Electronic Supplementary Information

For

Photoactivatable diazido Pt(IV) anticancer complex can bind to and oxidize all four nucleosides

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Table of contents

Table S1. Ions identified by MS in the reaction mixture between Pt(IV) complex **1** and guanosine at a molar ratio of Pt/guanosine = 1.0 and 2.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleosides and the protons for balancing the charges of the ions are omitted for clarity; The oxidation state of Pt in the Pt species is 2+ if not specified).

Ions	Formula	*m/z* observed (calculated)	
		Pt/guanosine = 1.0	Pt/guanosine = 2.0
{[guanine] + [Pt(py)] + CH_3CN}$^{2+}$	$C_{12}H_{11}N_7OPt$	233.041 (233.039)	233.039 (233.039)
{[guanine] + [Pt(py)$_2$]}$^{2+}$	$C_{15}H_{13}N_7OPt$	252.048 (252.049)	252.049 (252.049)
{[guanine] + [Pt(py)$_2$] + CH_3CN}$^{2+}$	$C_{17}H_{16}N_8OPt$	272.561 (272.563)	272.562 (272.563)
[guanosine]$^+$	$C_{10}H_{13}N_5O_5$	284.098 (284.102)	284.100 (284.102)
[Pt^{III}(OH)(py)]$^+$	C_5H_4NOPt	290.004 (290.000)	290.002 (290.000)
[Pt^{I}(py) + CH_3CN]$^+$	$C_7H_7N_2Pt$	315.033 (315.031)	315.034 (315.031)
[Pt(py)$_2$]$^+$	$C_{10}H_8N_2Pt$	352.042 (352.039)	352.040 (352.039)
{[Pt^{III}(py)] + 2CH_3CN]}$^+$	$C_{10}H_{10}N_2Pt$	354.056 (354.047)	354.053 (354.047)
[Pt(N)(py)$_2$]$^+$	$C_{10}H_9N_3Pt$	367.048 (367.055)	367.045 (367.055)
[Pt^{III}(OH)(py)$_2$]$^+$	$C_{10}H_9N_2OPt$	369.045 (369.047)	369.042 (369.047)
[Pt^{III}(N)(OH)(py)$_2$]$^+$	$C_{10}H_{10}N_3OPt$	384.055 (384.055)	384.052 (384.055)
[Pt^{III}(OH)$_2$(py)$_2$]$^+$	$C_{10}H_{11}N_2O_2Pt$	387.057 (387.055)	387.053 (387.055)
{[guanine] + [Pt(py)]}$^+$	$C_{10}H_8N_6OPt$	424.047 (424.047)	424.048 (424.047)
{[guanosine]$_3$ + K}$^{2+}$	$C_{30}H_{38}N_{15}O_{15}K$	444.617 (444.625)	444.613 (444.625)
{[guanine] + [Pt(py)] + CH_3CN}$^+$	$C_{12}H_{11}N_7OPt$	465.073 (465.078)	465.074 (465.078)
{[guanine] + [Pt(py)$_2$]}$^+$	$C_{15}H_{13}N_7OPt$	503.091 (503.094)	503.087 (503.094)
{[guanine] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{15}H_{14}N_{10}OPt$	546.107 (546.109)	546.107 (546.109)
[guanosine]$_2^+$	$C_{20}H_{26}N_{10}O_{10}$	567.190 (567.188)	567.186 (567.188)
{[guanosine]$_4$ + K}$^{2+}$	$C_{40}H_{51}N_{20}O_{20}K$	586.165 (586.172)	586.160 (586.172)
{[guanosine] + [Pt(N$_3$)(py)]}$^+$	$C_{15}H_{17}N_9O_5Pt$	599.110 (599.109)	599.105 (599.109)
{[guanosine] + [Pt(py)] + 2CH_3CN}$^+$	$C_{19}H_{22}N_8O_5Pt$	638.151 (638.141)	638.152 (638.141)
{[guanosine] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{22}N_{10}O_5Pt$	678.148 (678.148)	678.148 (678.148)
{[guanosine + O] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{22}N_{10}O_6Pt$	694.138 (694.148)	694.144 (694.148)
{[guanosine + (OH)$_2$] + [Pt(N$_3$)(py)$_2$]}$^+$	$C_{20}H_{24}N_{10}O_7Pt$	712.156 (712.156)	712.156 (712.156)

{[guanosine] + $[Pt^{IV}(N_3)_2(OH)(py)_2]\}^+$	$C_{20}H_{23}N_{13}O_6Pt$	737.167 (737.164)	737.161 (737.164)
$[guanosine]_3^+$	$C_{30}H_{39}N_{15}O_{15}$	850.285 (850.281)	850.278 (850.281)
$\{[guanosine]_6 + K\}^{2+}$	$C_{60}H_{77}N_{30}O_{30}K$	869.254 (869.258)	869.247 (869.258)
$\{[guanosine]_3 + K\}^+$	$C_{30}H_{38}N_{15}O_{15}K$	888.231 (888.234)	888.230 (888.234)
$\{[guanosine]_2 + [Pt(N_3)(py)_2]\}^+$	$C_{30}H_{35}N_{15}O_{10}Pt$	——	961.237 (961.242)
$\{[guanosine] + [Pt(N_3)(py)_2]_2\}^+$	$C_{30}H_{31}N_{15}O_5Pt_2$	1072.191 (1072.203)	1072.196 (1072.203)
$[guanosine]_4^+$	$C_{40}H_{52}N_{20}O_{20}$	1133.376 (1133.375)	1133.368 (1133.375)
$\{[guanosine]_4 + K\}^+$	$C_{40}H_{51}N_{20}O_{20}K$	1171.315 (1171.328)	1171.320 (1171.328)
$\{[guanosine]_8 + K\}^{2+}$	$C_{80}H_{103}N_{40}O_{40}K$	1152.845 (1152.852)	1152.843 (1152.852)
$[guanosine]_5^+$	$C_{50}H_{65}N_{25}O_{25}$	1416.469 (1416.469)	1416.458 (1416.469)

Table S2. Ions identified by MS in the reaction mixture between Pt(IV) complex **1** and adenosine at a molar ratio of Pt/adenosine = 1.0 and 2.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleosides and the protons for balancing the charges of the ions are omitted for clarity; The oxidation state of Pt in the Pt species is 2+ if not specified).

Ions	Formula	*m/z* observed (calculated)	
		Pt/adenosine = 1.0	Pt/adenosine = 2.0
{[adenine] + $[Pt(py)_2]$}$^{2+}$	$C_{15}H_{13}N_7Pt$	244.053 (244.055)	244.051 (244.055)
{[adenine] + $[Pt(py)_2]$ + CH_3CN}$^{2+}$	$C_{17}H_{16}N_8Pt$	264.567 (264.563)	264.565 (264.563)
[adenosine]$^+$	$C_{10}H_{13}N_5O_4$	268.105 (268.102)	268.107 (268.102)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.048 (352.039)	352.049 (352.039)
{$[Pt^{III}(py)]$ + $2CH_3CN$]}$^+$	$C_{10}H_{10}N_2Pt$	354.058 (354.047)	354.059 (354.047)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.050 (367.055)	367.051 (367.055)
$[Pt^{III}(OH)(py)_2]^+$	$C_{10}H_9N_2OPt$	369.047 (369.047)	369.048 (369.047)
$[Pt^{III}(N)(OH)(py)_2]^+$	$C_{10}H_{10}N_3OPt$	384.057 (384.055)	384.058 (384.055)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.054 (387.055)	387.055 (387.055)
{[adenine] + $[Pt(py)]$}$^+$	$C_{10}H_8N_6Pt$	408.058 (408.055)	408.059 (408.055)
{[adenine] + $[Pt(py)]$ + CH_3CN}$^+$	$C_{12}H_{11}N_7Pt$	449.080 (449.078)	449.081 (449.078)
$[Pt(N_3)_2(OH)_2(py)_2]^+$	$C_{10}H_{14}N_8O_2Pt$	474.102 (474.094)	474.103 (474.094)
{[adenine] + $[Pt(py)_2]$}$^+$	$C_{15}H_{13}N_7Pt$	487.099 (487.094)	487.099 (487.094)
{[adenine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{15}H_{14}N_{10}Pt$	530.113 (530.109)	530.114 (530.109)
{[adenine] + $[Pt^{IV}(N_3)(OH)_2(py)_2]$ + Na}$^+$	$C_{15}H_{15}N_{10}O_2PtNa$	586.107 (586.102)	586.107 (586.102)
{[adenosine] + $[Pt(OH)(py)_2]$}$^+$	$C_{20}H_{23}N_7O_5Pt$	637.144 (637.148)	637.149 (637.148)
{[adenosine + 2O] + $[Pt^{III}(N)(OH)(py)]$ + CH_3CN}$^+$	$C_{17}H_{21}N_8O_7Pt$	645.135 (645.125)	645.130 (645.125)
{[adenosine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{20}H_{22}N_{10}O_4Pt$	662.156 (662.155)	662.156 (662.155)
{[adenosine + O] + $[Pt(N_3)(py)_2]$}$^+$	$C_{20}H_{22}N_{10}O_5Pt$	678.150 (678.148)	678.155 (678.148)
{[adenosine] + $[Pt^{IV}(N_3)(OH)_2(py)_2]$}$^+$	$C_{20}H_{24}N_{10}O_6Pt$	696.166 (696.164)	696.160 (696.164)
{[adenosine] +	$C_{20}H_{21}N_{13}O_4Pt$	——	703.153 (703.156)

$[Pt^{IV}(N_3)_2(py)_2]\}^+$ {[adenosine + H_2O] + $[Pt(NH_3)(OH)(py)]$ + $[Pt^{IV}(OH)_2(py)]\}^+$	$C_{20}H_{29}N_8O_8Pt_2$	——	900.137 (900.148)
{[adenine] + $[Pt(N_3)(py)_2]_2\}^+$	$C_{25}H_{23}N_{15}Pt_2$	924.157 (924.164)	924.162 (924.164)
{[adenosine + H_2O] + $[Pt(NH_3)(OH)(py)]$ + $[Pt^{IV}(N_3)(OH)_2(py)]\}^+$	$C_{20}H_{30}N_{11}O_8Pt_2$	——	943.159 (943.164)
{[adenosine] + $[Pt(N_3)(py)]$ + $[Pt(N_3)(py)_2]\}^+$	$C_{25}H_{26}N_{14}O_4Pt_2$	——	977.167 (977.164)
{[adenosine] + $[Pt(N_3)(py)_2]_2\}^+$	$C_{30}H_{31}N_{15}O_4Pt_2$	1056.202 (1056.203)	1056.214 (1056.203)
{[adenosine] + $[Pt^{III}(N_3)(OH)(py)_2]_2\}^+$ or {[adenosine] + $[Pt(N_3)(py)_2]$ + $[Pt^{IV}(N_3)(OH)_2(py)_2]\}^+$	$C_{30}H_{33}N_{15}O_6Pt_2$	1090.217 (1090.211)	1090.215 (1090.211)
{[adenosine] + $[Pt^{III}(N_3)(OH)(py)_2]$ + $[Pt^{III}(N_3)_2(py)_2]\}^+$ or {[adenosine] + $[Pt(N_3)(py)_2]$ + $[Pt^{IV}(N_3)_2(OH)(py)_2]\}^+$	$C_{30}H_{32}N_{18}O_5Pt_2$	1115.224 (1115.219)	1115.222 (1115.219)

Table S3. Ions identified by MS in the reaction mixture between Pt(IV) complex **1** and cytidine at a molar ratio of Pt/cytidine = 1.0 and 2.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleosides and the protons for balancing the charges of the ions are omitted for clarity; The oxidation state of Pt in the Pt species is 2+ if not specified).

Ions	Formula	*m/z* observed (calculated)	
		Pt/cytidine = 1.0	Pt/cytidine = 2.0
$[cytidine]^+$	$C_9H_{13}N_3O_4$	228.097 (228.102)	228.095 (228.102)
$[Pt(N)(py)]^+$	$C_5H_4N_2Pt$	288.001 (288.008)	288.001 (288.008)
$[Pt^{III}(OH)(py)]^+$	C_5H_4NOPt	290.000 (290.000)	290.001 (290.000)
$\{[cytosine + H_2O] + [Pt(NH_3)]\}^+$	$C_4H_8N_4O_2Pt$	340.042 (340.039)	340.039 (340.039)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.041 (352.039)	352.042 (352.039)
$\{[Pt^{III}(py)] + 2CH_3CN]\}^+$	$C_{10}H_{10}N_2Pt$	354.055 (354.047)	354.056 (354.047)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.043 (367.055)	367.046 (367.055)
$[Pt^{III}(OH)(py)_2]^+$	$C_{10}H_9N_2OPt$	369.043 (369.047)	369.044 (369.047)
$[Pt^{III}(N)(OH)(py)_2]^+$	$C_{10}H_{10}N_3OPt$	384.049 (384.055)	384.050 (384.055)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.055 (387.055)	387.051 (387.055)
$\{[cytosine] + [Pt(N)(py)]\}^+$	$C_9H_9N_5OPt$	399.051 (399.055)	399.048 (399.055)
$\{[Pt^{III}(N)(py)] + CH_3CN\}^+$	$C_{12}H_{11}N_4Pt$	407.069 (407.070)	407.066 (407.070)
$[Pt^{III}(N)(N_3)(py)_2]^+$	$C_{10}H_9N_6Pt$	409.060 (409.063)	409.061 (409.063)
$\{[cytosine] + [Pt(py)] + CH_3CN\}^+$	$C_{11}H_{11}N_5OPt$	425.066 (425.070)	425.067 (425.070)
$\{[cytosine] + [Pt(N_3)(py)]\}^+$	$C_9H_9N_7OPt$	427.058 (427.063)	427.059 (427.063)
$[cytidine]_2^+$	$C_{18}H_{26}N_6O_8$	455.184 (455.188)	455.185 (455.188)
$\{[Pt^{III}(py)_2] + 3CH_3CN\}^+$	$C_{16}H_{16}N_5Pt$	474.097 (474.109)	474.098 (474.109)
$\{[cytidine]_2 + Na\}^+$	$C_{18}H_{25}N_6O_8Na$	477.167 (455.172)	477.168 (455.172)
$\{[cytosine] + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{14}N_8OPt$	506. 097 (506.102)	506.098 (506.102)
$\{[cytosine + 2(OH)] + [Pt(OH)(py)_2]\}^+$	$C_{14}H_{17}N_5O_4Pt$	515.089 (515.102)	515.094 (515.102)
$\{[cytosine + H_2O] + [Pt(OH)(py)_2] + Na\}^+$	$C_{14}H_{16}N_5O_3PtNa$	521.097 (521.086)	521.093 (521.086)
$\{[cytosine + H_2O] + [Pt^{III}(N_3)(OH)(py)_2]\}^+$	$C_{14}H_{17}N_8O_3Pt$	541.114 (541.117)	541.115 (541.117)
$\{[cytidine] + [Pt(OH)(py)_2]\}^+$	$C_{19}H_{23}N_5O_5Pt$	597.140 (597.141)	597.140 (597.141)
$\{[cytidine] + [Pt(N_3)(py)_2]\}^+$	$C_{19}H_{22}N_8O_4Pt$	622.148 (622.148)	622.148 (622.148)
{[cytidine + O] +	$C_{19}H_{22}N_8O_5Pt$	638.140 (638.141)	638.140 (638.141)

$[[Pt(N_3)(py)_2]\}^+$			
$\{[cytidine + 2(OH)] + [[Pt(N_3)(py)_2]\}^+$	$C_{19}H_{24}N_8O_6Pt$	—	656.150 (656.156)
$\{[cytidine + H_2O] + [[Pt(N_3)(py)_2] + Na\}^+$	$C_{19}H_{23}N_8O_5PtNa$	662.148 (662.141)	—
$\{[cytidine] + [Pt^{IV}(N_3)_2(py)_2]\}^+$	$C_{19}H_{21}N_{11}O_4Pt$	—	663.145 (663.148)
$\{[cytidine] + [Pt^{IV}(N_3)_2(OH)(py)_2]\}^+$	$C_{19}H_{23}N_{11}O_5Pt$	—	681.159 (681.156)
$\{[cytidine + H_2O] + [Pt^{IV}(N_3)_2(OH)(py)_2]\}^+$	$C_{19}H_{25}N_{11}O_6Pt$	—	699.166 (699.172)
$\{[cytidine + H_2O] + [Pt^{IV}(N_3)_2(OH)(py)_2] + Na\}^+$	$C_{19}H_{24}N_{11}O_6PtNa$	—	721.151 (721.156)
$\{[cytidine]_2 + [Pt(N_3)(py)_2]\}^+$	$C_{28}H_{35}N_{11}O_8Pt$	—	849.229 (849.242)
$\{[cytidine] + [Pt(N_3)(py)_2]_2\}^+$	$C_{29}H_{31}N_{13}O_4Pt_2$	—	1016.194 (1016.195)

Table S4. Ions identified by MS in the reaction mixture between Pt(IV) complex **1** and thymidine at a molar ratio of Pt/thymidine = 1.0 and 2.0 after irradiated under blue light for 1 h (Charges for Pt moiety in platinated nucleosides and the protons for balancing the charges of the ions are omitted for clarity; The oxidation state of Pt in the Pt species is 2+ if not specified).

Ions	Formula	*m/z* observed (calculated)	
		Pt/thymidine = 1.0	Pt/thymidine = 2.0
$[thymidine]^+$	$C_{10}H_{14}N_2O_5$	243.099 (243.094)	243.099 (243.094)
$\{[thymidine] + Na\}^+$	$C_{10}H_{13}N_2O_5Na$	265.080 (265.078)	265.080 (265.078)
$[Pt(py)]^+$	C_5H_3NPt	273.005 (273.000)	273.005 (273.000)
$[Pt(N)(py)]^+$	$C_5H_4N_2Pt$	288.008 (288.008)	288.012 (288.008)
$[Pt(N)(N)(py)]^+$	$C_5H_5N_3Pt$	303.020 (303.023)	303.020 (303.023)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.042 (352.039)	352.045 (352.039)
$\{[Pt^{III}(py)] + 2CH_3CN\}^+$	$C_9H_8N_3Pt$	354.055 (354.047)	354.055 (354.047)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.050 (367.055)	367.050 (367.055)
$[Pt^{III}(N)(OH)(py)_2]^+$	$C_{10}H_{10}N_3OPt$	384.053 (384.055)	384.057 (384.055)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.055 (387.055)	387.055 (387.055)
$\{[Pt(N_3)(py)_2] + CH_3CN\}^+$	$C_{12}H_{12}N_6Pt$	436.083 (436.086)	436.083 (436.086)
$\{[Pt^{III}(py)_2] + 3CH_3CN\}^+$	$C_{16}H_{16}N_5Pt$	474.097 (474.109)	474.102 (474.109)
$[thymidine]_2^+$	$C_{20}H_{28}N_4O_{10}$	485.186 (485.188)	485.186 (485.188)
$\{[thymidine]_2 + K\}^+$	$C_{20}H_{28}N_4O_{10}K$	523.133 (523.141)	523.133 (523.141)
$\{[thymine] + [Pt(N_3)(py)_2]\}^+$	$C_{15}H_{15}N_7O_2Pt$	521.101 (521.102)	521.101 (521.102)
$\{[thymidine]_4 + 2K\}^{2+}$	$C_{40}H_{54}N_8O_{20}K_2$	523.133 (523.141)	523.133 (523.141)
$\{[thymidine] + [Pt(py)] + CH_3CN\}^+$	$C_{17}H_{20}N_4O_5Pt$	556.117 (556.117)	556.117 (556.117)
$\{[thymidine] + [Pt(py)_2]\}^+$	$C_{20}H_{22}N_4O_5Pt$	594.128 (594.133)	594.128 (594.133)
$\{[thymidine] + [Pt(py)_2] + CH_3CN\}^+$	$C_{22}H_{25}N_5O_5Pt$	635.161 (635.156)	635.161 (635.156)
$\{[thymidine] + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_7O_5Pt$	637.151 (637.148)	637.151 (637.148)
$\{[thymidine + O] + [Pt(N_3)(py)_2]\}^+$	$C_{20}H_{23}N_7O_6Pt$	653.141 (653.150)	653.145 (653.150)
$\{[Pt(OH)_2(py)_2] + [Pt(OH)(py)_2]\}^+$	$C_{20}H_{22}N_4O_3Pt_2$	757.103 (757.102)	757.103 (757.102)
$\{[thymidine]_3 + K\}^+$	$C_{30}H_{41}N_6O_{15}K$	765.221 (765.234)	765.227 (765.234)
$\{[Pt^{III}(N_3)(OH)(py)_2] + [Pt(OH)(py)_2]\}^+$	$C_{20}H_{20}N_7O_2Pt_2$	781.106 (781.102)	781.106 (781.102)
$\{[thymidine]_4 + K\}^+$	$C_{40}H_{55}N_8O_{20}K$	1007.315 (1007.328)	1007.315 (1007.328)

Table S5. Fragment ions observed by MS/MS analysis under positive ion mode of the mono-platinated guanosine ({[guanosine] + $[Pt(N_3)(py)_2]$}$^+$). (Charges for Pt moiety in platinated fragments and the protons for balancing the charges of the ions are omitted for clarity).

Fragment Ions	Formula	*m/z*[a] observed (calculated)
[guanine]$^+$	$C_5H_5N_5O$	152.055 (152.056)
[Pt(py)]$^+$	C_5H_3NPt	273.004 (273.000)
[Pt(py) + OH]$^+$	C_5H_4NOPt	290.004 (290.000)
$[Pt(N_3)(OH)(O)(py)]^+$	$C_5H_6N_4O_2Pt$	350.027 (350.023)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.039 (352.039)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.052 (367.055)
$[Pt(N_3)(O)(py)_2]^+$	$C_{10}H_9N_5OPt$	411.062 (411.055)
{[guanine] + [Pt(py)]}$^+$	$C_{10}H_8N_6OPt$	424.047 (424.047)
{[guanine] + [Pt(N)(py)]}$^+$	$C_{10}H_9N_7OPt$	439.056 (439.063)
{[guanine] + $[Pt(N_3)(py)]$}$^+$	$C_{10}H_9N_9OPt$	467.064 (467.063)
{[guanosine] + [Pt(N)]}$^+$	$C_{10}H_{12}N_6O_5Pt$	492.066 (492.063)
{[guanine] + $[Pt(py)_2]$}$^+$	$C_{15}H_{13}N_7OPt$	503.091 (503.094)
{[guanine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{15}H_{14}N_{10}OPt$	546.107 (546.109)
{[guanosine] + [Pt(N)(py)]}$^+$	$C_{15}H_{17}N_7O_5Pt$	571.101 (571.102)
{[guanosine] + $[Pt(N_3)(py)]$}$^+$	$C_{15}H_{17}N_9O_5Pt$	599.105 (599.109)
{[guanosine] + [Pt(py)] + $2CH_3CN$}$^+$	$C_{19}H_{22}N_8O_5Pt$	638.151 (638.141)
{[guanosine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{20}H_{22}N_{10}O_5Pt$	678.148 (678.148)

Table S6. Fragment ions observed by MS/MS analysis under positive ion mode of the mono-platinated adenosine ({[adenosine] + $[Pt(N_3)(py)_2]$}$^+$). (Charges for Pt moiety in platinated fragments and the protons for balancing the charges of the ions are omitted for clarity).

Fragment Ions	Formula	*m/z*[a] observed (calculated)
[adenine]$^+$	$C_5H_5N_5$	136.060 (136.063)
[adenosine]$^+$	$C_{10}H_{13}N_5O_4$	268.103 (268.103)
$[Pt(N)(py)]^+$	$C_5H_4N_2Pt$	288.007 (288.008)
$[Pt(py) + OH]^+$	C_5H_4NOPt	290.004 (290.000)
$[Pt(N_3)(OH)(O)(py)]^+$	$C_5H_6N_4O_2Pt$	350.026 (350.023)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.045 (352.039)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.051 (367.055)
{[adenine] + $[Pt(py)]$}$^+$	$C_{10}H_8N_6Pt$	408.050 (408.055)
{[adenine] + $[Pt(N)(py)]$}$^+$	$C_{10}H_9N_7Pt$	423.063 (423.063)
{[adenine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{15}H_{14}N_{10}Pt$	530.114 (530.109)
{[adenosine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{20}H_{22}N_{10}O_4Pt$	662.156 (662.155)

Table S7. Fragment ions observed by MS/MS analysis under positive ion mode of the mono-platinated cytidine ({[cytidine] + $[Pt(N_3)(py)_2]$}$^+$). (Charges for Pt moiety in platinated fragments and the protons for balancing the charges of the ions are omitted for clarity).

Fragment Ions	Formula	*m/z*[a] observed (calculated)
[cytosine]$^+$	$C_4H_5N_3O$	112.048 (112.047)
[cytidine]$^+$	$C_9H_{13}N_3O_4$	228.097 (228.102)
[Pt(py) + OH]$^+$	C_5H_4NOPt	290.003 (290.000)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.041 (352.039)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.050 (367.055)
{[cytosine] + [Pt(py)]}$^+$	$C_9H_8N_4OPt$	384.045 (384.039)
{[cytosine] + [Pt(N)(py)]}$^+$	$C_9H_9N_5OPt$	399.051 (399.055)
{[cytosine] + [Pt(py)] + CH_3CN}$^+$	$C_{11}H_{11}N_5OPt$	425.066 (425.070)
{[cytosine] + $[Pt(N_3)(py)]$}$^+$	$C_9H_9N_7OPt$	427.058 (427.063)
{[cytosine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{15}H_{14}N_{10}Pt$	506.097 (506.102)
{[cytidine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{19}H_{22}N_8O_4Pt$	622.148 (622.148)

Table S8. Fragment ions observed by MS/MS analysis under positive ion mode of the mono-platinated thymidine ({[thymidine] + $[Pt(N_3)(py)_2]$}$^+$). (Charges for Pt moiety in platinated fragments and the protons for balancing the charges of the ions are omitted for clarity).

Fragment Ions	Formula	*m/z*[a] observed (calculated)
[thymine]$^+$	$C_5H_6N_2O_2$	127.050 (127.047)
[thymidine]$^+$	$C_{10}H_{14}N_2O_5$	243.094 (243.099)
{[thymidine] + Na}$^+$	$C_{10}H_{13}N_2O_5Na$	265.080 (265.078)
[Pt(N)(py)]$^+$	$C_5H_4N_2Pt$	288.012 (288.008)
[Pt(py) + OH]$^+$	C_5H_4NOPt	290.004 (290.000)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.042 (352.039)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.050 (367.055)
{[thymine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{15}H_{15}N_7O_2Pt$	521.097 (521.102)
{[thymidine] + [Pt(py)] + CH_3CN}$^+$	$C_{17}H_{20}N_4O_5Pt$	556.117 (556.117)
{[thymidine] + $[Pt(py)_2]$}$^+$	$C_{20}H_{22}N_4O_5Pt$	594.128 (594.133)
{[thymidine] + $[Pt(py)_2]$ + CH_3CN}$^+$	$C_{22}H_{25}N_5O_5Pt$	635.156 (635.156)
{[thymidine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{20}H_{23}N_7O_5Pt$	637.146 (637.148)

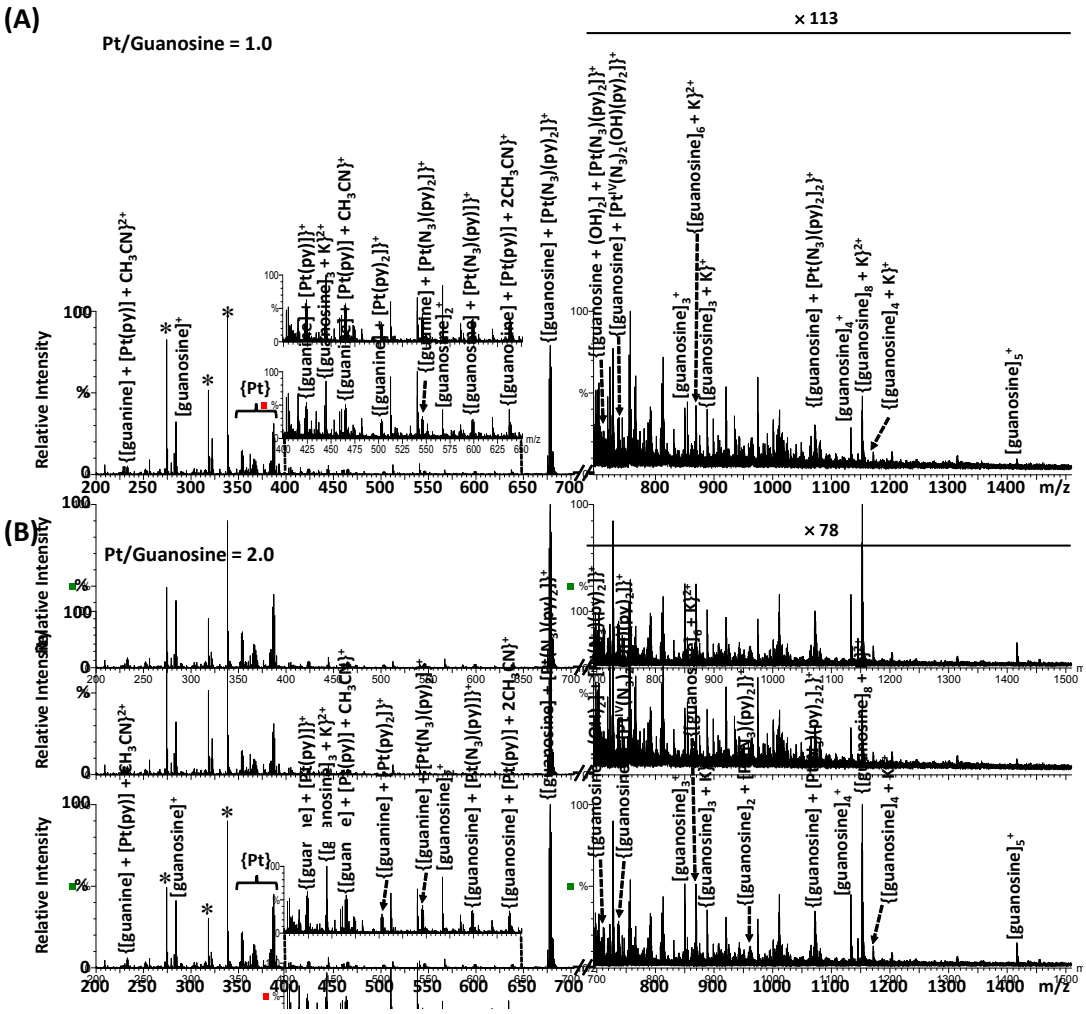

Fig. S1 Mass spectrum of the reaction mixture between Pt(IV) complex **1** and guanosine at a molar ratio of (A) Pt/guanosine = 1.0 and (B) 2.0 after irradiated under blue light for 1 h. ∗ indicates the impurity.

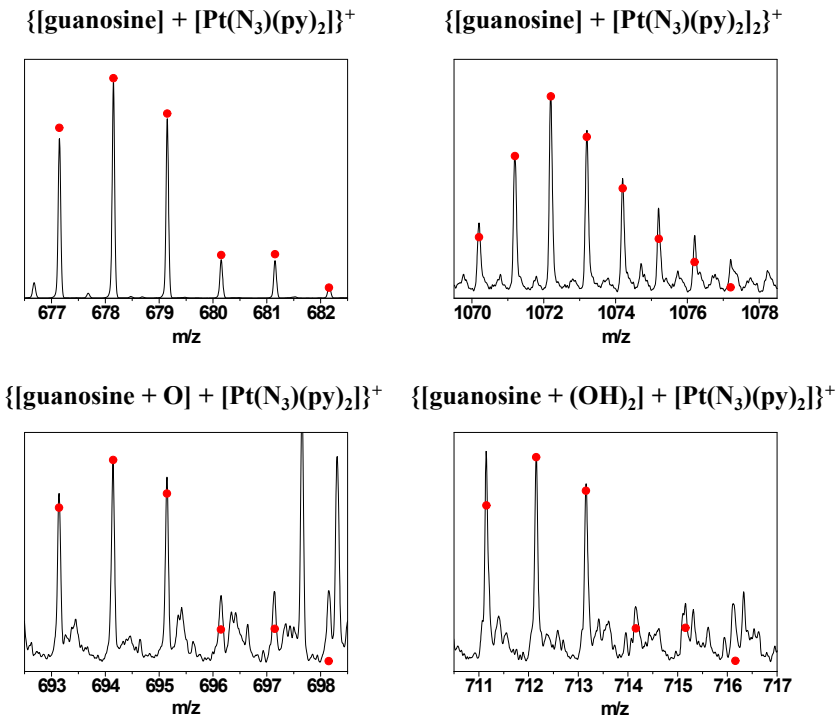

Fig. S2 The isotopic models (dots) and mass spectra (lines) of the representative ions detected by MS from the reaction mixture of complex **1** and guanosine after irradiation under blue light for 1 h.

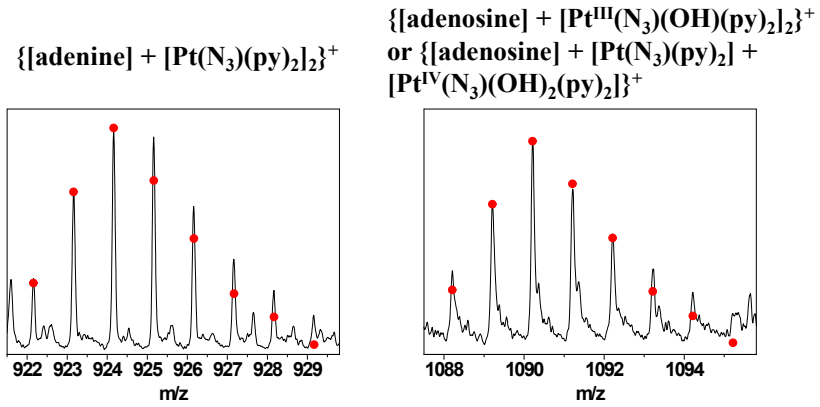

Fig. S3 The isotopic models (dots) and mass spectra (lines) of the representative ions detected by MS from the reaction mixture of complex **1** and adenosine after irradiation under blue light for 1 h.

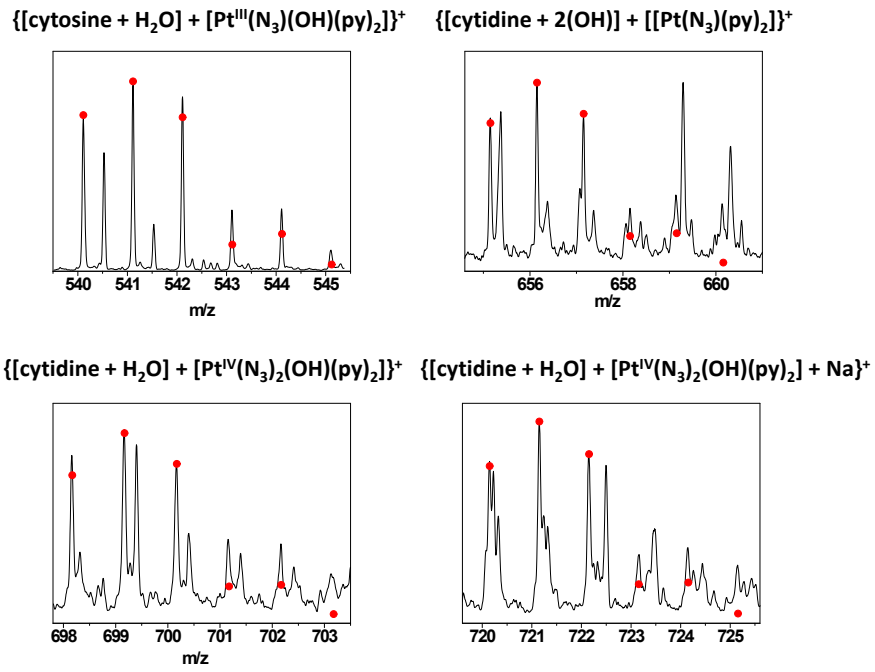

Fig. S4 The isotopic models (dots) and mass spectra (lines) of the representative ions detected by MS from the reaction mixture of complex **1** and cytidine after irradiation under blue light for 1 h.

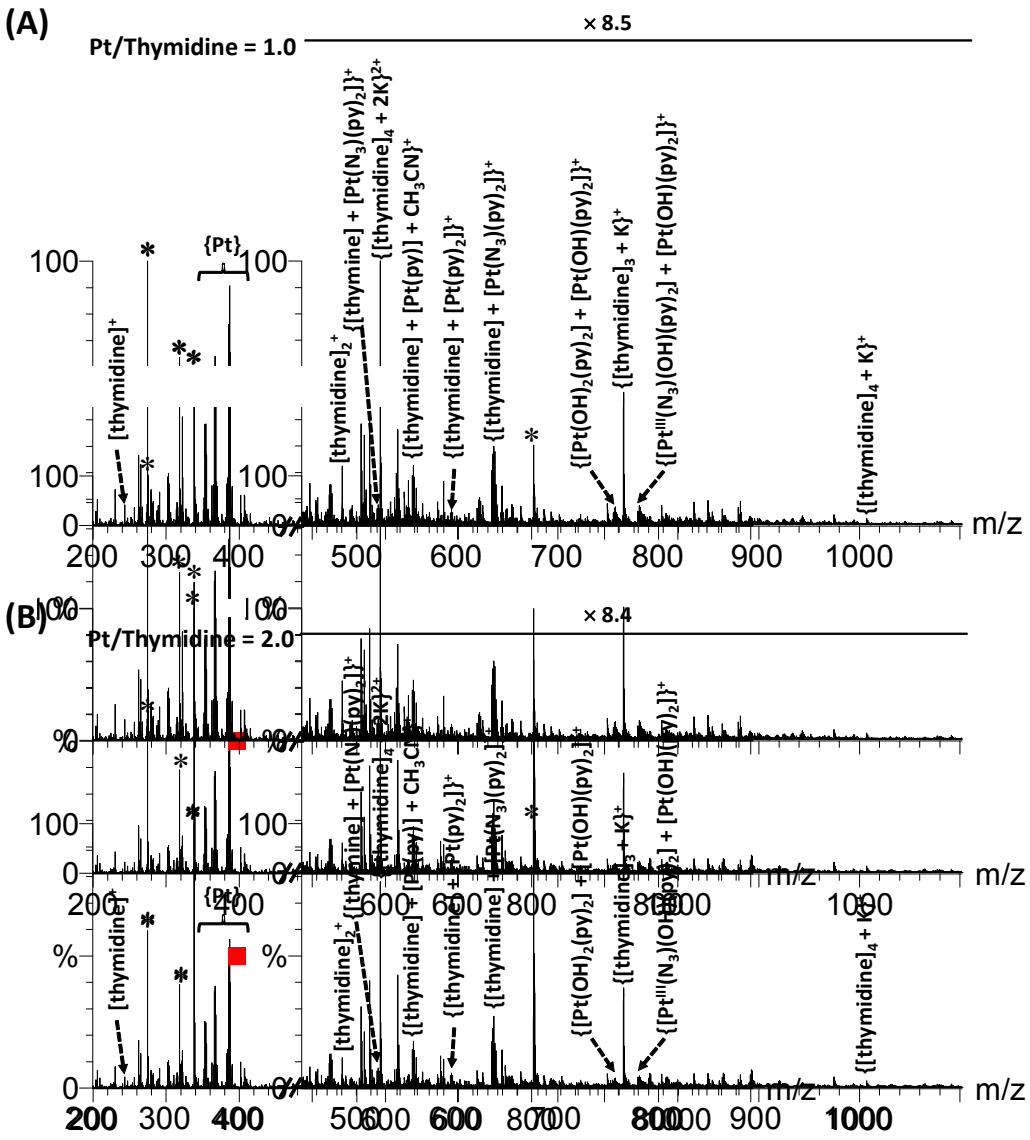

Fig. S5 Mass spectrum of the reaction mixture between Pt(IV) complex **1** and thymidine at a molar ratio of (A) Pt/thymidine = 1.0 and (B) 2.0 after irradiated under blue light for 1 h. ∗ indicates the impurity.

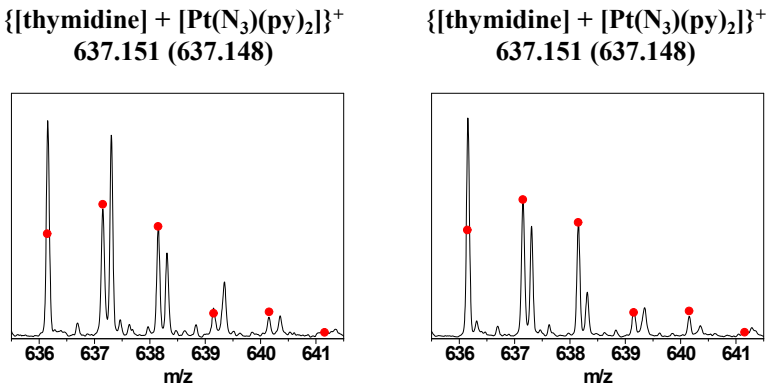

Fig. S6 The isotopic models (dots) and mass spectra (lines) of the representative ions detected by MS from the reaction mixture of complex **1** and thymidine after irradiation under blue light for 1 h.