Electronic Supplementary Information

for

Reactions of a photoactivatable diazido Pt(IV) anticancer complex with a single-stranded oligodeoxynucleotide

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Table S1. MS data 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).

Ion	Formula	m/z observed	m/z calculated	Error (ppm)
{**I** + [Pt(N_3)(py_2)]}$^{6-}$	$C_{154}H_{198}N_{44}O_{96}P_{14}Pt$	688.962	688.961	1.45
{**I** + [Pt(N_3)(py_2)]$_2$}$^{6-}$	$C_{164}H_{207}N_{49}O_{96}P_{14}Pt_2$	869.635	869.633	2.30
[**I**]$^{5-}$	$C_{144}H_{189}N_{39}O_{96}P_{14}$	886.138	886.141	-3.39
{**I** + [Pt(N_3)(py_2)]$_3$}$^{6-}$	$C_{174}H_{216}N_{54}O_{96}P_{14}Pt_3$	935.305	935.320	-16.04
{**I** + [Pt(py_2)]}$^{5-}$	$C_{164}H_{207}N_{49}O_{96}P_{14}Pt$	956.349	956.352	-3.14
{**I** + [Pt(N_3)(py_2)]}$^{5-}$	$C_{154}H_{198}N_{44}O_{96}P_{14}Pt$	964.949	964.953	-4.15
{**I** + [Pt(py_2)] + [Pt(N_3)(py_2)]}$^{5-}$	$C_{164}H_{206}N_{46}O_{96}P_{14}Pt_2$	1035.159	1035.156	2.90
{**I** + [Pt(N_3)(py_2)]$_2$}$^{5-}$	$C_{164}H_{207}N_{49}O_{96}P_{14}Pt_2$	1043.761	1043.766	-4.79
[**I**]$^{4-}$	$C_{144}H_{189}N_{39}O_{96}P_{14}$	1107.931	1107.930	0.90
{**I** + [Pt(N_3)(py_2)]$_3$}$^{5-}$	$C_{174}H_{216}N_{54}O_{96}P_{14}Pt_3$	1122.573	1122.570	2.67
{**I** + [Pt(py_2)]}$^{4-}$	$C_{154}H_{198}N_{41}O_{96}P_{14}Pt$	1195.686	1195.688	-1.67
{**I** + [Pt(N_3)(py_2)]}$^{4-}$	$C_{154}H_{198}N_{44}O_{96}P_{14}Pt$	1206.439	1206.445	-4.97
{**I** + [Pt(py_2)] + [Pt(N_3)(py_2)]}$^{4-}$	$C_{164}H_{206}N_{46}O_{96}P_{14}Pt_2$	1294.204	1294.204	0.00
{**I** + [Pt(N_3)(py_2)]$_2$}$^{4-}$	$C_{164}H_{207}N_{49}O_{96}P_{14}Pt_2$	1304.953	1304.953	0.00
{**I** + [Pt(py_2)] + [Pt(N_3)(py_2)]$_2$}$^{4-}$	$C_{174}H_{216}N_{51}O_{96}P_{14}Pt_3$	1392.715	1392.711	2.87
{**I** + [Pt(N_3)(py_2)]$_3$}$^{4-}$	$C_{174}H_{216}N_{54}O_{96}P_{14}Pt_3$	1403.473	1403.469	2.85
[**I**]$^{3-}$	$C_{144}H_{189}N_{39}O_{96}P_{14}$	1477.242	1477.242	0.00
[**I** + Na]$^{3-}$	$C_{144}H_{188}N_{39}O_{96}P_{14}Na$	1484.573	1484.570	2.02
{**I** + [Pt(py_2)]$_2$ + [Pt(N_3)(py_2)]$_2$}$^{4-}$	$C_{184}H_{224}N_{56}O_{96}P_{14}Pt_4$	1491.226	1491.227	-0.67
{**I** + [Pt(N_3)(py_2)]$_4$}$^{4-}$	$C_{184}H_{225}N_{59}O_{96}P_{14}Pt_4$	1502.230	1502.234	-2.66
{**I** + [Pt(py_2)]}$^{3-}$	$C_{154}H_{198}N_{41}O_{96}P_{14}Pt$	1594.593	1594.587	3.76
{**I** + [Pt(N_3)(py_2)]}$^{3-}$	$C_{154}H_{198}N_{44}O_{96}P_{14}Pt$	1608.932	1608.922	6.22
{**I** + [Pt^{III}(N_3)(OH)(py_2)]}$^{3-}$	$C_{154}H_{199}N_{44}O_{97}P_{14}Pt$	1614.594	1614.596	1.24
{[**I** + 3O] + [Pt^{III}(OH)(py_2)]}$^{3-}$	$C_{154}H_{198}N_{41}O_{100}P_{14}Pt$	1616.261	1616.250	6.80
{[**I** + H_2O + $(OH)_2$] + [Pt(N_3)(py_2)]}$^{3-}$ or {[**I** + O + $(H_2O)_2$] + [Pt(N_3)(py_2)] }$^{3-}$	$C_{154}H_{202}N_{44}O_{99}P_{14}Pt$	1626.269	1626.266	1.84
{[**I** + $(OH)_2$] + [$Pt^{III}$$(N_3)_2$($py_2$)] + Na}$^{3-}$ or {[**I** + O + H_2O] + [$Pt^{III}$$(N_3)_2$($py_2$)] + Na}$^{3-}$	$C_{154}H_{200}N_{47}O_{98}P_{14}PtNa$	1641.588	1641.594	-3.65
{**I** + [Pt(py_2)]$_2$}$^{3-}$	$C_{164}H_{205}N_{43}O_{96}P_{14}Pt_2$	1711.599	1711.602	-1.75
{**I** + [Pt(py_2)] + [Pt(N_3)(py_2)]}$^{3-}$	$C_{164}H_{206}N_{46}O_{96}P_{14}Pt_2$	1725.941	1725.938	1.74

{[**I** + H_2O] + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]}$^{3-}$	$C_{164}H_{209}N_{46}O_{97}P_{14}Pt_2$	1731.938	1731.944	-3.46
{[**I** +2O] + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]}$^{3-}$	$C_{164}H_{206}N_{46}O_{98}P_{14}Pt_2$	1736.608	1736.602	3.46
{**I** + [Pt(N_3)(py)$_2$]$_2$}$^{3-}$	$C_{164}H_{207}N_{49}O_{96}P_{14}Pt_2$	1740.284	1740.273	6.32
{**I** + [Pt^{III}(N_3)(OH)(py)$_2$] + [Pt(N_3)(py)$_2$]}$^{3-}$	$C_{164}H_{208}N_{49}O_{97}P_{14}Pt_2$	1745.952	1745.945	4.01
{**I** + [Pt(N_3)(py)$_2$]$_2$ + Na}$^{3-}$	$C_{164}H_{206}N_{49}O_{96}P_{14}Pt_2Na$	1747.606	1747.602	2.29
{[**I** + H_2O] + [Pt^{III}(N_3)(OH)(py)$_2$]$_2$}$^{3-}$	$C_{164}H_{211}N_{49}O_{99}P_{14}Pt_2$	1757.617	1757.617	0.00
{[**I** + 4O] + [Pt^{III}(N_3)(OH)(py)$_2$]$_2$}$^{3-}$	$C_{164}H_{209}N_{49}O_{102}P_{14}Pt_2$	1772.937	1772.938	-0.56
{**I** + [Pt(py)$_2$]$_2$ + [Pt(N_3)(py)$_2$]}$^{3-}$	$C_{174}H_{215}N_{48}O_{96}P_{14}Pt_3$	1843.288	1843.281	3.80
{**I** + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]$_2$}$^{3-}$	$C_{174}H_{216}N_{51}O_{96}P_{14}Pt_3$	1857.297	1857.289	4.31
{[**I** + O] + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]$_2$}$^{3-}$	$C_{174}H_{216}N_{51}O_{97}P_{14}Pt_3$	1862.957	1862.953	2.15
{**I** + [Pt(N_3)(py)$_2$]$_3$}$^{3-}$	$C_{174}H_{216}N_{54}O_{96}P_{14}Pt_3$	1871.633	1871.625	4.27
{**I** + [Pt^{III}(N_3)(OH)(py)$_2$] + [Pt(N_3)(py)$_2$]$_2$}$^{3-}$	$C_{174}H_{217}N_{54}O_{97}P_{14}Pt_3$	1877.307	1877.297	5.33
{[**I** + H_2O] + [Pt^{III}(N_3)(OH)(py)$_2$]$_2$ + [Pt(N_3)(py)$_2$]}$^{3-}$	$C_{174}H_{220}N_{54}O_{99}P_{14}Pt_3$	1888.973	1888.961	6.35
{**I** + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]$_3$}$^{3-}$	$C_{184}H_{224}N_{56}O_{96}P_{14}Pt_4$	1988.986	1988.969	8.55
{**I** + [Pt(N_3)(py)$_2$]$_4$}$^{3-}$	$C_{184}H_{225}N_{59}O_{96}P_{14}Pt_4$	2003.325	2003.313	5.99
{[**I** + $(OH)_2$ + H_2O] + [Pt(N_3)(py)$_2$]$_4$}$^{3-}$ or {[**I** + O + $(H_2O)_2$] + [Pt(N_3)(py)$_2$]$_4$}$^{3-}$	$C_{184}H_{229}N_{59}O_{99}P_{14}Pt_4$	2020.665	2020.648	8.41
{[**I**]$_2$ + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]$_3$}$^{5-}$	$C_{328}H_{413}N_{95}O_{192}P_{28}Pt_4$	2080.143	2080.133	4.81
{**I** + [Pt(N_3)(py)$_2$]$_2$}$_2$$^{5-}$	$C_{328}H_{414}N_{98}O_{192}P_{28}Pt_4$	2088.748	2088.734	6.70
{**I** + [Pt(py)$_2$] + [Pt(N_3)(py)$_2$]$_4$}$^{3-}$	$C_{194}H_{233}N_{61}O_{96}P_{14}Pt_5$	2120.340	2120.320	9.43
{**I** + [Pt(N_3)(py)$_2$]$_5$}$^{3-}$	$C_{194}H_{234}N_{64}O_{96}P_{14}Pt_5$	2134.681	2134.656	11.71
{[**I** + $(OH)_2$ + H_2O] + [Pt(N_3)(py)$_2$]$_5$}$^{3-}$ or {[**I** + O + $(H_2O)_2$] + [Pt(N_3)(py)$_2$]$_5$}$^{3-}$	$C_{194}H_{238}N_{64}O_{99}P_{14}Pt_5$	2152.017	2152.000	7.90
{**I** + [Pt(N_3)(py)$_2$]$_3$}$_2$$^{5-}$	$C_{348}H_{432}N_{108}O_{192}P_{28}Pt_6$	2246.381	2246.352	12.91

Table S2. Fragment ions observed by MS/MS analysis in negative-ion mode of mono-platinated **I** ([**I** + **1′**]$^{3-}$, *m/z* 1608.932) 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	*m/z*[a] observed (calculated)	Fragments	*m/z*[a] observed (calculated)
w_1^-	306.045 (306.047)	$[a_2 - T_2^b]^-$	386.068 (386.078)
w_2^-	610.087 (610.094)	a_2^-	512.106 (512.117)
w_3^-	899.136 (899.141)	$[a_3 - C_3^b]^-$	690.117 (690.125)
w_4^-	1203.182 (1203.188)	$\{[a_3 - C_3] + \mathbf{1'}\}^-$	1084.163 (1084.172)
w_5^-	1507.229 (1507.234)	$[a_4 - T_4]^-$	979.152 (979.168)
w_5^{2-}	753.100 (753.117)	a_4^-	1105.212 (1105.211)
$[w_5 + \mathbf{1'}]^-$	1902.280 (1902.289)	$[a_5 - C_5]^-$	1283.208 (1283.211)
w_6^{2-}	897.630 (897.633)	$\{[a_5 - C_5] + \mathbf{1'}\}^-$	1678.269 (1678.266)
w_7^-	2100.332 (2100.328)	$[a_8 - G_8^b]^-$	2180.369 (2180.352)
w_7^{2-}	1049.656 (1049.656)	$[a_8 - G_8]^{2-}$	1089.669 (1089.672)
$[w_7 + \mathbf{1'}]^{2-}$	1247.175 (1247.188)	$\{[a_8 - G_8] + \mathbf{1'}\}^{2-}$	1287.186 (1287.195)
w_{10}^-	1518.731 (1518.734)	$[a_{10} - C_{10}]^{2-}$	1406.720 (1406.727)
$[w_{10} + \mathbf{1'}]^{2-}$	1715.761 (1715.758)	$\{[a_{10} - C_{10}] + \mathbf{1'}\}^{2-}$	1603.748 (1603.750)
w_{12}^{2-}	1815.267 (1815.281)	$[a_{13} - C_{13}]^{2-}$	1855.293 (1855.290)
$[w_{12} + \mathbf{1'}]^{2-}$	2012.315 (2012.305)	$\{[a_{13} - C_{13}] + \mathbf{1'}\}^{2-}$	2052.337 (2052.333)
$[w_{14} + \mathbf{1'}]^{3-}$	1539.235 (1539.234)	$\{[a_{15} - C_{15}] + \mathbf{1'}\}^{2-}$	1565.909 (1565.906)
$\{w_{14} + [\mathbf{1'} - N_3]\}^{3-}$	1524.899 (1524.891)		
$\{w_{14} + [\mathbf{1'} - py]\}^{3-}$	1512.887 (1512.883)		
$[w_{14} + \mathbf{1'} - C^c]^{3-}$	1502.217 (1502.219)		
$[w_{14} + \mathbf{1'} - G^c]^{3-}$	1488.886 (1488.883)		
$[\mathbf{I} + \mathbf{1'}]^{3-}$	1608.926 (1608.922)	$\{[\mathbf{I} + \mathbf{1'}] - N_3\}^{3-}$	1594.588 (1594.586)
$[\mathbf{I} - G]^{3-}$	1426.890 (1426.891)	$\{[\mathbf{I} + \mathbf{1'}] - py\}^{3-}$	1582.581 (1582.578)
$\{[\mathbf{I} + \mathbf{1'}] - C\}^{3-}$	1571.912 (1571.904)	$\{[\mathbf{I} + \mathbf{1'}] - N_2 - py\}^{3-}$	1573.245 (1571.242)
$\{[\mathbf{I} + \mathbf{1'}] - G\}^{3-}$	1558.241 (1558.242)	$\{[\mathbf{I} + \mathbf{1'}] - py - C\}^{3-}$	1545.566 (1545.563)
$\{[\mathbf{I} + \mathbf{1'}] - 2C\}^{3-}$	1534.894 (1534.898)	$\{[\mathbf{I} + \mathbf{1'}] - py - G\}^{3-}$	1532.228 (1532.227)
$\{[\mathbf{I} + \mathbf{1'}] - G - C\}^{3-}$	1521.562 (1521.563)		
Internal fragments[d]			
$[T_6{:}T_9]^-$	1418.181 (1418.188)	$[T_x{:}T_x]^-$ (x=2,4,9,12,14)	481.035 (481.039)
$\{[T_6{:}T_9] - G\}^-$	1267.127 (1267.144)	$[T_4{:}T_7]^-/[T_9{:}T_{12}]^-/[T_{11}{:}T_{14}]^-$	1378.177 (1378.180)

$[T_2{:}T_4]^-/[C_5{:}T_7]^-/[C_{10}{:}T_{12}]^-$	1074.127 (1074.133)	$\{[T_4{:}T_7]/[T_9{:}T_{12}]/[T_{11}{:}T_{14}] + \mathbf{1'}\}^-$	1773.223 (1773.234)
$\{[T_2{:}T_4]/[C_5{:}T_7]/[C_{10}{:}T_{12}] + \mathbf{1'}\}^-$	1468.187 (1468.188)	$[T_6{:}T_7]^-/[T_{11}{:}T_{12}]^-$	785.079 (785.086)
$[T_2{:}T_7]^{2-}/[T_9{:}T_{14}]^{2-}$	985.129 (985.133)	$\{[T_2{:}T_{14}] + \mathbf{1'}\}^{3-}$	1496.219 (1496.211)
$[T_2{:}T_7]^-/[T_9{:}T_{14}]^-$	1971.275 (1971.273)	$[T_2{:}T_9]^{2-}/[C_5{:}T_{12}]^{2-}$	1302.184 (1302.180)
$\{[T_2{:}T_7]/[T_9{:}T_{14}] + \mathbf{1'}\}^{2-}$	1182.656 (1182.656)	$\{[T_2{:}T_9]/[C_5{:}T_{12}] + \mathbf{1'}\}^{2-}$	1499.206 (1499.211)
$[T_2{:}T_{12}]^{2-}/[T_4{:}T_{14}]^{2-}$	1750.765 (1750.750)	$\{[T_4{:}T_9] - G\}^-$	1860.234 (1860.227)
$\{[T_2{:}T_{12}]/[T_4{:}T_{14}] + \mathbf{1'}\}^{2-}$	1947.790 (1947.781)	$[T_4{:}T_{12}]^{2-}/[T_6{:}T_{14}]^{2-}$	1454.210 (1454.203)
		$\{[T_4{:}T_{12}]/[T_6{:}T_{14}] + \mathbf{1'}\}^{2-}$	1651.226 (1651.234)

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

[b]T_n, C_n and G_n represent the loss of a cytosine 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.

[c]C and G represent the neutral loss of a cytosine and a guanine base, respectively.

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

Table S3. Fragment ions observed by MS/MS analysis in negative-ion mode of di-platinated **I** ($[\mathbf{I} + \mathbf{1'}_2]^{3-}$, *m/z* 1740.284) 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). $\mathbf{1'} = [Pt(N_3)(py)_2]^+$.

Fragments	*m/z*[a] observed (calculated)	Fragments	*m/z*[a] observed (calculated)
w_1^-	306.045 (306.047)	$[a_2 - T_2^{b}]^-$	386.068 (386.078)
w_2^-	610.093 (610.094)	a_2^-	512.119 (512.117)
w_3^-	899.136 (899.141)	$[a_3 - C_3^{b}]^-$	690.117 (690.125)
w_4^-	1203.182 (1203.188)	$\{[a_3 - C_3] + \mathbf{1'}\}^-$	1084.168 (1084.172)
w_5^-	1507.237 (1507.234)	$[a_4 - T_4]^-$	979.159 (979.168)
w_5^{2-}	753.107 (753.117)	a_4^-	1105.212 (1105.211)
$[w_5 + \mathbf{1'}]^-$	1902.298 (1902.289)	$[a_5 - C_5]^-$	1283.208 (1283.211)
w_6^{2-}	897.630 (897.633)	$\{[a_5 - C_5] + \mathbf{1'}\}^-$	1678.261 (1678.266)
w_7^{2-}	1049.656 (1049.656)	$[a_8 - G_8^{b}]^-$	2180.379 (2180.352)
$[w_7 + \mathbf{1'}]^{2-}$	1247.182 (1247.188)	$[a_8 - G_8]^{2-}$	1089.669 (1089.672)
w_7^-	2100.351 (2100.328)	$\{[a_8 - G_8] + \mathbf{1'}\}^{2-}$	1287.193 (1287.195)
$[w_{10} + \mathbf{1'}]^{2-}$	1715.769 (1715.758)	$\{[a_{10} - C_{10}] + \mathbf{1'}\}^{2-}$	1603.748 (1603.750)
$[w_{10} + \mathbf{1'}_2]^{2-}$	1912.795 (1912.781)	$\{[a_{10} - C_{10}] + \mathbf{1'}_2\}^{2-}$	1800.775 (1800.773)
$[w_{12} + \mathbf{1'}]^{2-}$	2012.333 (2012.305)	$\{[a_{13} - C_{13}] + \mathbf{1'}\}^{2-}$	2052.330 (2052.333)
$[w_{12} + \mathbf{1'}_2]^{2-}$	2209.858 (2209.828)	$\{[a_{13} - C_{13}] + \mathbf{1'}_2\}^{2-}$	2249.848 (2249.844)
$[w_{14} + \mathbf{1'}]^{3-}$	1539.235 (1539.234)	$\{[a_{15} - C_{15}] + \mathbf{1'}_2\}^{3-}$	1697.276 (1697.258)
$\{[w_{14} + \mathbf{1'}] - C^{c}\}^{3-}$	1502.217 (1502.219)		
$\{[w_{14} + \mathbf{1'}] - G^{c}\}^{3-}$	1488.894 (1488.883)		
$[w_{14} + \mathbf{1'}_2]^{3-}$	1670.591 (1670.586)		
$\{[w_{14} + \mathbf{1'}_2] - py\}^{3-}$	1644.242 (1644.234)		
$\{[w_{14} + \mathbf{1'}_2] - C\}^{3-}$	1633.582 (1633.570)		
$\{[w_{14} + \mathbf{1'}_2] - G\}^{3-}$	1620.231 (1620.234)		
$[\mathbf{I} + \mathbf{1'}_2]^{3-}$	1740.287 (1740.273)	$\{[\mathbf{I} + \mathbf{1'}_2] - G\}^{3-}$	1689.934 (1689.930)
$\{[\mathbf{I} + \mathbf{1'}_2] - N_3\}^{3-}$	1725.953 (1725.938)	$\{[\mathbf{I} + \mathbf{1'}] - N_3\}^{3-}$	1594.590 (1594.586)
$\{[\mathbf{I} + \mathbf{1'}_2] - py\}^{3-}$	1713.935 (1713.930)	$\{[\mathbf{I} + \mathbf{1'}] - C\}^{3-}$	1571.906 (1571.904)
$\{[\mathbf{I} + \mathbf{1'}_2] - C\}^{3-}$	1703.271 (1703.258)	$\{[\mathbf{I} + \mathbf{1'}] - G\}^{3-}$	1558.249 (1558.242)
$\{[\mathbf{I} + \mathbf{1'}_2] - 2py\}^{3-}$	1687.599 (1687.578)	$\{[\mathbf{I} + \mathbf{1'}] - py - G\}^{3-}$	1532.222 (1532.227)
$\{[\mathbf{I} + \mathbf{1'}_2] - C - py\}^{3-}$	1676.917 (1676.914)	$\{[\mathbf{I} + \mathbf{1'}] - G - C\}^{3-}$	1521.564 (1521.563)
Internal fragments[d]			
$[T_6{:}T_9]^-$	1418.181 (1418.188)	$[T_x{:}T_x]^-$ (x=2,4,9,12,14)	481.035 (481.039)

$\{[T_6{:}T_9] - G\}^-$	1267.127 (1267.144)	$[T_4{:}T_7]^-/[T_9{:}T_{12}]^-/[T_{11}{:}T_{14}]^-$	1378.177 (1378.180)
$[T_2{:}T_4]^-/[C_5{:}T_7]^-/[C_{10}{:}T_{12}]^-$	1074.127 (1074.133)	$\{[T_4{:}T_7]/[T_9{:}T_{12}]/[T_{11}{:}T_{14}] + \mathbf{1'}\}^-$	1773.250 (1773.234)
$\{[T_2{:}T_4]/[C_5{:}T_7]/[C_{10}{:}T_{12}] + \mathbf{1'}\}^-$	1468.187 (1468.188)	$[T_6{:}T_7]^-/[T_{11}{:}T_{12}]^-$	785.084 (785.086)
$[T_2{:}T_7]^{2-}/[T_9{:}T_{14}]^{2-}$	985.129 (985.133)	$\{[T_2{:}T_{14}] + \mathbf{1'}_2\}^{3-}$	1627.570 (1627.563)
$[T_2{:}T_7]^-/[T_9{:}T_{14}]^-$	1971.284 (1971.273)	$[T_6{:}T_{14}]^{2-}$	1454.178 (1454.203)
$\{[T_2{:}T_7]/[T_9{:}T_{14}] + \mathbf{1'}\}^{2-}$	1182.642 (1182.656)	$\{[T_4{:}T_9] - G\}^-$	1860.234 (1860.227)
$\{[T_2{:}T_9]/[C_5{:}T_{12}] + \mathbf{1'}\}^{2-}$	1499.222 (1499.211)	$\{[T_2{:}T_{12}]/[T_4{:}T_{14}] + \mathbf{1'}_2\}^{2-}$	2145.318 (2145.305)

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

[b]T_n, C_n and G_n represent the loss of a cytosine 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.

[c]C and G represent the neutral loss of a cytosine and a guanine base, respectively.

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

Table S4. Fragment ions observed by MS/MS analysis in negative-ion mode of tri-platinated **I** ([**I** + $\mathbf{1'}_3$]$^{3-}$, *m/z* 1857.297) 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). $\mathbf{1'}$ = [Pt(N_3)(py)$_2$]$^+$.

Fragments	*m/z*[a] observed (calculated)	Fragments	*m/z*[a] observed (calculated)
w_1^-	306.042 (306.047)	$[a_2 - T_2^b]^-$	386.073 (386.078)
w_2^-	610.087 (610.094)	$[a_3 - C_3^b]^-$	690.111 (690.125)
w_3^-	899.128 (899.141)	$\{[a_3 - C_3] + \mathbf{1'}\}^-$	1084.160 (1084.172)
w_4^-	1203.192 (1203.188)	$[a_4 - T_4]^-$	979.162 (979.168)
w_5^-	1507.214 (1507.234)	$[a_5 - C_5]^-$	1283.203 (1283.211)
$[w_5 + \mathbf{1'}]^-$	1902.280 (1902.289)	$\{[a_5 - C_5] + \mathbf{1'}\}^-$	1678.253 (1678.266)
w_6^{2-}	897.628 (897.633)	$[a_8 - G_8^b]^{2-}$	1089.658 (1089.672)
w_7^{2-}	1049.646 (1049.656)	$\{[a_8 - G_8] + \mathbf{1'}\}^{2-}$	1287.188 (1287.195)
$[w_7 + \mathbf{1'}]^{2-}$	1247.177 (1247.188)	$\{[a_{10} - C_{10}] + \mathbf{1'}\}^{2-}$	1603.749 (1603.750)
$[w_7 + \mathbf{1'}_2]^{2-}$	1444.203 (1444.211)	$\{[a_{10} - C_{10}] + \mathbf{1'}_2\}^{2-}$	1800.807 (1800.773)
$[w_{10} + \mathbf{1'}_2]^{2-}$	1912.795 (1912.781)	$\{[a_{13} - C_{13}] + \mathbf{1'}_2\}^{2-}$	2249.862 (2249.844)
$[w_{10} + \mathbf{1'}_3]^{2-}$	2110.333 (2110.313)	$\{[a_{13} - C_{13}] + \mathbf{1'}_3\}^{2-}$	2446.894 (2446.867)
$[w_{12} + \mathbf{1'}_2]^{2-}$	2209.866 (2209.828)	$\{[a_{15} - C_{15}] + \mathbf{1'}_3 - py\}^{3-}$	1802.272 (1802.258)
$[w_{12} + \mathbf{1'}_3]^{2-}$	2406.894 (2406.859)		
$[w_{14} + \mathbf{1'}_2]^{3-}$	1670.575 (1670.585)		
$\{[w_{14} + \mathbf{1'}_2] - py\}^{3-}$	1644.210 (1644.234)		
$[w_{14} + \mathbf{1'}_3]^{3-}$	1801.932 (1801.930)		
$\{[w_{14} + \mathbf{1'}_3] - py\}^{3-}$	1775.583 (1775.586)		
$[\mathbf{I} + \mathbf{1'}_3]^{3-}$	1871.635 (1871.625)	$\{[\mathbf{I} + \mathbf{1'}_2] - N_3\}^{3-}$	1725.928 (1725.938)
$\{[\mathbf{I} + \mathbf{1'}_3] - N_3\}^{3-}$	1857.299 (1857.289)	$\{[\mathbf{I} + \mathbf{1'}_2] - C^c\}^{3-}$	1703.255 (1703.258)
$\{[\mathbf{I} + \mathbf{1'}_3] - py\}^{3-}$	1845.281 (1845.281)	$\{[\mathbf{I} + \mathbf{1'}_2] - G^c\}^{3-}$	1689.926 (1689.930)
$\{[\mathbf{I} + \mathbf{1'}_3] - C\}^{3-}$	1834.620 (1834.609)	$\{[\mathbf{I} + \mathbf{1'}_2] - G - py\}^{3-}$	1663.567 (1663.578)
$\{[\mathbf{I} + \mathbf{1'}_3] - G\}^{3-}$	1821.273 (1821.273)	$\{[\mathbf{I} + \mathbf{1'}_2] - G - C\}^{3-}$	1652.903 (1652.914)
$\{[\mathbf{I} + \mathbf{1'}_3] - 2py\}^{3-}$	1818.930 (1818.928)		
$\{[\mathbf{I} + \mathbf{1'}_3] - C - py\}^{3-}$	1808.267 (1808.266)		
Internal fragments[d]			
$[T_2{:}T_4]^-/[C_5{:}T_7]^-/[C_{10}{:}T_{12}]^-$	1074.124 (1074.133)	$[T_x{:}T_x]^-$ (x=2,4,9,12,14)	481.035 (481.039)
$[T_2{:}T_7]^{2-}/[T_9{:}T_{14}]^{2-}$	985.126 (985.133)	$[T_4{:}T_7]^-/[T_9{:}T_{12}]^-/$	1378.171 (1378.180)

		$[T_{11}:T_{14}]^{-}$	
$\{[T_2:T_7]^{2-}/[T_9:T_{14}]^{2-}$ + **1′**}	1182.652 (1182.656)	$\{[T_4:T_7]^{-}/[T_9:T_{12}]^{-}/$ $[T_{11}:T_{14}]^{-}$ + **1′**}	1773.216 (1773.234)
$[T_6:T_7]^{-}/[T_{11}:T_{12}]^{-}$	785.077 (785.086)		

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

[b]T_n, C_n and G_n represent the loss of a cytosine 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.

[c]C and G represent the neutral loss of a cytosine and a guanine base, respectively.

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

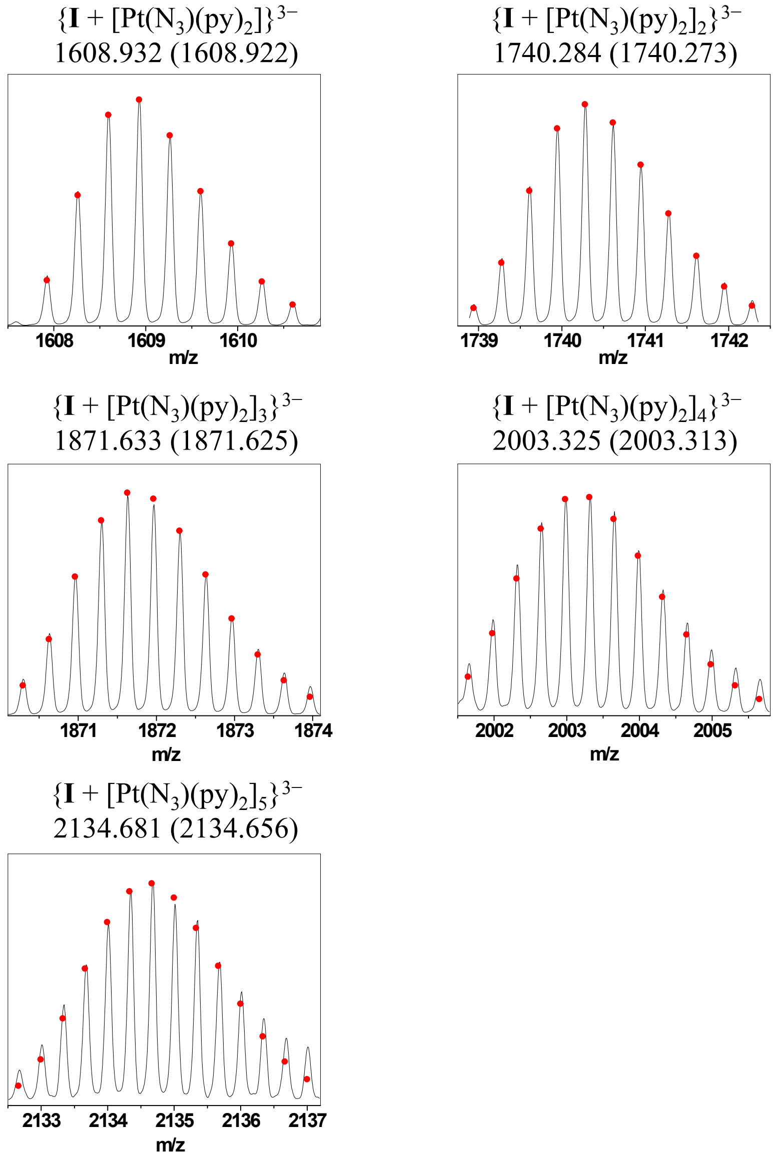

Figure S1. The isotopic models (dots) and mass spectra (lines) for mono-, di-, tri-, tetra- and penta-platinated ODN **I** by complex **1** from their reaction mixture after irradiation under blue light for 1 h.

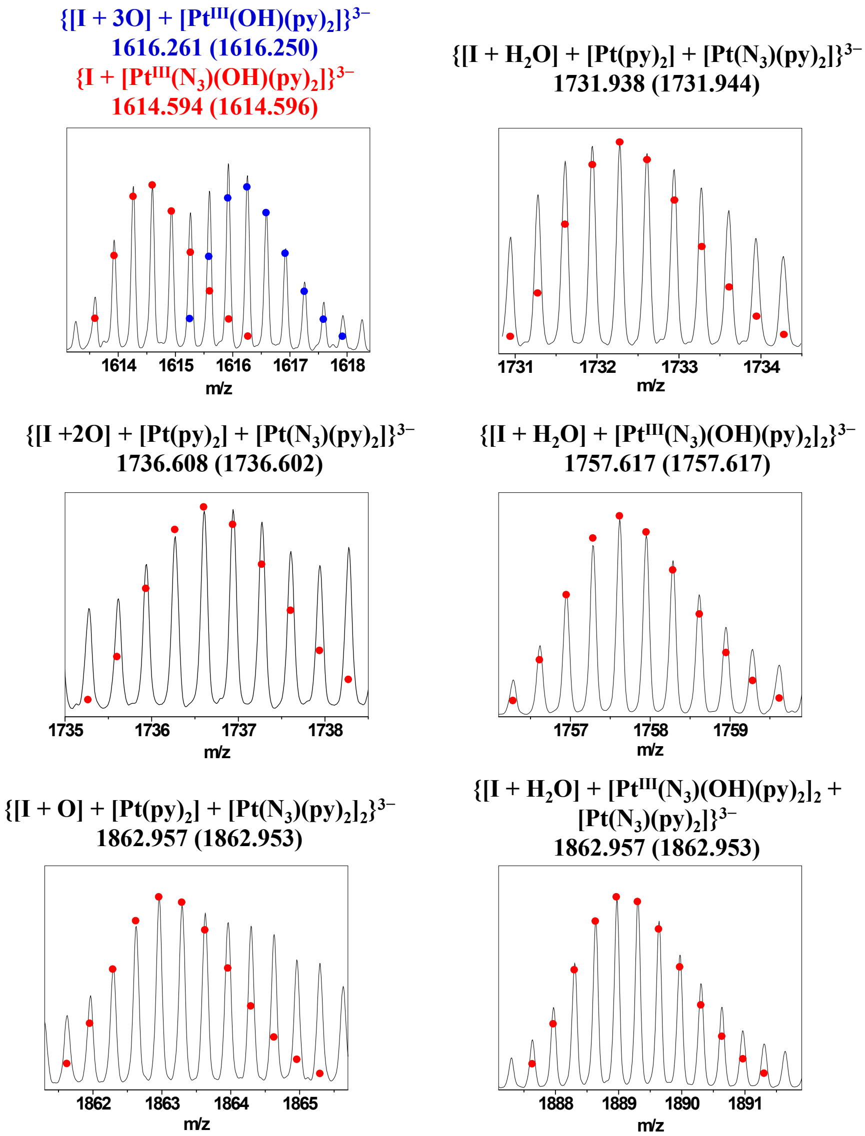

Figure S2. The isotopic models (dots) and mass spectra (lines) for the adducts at *m/z* 1614.594, 1616.261, 1731.938, 1736.608, 1757.617, 1862.957 and 1888.973.

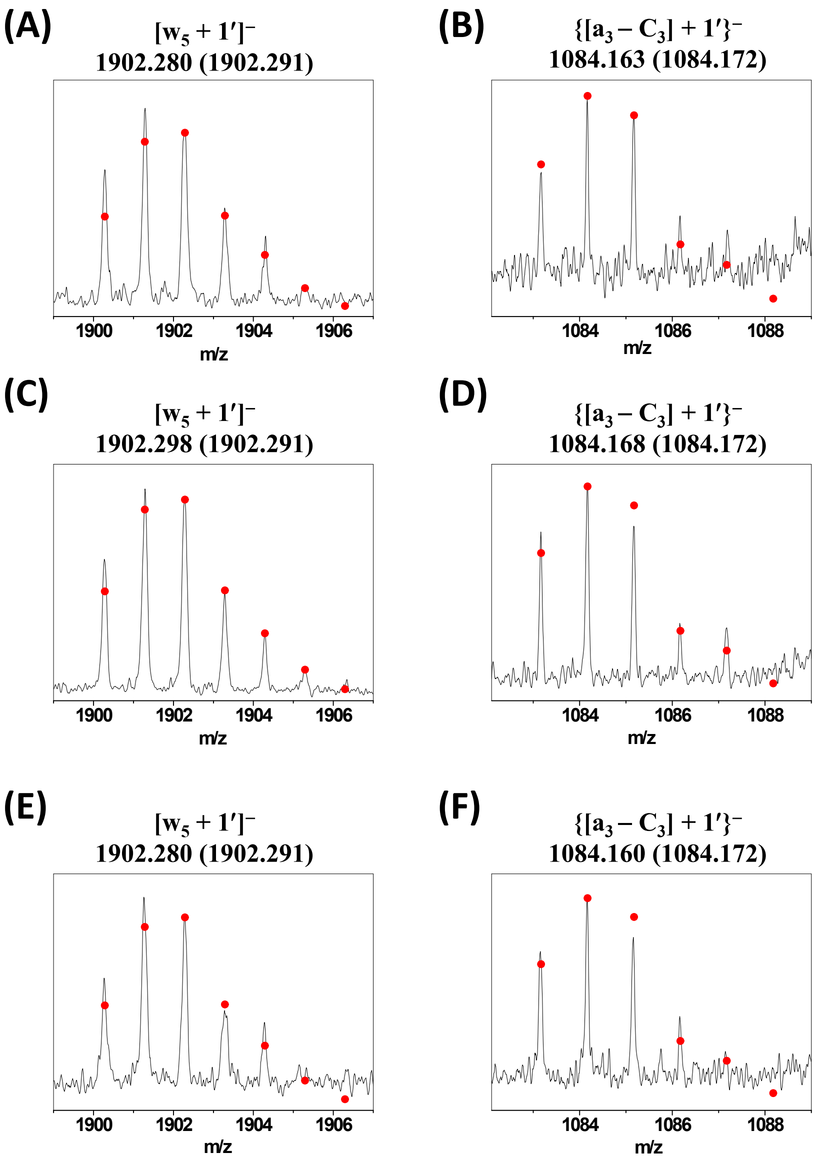

Figure S3. The isotopic models (dots) and mass spectra (lines) for the fragments of $[w_5 + \mathbf{1'}]^-$ and $\{[a_3 - C_3] + \mathbf{1'}\}^-$ observed in the CID fragmentation of $\{\mathbf{I} + \mathbf{1'}\}^+$ (A, B), $\{\mathbf{I} + \mathbf{1'}_2\}^+$ (C, D) and $\{\mathbf{I} + \mathbf{1'}_3\}^+$ (E, F), respectively. $\mathbf{1'} = [Pt(N_3)(py)_2]^+$.

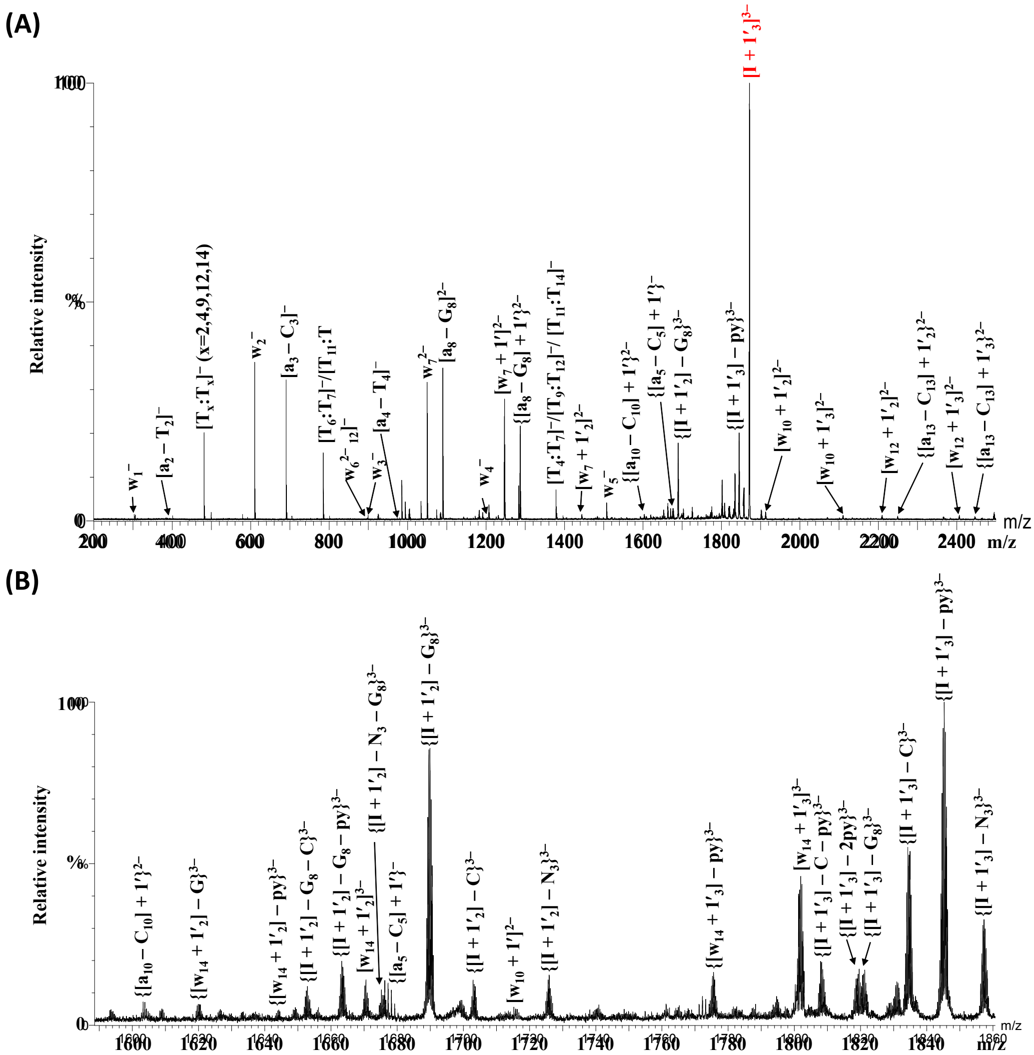

Figure S4. Tandem mass spectra of parent ion $[\mathbf{I} + \mathbf{1'}_3]^+$ with the parent ion shown in red (A) and the enlarged spectrum during the MS range of *m/z* 1590-1860 (B). The corresponding MS/MS data in detail are listed in Tables S4. $\mathbf{1'} = [Pt(N_3)(py)_2]^+$.