Adenine-adenine, adenine-cytosine and cytosine-cytosine crosslinks in trinucleotides induced by a photoactivatable Pt(IV) anticancer prodrug

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Electronic Supplementary Information

Table S4. MS data for the photo-reaction between Pt(IV) complex **1** and ODN **IV**

Table S5. MS/MS data of mono-platinated **I** adduct ([**I** + **1′**]$^+$)

Table S6. MS/MS data of mono-platinated **I** adduct ([**II** + **1′**]$^+$)

Table S7. MS/MS data of mono-platinated **I** adduct ([**III** + **1′**]$^+$)

Table S8. MS/MS data of mono-platinated **I** adduct ([**IV** + **1′**]$^+$)

Table S9. MS/MS data of mono-platinated **I** adduct ([**I** + **1″**]$^+$)

Table S10. MS/MS data of mono-platinated **I** adduct ([**II** + **1″**]$^+$)

Table S11. MS/MS data of mono-platinated **I** adduct ([**III** + **1″**]$^+$)

Table S12. MS/MS data of mono-platinated **I** adduct ([**IV** + **1″**]$^+$)

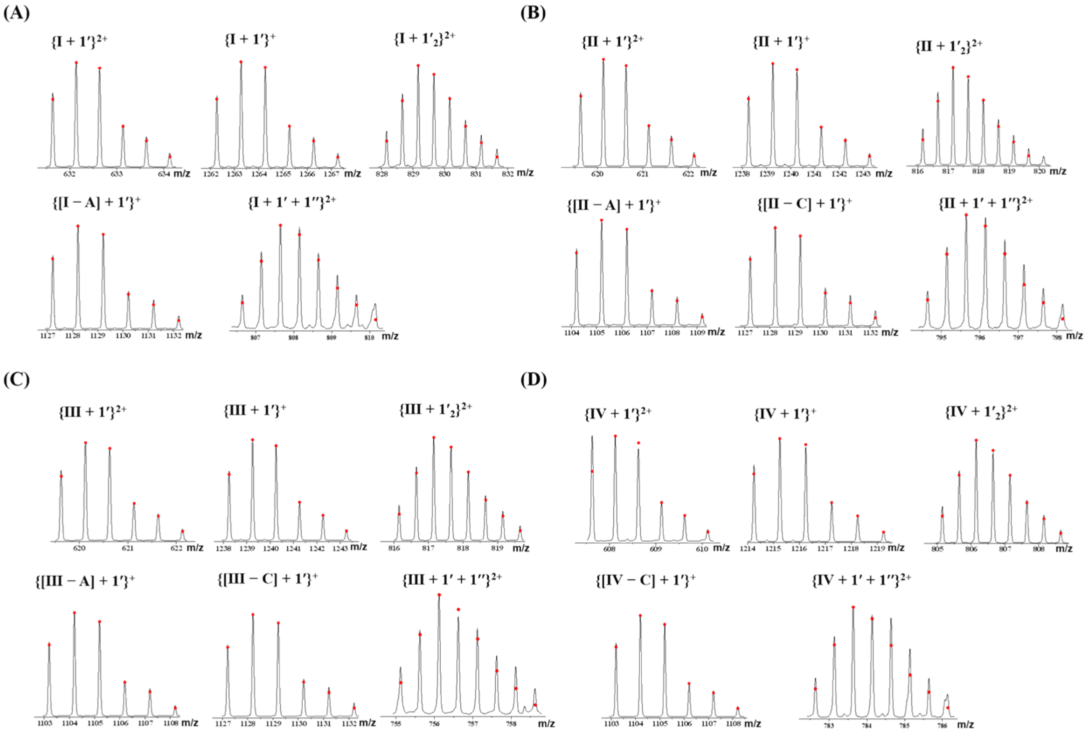


Figure S1. (A – D) The isotopic models (dots) and mass spectra (lines) of the major platinated adducts under positive-ion mode arising from the reaction of complex **1** and ODN **I** (A), **II** (B), **III** (C) or **IV** (D) upon irradiation under blue light for 1 h. **1′** = $[Pt(N_3)(py)_2]^+$ and **1″** = $[Pt(py)_2]^{2+}$.

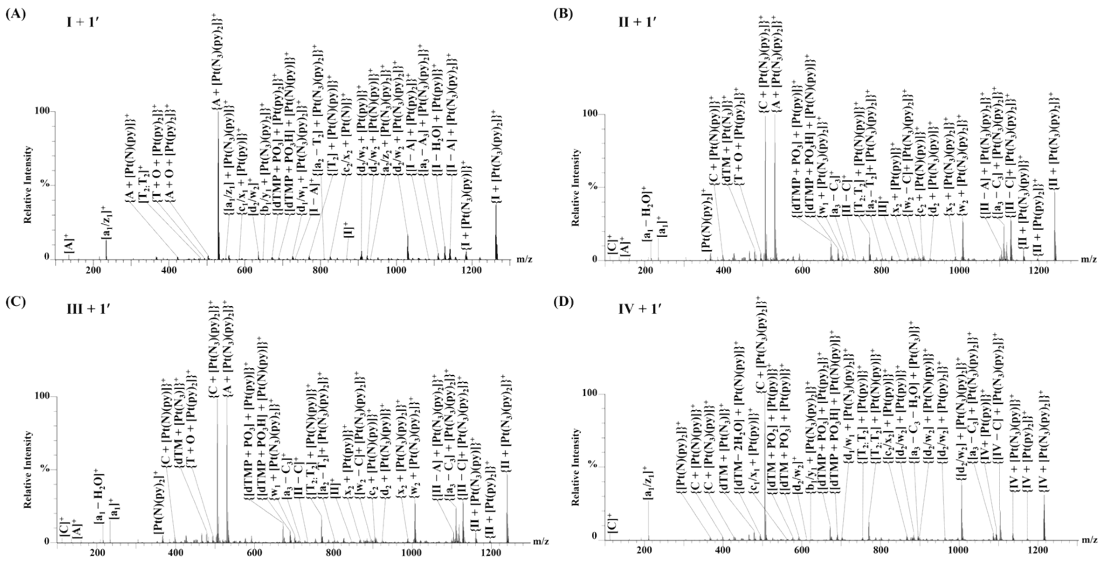


Figure S2. Tandem mass spectra of the parent ions {**I** + **1′**}$^+$ (A), {**II** + **1′**}$^+$ (B), {**III** + **1′**}$^+$ (C), {**IV** + **1′**}$^+$ (D) in the mass range of *m/z* 100 – 1250 with the main peaks labeled. The corresponding MS/MS data in detail are listed in Tables S5 – S8 in the Supporting Information. **1′** = $[Pt(N_3)(py)_2]^+$.

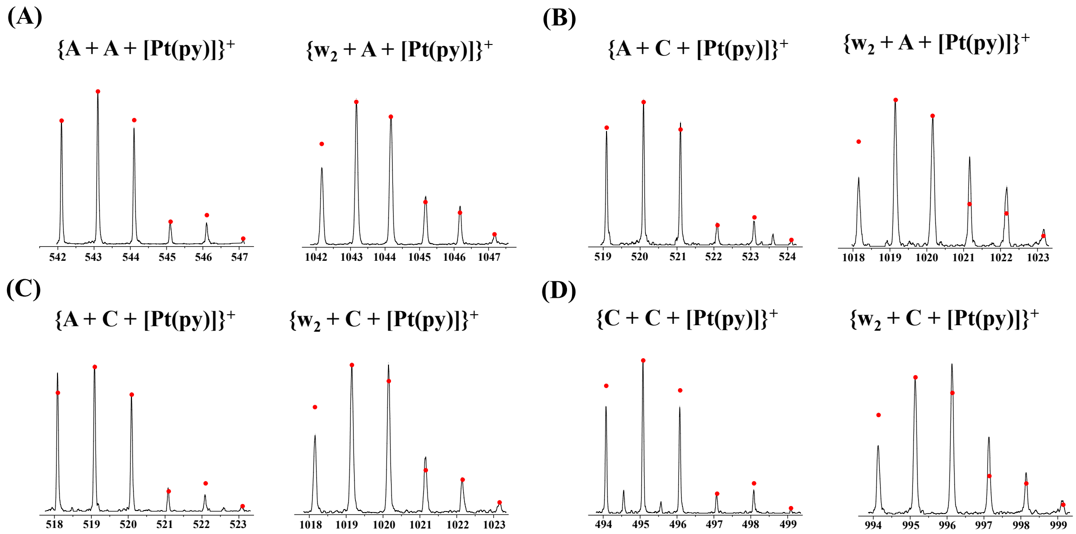


Figure S3. The isotopic models (dots) and mass spectra (lines) of the representative platinated fragments from the tandem mass spectrum of the parent ions {**I** + $[Pt(py)_2]$}$^+$ (A), {**II** + $[Pt(py)_2]$}$^+$ (B), {**III** + $[Pt(py)_2]$}$^+$ (C) and {**IV** + $[Pt(py)_2]$}$^+$ (D).

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** = $[Pt(N_3)_2(OH)_2(Py)_2]$.

Ions	Formula	*m/z*[a] observed(calculated)
$[A]^+$	$C_5H_5N_5$	136.058(136.062)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.055(387.054)
$[\mathbf{I}]^{2+}$	$C_{30}H_{38}N_{12}O_{15}P_2$	435.106(435.110)
$[Pt^{IV}(N_3)_2(OH)_2(py)_2]^+$	$C_{10}H_{14}O_2N_8Pt$	474.096(474.096)
$\{A + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}Pt$	530.108(530.112)
$\{\mathbf{I} + [Pt(py)_2]\}^{2+}$	$C_{40}H_{46}N_{14}O_{15}P_2Pt$	610.625(610.627)
$\{\mathbf{I} + [Pt(N_3)(py)_2]\}^{2+}$	$C_{40}H_{47}N_{17}O_{15}P_2Pt$	632.133(632.135)
$[\mathbf{I} - A^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.155(734.158)
$\{\mathbf{I} + [Pt(N_3)(py)_2] + [Pt(py)_2]\}^{2+}$	$C_{50}H_{55}N_{19}O_{15}P_2Pt_2$	807.654(807.652)
$\{\mathbf{I} + [Pt(N_3)(py)_2]_2\}^{2+}$	$C_{50}H5_6N_{22}O_{15}P_2Pt_2$	829.163(829.160)
$[\mathbf{I}]^+$	$C_{30}H_{38}N_{12}O_{15}P_2$	869.213(869.213)
$\{[\mathbf{I}]_2 + K\}^{2+}$	$C_{60}H_{75}N_{24}O_{30}P_4K$	888.191(888.191)
$\{d_2/w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{13}P_2Pt$	1030.178(1030.172_
$\{[\mathbf{I}]_2 + [Pt(N_3)(py)_2] + K\}^{2+}$	$C_{70}H_{84}N_{29}O_{30}P_4PtK$	1085.717(1085.717)
$\{[\mathbf{I} - A^b] + [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.215(1128.209)
$\{\mathbf{I} + [Pt(py)_2]\}^+$	$C_{40}H_{46}N_{14}O_{15}P_2Pt$	1220.253(1220.246)
$\{\mathbf{I} + [Pt(N_3)(py)_2]\}^+$	$C_{40}H_{47}N_{17}O_{15}P_2Pt$	1263.271(1263.264)

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

[b]A represent the neutral loss of an adenine.

Table S2. MS data under positive-ion mode for the reaction between Pt(IV) complex **1** and ODN **II** at a molar ratio of **1**/**II** = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety and the loss of protons from **II** for balancing the charges of the ions are omitted for clarity). **1** = $[Pt(N_3)_2(OH)_2(Py)_2]$.

Ions	Formula	m/z^a observed(calculated)
$[A]^+$	$C_5H_5N_5$	136.058(136.062)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.049(387.054)
$[Pt^{IV}(N_3)_2(OH)_2(py)_2]^+$	$C_{10}H_{14}N_8O_2Pt$	474.095(474.096)
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.100(506.101)
$\{A + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}Pt$	530.111(530.112)
$\{\mathbf{II} + [Pt(py)_2]\}^{2+}$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	598.618(598.621)
$\{\mathbf{II} + [Pt(N_3)(py)_2]\}^{2+}$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	620.130(620.130)
$[\mathbf{II} - C^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.158(734.158)
$\{\mathbf{II} + [Pt(N_3)(py)_2] + [Pt(py)_2]\}^{2+}$	$C_{49}H_{55}N_{17}O_{16}P_2Pt_2$	795.643(795.646)
$\{\mathbf{II} + [Pt(N_3)(py)_2]_2\}^{2+}$	$C_{49}H_{56}N_{20}O_{16}P_2Pt_2$	817.156(817.155)
$[\mathbf{II}]^+$	$C_{29}H_{38}N_{10}O_{16}P_2$	845.202(845.202)
$\{w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{36}N_{10}O_{14}P_2Pt$	1006.166(1006.161)
$\{[\mathbf{II}]_2 + [Pt(py)_2]\}^{2+}$	$C_{68}H_{84}N_{22}O_{32}P_4Pt$	1021.222(1021.219)
$\{[\mathbf{II}]_2 + [Pt(N_3)(py)_2]\}^{2+}$	$C_{68}H_{85}N_{25}O_{32}P_4Pt$	1042.729(1042.728)
$\{[\mathbf{II} - A^b] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.198(1104.202)
$\{[\mathbf{II} - C^b] + [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.212 (1128.209)
$\{\mathbf{II} + [Pt(py)_2]\}^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.245(1196.235)
$\{\mathbf{II} + [Pt(N_3)(py)_2]\}^+$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	1239.260(1239.252)
$[\mathbf{II}]_3^{2+}$	$C_{87}H_{114}N_{30}O_{48}P_6$	1267.807(1267.800)

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

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

Table S3. MS data under positive-ion mode for the reaction between Pt(IV) complex **1** and ODN **III** at a molar ratio of **1**/**III** = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety and the loss of protons from **III** for balancing the charges of the ions are omitted for clarity). **1** = $[Pt(N_3)_2(OH)_2(Py)_2]$.

Ions	Formula	*m/z*[a] observed(calculated)
$[C]^+$	$C_4H_5N_3O$	112.056(112.051)
$[A]^+$	$C_5H_5N_5$	136.058(136.062)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.049(387.054)
$[Pt^{IV}(N_3)_2(OH)_2(py)_2]^+$	$C_{10}H_{14}N_8O_2Pt$	474.095(474.096)
$[C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.095(506.101)
$\{\mathbf{III} + [Pt(py)_2]\}^{2+}$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	598.618(598.621)
$\{\mathbf{III} + [Pt(N_3)(py)_2]\}^{2+}$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	620.124(620.130)
$[w_2]^+$	$C_{20}H_{27}N_7O_{13}P_2$	636.118(636.121)
$[\mathbf{III} - C^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.153(734.158)
$\{\mathbf{III} + [Pt(N_3)(py)_2] + [Pt(py)_2]\}^{2+}$	$C_{49}H_{55}N_{17}O_{16}P_2Pt_2$	795.643(795.646)
$\{\mathbf{III} + [Pt(N_3)(py)_2]_2\}^{2+}$	$C_{49}H_{56}N_{20}O_{16}P_2Pt_2$	817.150(817.155)
$[\mathbf{III}]^+$	$C_{29}H_{38}N_{10}O_{16}P_2$	845.202(845.202)
$\{w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{13}P_2Pt$	1030.175(1030.172)
$\{[\mathbf{III} - A^b] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.202(1104.198)
$\{[\mathbf{III} - C^b]+ [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.205(1128.209)
$\{\mathbf{III} + [Pt(py)_2]\}^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.231(1196.235)
$\{\mathbf{III} + [Pt(N_3)(py)_2]\}^+$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	1239.253(1239.252)

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

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

Table S4. MS data under positive-ion mode for the reaction between Pt(IV) complex **1** and ODN **IV** at a molar ratio of **1**/**IV** = 1.0 after irradiated under blue light for 1 h (Charges for Pt moiety and the loss of protons from **IV** for balancing the charges of the ions are omitted for clarity). **1** = $[Pt(N_3)_2(OH)_2(Py)_2]$.

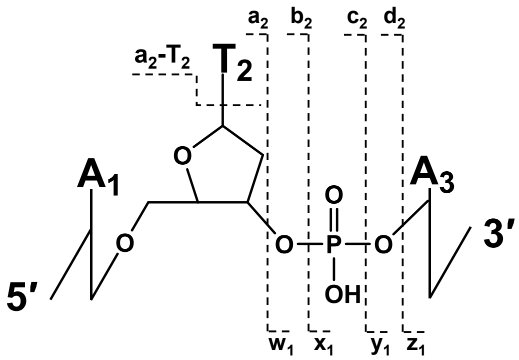
Ions	Formula	*m/z*[a] observed(calculated)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.049(387.054)
$[Pt^{IV}(N_3)_2(OH)_2(py)_2]^+$	$C_{10}H_{14}N_8O_2Pt$	474.095(474.096)
$[T_2{:}T_2{}^c]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.051(483.056)
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.096(506.101)
$\{\mathbf{IV} + [Pt(py)_2]\}^{2+}$	$C_{38}H_{46}N_{10}O_{17}P_2Pt$	586.614(586.616)
$\{\mathbf{IV} + [Pt(N_3)(py)_2]\}^{2+}$	$C_{38}H_{47}N_{13}O_{17}P_2Pt$	608.122(608.124)
$[\mathbf{IV} - C^b]^+$	$C_{24}H_{33}N_5O_{16}P_2$	710.147(710.147)
$\{\mathbf{IV} + [Pt(N_3)(py)_2] + [Pt(py)_2]\}^{2+}$	$C_{48}H_{55}N_{15}O_{17}P_2Pt_2$	783.639(783.641)
$\{\mathbf{IV} + [Pt(N_3)(py)_2]_2\}^{2+}$	$C_{48}H_{56}N_{18}O_{17}P_2Pt_2$	805.147(805.149)
$[\mathbf{IV}]^+$	$C_{28}H_{38}N_8O_{17}P_2$	821.190(821.190)
$\{[d_2/w_2] + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{36}N_{10}O_{14}P_2Pt$	1006.160(1006.161)
$\{[\mathbf{IV} - C^b] + [Pt(py)_2]\}^+$	$C_{34}H_{41}N_7O_{16}P_2Pt$	1061.184(1061.181)
$\{[\mathbf{IV} - C^b] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.203(1104.198)
$\{\mathbf{IV} + [Pt(py)_2]\}^+$	$C_{38}H_{46}N_{10}O_{17}P_2Pt$	1172.228(1172.224)
$\{\mathbf{IV} + [Pt(N_3)(py)_2]\}^+$	$C_{38}H_{47}N_{13}O_{17}P_2Pt$	1215.249(1215.254)

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

[b]C represent the neutral loss of a cytosine base.

[c]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 S5. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **I** ([**I** + **1′**]$^+$) 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′** = $[Pt(N_3)(py)_2]^{2+}$



Ions	Formula	*m/z*[a] observed(calculated)
$[A]^+$	$C_5H_5N_5$	136.055(136.062)
$[a_1/z_1 - H_2O]^+$	$C_{10}H_9N_5O$	216.084(216.088)
$[a_1/z_1]^+$	$C_{10}H_{11}N_5O_2$	234.093(234.099)
$[Pt(N_3)(py)_2]^+$	$C_{10}H_9N_5Pt$	395.053(395.058)
$\{A + [Pt(N)(py)]\}^+$	$C_{10}H_9N_7Pt$	423.054(423.064)
$\{dTM^e + [Pt(N_3)]\}^+$	$C_{10}H_{13}N_5O_5Pt$	479.077(479.064)
$[T_2{:}T_2{}^d]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.052(483.056)
$\{A + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{14}N_{10}Pt$	530.102(530.112)
$\{A + A + [Pt(N_3)(py)]\}^+$	$C_{15}H_{13}N_{11}Pt$	543.102(543.108)
$\{[a_1/z_1] + [Pt(N_3)(py)]\}^+$	$C_{15}H_{15}N_9O_2Pt$	550.089(550.107)
$\{A + A + [Pt(N)(py)]\}^+$	$C_{15}H_{14}N_{12}Pt$	558.114(558.118)
$\{[dTM^e + PO_2] + [Pt(py)]\}^+$	$C_{15}H_{16}N_3O_7PPt$	577.041(577.045)
$\{c_1/x_1 + [Pt(py)]\}^+$	$C_{15}H_{15}N_6O_5PPt$	586.059(586.056)
$\{[dTM^e + PO_2] + [Pt(N)(py)]\}^+$	$C_{15}H_{17}N_4O_7PPt$	592.049(592.056)
$\{c_1/x_1 + [Pt(N)(py)]\}^+$	$C_{15}H_{16}N_7O_5PPt$	601.061(601.067)
$\{d_1/w_1 + [Pt(N)(py)]\}^+$	$C_{15}H_{18}N_7O_6PPt$	619.066(619.078)
$[d_2/w_2]^+$	$C_{20}H_{27}N_7O_{13}P_2$	636.120(636.121)
$\{b_1/y_1 + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{22}N_{10}O_3Pt$	646.154(646.160)

$\{[dTMP^e + PO_3] + [Pt(py)]\}^+$	$C_{20}H_{21}N_4O_8PPt$	672.081(672.082)
$\{[dTMP^e + PO_3H] + [Pt(N)(py)]\}^+$	$C_{15}H_{20}N_4O_{11}P_2Pt$	690.033(690.028)
$\{c_1/x_1 + T + [Pt(py)]\}^+$	$C_{20}H_{21}N_8O_7PPt$	712.087(712.099)
$\{d_1/w_1 + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_6PPt$	726.119(726.126)
$[\mathbf{I} - A^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.155(734.158)
$\{[T_2{:}T_2^d] + [Pt(py)]\}^+$	$C_{20}H_{23}N_3O_{12}P_2Pt$	755.050(755.048)
$\{[T_2{:}T_2^d] + [Pt(N)(py)]\}^+$	$C_{20}H_{24}N_4O_{12}P_2Pt$	770.054(770.059)
$\{[a_2 - T_2^c] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{27}N_{10}O_7PPt$	806.154(806.152)
$\{c_2/x_2 + [Pt(N)]\}^+$	$C_{20}H_{24}N_8O_{12}P_2Pt$	826.076(829.071)
$\{d_2/w_2 + [Pt(N)]\}^+$	$C_{20}H_{26}N_8O_{13}P_2Pt$	844.082(844.072)
$[\mathbf{I}]^+$	$C_{30}H_{38}N_{12}O_{15}P_2$	869.213(869.213)
$\{[T_2{:}T_2^d] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_7O_{12}P_2Pt$	877.123(877.107)
$\{c_2/x_2 +[Pt(py)]\}^+$	$C_{25}H_{28}N_8O_{12}P_2Pt$	890.103(890.102)
$\{c_2/x_2 + [Pt(N)(py)]\}^+$	$C_{25}H_{29}N_9O_{12}P_2Pt$	905.118(905.113)
$\{d_2/w_2 + [Pt(py)]\}^+$	$C_{25}H_{30}N_8O_{13}P_2Pt$	908.115(908.113)
$\{d_2/w_2 + [Pt(N)(py)]\}^+$	$C_{25}H_{31}N_9O_{13}P_2Pt$	923.125(923.124)
$\{a_2/z_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{33}N_{12}O_9PPt$	932.201(932.195)
$\{d_2/w_2 + [Pt(N_3)(py)]\}^+$	$C_{25}H_{31}N_{11}O_{13}P_2Pt$	951.130(951.130)
$\{[\mathbf{I} - T^b] + [Pt(N_3)]\}^+$	$C_{25}H_{31}N_{13}O_{13}P_2Pt$	979.136(979.138)
$\{d_2/w_2 + [Pt(py)_2]\}^+$	$C_{30}H_{35}N_9O_{13}P_2Pt$	987.153(987.155)
$\{d_2/w_2 + [Pt(N)(py)_2]\}^+$	$C_{30}H_{36}N_{10}O_{13}P_2Pt$	1002.159(1002.166)
$\{c_2/x_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{34}N_{12}O_{12}P_2Pt$	1012.151(1012.167)
$\{d_2/w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{13}P_2Pt$	1030.172(1030.172)
$\{[\mathbf{I} - T^b] + [Pt(N_3)(py)]\}^+$	$C_{30}H_{36}N_{14}O_{13}P_2Pt$	1058.179(1058.178)
$\{[a_3 - A_3^c] + [Pt(py)_2]\}^+$	$C_{35}H_{39}N_9O_{14}P_2Pt$	1067.185(1067.182)
$\{\mathbf{I} + [Pt(N)]\}^+$	$C_{30}H_{37}N_{13}O_{15}P_2Pt$	1077.171(1077.173)
$\{[\mathbf{I} - A^b] + [Pt(py)_2]\}^+$	$C_{35}H_{41}N_9O_{15}P_2Pt$	1085.184(1085.192)
$\{[a_3 - A_3^c] + [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{40}N_{12}O_{14}P_2Pt$	1110.195(1110.198)
$\{[\mathbf{I} - H_2O] + [Pt(py)]\}^+$	$C_{35}H_{39}N_{13}O_{14}P_2Pt$	1123.185(1123.194)
$\{[\mathbf{I} - A^b] + [Pt(N_3)(py)_2]\}^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.215(1128.209)

{**I** + [Pt(py)]}$^+$	$C_{35}H_{41}N_{13}O_{15}P_2Pt$	1141.206(1141.204)
{**I** + [Pt(N)(py)]}$^+$	$C_{35}H_{42}N_{14}O_{15}P_2Pt$	1156.220(1156.215)
{[**I** − H_2O] + [Pt(N_3)(py)]}$^+$	$C_{35}H_{40}N_{16}O_{14}P_2Pt$	1166.235(1166.211)
{**I** + [Pt(N_3)(py)]}$^+$	$C_{35}H_{42}N_{16}O_{15}P_2Pt$	1185.230(1185.221)
{**I** + [Pt$(py)_2$]}$^+$	$C_{40}H_{46}N_{14}O_{15}P_2Pt$	1220.260(1220.246)
{**I** + [Pt(N_3)$(py)_2$]}$^+$	$C_{40}H_{47}N_{17}O_{15}P_2Pt$	1263.264(1263.264)

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

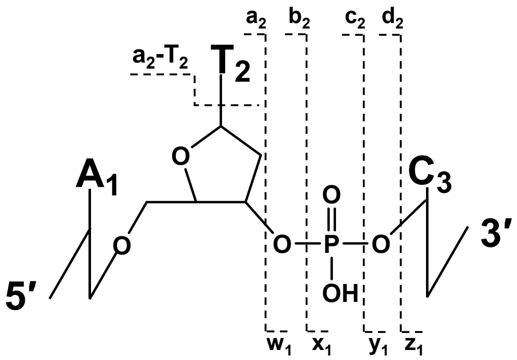
[b]A and T represent the neutral loss of an adenine and a thymine base, respectively.

[c]T_n and A_n represent the loss of a thymine or an adenine base, 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]dTM and dTMP represent the thymidine and thymidine monophosphate, respectively.

Table S6. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **II** ([**II** + **1′**]$^+$) produced by the reaction of complex **1** with ODN **II** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **II** for balancing the charges of the ions are omitted for clarity). **1′** = [Pt(N$_3$)(py)$_2$]$^+$



Ions	Formula	*m/z*[a] observed(calculated)
[C]$^+$	$C_4H_5N_3O$	112.045(112.051)
[A]$^+$	$C_5H_5N_5$	136.057(136.062)
[a$_1$ − H$_2$O]$^+$	$C_{10}H_9N_5O$	216.082(216.088)
[a$_1$]$^+$	$C_{10}H_{11}N_5O_2$	234.094(234.099)
[Pt(N)(py)$_2$]$^+$	$C_{10}H_9N_3Pt$	367.037(367.052)
{C + [Pt(N)(py)]}$^+$	$C_9H_9N_5OPt$	399.048(399.053)
{C + [Pt(N$_3$)(py)]}$^+$	$C_9H_9N_7OPt$	427.052(427.059)
{dTM[e] + [Pt(N$_3$)]}$^+$	$C_{10}H_{13}N_5O_5Pt$	479.072(479.64)
{C + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{14}H_{14}N_8OPt$	506.092(506.101)
{A + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}Pt$	530.108(530.112)
{[dTM[e] + PO$_2$] + [Pt(py)]}$^+$	$C_{15}H_{16}N_3O_7PPt$	577.040(577.045)
{[dTM[e] + PO$_3$] + [Pt(py)]}$^+$	$C_{15}H_{16}N_3O_8PPt$	593.035(593.040)
{[dTMP[e] + PO$_3$] + [Pt(py)]}$^+$	$C_{20}H_{21}N_4O_8PPt$	672.074(672.082)
{[dTMP[e] + PO$_3$H] + [Pt(N)(py)]}$^+$	$C_{15}H_{20}N_4O_{11}P_2Pt$	690.022(690.033)
{w$_1$ + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{19}H_{23}N_8O_7PPt$	702.109(702.115)
{c$_1$ + T + [Pt(py)]}$^+$	$C_{20}H_{21}N_8O_7PPt$	712.097(712.099)

$[a_3 - C_3^c]^+$	$C_{25}H_{31}N_7O_{14}P_2$	716.161(716.148)
$\{[a_2 - T_2^c] + [Pt(N_3)(py)]\}^+$	$C_{20}H_{22}N_9O_7PPt$	727.105(725.110)
$[\mathbf{II} - C^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.154(734.158)
$\{[T_2{:}T_2^d] + [Pt(N)(py)]\}^+$	$C_{20}H_{24}N_4O_{12}P_2Pt$	770.053(770.059)
$\{[w_2 - C^b] + [Pt(N)(py)]\}^+$	$C_{20}H_{26}N_5O_{13}P_2Pt$	802.066(802.072)
$\{[a_2 - T_2^c] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{27}N_{10}O_7PPt$	806.152(806.152)
$\{[x_2 - C^b] + [Pt(py)_2]\}^+$ or $\{[T_2^d] + [Pt(py)_2]\}^+$	$C_{25}H_{28}N_4O_{12}P_2Pt$	834.087(834.090)
$[\mathbf{II}]^+$	$C_{29}H_{38}N_{10}O_{16}P_2$	845.191(845.202)
$\{x_2 + [Pt(py)]\}^+$	$C_{24}H_{28}N_6O_{13}P_2Pt$	866.086(866.091)
$\{[x_2 - C^b] + [Pt(N_3)(py)_2]\}^+$ or $\{[T_2^d] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_7O_{12}P_2Pt$	877.103(877.107)
$\{x_2 + [Pt(N_3)(py)]\}^+$	$C_{24}H_{29}N_7O_{13}P_2Pt$	881.099(880.102)
$\{w_2 + [Pt(py)]\}^+$	$C_{24}H_{30}N_6O_{14}P_2Pt$	884.110(884.102)
$\{c_2 + [Pt(py)]\}^+$	$C_{25}H_{28}N_8O_{12}P_2Pt$	890.095(890.102)
$\{[w_2 - C^b] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{31}N_7O_{13}P_2Pt$	895.118(895.118)
$\{c_2 + [Pt(N)(py)]\}^+$	$C_{25}H_{29}N_9O_{12}P_2Pt$	905.115(905.113)
$\{d_2 + [Pt(py)]\}^+$	$C_{25}H_{30}N_8O_{13}P_2Pt$	908.119(908.113)
$\{d_2 + [Pt(N_3)(py)]\}^+$	$C_{25}H_{31}N_9O_{13}P_2Pt$	923.104(923.124)
$\{a_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{33}N_{12}O_9PPt$	932.186(932.195)
$\{w_2 + [Pt(py)_2]\}^+$	$C_{29}H_{35}N_7O_{14}P_2Pt$	963.135(963.144)
$\{d_2 + [Pt(py)_2]\}^+$	$C_{30}H_{35}N_9O_{13}P_2Pt$	987.143(987.155)
$\{x_2 + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{34}N_{10}O_{13}P_2Pt$	988.135(988.150)
$\{w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{36}N_{10}O_{14}P_2Pt$	1006.165(1006.161)
$\{c_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{34}N_{12}O_{12}P_2Pt$	1012.151(1012.162)
$\{[\mathbf{II} - H_2O] + [Pt]\}^+$	$C_{29}H_{34}N_{10}O_{15}P_2Pt$	1020.155(1020.140)
$\{d_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{13}P_2Pt$	1030.162(1030.172)
$\{[\mathbf{II} - H_2O] + [Pt(N)]\}^+$	$C_{29}H_{35}N_{11}O_{15}P_2Pt$	1035.151(1035.151)
$\{\mathbf{II} + [Pt(N)]\}^+$	$C_{29}H_{37}N_{11}O_{16}P_2Pt$	1053.151(1053.162)
$\{[\mathbf{II} - A^b] + [Pt(py)_2]\}^+$	$C_{34}H_{41}N_7O_{16}P_2Pt$	1061.162(1061.181)
$\{[a_3 - C_3^c] + [Pt(py)_2]\}^+$	$C_{35}H_{39}N_9O_{14}P_2Pt$	1067.182(1067.182)

{[**II** − C[b]]+ [Pt(py)$_2$]}$^+$	$C_{35}H_{41}N_9O_{15}P_2Pt$	1085.181(1085.192)
{[**II** − H_2O]+ [Pt(py)]}$^+$	$C_{34}H_{39}N_{11}O_{15}P_2Pt$	1099.192(1099.182)
{[**II** − A[b]] + [Pt(N_3)(py)$_2$]}$^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.195(1104.198)
{[a_3 − C_3[c]] + [Pt(N_3)(py)$_2$]}$^+$	$C_{35}H_{40}N_{12}O_{14}P_2Pt$	1110.199(1110.198)
{**II** + [Pt(py)]}$^+$	$C_{34}H_{41}N_{11}O_{16}P_2Pt$	1117.198(1117.193)
{[**II** − C[b]]+ [Pt(N_3)(py)$_2$]}$^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.205(1128.209)
{**II** + [Pt(N_3)(py)]}$^+$	$C_{34}H_{42}N_{14}O_{16}P_2Pt$	1160.203(1160.210)
{**II** + [Pt(py)$_2$]}$^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.230(1196.235)
{**II** + [Pt(N_3)(py)$_2$]}$^+$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	1239.252(1239.252)

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

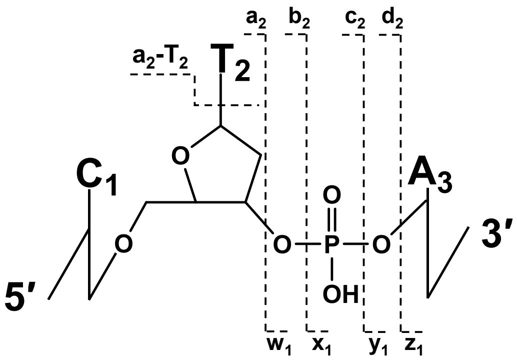
[b]A and C represent the neutral loss of an adenine and a cytosine base, respectively.

[c]T_n and C_n represent the loss of a thymine and a cytosine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **II**.

[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]dTM and dTMP represent the thymidine and thymidine monophosphate, respectively.

Table S7. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **III** ([**III** + **1′**]$^+$) produced by the reaction of complex **1** with ODN **III** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **III** for balancing the charges of the ions are omitted for clarity). **1′** = $[Pt(N_3)(py)_2]^+$



Ions	Formula	m/z[a] observed(calculated)
$[C]^+$	$C_4H_5N_3O$	112.047(112.051)
$[A]^+$	$C_5H_5N_5$	136.056(136.062)
$[a_1]^+$	$C_9H_{11}N_3O_3$	210.084(210.087)
$[Pt(N_3)(py)]^+$	$C_{10}H_9N_5Pt$	395.051(395.058)
$\{C + [Pt(N)(py)]\}^+$	$C_9H_9N_5OPt$	399.050(399.053)
$\{A + [Pt(N)(py)]\}^+$	$C_{10}H_9N_7Pt$	423.048(423.064)
$\{C + [Pt(N_3)(py)]\}^+$	$C_9H_9N_7OPt$	427.055(427.059)
$\{[C - NH_2] + [Pt(py)_2]\}^+$	$C_{14}H_{11}N_4OPt$	447.066(447.065)
$\{A + [Pt(N_3)(py)]\}^+$	$C_{10}H_9N_9Pt$	451.072(451.070)
$\{dTM^e + [Pt(N_3)]\}^+$	$C_{10}H_{13}N_5O_5Pt$	479.079(479.064)
$[T_2{:}T_2^d]^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.041(483.056)
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.095(506.101)
$\{A + [Pt(N_3)(py)_2]\}^{2+}$	$C_{15}H_{14}N_{10}Pt$	530.111(530.112)
$\{[dTM^e + PO_2] + [Pt(py)]\}^+$	$C_{15}H_{16}N_3O_7PPt$	577.043(577.045)
$\{x_1 + [Pt(py)]\}^+$	$C_{15}H_{15}N_6O_5PPt$	586.052(586.056)
$\{[dTM^e + PO_2] + [Pt(N)(py)]\}^+$	$C_{15}H_{17}N_4O_7PPt$	592.042(592.056)

$[d_2]^+$	$C_{20}H_{27}N_7O_{13}P_2$	636.118(636.121)
$\{[dTMP^e + PO_3] + [Pt(py)_2]\}^+$	$C_{20}H_{21}N_4O_8PPt$	672.083(672.082)
$\{[dTMP^e + PO_3H] + [Pt(N)(py)]\}^+$	$C_{15}H_{20}N_4O_{11}P_2Pt$	690.026(690.033)
$\{c_1 + T + [Pt(py)]\}^+$	$C_{20}H_{21}N_8O_7PPt$	712.096(712.099)
$\{w_1 + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_{10}O_6PPt$	726.125(726.126)
$[\mathbf{III} - C^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.152(734.158)
$\{[dTMP^e + PO_3H] + [Pt(py)_2]\}^+$	$C_{20}H_{24}N_4O_{11}P_2Pt$	754.063(754.064)
$\{[T_2:T_2^d] + [Pt(N)(py)]\}^+$	$C_{20}H_{24}N_4O_{12}P_2Pt$	770.052(770.059)
$\{x_2 + [Pt(N)]\}^+$	$C_{20}H_{26}N_8O_{13}P_2Pt$	826.076(829.071)
$\{[d_2 - T^b - 2H_2O] + [Pt(N_3)(py)_2]\}^+$	$C_{24}H_{26}N_8O_{10}P_2Pt$	844.088(844.097)
$\{[c_2 - C^b] + [Pt(N_3)(py)_2]\}^+$ or $\{[T_2^d] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_7O_{12}P_2Pt$	877.108(877.107)
$\{c_2 + [Pt(N_3)(py)]\}^+$	$C_{24}H_{29}N_7O_{13}P_2Pt$	881.108(880.102)
$\{x_2 + [Pt(N)(py)]\}^+$	$C_{25}H_{29}N_9O_{12}P_2Pt$	905.108(905.113)
$\{w_2 + [Pt(py)]\}^+$	$C_{25}H_{30}N_8O_{13}P_2Pt$	908.109(908.113)
$\{w_2 + [Pt(N)(py)]\}^+$	$C_{25}H_{31}N_9O_{13}P_2Pt$	923.128(923.120)
$\{d_2 + A + [Pt]\}^+$ or $\{w_2 + C + [Pt]\}^+$	$C_{24}H_{30}N_{10}O_{14}P_2Pt$	940.112(940.114)
$\{w_2 + [Pt(N_3)(py)]\}^+$	$C_{25}H_{31}N_{11}O_{13}P_2Pt$	951.144(951.130)
$\{d_2 + [Pt(py)_2]\}^+$	$C_{29}H_{35}N_7O_{14}P_2Pt$	963.128(963.144)
$\{[a_3 - A_3^c - C^b] + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{35}N_7O_{14}P_2Pt$	975.133(975.144)
$\{w_2 + [Pt(py)_2]\}^+$	$C_{30}H_{35}N_9O_{13}P_2Pt$	987.146(987.155)
$\{w_2 + [Pt(N)(py)_2]\}^+$	$C_{30}H_{36}N_{10}O_{13}P_2Pt$	1002.160(1002.166)
$\{[\mathbf{III} - C^b] + [Pt(py)]\}^+$	$C_{30}H_{36}N_8O_{15}P_2Pt$	1006.152(1006.150)
$\{d_2 + A + [Pt(py)]\}^+$ or $\{w_2 + C + [Pt(py)]\}^+$	$C_{29}H_{35}N_{11}O_{14}P_2Pt$	1019.150(1019.156)
$\{[\mathbf{III} - H_2O] + [Pt]\}^+$	$C_{29}H_{34}N_{10}O_{15}P_2Pt$	1020.161(1020.140)
$\{w_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{13}P_2Pt$	1030.174(1030.172)
$\{\mathbf{III} + [Pt(N)]\}^+$	$C_{29}H_{37}N_{11}O_{16}P_2Pt$	1053.157(1053.162)
$\{[w_2 + 2O + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{36}N_{12}O_{15}P_2Pt$	1062.162(1062.162)
$\{[a_3 - A_3^c] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{40}N_{10}O_{15}P_2Pt$	1086.193(1086.187)
$\{d_2 + A + [Pt(py)_2]\}^+$ or $\{w_2 + C + [Pt(py)_2]\}^+$	$C_{34}H_{40}N_{12}O_{14}P_2Pt$	1098.207(1098.198)

{[**III** − A[b]] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.208(1104.198)
{**III** + [Pt(py)]}$^+$	$C_{34}H_{41}N_{11}O_{16}P_2Pt$	1117.190(1117.193)
{[**III** − C[b]]+ [Pt(py)$_2$]}$^+$	$C_{35}H_{42}N_{12}O_{15}P_2Pt$	1128.211(1128.209)
{**III** + [Pt(N$_3$)(py)]}$^+$	$C_{34}H_{42}N_{14}O_{16}P_2Pt$	1160.210(1160.210)
{**III** + [Pt(py)$_2$]}$^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.237(1196.235)
{**III** + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{39}H_{47}N_{15}O_{16}P_2Pt$	1239.252(1239.252)

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

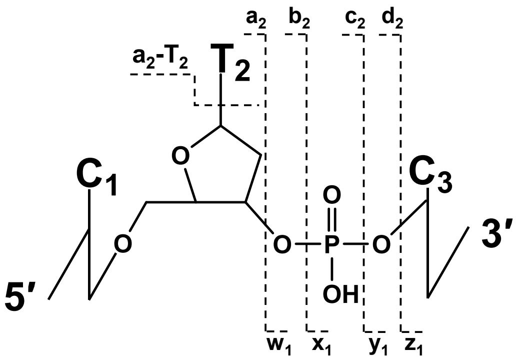
[b]A, T and C represent the neutral loss of an adenine, thymine and a cytosine base, respectively.

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

[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]dTM and dTMP represent the thymidine and thymidine monophosphate, respectively.

Table S8. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **IV** ([**IV** + **1′**]$^+$) produced by the reaction of complex **1** with ODN **IV** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **IV** for balancing the charges of the ions are omitted for clarity). **1′** = $[Pt(N_3)(py)_2]^+$



Ions	Formula	*m/z*[a] observed(calculated)
$[C]^+$	$C_4H_5N_3O$	112.045(112.051)
$[a_1/z_1]^+$	$C_9H_{11}N_3O_3$	210.083(210.087)
$\{[Pt(N)(py)_2]\}^+$	$C_{10}H_9N_3Pt$	367.034(367.052)
$\{[Pt(N_3)(py)_2]\}^+$	$C_{10}H_9N_5Pt$	395.058(395.058)
$\{C + [Pt(N)(py)]\}^+$	$C_9H_9N_5OPt$	399.049(399.053)
$\{C + [Pt(N_3)(py)]\}^+$	$C_9H_9N_7OPt$	427.053(427.059)
$\{dTM^e + [Pt(N_3)]\}^+$	$C_{10}H_{13}N_5O_5Pt$	479.073(479.064)
$\{[dTM^e - 2H_2O] + [Pt(N)(py)]\}^+$	$C_{15}H_{14}N_4O_3Pt$	494.071(494.079)
$\{C + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506.093(506.101)
$\{C + C + [Pt(N_3)(py)]\}^+$	$C_{13}H_{14}N_{10}O_2Pt$	538.103(538.102)
$\{c_1/x_1 + [Pt(py)]\}^+$	$C_{14}H_{15}N_4O_6PPt$	562.036(562.045)
$\{C + C + [Pt(py)_2]\}^+$	$C_{18}H_{18}N_8O_2Pt$	574.113(574.127)
$\{[dTM^e + PO_2] + [Pt(py)]\}^+$	$C_{15}H_{16}N_3O_7PPt$	577.036(577.045)
$\{[dTM^e + PO_3] + [Pt(py)]\}^+$	$C_{15}H_{16}N_3O_8PPt$	593.036(593.040)
$[d_2/w_2]^+$	$C_{19}H_{27}N_5O_{14}P_2$	612.100(612.110)
$\{b_1/y_1 + [Pt(N_3)(py)_2]\}^+$	$C_{19}H_{22}N_8O_4Pt$	622.143(622.149)
$\{b_2/y_2 + [Pt(N_3)]\}^+$	$C_{14}H_{19}N_6O_9PPt$	642.064(642.067)
$\{[dTMP^e + PO_3] + [Pt(py)_2]\}^+$	$C_{20}H_{21}N_4O_8PPt$	672.075(672.082)

$\{[dTMP^{e} + PO_3H] + [Pt(N)(py)]\}^+$	$C_{15}H_{20}N_4O_{11}P_2Pt$	690.023(690.033)
$\{d_1/w_1 + [Pt(N_3)(py)_2]\}^+$	$C_{19}H_{23}N_8O_7PPt$	702.105(702.115)
$[\mathbf{IV} - C^{b}]^+$	$C_{24}H_{33}N_5O_{16}P_2$	710.143(710.147)
$\{[T_2{:}T_2^{d}] + [Pt(py)]\}^+$	$C_{20}H_{23}N_3O_{12}P_2Pt$	755.056(755.048))
$\{[T_2{:}T_2^{d}] + [Pt(N)(py)]\}^+$	$C_{20}H_{24}N_4O_{12}P_2Pt$	770.054(770.059)
$\{[c_2/x_2] + [Pt]\}^+$	$C_{24}H_{28}N_6O_{13}P_2Pt$	788.061(788.049)
$\{[c_2/x_2] + [Pt(N)]\}^+$	$C_{24}H_{29}N_7O_{13}P_2Pt$	802.059(802.060)
$\{[d_2/w_2] + [Pt(N)]\}^+$	$C_{19}H_{26}N_6O_{14}P_2Pt$	820.070(820.070)
$\{[T_2{:}T_2^{d}] + [Pt(py)_2]\}^+$	$C_{25}H_{28}N_4O_{12}P_2Pt$	834.088(834.090)
$\{[T_2{:}T_2^{d}] + [Pt(N)(py)_2]\}^+$	$C_{25}H_{29}N_5O_{12}P_2Pt$	849.102(849.101)
$\{[c_2/x_2] + [Pt(py)]\}^+$	$C_{29}H_{33}N_7O_{13}P_2Pt$	866.088(866.091)
$\{[T_2^{d}] + [Pt(N_3)(py)_2]\}^+$	$C_{25}H_{29}N_7O_{12}P_2Pt$	877.104(877.107)
$\{[d_2/w_2] + [Pt(py)]\}^+$	$C_{24}H_{30}N_6O_{14}P_2Pt$	884.100(884.102)
$\{[a_3 - C_3^{c} - H_2O] + [Pt(N_3)]\}^+$	$C_{24}H_{29}N_8O_{13}P_2Pt$	895.114(895.105)
$\{[d_2/w_2] + [Pt(N)(py)]\}^+$	$C_{24}H_{31}N_7O_{14}P_2Pt$	899.107(899.113)
$\{a_2 + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{33}N_{10}O_{10}PPt$	908.181(908.184)
$\{d_2/w_2 + C + [Pt]\}^+$	$C_{23}H_{30}N_8O_{15}P_2Pt$	916.099(916.103)
$\{[c_2/x_2 - H_2O] + [Pt(py)_2]\}^+$	$C_{29}H_{31}N_7O_{12}P_2Pt$	927.117(927.123)
$\{[\mathbf{IV} - T^{b}] + [Pt(py)_2]\}^+$	$C_{23}H_{31}N_9O_{15}P_2Pt$	931.113(931.114)
$\{[c_2/x_2] + [Pt(py)_2]\}^+$	$C_{29}H_{33}N_7O_{13}P_2Pt$	945.113(945.133)
$\{[d_2/w_2] + [Pt(py)_2]\}^+$	$C_{29}H_{35}N_7O_{14}P_2Pt$	963.137(963.144)
$\{[a_3 - C_3^{c} - C^{b}] + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{35}N_7O_{14}P_2Pt$	975.136(975.144)
$\{[d_2/w_2] + [Pt(N_3)(py)_2]\}^+$	$C_{29}H_{36}N_{10}O_{14}P_2Pt$	1006.161(1006.161)
$\{[a_3 - C_3^{c}] + [Pt(py)_2]\}^+$	$C_{34}H_{39}N_7O_{15}P_2Pt$	1043.167(1043.170)
$\{[\mathbf{IV} - C^{b}] + [Pt(py)_2]\}^+$	$C_{34}H_{41}N_7O_{16}P_2Pt$	1061.184(1061.181)
$\{[\mathbf{IV} - H_2O] + [Pt(py)]\}^+$	$C_{33}H_{39}N_9O_{16}P_2Pt$	1075.187(1075.171)
$\{[a_3 - C_3^{c}] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{40}N_{10}O_{15}P_2Pt$	1086.182(1086.187)
$\{\mathbf{IV} + [Pt(py)]\}^+$	$C_{33}H_{41}N_9O_{17}P_2Pt$	1093.179(1093.182)
$\{[\mathbf{IV} - C^{b}] + [Pt(N_3)(py)_2]\}^+$	$C_{34}H_{42}N_{10}O_{16}P_2Pt$	1104.197(1104.198)
$\{\mathbf{IV} + [Pt(N_3)(py)]\}^+$	$C_{33}H_{42}N_{12}O_{17}P_2Pt$	1136.194(1136.199)

{**IV** + [Pt(py)$_2$]}$^+$	$C_{38}H_{46}N_{10}O_{17}P_2Pt$	1172.221(1172.224)
{**IV** + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{38}H_{47}N_{13}O_{17}P_2Pt$	1215.241(1215.241)

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

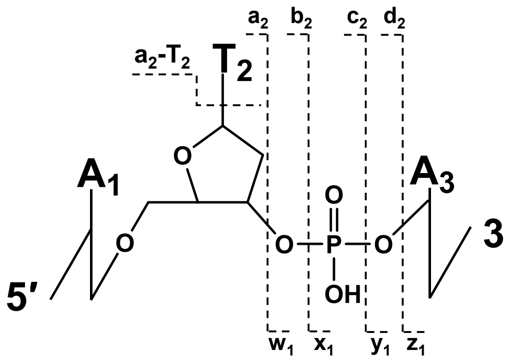
[b]T and C represent the neutral loss of a thymine and a cytosine base, respectively.

[c]T_n and C_n represent the loss of a thymine and a cytosine base, respectively, followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **IV**.

[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]dTM and dTMP represent the thymidine and thymidine monophosphate, respectively.

Table S9. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **I** ([**I** + **1″**]$^+$) 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″** = $[Pt(py)_2]^{2+}$



Ions	Formula	m/z^a observed(calculated)
$[A]^+$	$C_5H_5N_5$	136.058(136.062)
$\{A + [Pt(py)]\}^+$	$C_{10}H_8N_6Pt$	408.029(408.053)
$\{A + [Pt(py)_2]\}^+$	$C_{15}H_{13}N_7Pt$	487.071(487.095)
$\{A + T + [Pt(py)]\}^+$	$C_{15}H_{14}N_8O_2Pt$	534.090(534.096)
$\{A + A + [Pt(py)]\}^+$	$C_{15}H_{13}N_{11}Pt$	543.102(543.108)
$\{c_1/x_1 + [Pt(py)]\}^+$	$C_{15}H_{15}N_6O_5PPt$	586.059(586.056)
$\{A + A + [Pt(py)_2]\}^+$	$C_{20}H_{18}N_{12}Pt$	622.148(622.150)
$\{d_2/w_2\}^+$	$C_{20}H_{27}N_7O_{13}P_2$	636.120(636.121)
$\{c_1/x_1 + T + [Pt(py)]\}^+$	$C_{20}H_{21}N_8O_7PPt$	712.098(712.099)
$\{d_1/w_1 + T + [Pt(py)]\}^+$	$C_{20}H_{23}N_8O_8PPt$	730.098(730.110)
$[\mathbf{I} - A^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.161(734.158)
$\{d_1/w_1 + A + [Pt(py)]\}^+$	$C_{20}H_{22}N_{11}O_6PPt$	739.113(739.121)
$\{[T_2{:}T_2^c] + [Pt(py)]\}^+$	$C_{20}H_{23}N_3O_{12}P_2Pt$	755.050(755.048)
$\{[a_2/z_2 - H_2O] + [Pt(py)]\}^+$	$C_{25}H_{25}N_8O_8PPt$	792.131(792.126)
$[\mathbf{I}]^+$	$C_{30}H_{38}N_{12}O_{15}P_2$	869.207(869.213)
$\{c_2/x_2 + [Pt(py)]\}^+$	$C_{25}H_{28}N_8O_{12}P_2Pt$	890.103(890.102)
$\{w_2 + [Pt(py)]\}^+$	$C_{25}H_{30}N_8O_{13}P_2Pt$	908.115(908.113)
$\{a_2/z_2 + A + [Pt(py)]\}^+$	$C_{30}H_{32}N_{13}O_9PPt$	945.203(945.191)

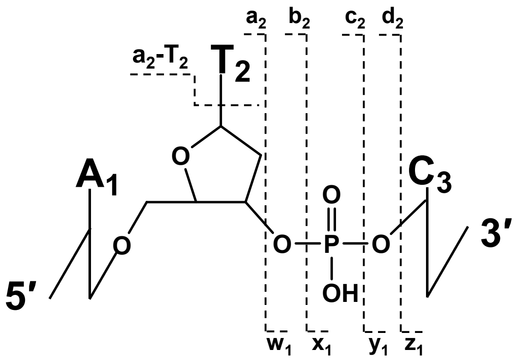
$\{w_2 + A + [Pt]\}^+$	$C_{25}H_{30}N_{12}O_{13}P_2Pt$	964.130(964.125)
$\{w_2 + [Pt(py)_2]\}^+$	$C_{30}H_{35}N_9O_{13}P_2Pt$	987.153(987.155)
$\{[\mathbf{I} - A^b] + [Pt(py)]\}^+$	$C_{30}H_{36}N_8O_{15}P_2Pt$	1006.155(1006.150)
$\{c_2/x_2 + A + [Pt(py)]\}^+$	$C_{30}H_{33}N_{13}O_{12}P_2Pt$	1025.175(1025.157)
$\{w_2 + A + [Pt(py)]\}^+$	$C_{30}H_{35}N_{13}O_{13}P_2Pt$	1043.176(1043.167)
$\{\mathbf{I} + [Pt]\}^+$	$C_{30}H_{36}N_{12}O_{15}P_2Pt$	1062.167(1062.162)
$\{w_2 + A + [Pt(py)_2]\}^+$	$C_{35}H_{40}N_{14}O_{13}P_2Pt$	1122.204(1122.210)
$\{[\mathbf{I} – H_2O]+ [Pt(py)]\}^+$	$C_{35}H_{39}N_{13}O_{14}P_2Pt$	1123.199(1123.194)
$\{\mathbf{I} + [Pt(py)]\}^+$	$C_{35}H_{41}N_{13}O_{15}P_2Pt$	1141.213(1141.204)
$\{\mathbf{I} + [Pt(py)_2]\}^+$	$C_{40}H_{46}N_{14}O_{15}P_2Pt$	1220.246(1220.246)

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

[b]A represent the neutral loss of an adenine.

[c]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 S10. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **II** ([**II** + **1′′**]$^+$) produced by the reaction of complex **1** with ODN **II** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **II** for balancing the charges of the ions are omitted for clarity). **1′′** = $[Pt(py)_2]^{2+}$



Ions	Formula	m/z^a observed(calculated)
$[C]^+$	$C_4H_5N_3O$	112.045(112.051)
$[A]^+$	$C_5H_5N_5$	136.060(136.062)
$\{A + C + [Pt(py)]\}^+$	$C_{14}H_{13}N_9OPt$	519.091(519.096)
$\{A + C + [Pt(py)_2]\}^+$	$C_{19}H_{18}N_{10}OPt$	598.131(598.139)
$[\mathbf{II} - C^b]^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.151(734.158)
$\{[T_2{:}T_2^d] + [Pt(py)]\}^+$	$C_{20}H_{23}N_3O_{12}P_2Pt$	755.046(755.048)
$\{c_2 + [Pt]\}^+$	$C_{20}H_{23}N_7O_{12}P_2Pt$	811.077(811.060)
$[\mathbf{II}]^+$	$C_{29}H_{38}N_{10}O_{16}P_2$	845.212(845.202)
$\{x_2 + [Pt(py)]\}^+$	$C_{24}H_{28}N_6O_{13}P_2Pt$	866.096(866.091)
$\{w_2 + [Pt(py)]\}^+$	$C_{24}H_{30}N_6O_{14}P_2Pt$	884.096(884.102)
$\{c_2 + [Pt(py)]\}^+$	$C_{25}H_{28}N_8O_{12}P_2Pt$	890.098(890.102)
$\{[a_3 - C_3^c]+ [Pt]\}^+$	$C_{25}H_{29}N_7O_{14}P_2Pt$	908.098(908.097)
$\{a_2 + C + [Pt(py)]\}^+$	$C_{29}H_{32}N_{11}O_{10}PPt$	921.185(921.179)
$\{w_2 + A + [Pt]\}^+$	$C_{24}H_{30}N_{10}O_{14}P_2Pt$	939.103(939.114)
$\{[\mathbf{II} - A^b]+ [Pt(py)]\}^+$	$C_{29}H_{36}N_6O_{16}P_2Pt$	982.135(982.139)
$\{[a_3 - C_3^c]+ [Pt(py)]\}^+$	$C_{30}H_{34}N_8O_{14}P_2Pt$	988.139(988.139)

{x_2 + A + [Pt(py)]}+ or {c_2 + C + [Pt(py)]}+	$C_{29}H_{33}N_{11}O_{13}P_2Pt$	1001.140(1001.146)
{[**II** − C^b]+ [Pt(py)]}$^+$	$C_{30}H_{36}N_8O_{15}P_2Pt$	1006.156(1006.150)
{w_2 + A + [Pt(py)]}$^+$	$C_{29}H_{35}N_{11}O_{14}P_2Pt$	1019.145(1019.156)
{[**II** − C^b]+ [Pt(py)$_2$]}$^+$	$C_{35}H_{41}N_9O_{15}P_2Pt$	1085.185(1085.192)
{[**II** − H_2O]+ [Pt(py)]}$^+$	$C_{34}H_{39}N_{11}O_{15}P_2Pt$	1099.189(1099.182)
{**II** + [Pt(py)]}$^+$	$C_{34}H_{41}N_{11}O_{16}P_2Pt$	1117.195(1117.193)
{**II** + [Pt(py)$_2$]}$^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.235(1196.235)

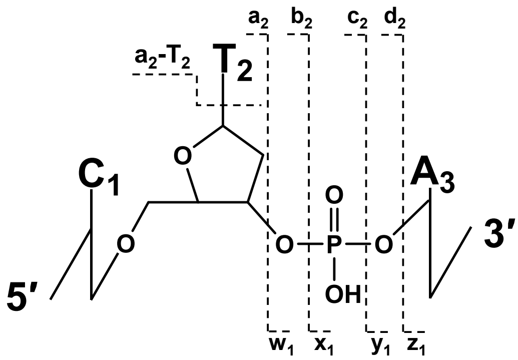
[a]The most abundant isotopic mass-to-charge ratio.

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

[c]C_n represent the loss of a cytosine base followed by elimination of a H_2O molecule to form a furan ring, n indicates the position of the base in strand **II**.

[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 S11. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **III** ([**III** + **1″**]$^+$) produced by the reaction of complex **1** with ODN **III** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **III** for balancing the charges of the ions are omitted for clarity). **1″** = [Pt(py)$_2$]$^+$



Ions	Formula	*m/z*[a] observed(calculated)
[C]$^+$	$C_4H_5N_3O$	112.047(112.051)
[A]$^+$	$C_5H_5N_5$	136.056(136.062)
[a_1]$^+$	$C_9H_{11}N_3O_3$	210.082(210.087)
[T_2:T_2^c]$^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.042(483.056)
{a_1 + [Pt(py)]}$^+$	$C_{15}H_{14}N_6O_2Pt$	506.087(506.090)
{A + C + [Pt(py)]}$^+$	$C_{14}H_{13}N_9OPt$	519.083(519.096)
{A + T + [Pt(py)]}$^+$	$C_{15}H_{14}N_8O_2Pt$	534.094(534.096)
{A + C + [Pt(py)$_2$]}$^+$	$C_{19}H_{18}N_{10}OPt$	598.122(598.139)
[d_2]$^+$	$C_{20}H_{27}N_7O_{13}P_2$	636.118(636.121)
{c_1 + T + [Pt(py)]}$^+$	$C_{20}H_{21}N_8O_7PPt$	712.101(712.099)
{w_1 + T + [Pt(py)]}$^+$	$C_{20}H_{23}N_8O_8PPt$	730.101(730.110)
[**III** − A^b]$^+$	$C_{25}H_{33}N_7O_{15}P_2$	734.147(734.158)
{[T_2:T_2^c] + [Pt(py)]}$^+$	$C_{20}H_{23}N_3O_{12}P_2Pt$	755.053(755.048)
{[z_2 − H_2O] + [Pt(py)]}$^+$	$C_{25}H_{25}N_8O_8PPt$	792.122(792.126)
{x_2 + [Pt]}$^+$	$C_{20}H_{23}N_7O_{12}P_2Pt$	811.060(811.060)
[**III**]$^+$	$C_{29}H_{38}N_{10}O_{16}P_2$	845.195(845.202)

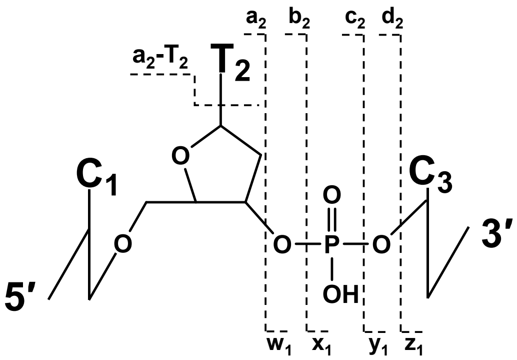
$\{c_2 + [Pt(py)]\}^+$	$C_{24}H_{28}N_6O_{13}P_2Pt$	866.079(866.091)
$\{x_2 + [Pt(py)]\}^+$	$C_{25}H_{28}N_8O_{12}P_2Pt$	890.099(890.102)
$\{w_2 + [Pt(py)]\}^+$	$C_{25}H_{30}N_8O_{13}P_2Pt$	908.105(908.113)
$\{w_2 + C + [Pt]\}^+$	$C_{24}H_{30}N_{10}O_{14}P_2Pt$	940.117(940.114)
$\{w_2 + A + [Pt]\}^+$	$C_{25}H_{30}N_{12}O_{13}P_2Pt$	964.138(964.125)
$\{w_2 + [Pt(py)_2]\}^+$	$C_{30}H_{35}N_9O_{13}P_2Pt$	987.148(987.155)
$\{[\mathbf{III} - C^b] + [Pt(py)]\}^+$	$C_{30}H_{36}N_8O_{15}P_2Pt$	1006.144(1006.150)
$\{w_2 + C + [Pt(py)]\}^+$	$C_{29}H_{35}N_{11}O_{14}P_2Pt$	1019.153(1019.156)
$\{\mathbf{III} + [Pt]\}^+$	$C_{29}H_{36}N_{10}O_{16}P_2Pt$	1038.149(1038.151)
$\{[\mathbf{III} - C^b] + [Pt(py)_2]\}^+$	$C_{35}H_{41}N_9O_{15}P_2Pt$	1085.193(1085.192)
$\{w_2 + C + [Pt(py)_2]\}^+$	$C_{34}H_{40}N_{12}O_{14}P_2Pt$	1098.185(1098.198)
$\{[\mathbf{III} - H_2O] + [Pt(py)]\}^+$	$C_{34}H_{39}N_{11}O_{15}P_2Pt$	1099.183(1099.182)
$\{\mathbf{III} + [Pt(py)]\}^+$	$C_{34}H_{41}N_{11}O_{16}P_2Pt$	1117.189(1117.193)
$\{\mathbf{III} + [Pt(py)_2]\}^+$	$C_{39}H_{46}N_{12}O_{16}P_2Pt$	1196.235(1196.235)

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

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

[c]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 S12. Fragment ions observed by MS/MS analysis in positive-ion mode of mono-platinated **IV** ([**IV** + **1″**]$^+$) produced by the reaction of complex **1** with ODN **IV** at 310 K after irradiation under blue light for 1 h. (Charges for Pt moiety and the loss of protons from **IV** for balancing the charges of the ions are omitted for clarity). **1″** = [Pt(py)$_2$]$^+$



Ions	Formula	*m/z*[a] observed(calculated)
[C]$^+$	$C_4H_5N_3O$	112.044(112.051)
[a_1/z_1]$^+$	$C_9H_{11}N_3O_3$	210.079(210.087)
{C + C + [Pt]}$^+$	$C_8H_8N_6O_2Pt$	416.031(416.043)
[T_2:T_2^c]$^+$	$C_{15}H_{20}N_2O_{12}P_2$	483.047(483.056)
{C + C + [Pt(py)]}$^+$	$C_{13}H_{13}N_7O_2Pt$	495.076(495.085)
{C + C + [Pt(py)$_2$]}$^+$	$C_{18}H_{18}N_8O_2Pt$	574.116(574.127)
[d_2/w_2]$^+$	$C_{19}H_{27}N_5O_{14}P_2$	612.103(612.110)
[**IV** − C^b]$^+$	$C_{24}H_{33}N_5O_{16}P_2$	710.135(710.147)
{c_2/x_2 + [Pt]}$^+$	$C_{19}H_{23}N_5O_{13}P_2Pt$	787.059(786.049)
[**IV**]$^+$	$C_{28}H_{38}N_8O_{17}P_2$	821.182(821.190)
{c_2/x_2 + [Pt(py)]}$^+$	$C_{24}H_{28}N_6O_{13}P_2Pt$	866.091(866.091)
{w_2 + [Pt(py)]}$^+$	$C_{24}H_{30}N_6O_{14}P_2Pt$	884.091(884.102)
{w_2 + C + [Pt]}$^+$	$C_{23}H_{30}N_8O_{15}P_2Pt$	916.096(916.103)
{w_2 + [Pt(py)$_2$]}$^+$	$C_{29}H_{35}N_7O_{14}P_2Pt$	963.134(963.144)
{[**IV** − C^b] + [Pt(py)]}$^+$	$C_{29}H_{36}N_6O_{16}P_2Pt$	982.142(982.139)
{w_2 + C + [Pt(py)]}$^+$	$C_{28}H_{35}N_9O_{15}P_2Pt$	995.131(995.145)
{[**IV** − H_2O] + [Pt]}$^+$	$C_{28}H_{34}N_8O_{16}P_2Pt$	996.133(996.129)
{**IV** + [Pt]}$^+$	$C_{28}H_{36}N_8O_{17}P_2Pt$	1014.131(1014.140)

{[**IV** − C[b]] + [Pt(py)$_2$]}$^+$	$C_{34}H_{41}N_7O_{16}P_2Pt$	1061.174(1061.181)
{w$_2$ + C + [Pt(py)$_2$]}$^+$	$C_{33}H_{40}N_{10}O_{15}P_2Pt$	1074.157(1074.187)
{[**IV** − H_2O] + [Pt(py)]}$^+$	$C_{33}H_{39}N_9O_{16}P_2Pt$	1075.170(1075.171)
{**IV** + [Pt(py)]}$^+$	$C_{33}H_{41}N_9O_{17}P_2Pt$	1093.176(1093.182)
{**IV** + [Pt(py)$_2$]}$^+$	$C_{38}H_{46}N_{10}O_{17}P_2Pt$	1172.224(1172.224)

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

[b]T and C represent the neutral loss of a thymine and a cytosine base, respectively.

[c]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.