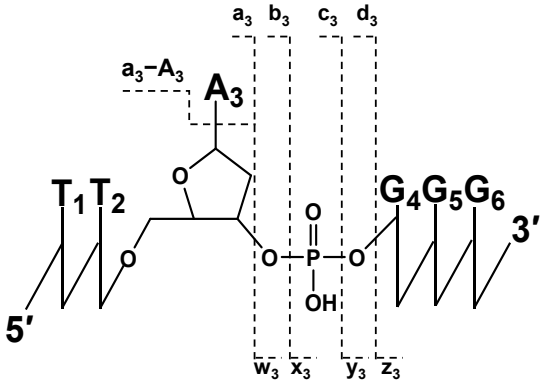
[a]The most abundant isotopic mass-to-charge ratio.

[b]A and G represent the neutral loss of an adenine and a guanine base, respectively.

[c]T_n, A_n and G_n represent the loss of a thymine, an adenine and a guanine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **I**.

[d]The internal fragment $B_m{:}B_n$ results from fragmentation at both the a- and w-sites, having a phosphate group at their 5′-terminus and a furan ring at the 3′-terminus.

Table S3. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **I** ([**I** + **1″**]$^{2+}$, *m/z* 1100.196) produced by the reaction of complex **1** with ODN **I** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **I** for balancing the charges of the ions are omitted for clarity). **1″** = $[Pt(py)_2]^{2+}$.



Fragments	Formula(neutral)	m/z[a] observed(calculated)
$[w_1]^+$	$C_{10}H_{14}N_5O_7P$	348.075(348.070)
$\{w_1 + G + \mathbf{1''}\}^+$	$C_{25}H_{27}N_{12}O_8PPt$	850.148(850.156)
$\{[w_2 - G^b] + \mathbf{1''}\}^+$	$C_{25}H_{29}N_7O_{12}P_2Pt$	877.114(877.109)
$\{w_2 + G + \mathbf{1''}\}^+$	$C_{35}H_{39}N_{17}O_{14}P_2Pt$	1179.202(1179.206)
$\{[w_3 - G^b] + \mathbf{1''}\}^{2+}$	$C_{35}H_{41}N_{12}O_{18}P_3Pt$	603.589(603.586)
$\{[w_3 - G^b] + \mathbf{1''}\}^+$	$C_{35}H_{41}N_{12}O_{18}P_3Pt$	1206.158(1206.156)
$\{[x_4 + \mathbf{1''} + Na\}^{2+}$	$C_{50}H_{57}N_{22}O_{23}P_4PtNa$	838.648(838.631)
$\{z_4 - G^b + \mathbf{1''}\}^{2+}$	$C_{45}H_{50}N_{17}O_{19}P_3Pt$	711.133(711.124)
$\{[w_5 - G^b] + \mathbf{1''}\}^{2+}$	$C_{55}H_{66}N_{19}O_{30}P_5Pt$	912.636(912.633)
$\{w_5 + G + \mathbf{1''}\}^{2+}$	$C_{65}H_{76}N_{29}O_{32}P_5Pt$	1063.685(1063.686)
$\{[a_2 - T_2^c] - H_2O\}^+$	$C_{15}H_{17}N_2O_8P$	385.088(385.078)
$[a_2]^+$	$C_{20}H_{25}N_4O_{11}P$	529.143(529.133)
$[d_2]^+$	$C_{20}H_{28}N_4O_{15}P_2$	627.116(627.109)
$[a_3]^+$	$C_{30}H_{37}N_9O_{16}P_2$	842.191(842.188)
$[a_4 - G_4^c]^+$	$C_{35}H_{44}N_9O_{21}P_3$	1020.196(1020.195)
$\{a_4 + [\mathbf{1''} - py]\}^{2+}$	$C_{45}H_{52}N_{15}O_{22}P_3Pt$	722.131(722.121)
$\{a_5 - G_5^c\}^+$	$C_{45}H_{56}N_{14}O_{27}P_4$	1349.245(1349.250)
$\{a_5 + \mathbf{1''}\}^{2+}$	$C_{60}H_{69}N_{21}O_{28}P_4Pt$	926.672(926.672)
$\{[a_5 - G_5^c] + \mathbf{1''}\}^+$	$C_{55}H_{64}N_{16}O_{27}P_4Pt$	1701.267(1701.281)
$\{[a_5 - G^b] + \mathbf{1''}\}^{2+}$	$C_{55}H_{66}N_{16}O_{28}P_4Pt$	860.154(860.150)
$\{[a_5 - G^b] + \mathbf{1''}\}^+$	$C_{55}H_{66}N_{16}O_{28}P_4Pt$	1719.288(1719.292)

$\{[b_5 - G^b] + [\mathbf{1''} - py]\}^{2+}$	$C_{50}H_{61}N_{15}O_{28}P_4Pt$	820.133(82.128)
$\{[b_5 - G^b] + [\mathbf{1''} - py]\}^{+}$	$C_{50}H_{61}N_{15}O_{28}P_4Pt$	1639.250(1639.248)
$\{[d_5 - G^b] + \mathbf{1''}\}^{2+}$	$C_{55}H_{67}N_{16}O_{31}P_5Pt$	900.146(900.133)
$\{[d_5 - G^b] + \mathbf{1''}\}^{+}$	$C_{55}H_{67}N_{16}O_{31}P_5Pt$	1799.256(1799.258)
$\{c_5 + A + \mathbf{1''}\}^{2+}$	$C_{65}H_{77}N_{26}O_{31}P_5Pt$	1035.182(1035.187)
$\{d_5 + \mathbf{1''} + MeCN\}^{2+}$	$C_{62}H_{75}N_{22}O_{32}P_5Pt$	996.164(996.171)
$\{[a_6 - G_6^c] + \mathbf{1''}\}^{2+}$	$C_{65}H_{76}N_{21}O_{33}P_5Pt$	1015.671(1015.671)
Other fragment ions		
$[A]^+$	$C_5H_5N_5$	136.067(136.062)
$[G]^+$	$C_5H_5N_5O$	152.062(152.057)
$[T_2^d]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.065(483.055)
$[A_3^d]^+$	$C_{15}H_{19}N_5O_{10}P_2$	492.074(492.070)
$\{G + G + \mathbf{1''}\}^{+}$	$C_{20}H_{18}N_{12}O_2Pt$	654.143(654.141)
$[T_2{:}A_3^d]^+$	$C_{25}H_{32}N_7O_{17}P_3$	796.121(796.117)
$\{[T_2{:}G_5^d] + G + \mathbf{1''}\}^{2+}$	$C_{60}H_{69}N_{24}O_{30}P_5Pt$	979.152(979.156)
$\{[G_4{:}G_5^d] - H_2O + \mathbf{1''}\}^{+}$	$C_{45}H_{51}N_{17}O_{21}P_4Pt$	1485.199(1485.213)
$\{[G_4/G_5^d] + G + \mathbf{1''}\}^{+}$	$C_{30}H_{32}N_{12}O_{12}P_2Pt$	1010.150(1010.146)
$\{[\mathbf{I} - G^b] + [\mathbf{1''} - py]\}^{2+}$	$C_{60}H_{73}N_{20}O_{34}P_5Pt$	985.157(985.156)
$\{[\mathbf{I} - G^b] + \mathbf{1''}\}^{2+}$	$C_{65}H_{78}N_{21}O_{34}P_5Pt$	1024.676(1024.680)
$\{\mathbf{I} + \mathbf{1''} - py\}^{2+}$	$C_{65}H_{78}N_{25}O_{35}P_5Pt$	1060.672(1060.672)

[a]The most abundant isotopic mass-to-charge ratio.

[b]A and G represent the neutral loss of an adenine and a guanine base, respectively.

[c]T_n, A_n and G_n represent the loss of a thymine, an adenine and a guanine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **I**.

[d]The internal fragment $B_m{:}B_n$ results from fragmentation at both the a- and w-sites, having a phosphate group at their 5′-terminus and a furan ring at the 3′-terminus.

Table S4. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **I** ($[\mathbf{I} + \mathbf{1'}_2]^{2+}$, *m/z* 1318.727) produced by the reaction of complex **1** with ODN **I** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **I** for balancing the charges of the ions are omitted for clarity). **1′** = $[Pt(N_3)(py)_2]^+$.

Fragments	**Formula(neutral)**	***m/z*[a] observed(calculated)**
$[w_1]^+$	$C_{10}H_{14}N_5O_7P$	348.084(348.070)
$\{w_1 + \mathbf{1'}\}^+$	$C_{20}H_{23}N_{10}O_7PPt$	742.133(742.121)
$[w_2 - G^b]^+$	$C_{15}H_{21}N_5O_{12}P_2$	526.082(526.070)
$[w_2]^+$	$C_{20}H_{26}N_{10}O_{13}P_2$	677.131(677.125)
$\{w_2 + \mathbf{1'}\}^{2+}$	$C_{30}H_{35}N_{15}O_{13}P_2Pt$	1071.181(1071.174)
$\{w_3 + \mathbf{1'}_2\}^{2+}$	$C_{50}H_{56}N_{25}O_{19}P_3Pt_2$	897.654(897.642)
$\{w_4 + \mathbf{1'}_2\}^{2+}$	$C_{60}H_{68}N_{30}O_{24}P_4Pt_2$	1054.176(1054.171)
$\{[z_4 - H_2O] + \mathbf{1'} - py\}^{2+}$	$C_{45}H_{49}N_{24}O_{19}P_3Pt$	759.626(759.631)
$[a_2]^+$	$C_{20}H_{25}N_4O_{11}P$	529.136(529.133)
$[a_4 - G_4^c]^+$	$C_{35}H_{44}N_9O_{21}P_3$	1020.201(1020.195)
$[a_5 - G_5^c]^+$	$C_{45}H_{56}N_{14}O_{27}P_4$	1349.266(1349.250)
$\{[a_5 - G_5^c] + \mathbf{1'}\}^+$	$C_{55}H_{65}N_{19}O_{27}P_4Pt$	1744.290(1744.299)
	Other fragment ions	
$[T_2^d]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.068(483.055)
$[G_4/G_5^d]^+$	$C_{15}H_{19}N_5O_{11}P_2$	508.074(508.063)
$\{G + \mathbf{1'}\}^+$	$C_{15}H_{14}N_{10}OPt$	546.117(546.109)
$[T_2{:}A_3^d]^+$	$C_{25}H_{32}N_7O_{17}P_3$	796.125(796.117)
$[G_4{:}G_5^d]^+$	$C_{25}H_{32}N_{10}O_{17}P_3$	837.126(837.115)
$[\mathbf{I}]^{2+}$	$C_{60}H_{75}N_{24}O_{35}P_5$	924.191(924.180)
$\{\mathbf{I} + \mathbf{1'}\}^{2+}$	$C_{70}H_{84}N_{29}O_{35}P_5Pt$	1121.710(1121.711)
$[T_2{:}G_4^d]^+$	$C_{35}H_{44}N_{12}O_{23}P_4$	1125.163(1125.164)
$\{\mathbf{I} + \mathbf{1'}_2 - 2N_3 - py + N\}^{2+}$	$C_{75}H_{87}N_{28}O_{35}P_5Pt_2$	1243.706(1243.702)
$\{[\mathbf{I} - A^b] + \mathbf{1'}_2\}^{2+}$	$C_{75}H_{88}N_{29}O_{35}P_5Pt_2$	1251.200(1251.207)

[a]The most abundant isotopic mass-to-charge ratio.

[b]A and G represent the neutral loss of an adenine and a guanine base, respectively.

[c]T_n, A_n and G_n represent the loss of a thymine, an adenine and a guanine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **I**.

[d]The internal fragment $B_m{:}B_n$ results from fragmentation at both the a- and w-sites, having a phosphate group at their 5′-terminus and a furan ring at the 3′-terminus.

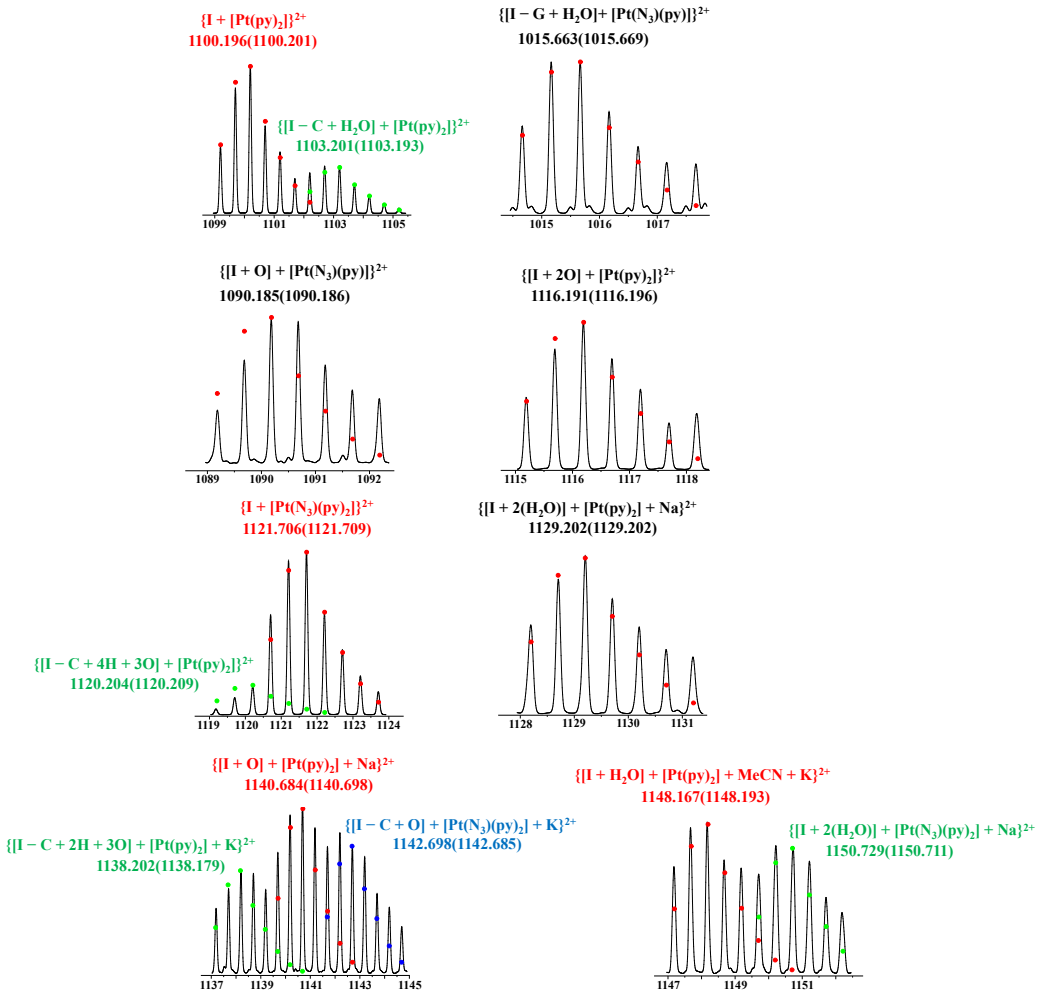


Figure S1. The isotopic models (dots) and mass spectra (lines) of several representative platinated adducts under positive-ion mode for the reaction of complex **1** and ODN **I** upon light irradiation. The C, O, H, G, K and Na represent carbon atom, oxygen atom, hydrogen atom, guanine base, potassium ion and sodium ion, respectively.