Appendix A Supplementary material accompanying the manuscript

Dual action photosensitive platinum(II) anticancer prodrugs with photoreleasable azide ligands

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Table S1. Crystal data and structure refinement for **1b** and **2b**.

Identification code	**1b**	**2b**
CDDC deposit number	1879095	1879096
Empirical formula	$C_{16}H_{11}F_3N_6O_3PtS$	$C_{16}H_{11}N_5Pt$
Formula weight	619.46	468.39
Temperature/K	150(2)	150(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a/Å	13.7623(3)	8.41153(16)
b/Å	19.3858(3)	8.56115(18)
c/Å	6.83652(13)	10.7240(2)
α/°	90	72.6488(19)
β/°	99.3479(18)	67.3179(19)
γ/°	90	82.0845(17)
Volume/Å^3	1799.71(6)	679.88(3)
Z	4	2
ρ_{calc}g/cm^3	2.286	2.288
μ/mm^{-1}	7.977	10.322
F(000)	1176.0	440.0
Crystal size/mm^3	0.28 × 0.02 × 0.02 orange needle	0.3 × 0.1 × 0.1 yellow block
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.396 to 68.064	4.986 to 61.572
Index ranges	$-20 \leq h \leq 20$, $-30 \leq k \leq 29$, $-10 \leq l \leq 10$	$-11 \leq h \leq 12$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	56560	42702
Independent reflections	6961 [R_{int} = 0.0706, R_{sigma} = 0.0404]	4042 [R_{int} = 0.0362, R_{sigma} = 0.0179]
Data/restraints/parameters	6961/0/271	4042/0/199
Goodness-of-fit on F^2	1.061	1.050
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0302, wR_2 = 0.0581	R_1 = 0.0164, wR_2 = 0.0367
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.0623	R_1 = 0.0177, wR_2 = 0.0372
Largest diff. peak/hole/e Å^{-3}	2.21/-1.57	0.97/-1.12

Table S2. Photophysical data for **1a** and **2a**, **1b** and **2b** in PBS and ACN at 298 K.

Complex	Solvent	λ_{abs}/nm (ε_{max}/dm^{3}mol^{-1}cm^{-1})	λ_{em}/nm	Φ_{em}[a]
1a	PBS	278(20700), 327(10150), 344(8890), 374(2060)		
	ACN	270(sh, 19270), 280(25450), 304(9290), 317(10330), 330(14590), 347(8310), 376(2210), 392(2010)		
1b	PBS	278(22440), 327(11350), 344(9980), 374(2300)		
	ACN	254(sh, 23440), 284(18780), 308(10130), 324(11880), 338(15030), 427(2590)		
2a	PBS	276(14430), 284(14310), 324(8310), 390(4830), 420(sh, 3360)	483, 515, 550(sh)	0.032
	ACN	287(18870), 327(6060), 359(sh, 3950), 376(6090), 398(sh, 4780)	489, 521, 558(sh)	0.059
2b	PBS	274(14410), 285(14470), 325(9450), 387(6660), 420(sh, 5450)	483, 515, 556, 604	0.026
	ACN	286(20730), 330(6630), 359(sh, 4470), 377(6720), 398(sh, 6010)	494, 524, 557(sh)	0.038

[a] $Ru(bpy)_3Cl_2$ was used as a reference.[1]

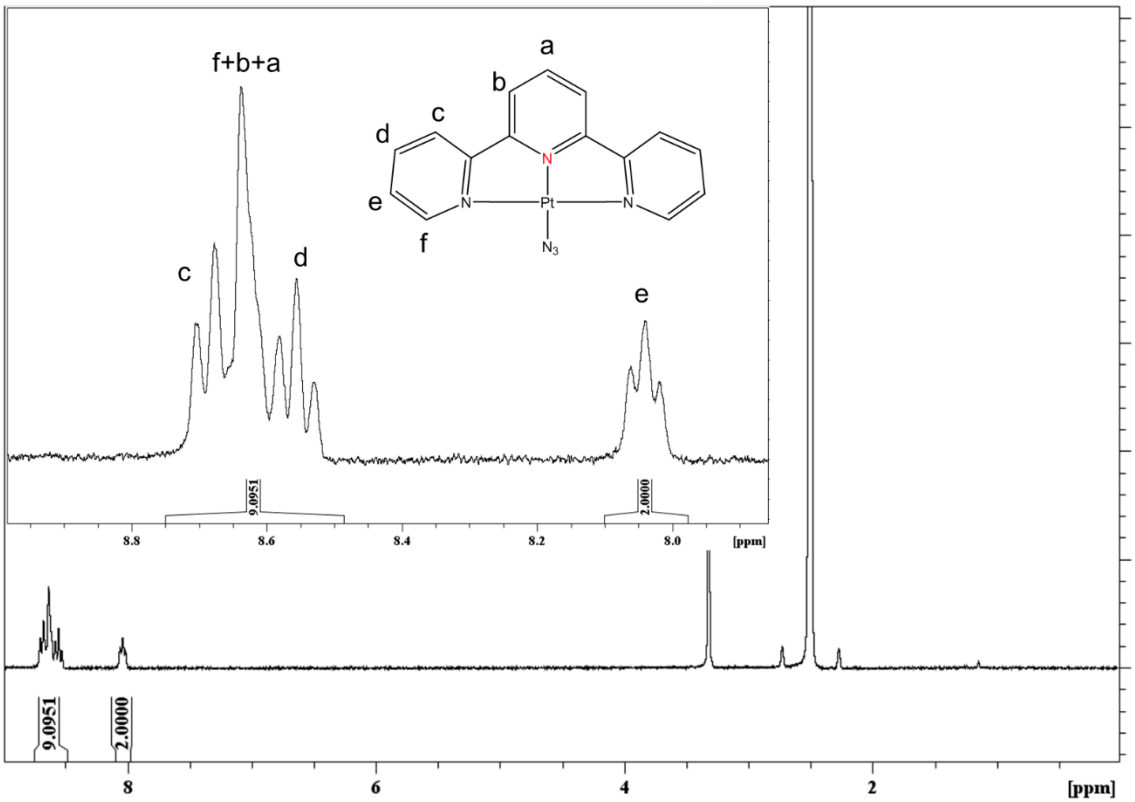

Figure S1. 300 MHz ^{1}H NMR spectrum of **1b** in DMSO-d_6 at 298 K.

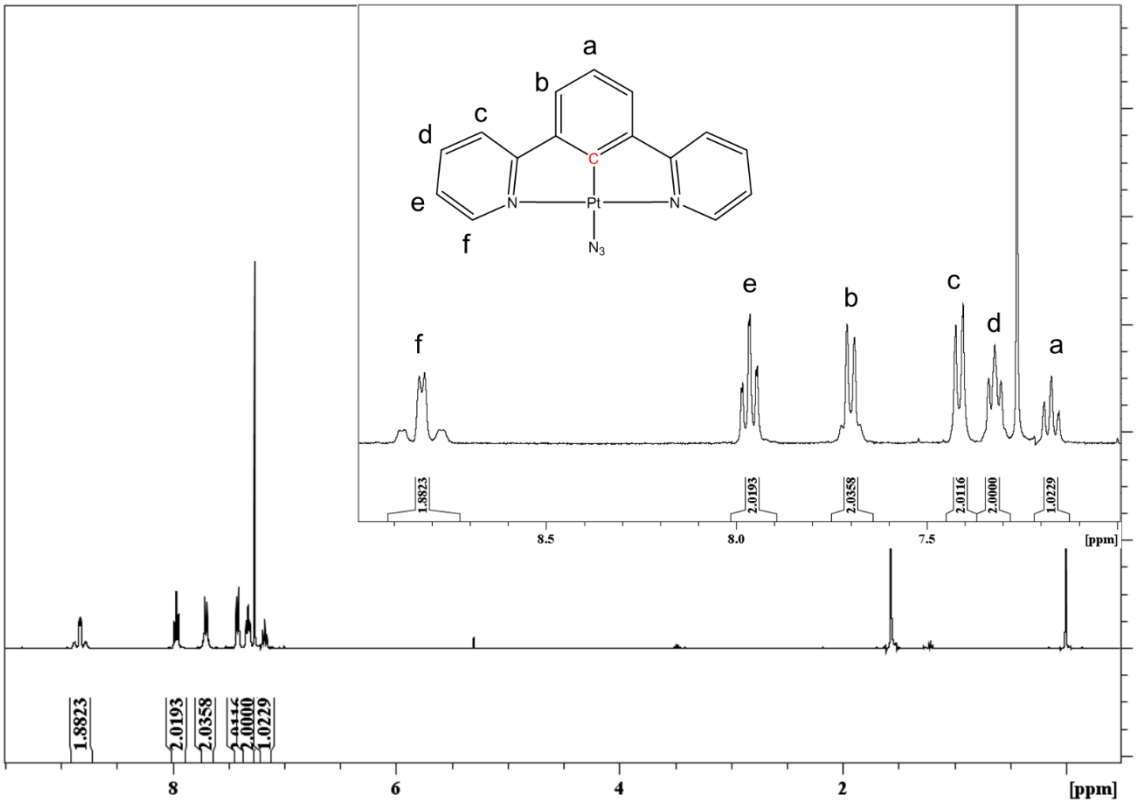

Figure S2. 400 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 298 K.

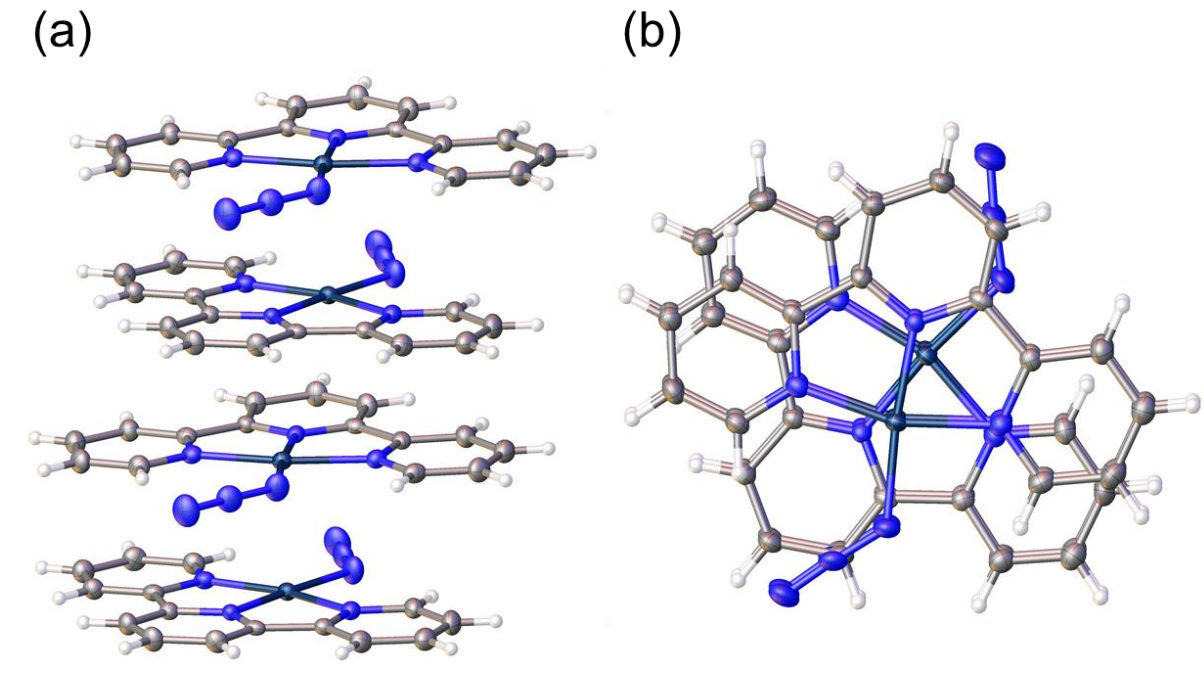

Figure S3. (a) π stack in the solid state structure of **1b**, and (b) π stacking viewed down the stacking axis.

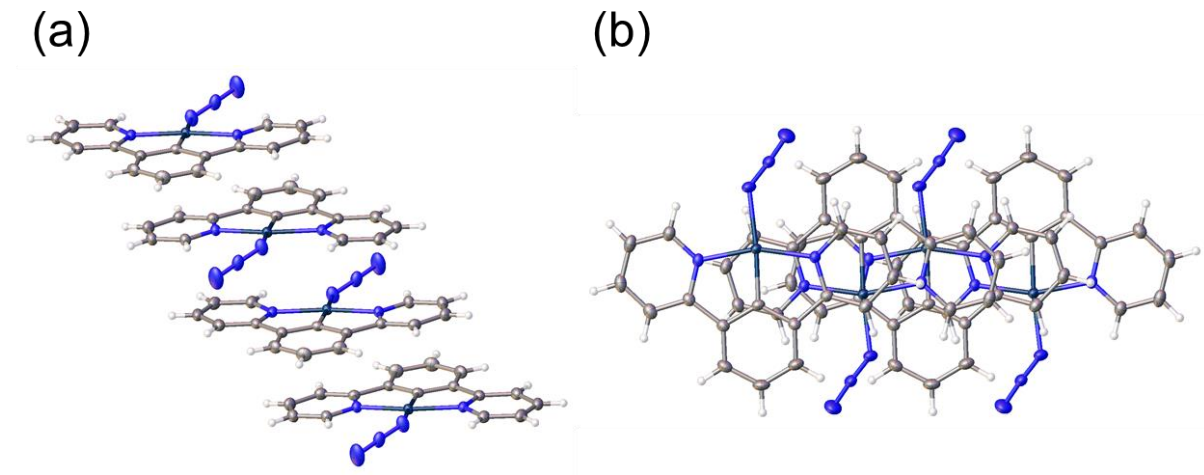

Figure S4. (a) π stack in the solid state structure of **2b**, and (b) π stacking viewed from above (molecules are viewed in the plane of the page and not looking directly down the stacking axis as each molecule is offset from the one above and below).

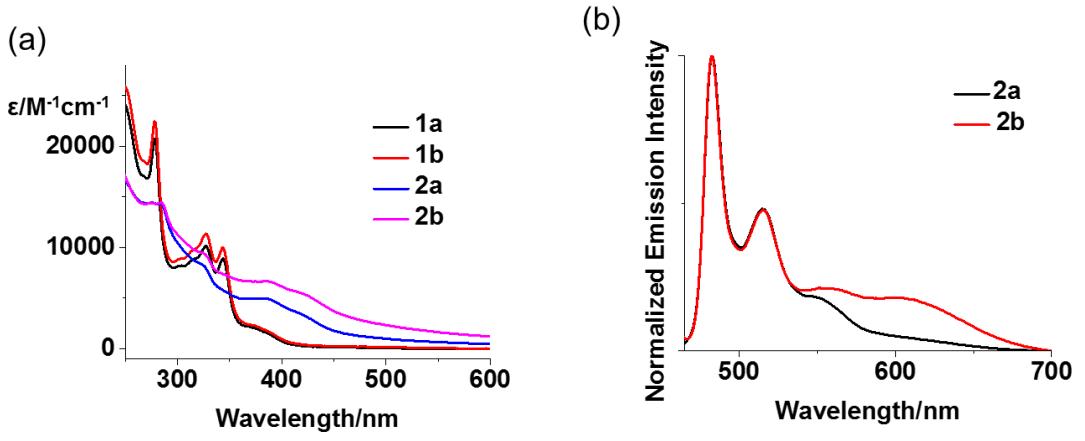

Figure S5. (a) Uv-vis absorption and (b) emission spectra of platinum(II) complexes in PBS.

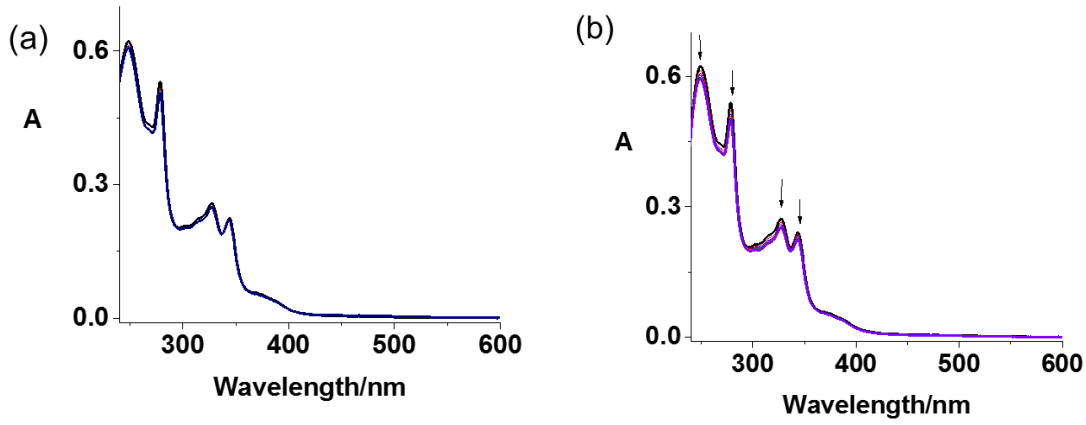

Figure S6. (a) Photochemical decomposition of **1a** and (b) **1b** in PBS determined by Uv-vis spectroscopy within 60 min (0, 5, 10, 20, 40, 60 min).

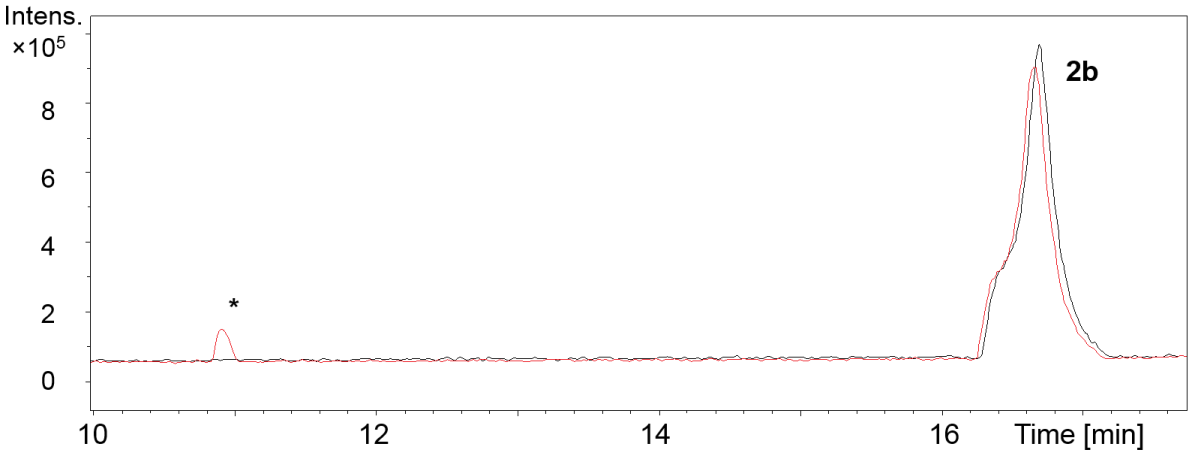

Figure S7. (a) LC-MS spectra of complex **2b** in PBS before (black) and after (red) irradiation with blue light (420 nm). * The species formed after irradiation with m/Z = 497.12.

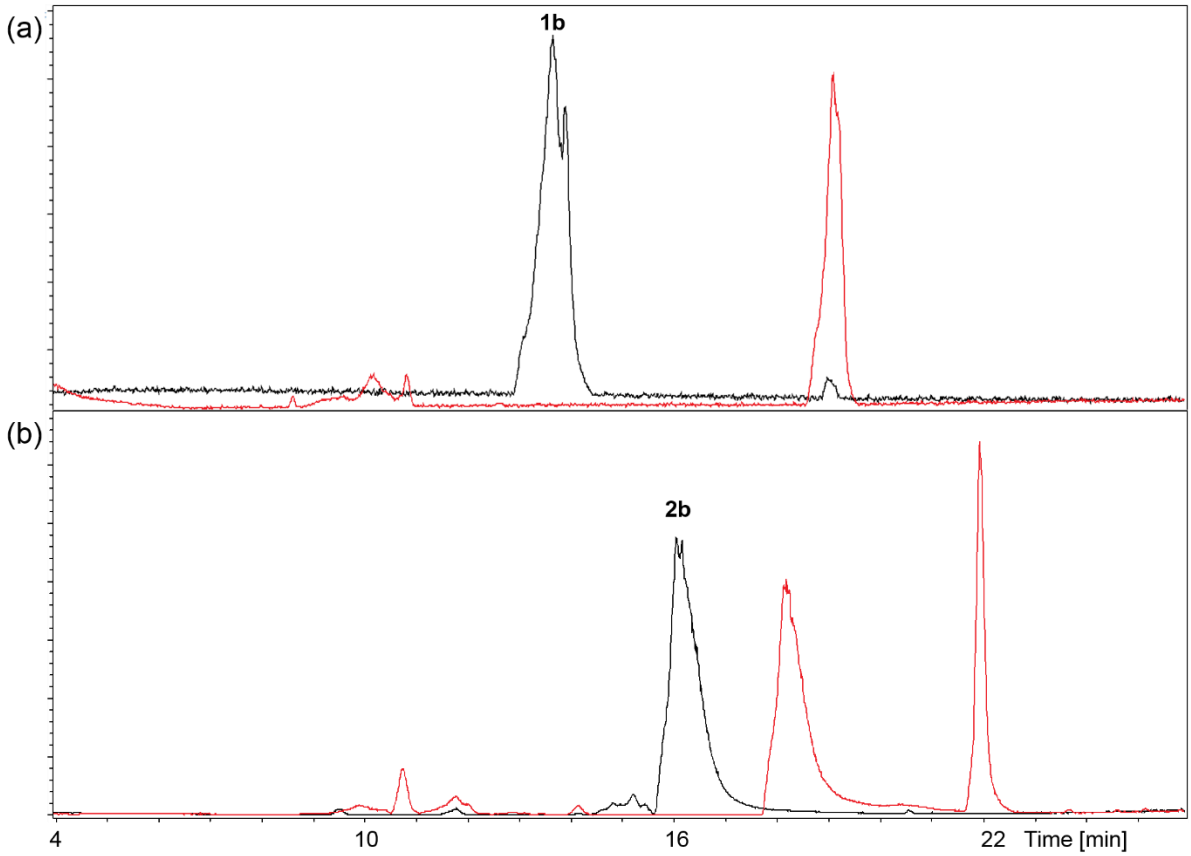

Figure S8. LC-MS spectra of complexes **1b** and **2b** in ACN before (black) and after (red) irradiation with blue light (420 nm).

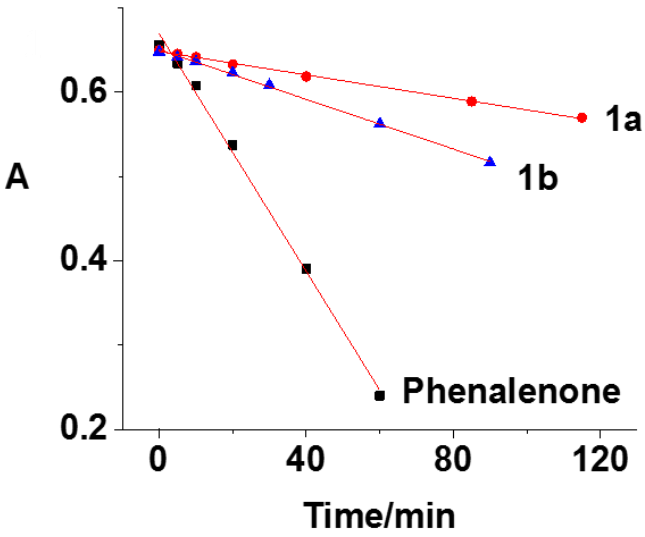

Figure S9. Plots of absorbance at 440 nm in PBS versus the irradiation times for complexes **1a**, **1b** and reference (phenalenone). The slope of the linear regression gives the singlet oxygen quantum yields.

Reference

1. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishic, S. Tobita, Phys. Chem. Chem. Phys. 11 (2009) 9850.