

Supplementary Material

Influence of initial speciation of platinum and palladium on their accumulation and toxicity towards phytoplankton

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Preparation of the AAP, AAP-rinse and AAP-EDTA medium

To prepare the AAP medium, five stock solutions were necessary (macronutrients #1 to #4 and micronutrients #1; Table S1). All five stock solutions were prepared in ultrapure water using high-purity chemicals. To prevent precipitation, the micronutrients solution was prepared in a 1% HNO₃ (v/v) solution. All solutions were filtered through a 0.2- μ m polycarbonate (PC) membrane under a laminar flow hood and then stored at 4°C. When preparing the growth media, all solutions were added to ultrapure water prior sterilisation at 121°C for 15 min, except for the micronutrients #1 and macronutrient #4 solutions. The two remaining solutions were sterilised by filtration to prevent metal precipitation at high temperature in the case of the micronutrients and to prevent CO₂ from degassing in the case of NaHCO₃. Both solutions were added to the medium under a laminar flow hood once cooled to room temperature.

Table S1. Composition and concentration (M) of AAP, AAP-rinse and AAP-EDTA medium.

Stock solution	Component	AAP	AAP-rinse	AAP-EDTA
Macronutrient #1	NaNO ₃	3.00×10 ⁻⁴	3.00×10 ⁻⁴	3.00×10 ⁻⁴
	MgCl ₂ ·6H ₂ O	5.98×10 ⁻⁵	5.98×10 ⁻⁵	5.98×10 ⁻⁵
	CaCl ₂ ·2H ₂ O	3.00×10 ⁻⁵	3.00×10 ⁻⁵	3.00×10 ⁻⁵
Macronutrient #2	MgSO ₄ ·7H ₂ O	5.92×10 ⁻⁵	5.92×10 ⁻⁵	5.92×10 ⁻⁵
Macronutrient #3	K ₂ HPO ₄	5.99×10 ⁻⁶	5.99×10 ⁻⁶	5.99×10 ⁻⁶
Macronutrient #4	NaHCO ₃	1.79×10 ⁻⁴	1.79×10 ⁻⁴	1.79×10 ⁻⁴
Micronutrients #1	H ₃ BO ₃	3.00×10 ⁻⁶	-	
	MnCl ₂ ·4H ₂ O	2.01×10 ⁻⁶		-
	ZnCl ₂	2.40×10 ⁻⁸		
	FeCl ₃ ·6H ₂ O	5.91×10 ⁻⁷		
	CoCl ₂ ·6H ₂ O	6.00×10 ⁻⁹		
	Na ₂ MoO ₄ ·2H ₂ O	3.00×10 ⁻⁸		
	CuCl ₂ ·2H ₂ O	7.04×10 ⁻¹¹		
	Na ₂ EDTA·2H ₂ O	8.06×10 ⁻⁷		

Table S2. Discrepancies between OECD (2011) guidelines for the testing of chemicals with freshwater algae and performed experiments.

Paragraph	Experimental
12	No reference substance was used to test the viability of our culture.
22	A geometric series was not used in the choice of the range of concentrations tested
29	Temperature (20.0 ± 0.1 °C) was lower than the recommended value but still in the recommended range of 21 to 24 °C when considering acceptable error for said recommended temperatures (21 ± 2 °C)
30	pH drifted by more than 1.5 unit in most Pt controls but no such drift was observed with Pd controls
31	Light intensity was slightly higher (121 ± 13 $\mu\text{E m}^{-2} \text{s}^{-1}$ compared to 60–120 $\mu\text{E m}^{-2} \text{s}^{-1}$ recommended)

Paragraph numbers in the Table refer to paragraph numbers in the original OECD report (OECD, 2011).

Table S3. Composition and concentration (M) of simplified growth medium (S-AAP)

Compound	[M] _{tot} (M)	[NaCl] (M)	[Na ₂ EDTA, 2 H ₂ O] (M)	[NaHCO ₃] (M)
(NH ₄) ₂ Pt ^{IV} Cl ₆	10 ⁻³	2.41×10 ⁻¹	1.44×10 ⁻⁵	1.79×10 ⁻⁴
(NO ₃) ₂ Pt ^{II} (NH ₃) ₄				
K ₂ Pt ^{II} Cl ₄	10 ⁻⁵	2.33×10 ⁻³	1.87×10 ⁻⁹	
(NO ₃) ₂ Pd(NH ₃) ₄	10 ⁻⁴	6.58×10 ⁻²	1.08×10 ⁻⁶	
H ₂ PdCl ₄	10 ⁻⁵	6.37×10 ⁻³	1.16×10 ⁻⁸	

Metal to ligand ratios were similar to those observed for the highest exposure concentrations, i.e. 30 $\mu\text{g Pd L}^{-1}$ (2.83×10^{-8} M) and 150 $\mu\text{g Pt L}^{-1}$ (7.69×10^{-7} M). Free EDTA⁴⁻ concentration in the AAP growth medium was calculated using MINEQL+ (Version 5.0).

Table S4. Rate constants used for kinetic simulation for the formation or dissociation of Pt^{II} chloro-complex and stability constants of Pt^{II} mono, di-hydroxo and tetra-amino complexes

Ligand	Equation	k_n (s ⁻¹ M ⁻¹)	k_{-n} (s ⁻¹)	log β_n
H ₂ O, Cl ^a	$\text{Pt}(\text{H}_2\text{O})_4^{2+} + \text{Cl}^- \xrightleftharpoons[k_{-1}]{k_1} \text{PtCl}(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	2.66×10 ⁻²	2.8×10 ⁻⁷	4.98
	$\text{PtCl}(\text{H}_2\text{O})_3^+ + \text{Cl}^- \xrightleftharpoons[k_{-2,\text{cis}}]{k_{2,\text{cis}}} \text{PtCl}_2(\text{H}_2\text{O})_{2,\text{cis}} + \text{H}_2\text{O}$	2×10 ⁻³	3×10 ⁻⁷	8.80
	$\text{PtCl}(\text{H}_2\text{O})_3^+ + \text{Cl}^- \xrightleftharpoons[k_{-2,\text{trans}}]{k_{2,\text{trans}}} \text{PtCl}_2(\text{H}_2\text{O})_{2,\text{trans}} + \text{H}_2\text{O}$	0.46	3×10 ⁻²	6.16
	$\text{PtCl}_2(\text{H}_2\text{O})_{2,\text{cis}} + \text{Cl}^- \xrightleftharpoons[k_{-3,\text{cis}}]{k_{3,\text{cis}}} \text{PtCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O}$	7.5×10 ⁻²	6×10 ⁻⁵	11.90
	$\text{PtCl}_2(\text{H}_2\text{O})_{2,\text{trans}} + \text{Cl}^- \xrightleftharpoons[k_{-3,\text{trans}}]{k_{3,\text{trans}}} \text{PtCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O}$	5.83×10 ⁻⁵	2.8×10 ⁻⁸	9.48
	$\text{PtCl}_3(\text{H}_2\text{O})^- + \text{Cl}^- \xrightleftharpoons[k_{-4}]{k_4} \text{PtCl}_4^{2-} + \text{H}_2\text{O}$	2.8×10 ⁻³	3.6×10 ⁻⁵	13.79
H ₂ O, OH ^b	$\text{Pt}(\text{H}_2\text{O})_4^{2+} + \text{OH}^- \xrightleftharpoons[k_{-1,\text{OH}}]{k_{1,\text{OH}}} \text{Pt}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	-	-	14.2
	$\text{Pt}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{OH}^- \xrightleftharpoons[k_{2,\text{OH}}]{k_{2,\text{OH}}} \text{Pt}(\text{OH})_2(\text{H}_2\text{O})_2^+ + \text{H}_2\text{O}$	-	-	28.3
H ₂ O, NH ₃ ^c	$\text{Pt}(\text{H}_2\text{O})_4^{2+} + 4\text{NH}_3 \xrightleftharpoons{\quad} \text{Pt}(\text{NH}_3)_4^{2+} + 4\text{H}_2\text{O}$	-	-	35.3

^a Elding (1970)

^b Wood *et al.* (1989)

^c Grinberg & Gelfman (1960)

Table S5. Rate constants used for kinetic simulations for the formation or dissociation of Pd chloro-complexes.

Ligand	Equation	k_n ($s^{-1} M^{-1}$)	k_{-n} (s^{-1})	$\log \beta_n$
H ₂ O, Cl ^a	$\text{Pd}(\text{H}_2\text{O})_4^{2+} + \text{Cl}^- \xrightleftharpoons[k_{-1}]{k_1} \text{PdCl}(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	1.83×10 ⁴	0.83	4.34
	$\text{PdCl}(\text{H}_2\text{O})_3^+ + \text{Cl}^- \xrightleftharpoons[k_{-2,\text{cis}}]{k_{2,\text{cis}}} \text{PdCl}_2(\text{H}_2\text{O})_{2,\text{cis}} + \text{H}_2\text{O}$	510	0.37	7.48
	$\text{PdCl}(\text{H}_2\text{O})_3^+ + \text{Cl}^- \xrightleftharpoons[k_{-2,\text{trans}}]{k_{2,\text{trans}}} \text{PdCl}_2(\text{H}_2\text{O})_{2,\text{trans}} + \text{H}_2\text{O}$	3.5×10 ⁴	56	7.14
	$\text{PdCl}_2(\text{H}_2\text{O})_{2,\text{cis}} + \text{Cl}^- \xrightleftharpoons[k_{-3,\text{cis}}]{k_{3,\text{cis}}} \text{PdCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O}$	5400	0.0027	12.78
	$\text{PdCl}_2(\text{H}_2\text{O})_{2,\text{trans}} + \text{Cl}^- \xrightleftharpoons[k_{-3,\text{trans}}]{k_{3,\text{trans}}} \text{PdCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O}$	21.7	2.7×10 ⁻²	10.04
	$\text{PdCl}_3(\text{H}_2\text{O})^- + \text{Cl}^- \xrightleftharpoons[k_{-4}]{k_4} \text{PdCl}_4^{2-} + \text{H}_2\text{O}$	180	8.9	14.04
H ₂ O, OH ^b	$\text{Pd}(\text{H}_2\text{O})_4^{2+} + \text{OH}^- \xrightleftharpoons[k_{-1,\text{OH}}]{k_{1,\text{OH}}} \text{Pd}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	-	-	11.7
	$\text{Pd}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{OH}^- \xrightleftharpoons[k_{2,\text{OH}}]{k_{2,\text{OH}}} \text{Pd}(\text{OH})_2(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	-	-	23.6

^a Reinhardt & Graham (1976)

^b Wood *et al.* (1989)

Table S6. Rate constants used for kinetic simulation for the formation or dissociation of Pd amino-complexes.

Ligand	Equation	k_n (s ⁻¹ M ⁻¹)	k_{-n} (s ⁻¹)	log β_n
H ₂ O, NH ₃ ^{a,b}	$\text{Pd}(\text{H}_2\text{O})_4^{2+} + \text{NH}_3 \xrightleftharpoons[k_{-1,\text{NH}_3}]{k_{1,\text{NH}_3}} \text{Pd}(\text{NH}_3)(\text{H}_2\text{O})_3^{2+} + \text{H}_2\text{O}$	13×10 ³	0.13×10 ⁻⁴	9.0
	$\text{Pd}(\text{NH}_3)(\text{H}_2\text{O})_3^{2+} + \text{NH}_3 \xrightleftharpoons[k_{-2(\text{cis}),\text{NH}_3}]{k_{2(\text{cis}),\text{NH}_3}} \text{Pd}(\text{NH}_3)_2(\text{H}_2\text{O})_{2(\text{cis})}^{2+} + \text{H}_2\text{O}$	21×10 ³	0.26×10 ⁻⁴	17.9
	$\text{Pd}(\text{NH}_3)_2(\text{H}_2\text{O})_{2(\text{cis})}^{2+} + \text{NH}_3 \xrightleftharpoons[k_{-3(\text{cis}),\text{NH}_3}]{k_{3(\text{cis}),\text{NH}_3}} \text{Pd}(\text{NH}_3)_3(\text{H}_2\text{O})^{2+} + \text{H}_2\text{O}$	6.7×10 ³	2.1×10 ⁻⁴	25.4 ²
	$\text{Pd}(\text{NH}_3)_3(\text{H}_2\text{O})^{2+} + \text{NH}_3 \xrightleftharpoons[k_{-4,\text{NH}_3}]{k_{4,\text{NH}_3}} \text{Pd}(\text{NH}_3)_4^{2+} + \text{H}_2\text{O}$	7×10 ³	2.75×10 ⁻⁴	32.8
H ₂ O, OH ^{-c}	$\text{Pd}(\text{H}_2\text{O})_4^{2+} + \text{OH}^- \xrightleftharpoons[k_{-1,\text{OH}}]{k_{1,\text{OH}}} \text{Pd}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$	-	-	11.7
	$\text{Pd}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{OH}^- \xrightleftharpoons[k_{2,\text{OH}}]{k_{2,\text{OH}}} \text{Pd}(\text{OH})_2(\text{H}_2\text{O})_2^+ + \text{H}_2\text{O}$	-	-	23.6
NH ₃ , H ^{+d}	$\text{NH}_3 + \text{H}^+ \xrightleftharpoons[k_{-\text{H},\text{NH}_3}]{k_{\text{H},\text{NH}_3}} \text{NH}_4^+$	4.3×10 ¹⁰	24.2	9.25

^a Reinhardt & Graham (1976)

^b DeBerry & Reinhardt (1972)

^c Wood *et al.* (1989)

^d Eigen (1964)

Table S7. pH measured every 24 h for all platinum algal exposure conditions.

Complex	[Pt] nominal in $\mu\text{g L}^{-1}$ (in M)	Replicate	Time (hours)				
			0	24	48	72	96
Pt^{IV}Cl₆²⁻	0	1	7.25	7.00	7.15	7.33	7.25
		2	7.24	7.06	7.12	7.53	7.42
		3	7.23	7.06	7.08	7.33	7.28
	10 (5.13×10^{-8})	1	7.23	6.93	7.03	7.17	7.06
		2	7.25	6.95	7.02	7.41	7.25
		3	7.23	7.06	7.03	7.54	7.27
	30 (1.54×10^{-7})	1	7.27	6.97	6.99	7.07	7.01
		2	7.12	7.07	7.13	7.07	7.02
		3	7.35	7.11	7.15	7.18	7.06
	50 (2.56×10^{-7})	1	7.19	7.03	7.11	7.19	7.08
		2	7.22	7.02	7.20	7.53	7.72
		3	7.14	7.15	7.17	7.42	7.40
	100 (5.13×10^{-7})	1	7.26	7.14	7.04	7.22	7.30
		2	7.25	6.97	7.08	7.11	7.15
		3	7.25	7.11	7.03	7.09	7.13
150 (7.69×10^{-7})	1	7.23	7.03	6.94	6.95	7.02	
	2	7.16	7.00	6.99	7.01	7.05	
	3	7.19	7.03	6.99	7.10	7.09	
Pt^{II}(NH₃)₄²⁺	0	1	7.27	7.22	7.19	7.32	7.20
		2	7.20	7.24	7.32	8.57	8.78
		3	7.20	7.27	7.26	7.35	7.59
	10 (5.13×10^{-8})	1	7.26	7.23	7.33	8.79	8.07
		2	7.15	7.19	7.18	7.39	7.48
		3	7.14	7.21	7.34	7.55	7.42
	30 (1.54×10^{-7})	1	7.16	7.15	7.29	7.41	7.41
		2	7.11	7.22	7.34	7.87	7.63
		3	7.19	7.20	7.38	7.64	7.58
	50 (2.56×10^{-7})	1	7.19	7.13	7.21	7.38	7.55
		2	7.14	7.22	7.32	8.00	7.71
		3	7.23	7.18	7.42	7.78	7.50
	100 (5.13×10^{-7})	1	7.16	7.14	7.26	7.36	7.42
		2	7.22	7.12	7.34	7.61	7.45
		3	7.19	7.24	7.39	7.67	7.44
150 (7.69×10^{-7})	1	7.19	7.17	7.26	7.18	7.40	
	2	7.14	7.12	7.42	8.55	8.49	
	3	7.10	7.16	7.34	7.49	7.72	
Pt^{II}Cl₄²⁻	0	1	7.12	7.13	7.36	7.75	8.58
		2	7.23	7.21	7.41	8.10	8.90
		3	7.27	7.29	7.49	8.27	8.74
	10 (5.13×10^{-8})	1	7.21	7.16	7.26	7.63	7.90
		2	7.22	7.15	7.33	7.96	8.54
		3	7.24	7.11	7.27	8.13	8.28
	30 (1.54×10^{-7})	1	7.23	7.06	7.20	7.80	8.46
		2	7.19	7.16	7.33	7.66	7.76
		3	7.13	7.27	7.42	8.18	8.66
	50 (2.56×10^{-7})	1	7.28	7.19	7.26	7.58	8.92
		2	7.18	7.18	7.30	7.70	8.74
		3	7.20	7.27	7.38	8.09	9.02
	100 (5.13×10^{-7})	1	7.10	7.17	7.26	7.43	7.47
		2	7.23	7.12	7.32	7.48	7.91
		3	7.27	7.18	7.34	7.77	8.70
150 (7.69×10^{-7})	1	7.18	7.12	7.24	7.28	7.84	
	2	7.20	7.16	7.23	7.42	7.74	
	3	7.14	7.15	7.22	7.50	7.48	

Table S8. pH measured every 24 h for all palladium algal exposure conditions.

Complex	[Pt] nominal in $\mu\text{g L}^{-1}$ (in M)	Replicate	pH versus time (Hours)				
			0	24	48	72	96
$\text{Pd}^{\text{II}}(\text{NH}_3)_4^{2+}$	0	1	7.24	7.09	7.14	7.21	7.32
		2	7.24	7.17	7.22	7.26	7.30
		3	7.23	7.14	7.28	7.32	7.44
	0.5 (4.72×10^{-9})	1	7.21	7.11	7.11	7.17	7.36
		2	7.18	7.20	7.20	7.20	7.30
		3	7.17	7.17	7.17	7.19	7.24
	2 (1.89×10^{-8})	1	7.16	7.14	7.05	7.11	7.29
		2	7.16	7.17	7.18	7.24	7.31
		3	7.14	7.18	7.14	7.28	7.34
	5 (4.72×10^{-8})	1	7.19	7.11	7.09	7.19	7.45
		2	7.18	7.01	7.02	7.10	7.19
		3	7.17	7.01	7.04	7.19	7.26
	10 (9.43×10^{-8})	1	7.19	7.09	7.06	7.07	7.24
		2	7.20	7.17	7.14	7.33	7.39
		3	7.21	7.13	7.15	7.16	7.25
20 (1.89×10^{-7})	1	7.21	7.09	7.08	7.10	7.26	
	2	7.18	7.12	7.09	7.11	7.21	
	3	7.20	7.15	7.13	7.16	7.22	
30 (2.83×10^{-7})	1	7.17	7.10	7.11	7.13	7.25	
	2	7.18	7.15	7.16	7.14	7.23	
	3	7.16	7.13	7.14	7.21	7.31	
$\text{Pd}^{\text{II}}\text{Cl}_4^{2-}$	0	1	7.16	7.17	7.17	7.33	7.28
		2	7.17	7.14	7.21	7.30	7.31
		3	7.22	7.21	7.27	7.35	7.32
	0.5 (4.72×10^{-9})	1	7.25	7.17	7.16	7.33	7.16
		2	7.24	7.17	7.15	7.22	7.40
		3	7.22	7.19	7.27	7.58	7.48
	2 (1.89×10^{-8})	1	7.20	7.15	7.17	7.32	7.23
		2	7.20	7.21	7.20	7.30	7.33
		3	7.25	7.17	7.18	7.35	7.37
	5 (4.72×10^{-8})	1	7.25	7.11	7.12	7.31	7.92
		2	7.24	7.16	7.18	7.32	7.55
		3	7.18	7.18	7.17	7.20	7.40
	10 (9.43×10^{-8})	1	7.18	7.13	7.15	7.09	7.27
		2	7.16	7.15	7.17	7.13	7.17
		3	7.23	7.12	7.19	7.13	7.18
20 (1.89×10^{-7})	1	7.18	7.13	7.11	7.08	7.15	
	2	7.23	7.18	7.18	7.11	7.15	
	3	7.25	7.15	7.12	7.15	7.18	
30 (2.83×10^{-7})	1	7.19	7.11	7.11	7.11	7.18	
	2	7.15	7.15	7.15	7.07	7.16	
	3	7.26	7.14	7.17	7.14	7.18	

Table S9. OECD validation criteria for all platinum and palladium experiments.

Compound	Replicate	Specific growth rate (d ⁻¹) at t72	Mean coefficient of variation for section-by-section specific growth rate	Coefficient of variation of average specific growth rates at t72
(NH ₄) ₂ Pt ^{IV} Cl ₆	1	0.96	17%	4%
	2	1.04		
	3	0.95		
(NO ₃) ₂ Pt ^{II} (NH ₃) ₄	1	1.19	8%	6%
	2	1.34		
	3	1.17		
K ₂ Pt ^{II} Cl ₄	1	1.13	5%	1%
	2	1.15		
	3	1.15		
(NO ₃) ₂ Pd(NH ₃) ₄	1	1.09	8%	1%
	2	1.07		
	3	1.10		
H ₂ PdCl ₄	1	1.02	5%	6%
	2	0.91		
	3	1.09		

Table S10. Maximal absorbances of the studied chloro- and amino-Pt and Pd complexes

Complex	Conditions	λ_{\max} (nm)	Reference
Pt ^{II} Cl ₄ ²⁻	[Pt] _{tot} = 1 x 10 ⁻³ M [NaCl] = 6.5 x 10 ⁻³ M [NaBr] = 1.5 x 10 ⁻³ M [HCl] = 2.0 x 10 ⁻³ M	217	Van Wyk <i>et al.</i> (2011)
	[H ₂ PtCl ₄] = 1 x 10 ⁻² M [HCl] = 1 M	217	This work
Pt ^{IV} Cl ₆ ²⁻	[H ₂ PtBr ₆] = 5 x 10 ⁻⁴ M [H ₂ PtCl ₆] = 5 x 10 ⁻⁴ M [HClO ₄] = 1 x 10 ⁻³ M	262 (ϵ = 24370 M ⁻¹ L ⁻¹ cm ⁻¹)	Van Wyk <i>et al.</i> (2011)
	[(NH ₄) ₂ PtCl ₆] = 5 x 10 ⁻³ M [HCl] = 1 M	262	This work
Pt ^{II} (NH ₃) ₄ ²⁺	[(ClO ₄) ₂ Pt(NH ₃) ₄] = N.A. [HClO ₄] = 1 x 10 ⁻¹ M	284 (ϵ = 44 M ⁻¹ L ⁻¹ cm ⁻¹)	Mason (1986)
	[(NO ₃) ₂ Pt(NH ₃) ₄] = 9 x 10 ⁻⁴ M	286	This work
Pd ^{II} Cl ₄ ²⁻	[PdCl ₄ ²⁻] = 5 x 10 ⁻⁴ M [HCl] = 0.1 M pH = 1	223 (ϵ = 19390 M ⁻¹ L ⁻¹ cm ⁻¹) 279 (ϵ = 5980 M ⁻¹ L ⁻¹ cm ⁻¹)	Wojnicki <i>et al.</i> (2011)
	[H ₂ PdCl ₄] = 1 x 10 ⁻⁵ M	222	This work
	[HCl] = 1 M	281	
Pd ^{II} (NH ₃) ₄ ²⁺	[K ₂ Pd]Cl ₄] = 0.5 M [NH ₃] = 10 M [NaClO ₄] = 1 M	295 (ϵ = 200 M ⁻¹ L ⁻¹ cm ⁻¹)	Rasmussen & Jørgensen (1968)

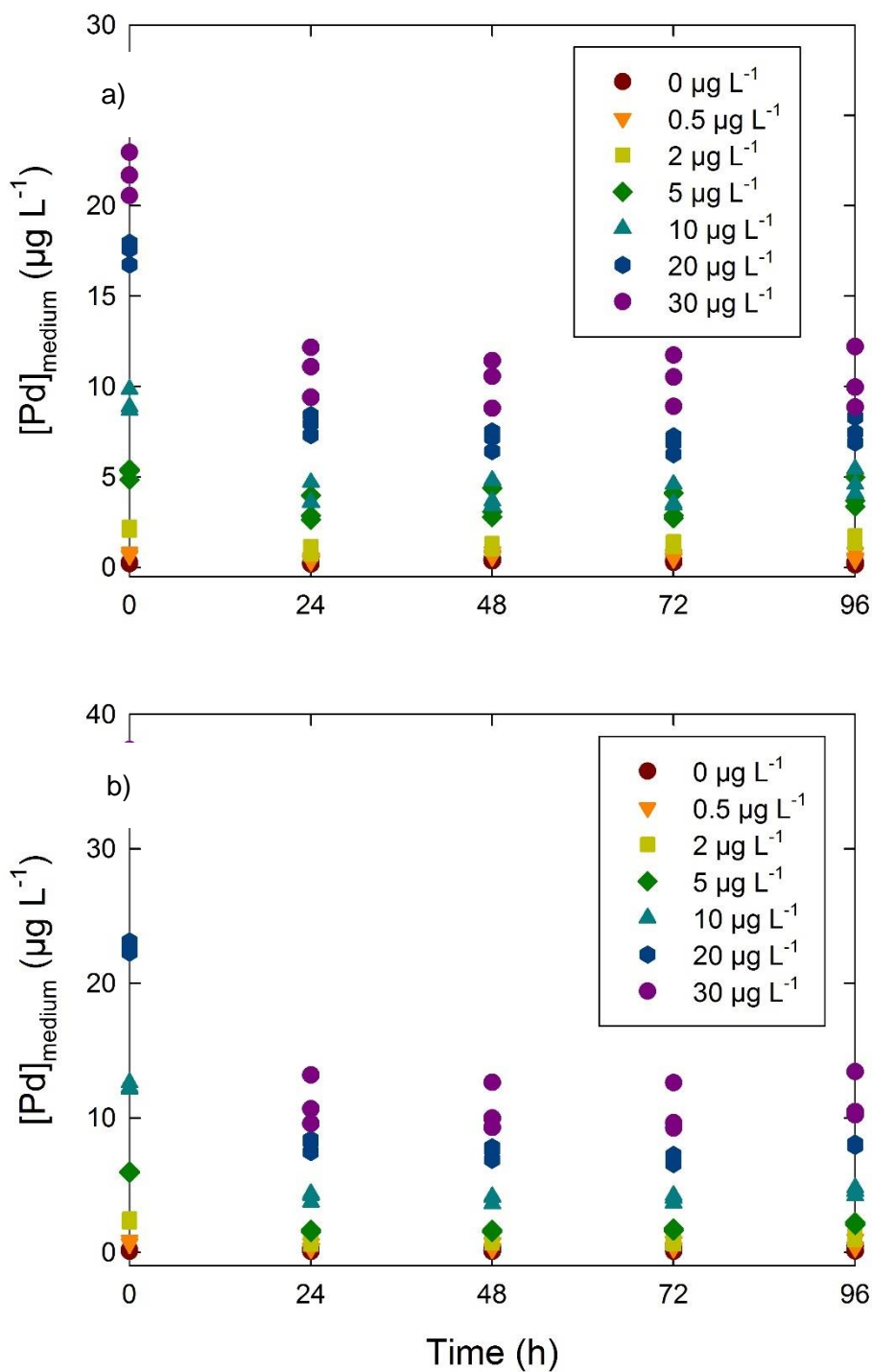


Figure S1. $[Pd]_{\text{tot}}$ measured in AAP medium over the duration of algae exposures (96 h) for different initial concentration (inset) of a) $Pd^{II}Cl_4^{2-}$ and b) $Pd^{II}(NH_3)_4^{2+}$.

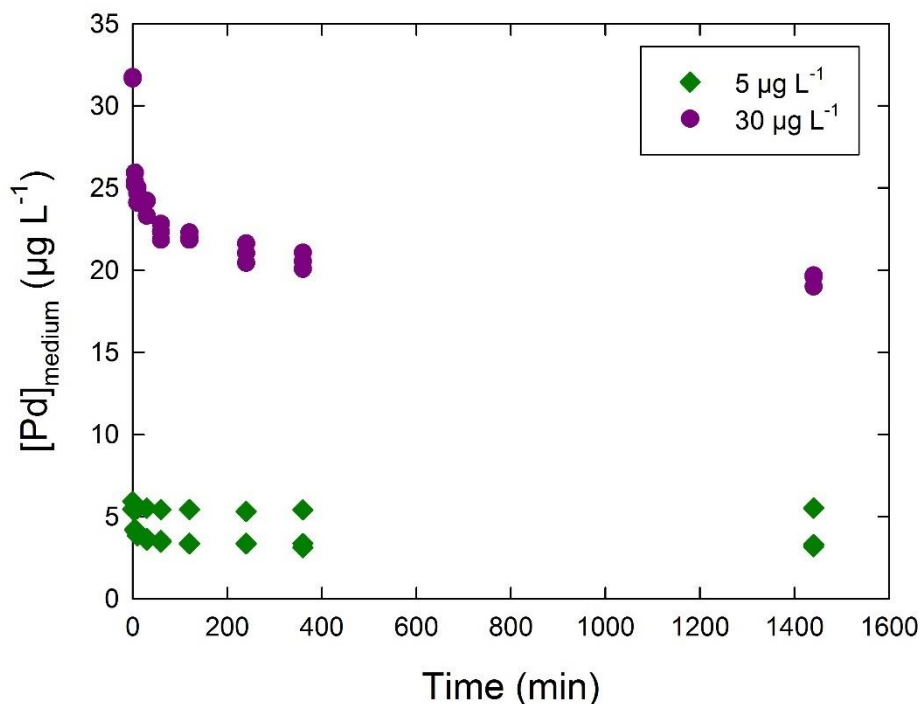


Figure S2. Total palladium concentrations over time in the absence of *R. subcapitata* at 5 and 30 µg L⁻¹ PdCl₄²⁻ initial concentration performed in triplicates.

Construction of theoretical absorbance spectra

The analysis of a mixture can be made by spectrophotometry using the following Beer–Lambert law:

$$A_{\lambda} = \epsilon_{\lambda} I C$$

where A_{λ} is the absorbance at the wavelength λ , ϵ_{λ} the absorptivity (mol⁻¹ L cm⁻¹) at the same wavelength λ , C the molar concentration of the absorbing solute (mol L⁻¹) and I the light path length (cm). This law is additive. The total absorbance of several absorbing component is thus equal to the sum of the absorbances of each species. Knowing the absorptivity of each species and their concentration under given experimental conditions (calculated here using the stability constants), the absorbance of the solution can be calculated. The electronic spectra of the complexes studied were reconstructed from literature data (Cox *et al.*, 1972; Elding & Olsson, 1978; Girard *et al.*, 2016) (Figure S3). The absorbance spectra of Pt and Pd species used in the exposure experiments were then calculated using the absorptivity found in the literature and their concentrations. In the case of the amino-Pt complex used ((NO₃)₂Pt^{II}(NH₃)₄), two absorbing species in solution at the initial time (Pt(NH₃)₄²⁺ and NO₃²⁻) were considered (Figure S3).

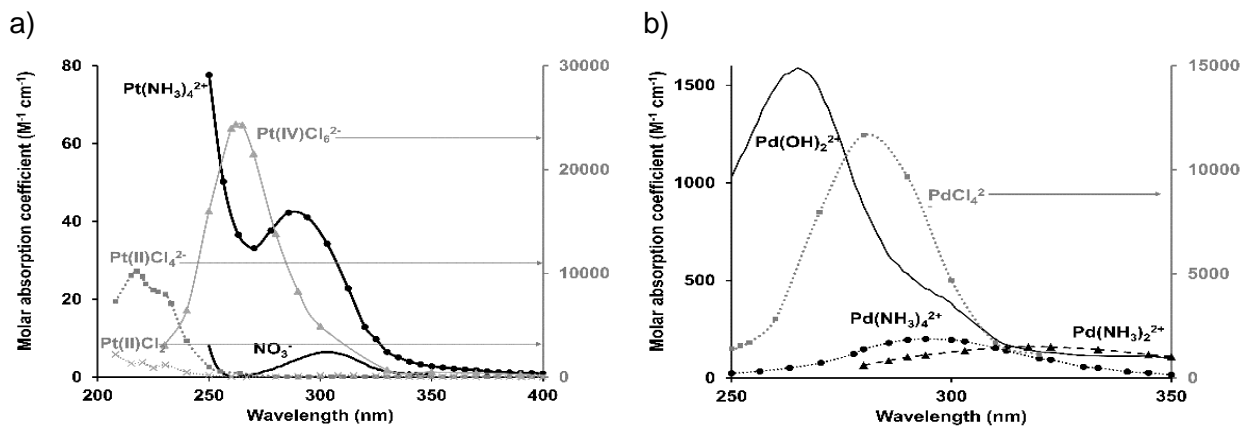


Figure S3. Absorptivity of chloro- and amino-complexes of platinum and palladium in water.

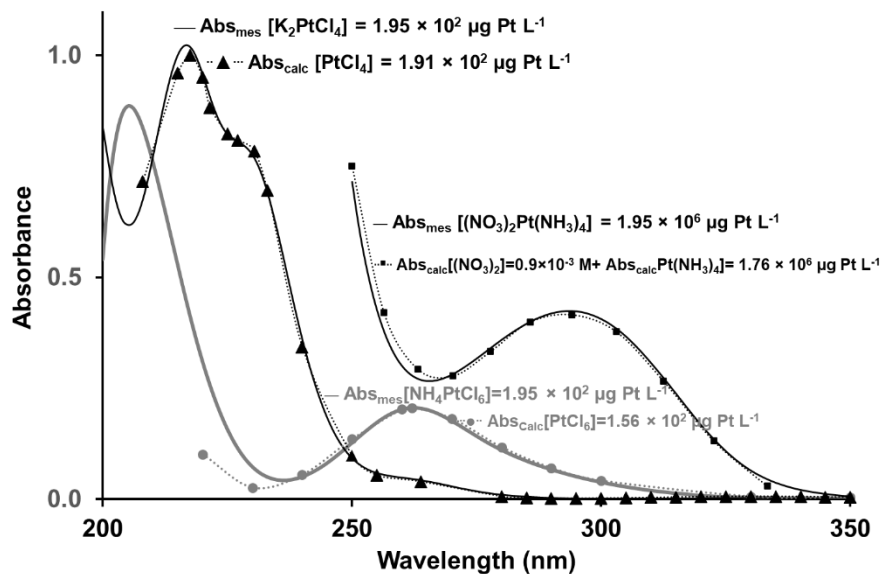


Figure S4. Experimental and calculated absorbance spectrum in water of $[K_2Pt^{II}Cl_4] = 1.92 \times 10^2 \mu g Pt L^{-1}$, $[HCl] = 1 M$, $l = 10 cm$; $[(NH_4)_2Pt^{IV}Cl_6] = 1.95 \times 10^2 \mu g Pt L^{-1}$, $[HCl] = 1 M$, $l = 1 cm$ and $[(NO_3)_2Pt^{II}(NH_3)_4]_{tot} = 1.95 \times 10^6 \mu g Pt L^{-1}$, $[HCl] = 1 M$, $l = 1 cm$ using absorptivity from Figure S3a.

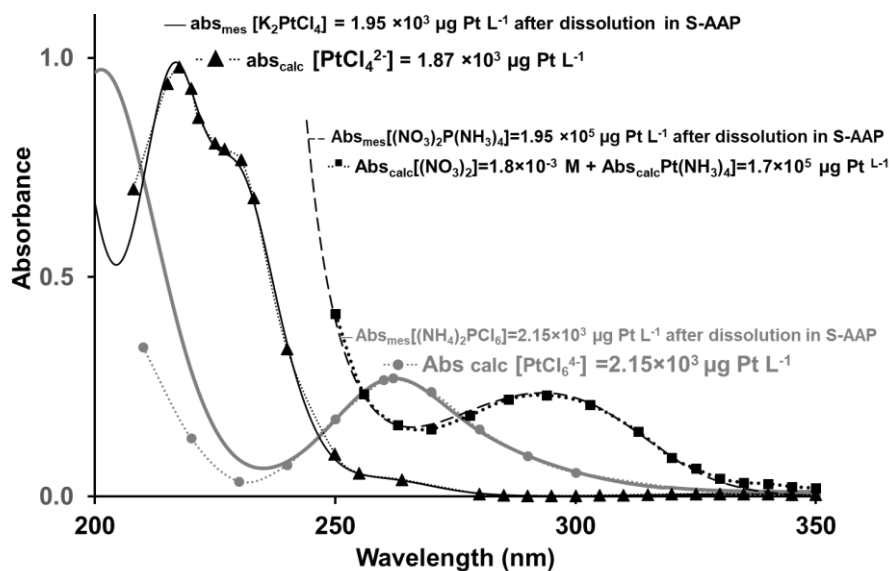


Figure S5. Experimental and calculated absorbance spectrum in the S-AAP medium measured after dissolution of $[K_2Pt^{II}Cl_4] = 1.95 \times 10^3 \mu\text{g Pt L}^{-1}$, $l = 10 \text{ cm}$; $[(NH_4)_2Pt^{IV}Cl_6] = 1.95 \times 10^2 \mu\text{g Pt L}^{-1}$, $l = 1 \text{ cm}$ and $[(NO_3)_2Pt^{II}(NH_3)_4]_{\text{tot}} = 1.95 \times 10^5 \mu\text{g Pt L}^{-1}$, $l = 5 \text{ cm}$ using absorptivity from Figure S3a.

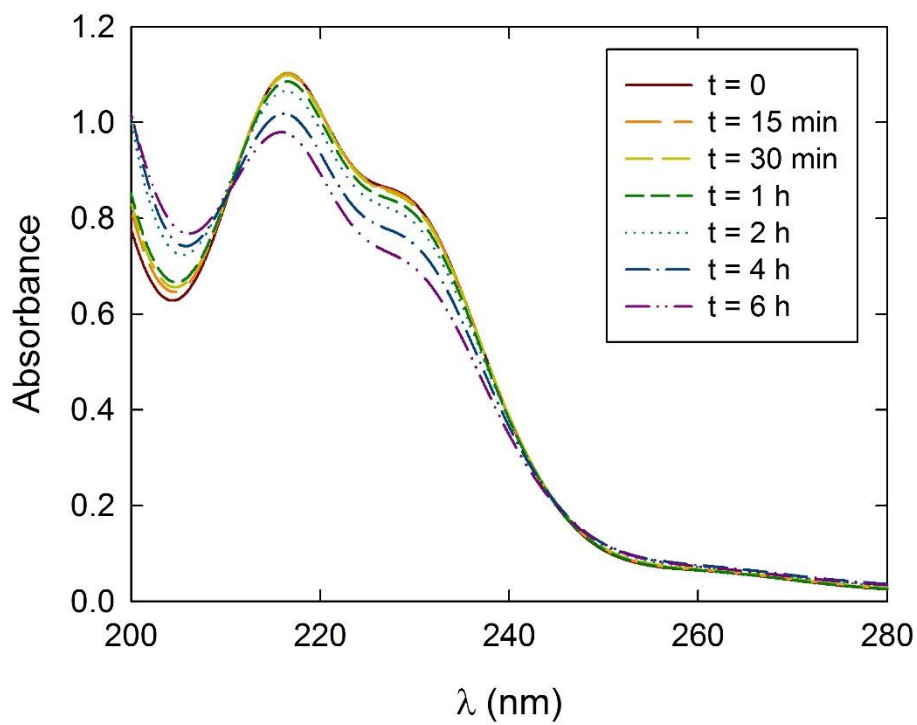


Figure S6. Absorbance spectrum for $[Pt^{II}Cl_4^{2-}]_0 = 10 \mu M$ in S-AAP exposed to light. Absorbance was monitored over a 6 h period. Although $Pt^{II}Cl_4^{2-}$ is still the dominant species in solution signs of re-speciation are visible as soon as 2 h after preparation of solution, pathlength = 10 cm, room temperature.

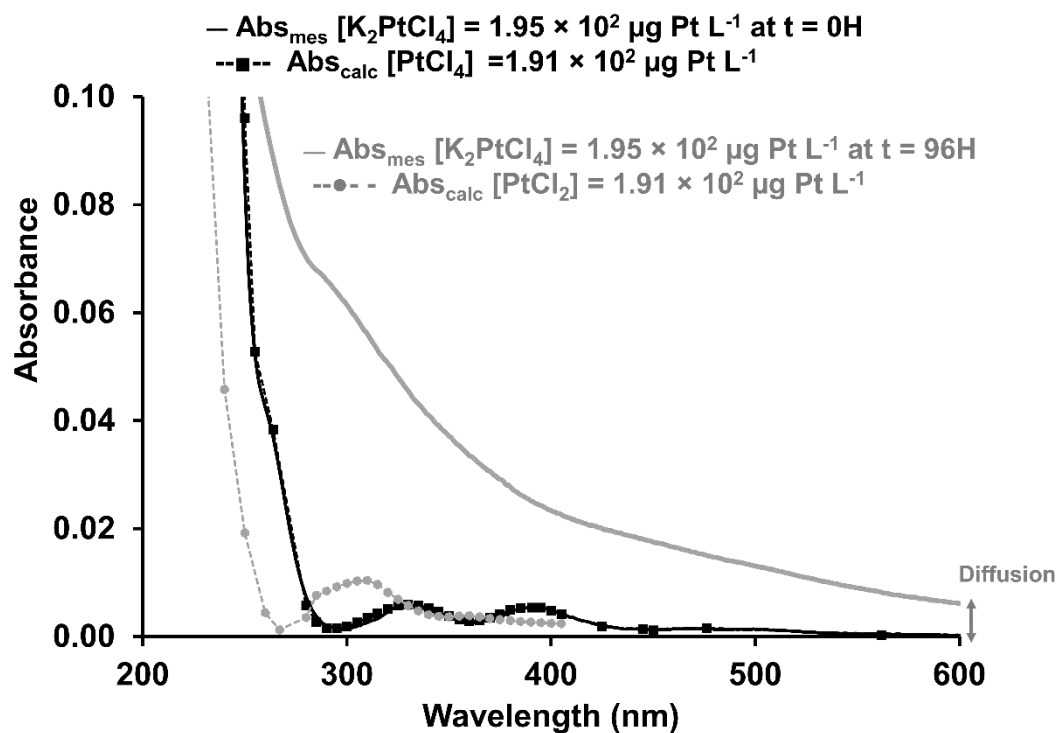


Figure S7. Experimental and calculated absorbance spectrum in S-AAP medium measured after dissolution and at 96 h of [K₂Pt^{II}Cl₄] = 1.95 × 10² μg Pt L⁻¹ and calculated [Pt^{II}Cl₂] = 1.91 × 10² μg Pt L⁻¹, l = 10 cm using literature absorptivity from Figure S3a.

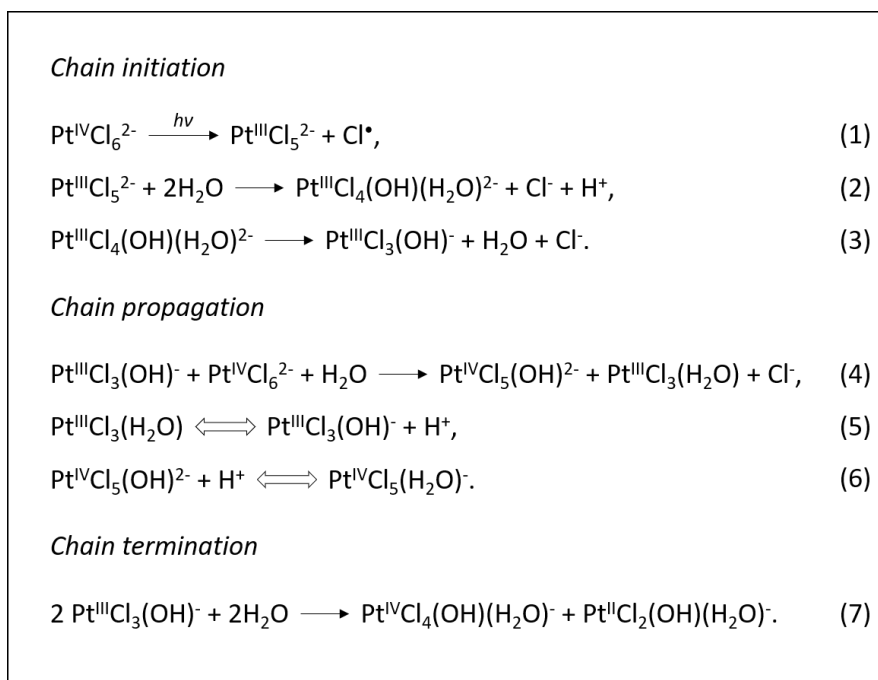


Figure S8. Proposed photodissociation mechanism of $\text{Pt}(\text{IV})\text{Cl}_6^-$ in aqueous solution (adapted from Pozdnyakov *et al.* 2015).

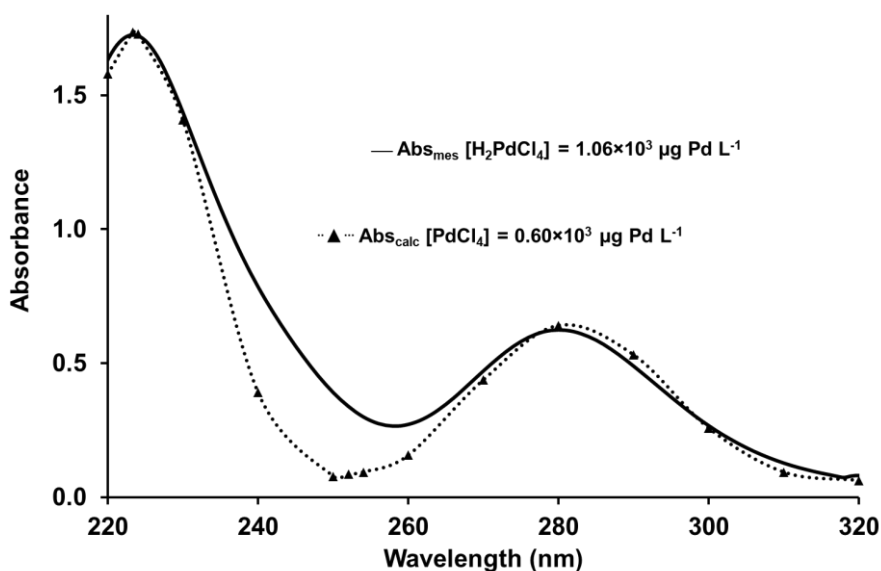


Figure S9. Absorbance spectrum measured in water at room temperature for $[\text{H}_2\text{Pd}^{\text{II}}\text{Cl}_4]_0 = 1.06 \times 10^3 \mu\text{g Pd L}^{-1}$ in 1 M HCl, $l = 10$ cm and calculated using absorptivity from Figure S3b.

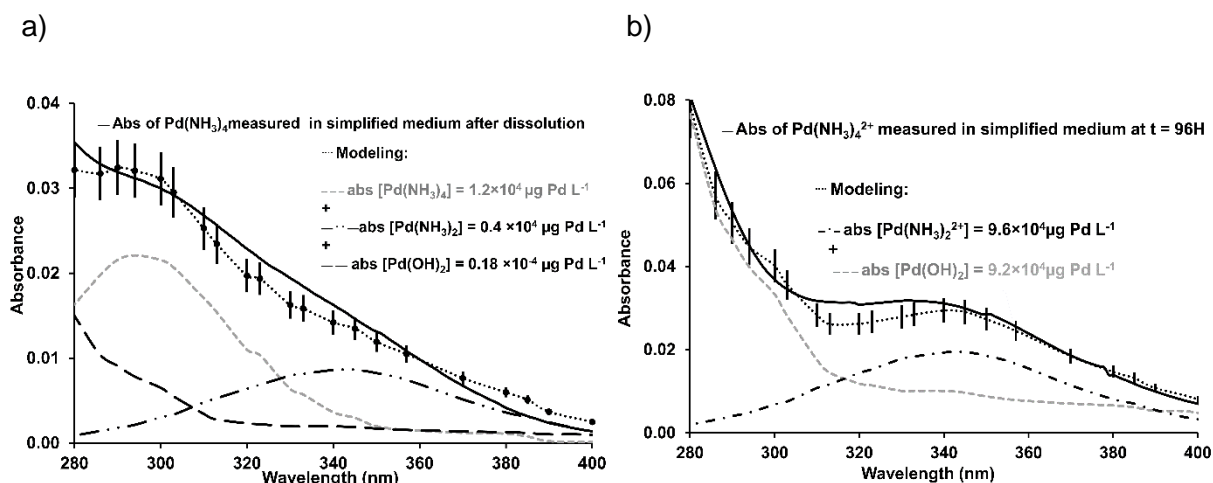


Figure S10. Absorbance spectrum at room temperature ($l = 1$ cm) of $\text{H}_2\text{Pd}(\text{NH}_3)_4$ in S-AAP medium exposed to light and measured a) after dissolution and at b) 96 h with $[\text{Pd}]_{\text{exp,tot}} = 0.94 \times 10^3 \mu\text{g Pd L}^{-1}$. The black lines represent measured absorbances. The dotted lines represent absorbances calculated from absorptivity (Figure S3) and kinetically modeled species concentrations at $[\text{Pd}]_{\text{tot}} = 1.7 \times 10^4 \mu\text{g Pd L}^{-1}$. The modelled species are a) $\text{Pd}(\text{NH}_3)_4^{2+}$, $\text{Pd}(\text{NH}_3)_2^{2+}$ and $\text{Pd}(\text{OH})_2$ and b) $\text{Pd}(\text{NH}_3)_4^{2+}$ and $\text{Pd}(\text{OH})_2$

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