Dual-platination and induced oxidation of uridine by a photoactivatable diazido Pt(IV) anticancer prodrug

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Electronic Supplementary Information

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Figure S5. Tandem mass spectra of parent ion $\{[\text{uridine}] + [Pt(py)_2]\}^+$

Table S1. Ions identified by MS in the reaction mixture of Pt(IV) complex **1** and uridine at a molar ratio of Pt/uridine = 1.0 upon 1 h of irradiation under blue light (λ_{max}=459 nm) 1 h. (Charges for Pt moiety and other ions are omitted for clarity).

Fragment ions	**Molecular formula**	**Observed (Theoretical)*m/z***
$[uracil]^+$	$C_4H_4N_2O_2$	113.033 (113.034)
$[uridine]^+$	$C_9H_{12}N_2O_6$	245.077 (245.077)
$\{[uridine] + Na\}^+$	$C_9H_{12}N_2O_6$	267.057 (267.059)
$[Pt(py)]^+$	C_5H_3NPt	272.998 (273.000)
$[Pt(N)(py)]^+$	$C_5H_4N_2Pt$	288.008 (288.008)
$[Pt(N)(N)(py)]^+$	$C_5H_5N_3Pt$	303.018 (303.023)
$\{[Pt(py)] + CH_3CN\}^+$	$C_7H_7N_2Pt$	315.037 (315.031)
$\{[uracil] + [Pt(NH_3)_2]\}^+$	$C_4H_8N_4O_2Pt$	340.040 (340.038)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.043 (352.039)
$\{[Pt^{III}(py)] + 2CH_3CN\}^+$	$C_9H_8N_3Pt$	354.055 (354.047)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.052 (367.055)
$[Pt^{III}(N)(OH)(py)_2]^+$	$C_{11}H_{10}N_3Pt$	384.053 (384.055)
$[Pt^{III}(OH)_2(py)_2]^+$	$C_{10}H_{11}N_2O_2Pt$	387.053 (387.055)
$\{[Pt(py)_2] + [HCOOH]\}^+$	$C_{11}H_{10}N_2O_2Pt$	398.043 (398.046)
$\{[Pt(N_3)(py)_2] + CH_3CN\}^+$	$C_{12}H_{12}N_6Pt$	436.083 (436.086)
$\{[uracil + O] + [Pt(N_3)(py)]\}^+$	$C_9H_8N_6O_3Pt$	444.040 (444.038)
$\{[uracil] + [Pt(py)_2]\}^+$	$C_{14}H_{12}N_4O_2Pt$	464.065 (464.068)
$[Pt(H_2O)_2(N_3)_2(py)_2]^+$	$C_{10}H_{14}N_8Pt$	474.102 (474.109)
$[uridine]_2^+$	$C_{18}H_{24}N_4O_{12}$	489.143 (489.146)
$\{[uracil] + [Pt(N_3)(py)_2]\}^+$	$C_{14}H_{13}N_7O_2Pt$	507.084 (507.085)
$\{[uracil + O] + [Pt(NH_3)(py)_2] + Na\}^+$	$C_{14}H_{14}N_5O_3PtNa$	519.082 (519.072)
unassigned		562.018
unassigned		572.011
$\{[uridine] + [Pt(py)_2]\}^+$ （**4**）	$C_{19}H_{20}N_4O_6Pt$	596.111 (596.112)
$\{[uridine] + [Pt(OH)(py)_2]\}^+$ （**3**）	$C_{19}H_{22}N_4O_7Pt$	614.118 (614.121)
$\{[uridine] + [Pt(N_3)(py)_2]\}^+$ （**2**）	$C_{19}H_{21}N_7O_6Pt$	639.128 (639.128)
$\{[uridine + O] + [Pt(N_3)(py)_2]\}^+$ （**6**）	$C_{19}H_{21}N_7O_7Pt$	655.118 (655.122)
$\{[Pt(OH)_2(py)_2] + [Pt(OH)(py)_2]\}^+$	$C_{20}H_{22}N_4O_3Pt_2$	757.103 (757.102)
$\{[Pt^{III}(N_3)(OH)(py)_2] + [Pt(OH)(py)_2]\}^+$	$C_{20}H_{20}N_7O_2Pt_2$	781.106 (781.102)
$\{[uridine] + [Pt(N_3)(py)_2]_2 + Na\}^+$（**5**）	$C_{29}H_{28}N_{12}O_6Pt_2Na$	1057.172 (1057.175)

Table S2. Fragment ions observed by MS/MS analysis under positive ion mode of the {[uridine] + $[Pt(N_3)(py)_2]$}$^+$. (Charges for Pt moiety in platinated adducts are omitted for clarity).

Fragment ions	**Molecular formula**	**Observed (Theoretical) *m/z***
{[uridine] + $[Pt(N_3)(py)_2]$}$^+$	$C_{19}H_{21}N_7O_6Pt$	639.128 (639.128)
{[uridine] + $[Pt(N)(py)_2]$}$^+$	$C_{19}H_{21}N_5O_6Pt$	611.117 (611.121)
{[uridine] + $[Pt(py)_2]$}$^+$	$C_{19}H_{20}N_4O_6Pt$	596.107 (596.112)
{[uridine] + [Pt(N)(py)]}$^+$	$C_{14}H_{16}N_4O_6Pt$	532.078 (532.079)
{[uracil] + $[Pt(N_3)(py)_2]$}$^+$	$C_{14}H_{13}N_7O_2Pt$	507.085 (507.085)
{[uracil] + $[Pt(N)(py)_2]$}$^+$	$C_{14}H_{13}N_5O_2Pt$	479.076 (479.079)
{[uracil] + $[Pt(py)_2]$}$^+$	$C_{14}H_{12}N_4O_2Pt$	464.065 (464.068)
{[uracil] + [Pt(N)(py)]}$^+$	$C_9H_8N_4O_2Pt$	400.036 (400.038)
$[Pt(N_3)(py)_2]^+$	$C_{10}H_9N_5Pt$	395.053 (395.058)
$[Pt(N)(py)_2]^+$	$C_{10}H_9N_3Pt$	367.051 (367.055)
[uridine]$^+$	$C_9H_{12}N_2O_6$	245.076 (245.077)
[uracil]$^+$	$C_4H_4N_2O_2$	113.032 (113.034)

Table S3. Fragment ions observed by MS/MS analysis under positive ion mode of the {[uridine] + $[Pt(OH)(py)_2]$}$^+$. (Charges for Pt moiety in platinated adducts are omitted for clarity).

Fragment ions	**Molecular formula**	**Observed (Theoretical) *m/z***
{[uridine] + $[Pt(OH)(py)_2]$}$^+$	$C_{19}H_{22}N_4O_7Pt$	614.121 (614.121)
{[uridine] + $[Pt(py)_2]$}$^+$	$C_{19}H_{20}N_4O_6Pt$	596.104 (596.112)
{[uridine] + [Pt(OH)(py)]}$^+$	$C_{14}H_{17}N_3O_7Pt$	535.076 (535.086)
{[uridine] + [Pt(py)]}$^+$	$C_{14}H_{15}N_3O_6Pt$	517.068 (517.070)
{[uracil] + $[Pt(OH)(py)_2]$}$^+$	$C_{14}H_{14}N_4O_3Pt$	482.073 (482.079)
{[uracil] + $[Pt(py)_2]$}$^+$	$C_{14}H_{12}N_4O_2Pt$	464.065 (464.068)
{[uracil] + [Pt(OH)(py)]}$^+$	$C_9H_9N_3O_3Pt$	403.037 (403.042)
{[uracil] + [Pt(py)]}$^+$	$C_9H_7N_3O_2Pt$	385.024 (385.026)
$[Pt(OH)(py)_2]^+$	$C_{10}H_{10}N_2OPt$	370.049 (370.052)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.043 (352.041)
[uridine]$^+$	$C_9H_{12}N_2O_6$	245.076 (245.077)
[uracil]$^+$	$C_4H_4N_2O_2$	113.032 (113.034)

Table S4. Fragment ions observed by MS/MS analysis under positive ion mode of the {[uridine] + $[Pt(py)_2]$}$^+$. (Charges for Pt moiety in platinated adducts are omitted for clarity).

Fragment ions	**Molecular formula**	**Observed (Theoretical) *m/z***
{[uridine] + $[Pt(py)_2]$}$^+$	$C_{19}H_{20}N_4O_6Pt$	596.114 (596.112)
{[uracil] + $[Pt(py)_2]$}$^+$	$C_{14}H_{12}N_4O_2Pt$	464.067 (464.068)
{[uracil] + [Pt(py)]}$^+$	$C_9H_7N_3O_2Pt$	385.032 (385.026)
$[Pt(py)_2]^+$	$C_{10}H_8N_2Pt$	352.043 (352.041)
[uridine]$^+$	$C_9H_{12}N_2O_6$	245.076 (245.077)
[uracil]$^+$	$C_4H_4N_2O_2$	113.033 (113.034)

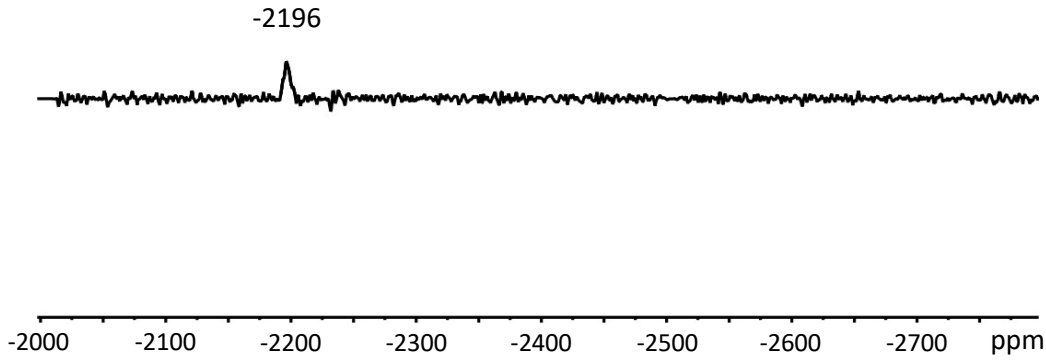

Figure S1. ^{195}Pt NMR (129.4 MHz, 298 K) spectrum of complex **1** (4 mM) with equal molar uridine in D_2O (initial pH adjusted to 7.4) after irradiation 1 h at 450 nm at 298 K.

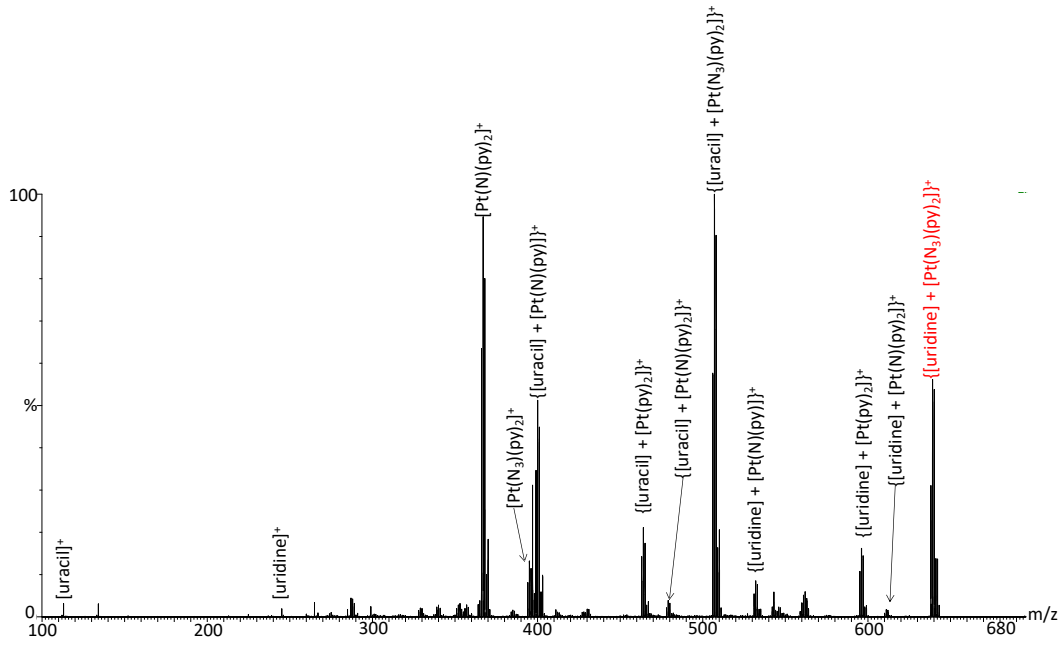

Figure S2. Tandem mass spectrum of adduct **2** $\{[Pt(N_3)(py)_2] + [uridine]\}^+$ in the *m/z* range of 100 – 690 with the main peaks labeled and the parent ions highlighted in red. The corresponding MS/MS data are listed in Table S2.

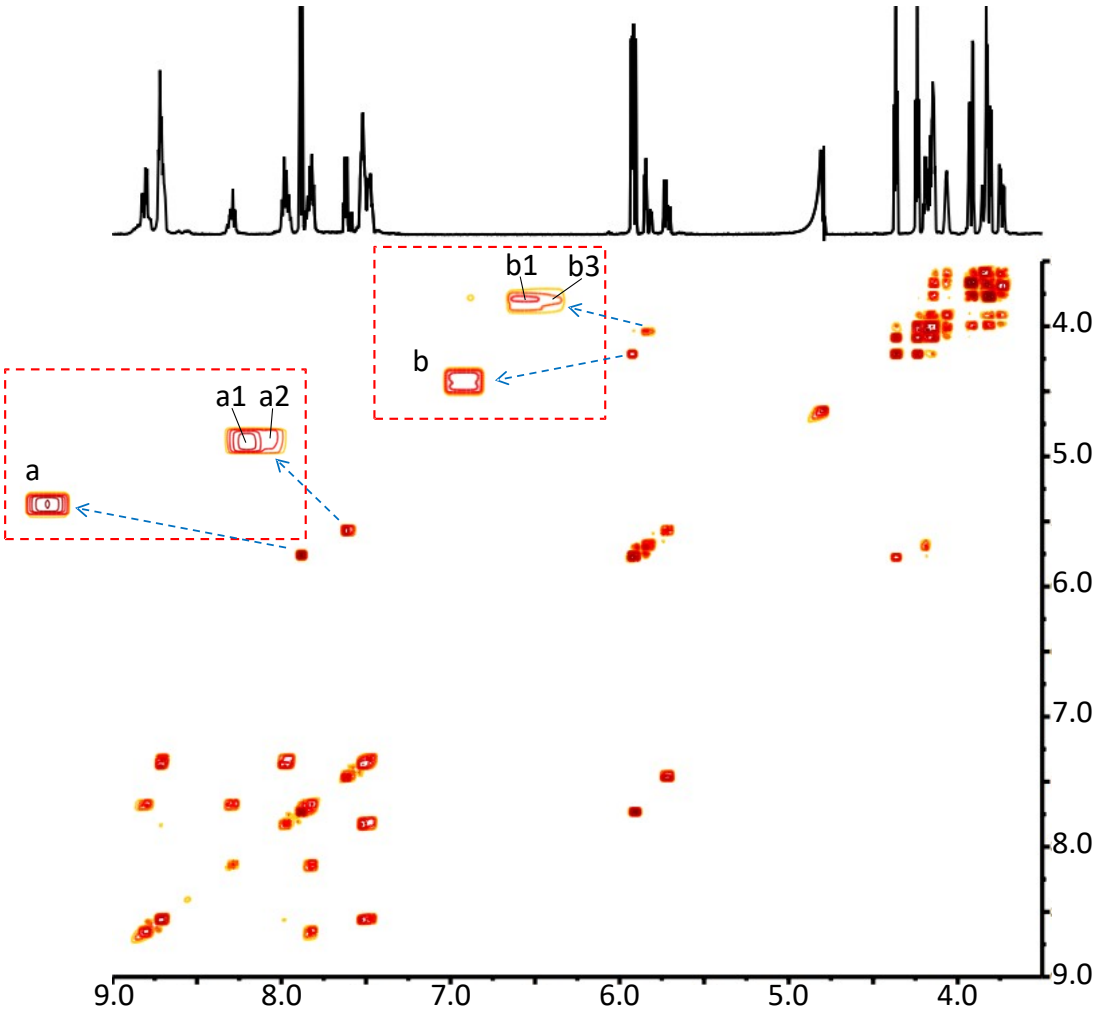

Figure S3. ^{1}H-^{1}H COSY NMR spectrum of reaction mixture of complex **1** (4 mM) with equal molar uridinein D_2O (initial pH adjusted to 7) upon irradiation at 460 nm (50 mW cm^{-2}, 310 K) for 1 h and further incubation for 71 h under 310 K in dark. a: C5-H/C6-H, free uridine; b: C5-H/H1′, free uridine; a1: C5-H/C6-H, complex **2** and **4** (overlap); a2: C5-H/C6-H, complex **3**; b1: H1′/H2′, complex **2**; b2: H1′/H2′, complex **3** and **4** (overlap).

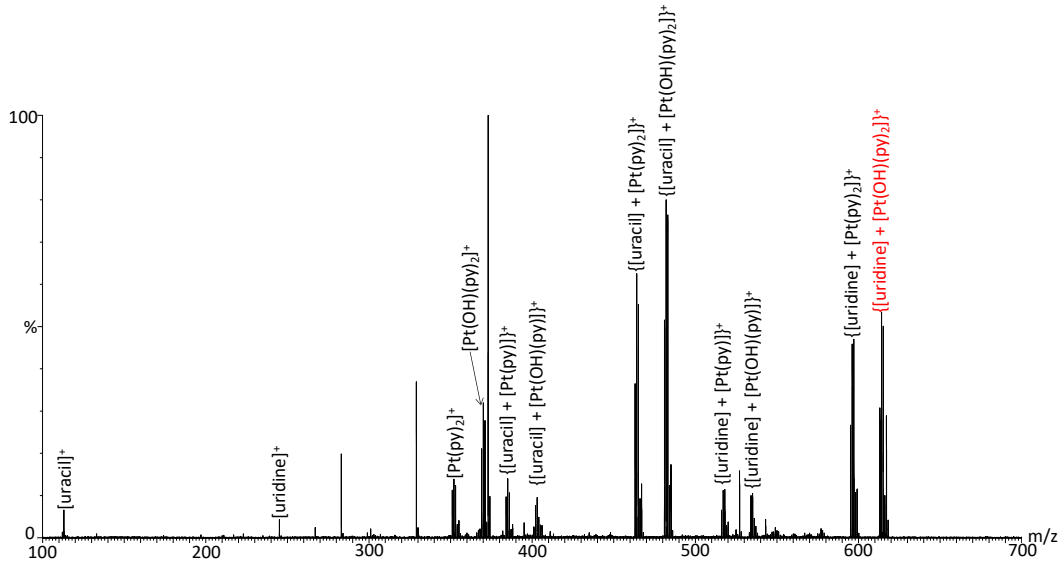

Figure S4. Tandem mass spectrum of $\{[Pt(OH)(py)_2] + [uridine]\}^+$ in the *m/z* range of 100 - 700 with the main peaks labeled and the parent ions highlighted in red. The corresponding MS/MS data are listed in Table S3.

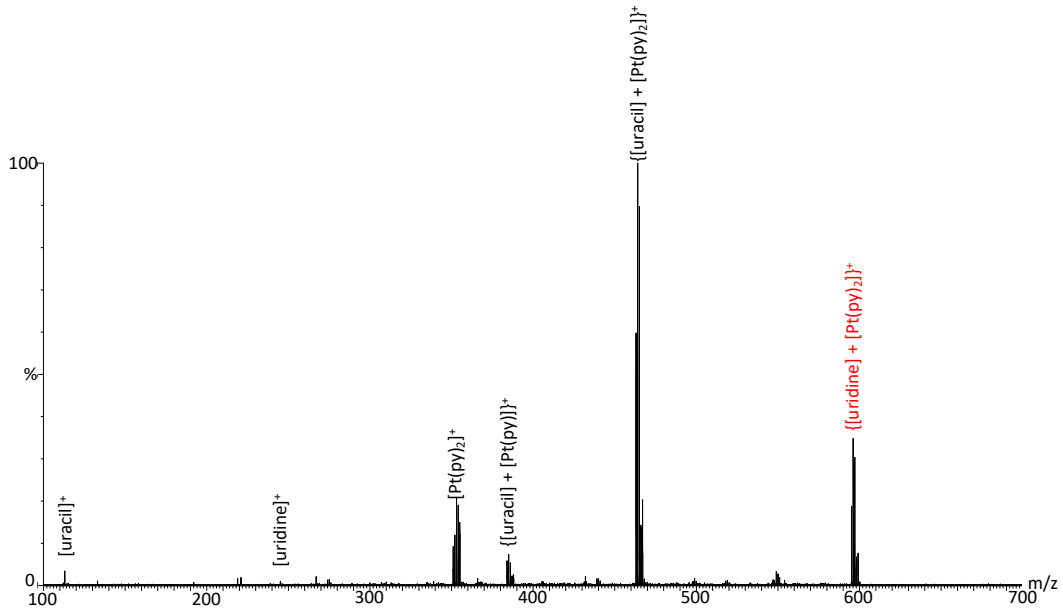

Figure S5. Tandem mass spectrum of $\{[Pt(py)_2] + [uridine]\}^+$ in the *m/z* range of 100 - 700 with the main peaks labeled and the parent ions highlighted in red. The corresponding MS/MS data are listed in Table S4.