Type of the Paper (Article, Review, Communication, etc.)

Synthesis, reactivity studies and cytotoxicity of two iodidoplatinum(II) complexes. Does photoactivation work?

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Supporting Information

Table S1. Crystal Data for complex **1** and **2**

	complex 1		**complex 2**	
Chemical formula	$C_8H_{14}I_2N_2Pt$		$C_6H_{10}I_2N_2Pt$	
Formula weight	587.10 g/mol		559.05 g/mol	
Temperature	296 K		296 K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal size	0.15 x 0.20 x 0.30 mm		0.28 x 0.32 x 0.37 mm	
Crystal habit	pyramidal		prismatic	
Crystal system	monoclinic		orthorhombic	
Space group	C 1 2/c 1		P 21 21 21	
Unit cell dimensions	a = 15.8255(5) Å b= 9.2481(3) Å c = 19.9604(8) Å	α = 90º β = 110.013(1)º γ = 90º	a = 9.5004(4) Å b= 9.8547(3) Å c = 12.2052(5) Å	α = 90º β = 90º γ = 90º
Volume	2744.36(15) $Å^3$		1142.85(6) $Å^3$	
Z	8		4	
Density (calculated)	2.842 g/cm^3		3.249 g/cm^3	
Absorption coefficient	14.692 mm^{-1}		17.631 mm^{-1}	
Theta range for data collection	2.59 to 25.35°		2.72 to 25.33°	
Index ranges	-18<=h<=18, -11<=k<=11, -23<=l<=24		-10<=h<=11, -10<=k<=11, -14<=l<=14	
Reflections collected	24220		7667	
Independent reflections	2499 [R(int) = 0.0421]		2084 [R(int) = 0.0307]	
Coverage of independent reflections	99.8%		99.5%	
Data / restraints / parameters	2499 / 0 / 120		2084 / 0 / 101	
Goodness-of-fit on F^2	1.198		1.325	
Final R indices	$I > 2\sigma(I)$: R1 = 0.0377, wR2= 0.1151 all data : R1 = 0.0439, wR2 = 0.1191		$I > 2\sigma(I)$: R1 = 0.0314, wR2= 0.0873 all data : R1 = 0.0405, wR2 = 0.1264	
Largest diff. peak and hole	1.258 and -1.420 e $Å^3$		1.737 and -4.975 e$Å^{-3}$	

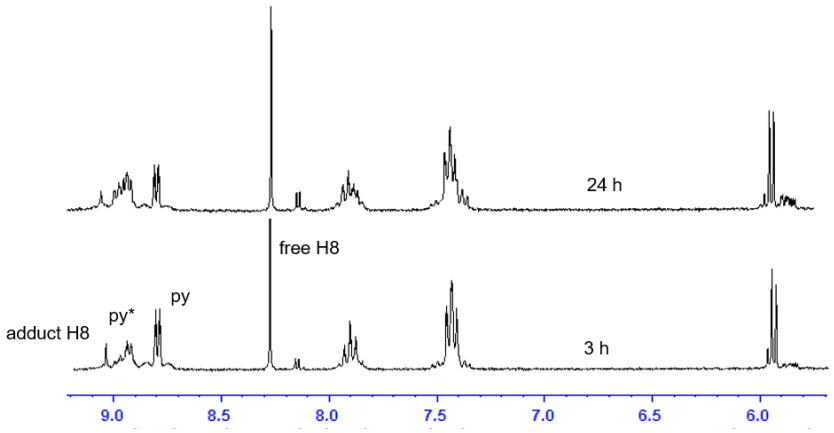


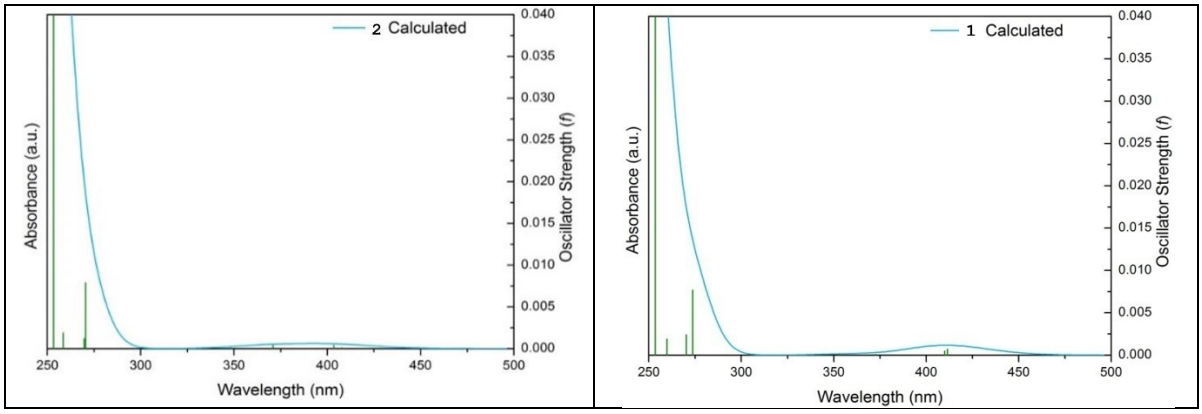
Figure S1. Progress of the reaction between complex **2** and 5′-GMP at 37 °C monitored by ^1H NMR showing changes in the aromatic area. Labels: free H8, free nucleotide; adduct H8, nucleotide adduct; py, pyridine ligand complex 1; py*, pyridine signal adducts.

Table S2. Selected bond distances (Å) for complexes **1** and **2** optimized with the DFT method at the PBE1PBE:LANL08/6-31G** level using the PCM solvent (water) model.

	Pt–I	Pt–I	Pt–N	Pt–N(py)
1	2.687	2.687	2.065	2.030
1 – X-ray	2.596	2.592	2.067	2.025
2	2.689	2.686	2.068	2.032
2 – X-ray	2.597	2.591	2.070	2.022

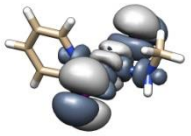
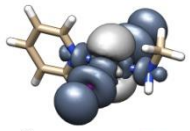
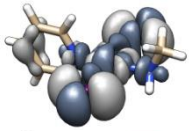
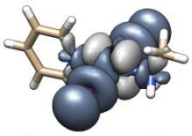
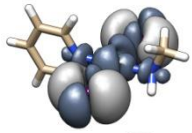
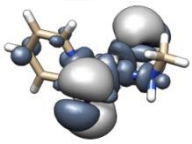
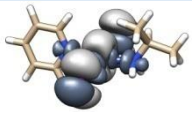
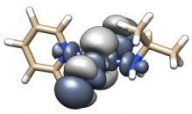
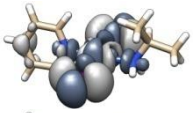
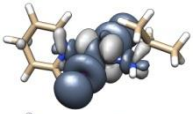
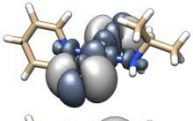
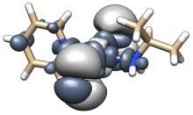
X-ray structural parameters are reported for comparison when available.

Table S3. Experimental and theoretical absorption spectra for **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level.



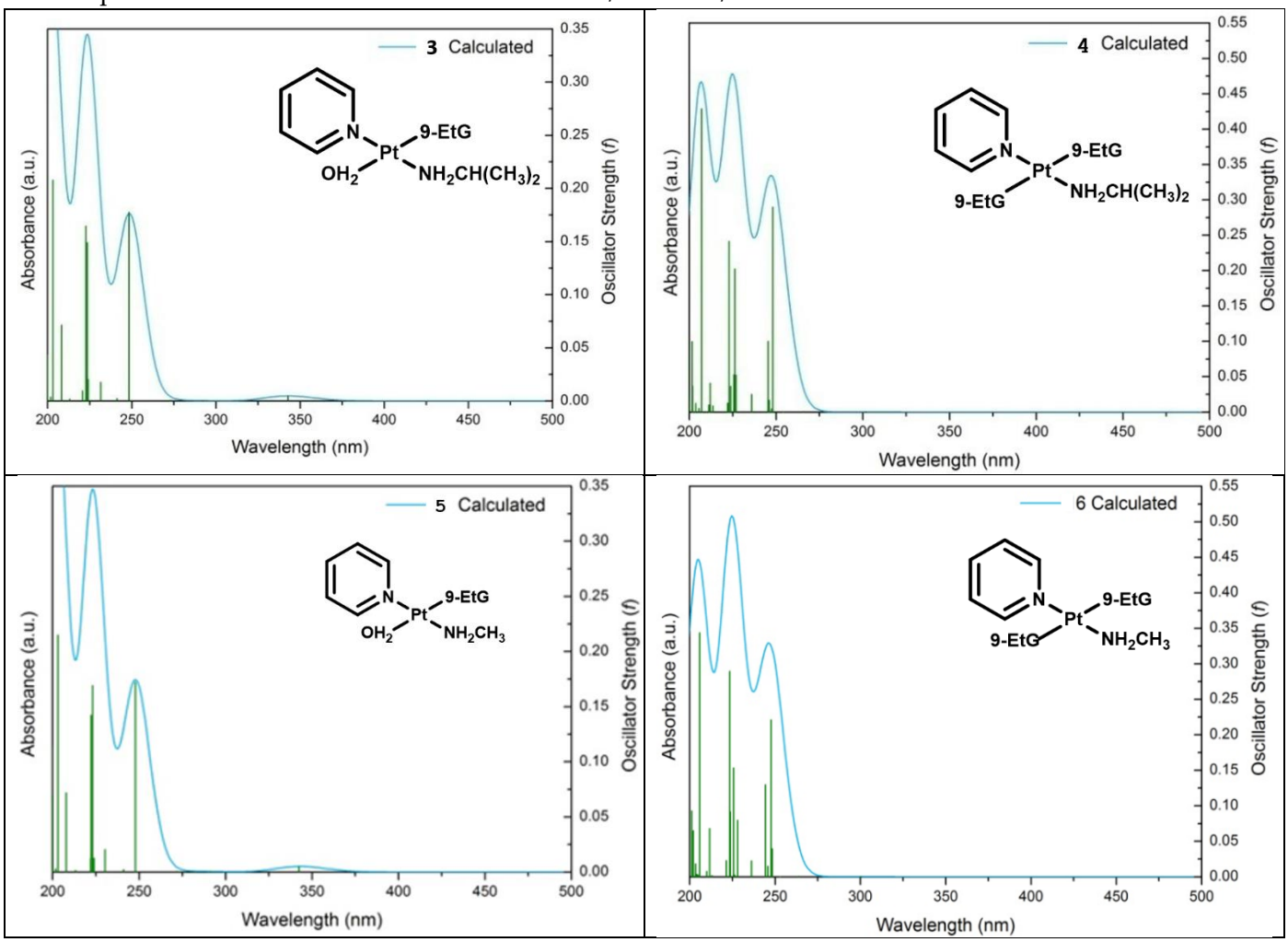
Singlet-singlet transitions are shown as vertical bars with heights equal to their oscillator strengths. The theoretical curves were obtained using GAUSSSUM 2.2.[32]

Table S4. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level.

Complex 1					
Tr.	**E_{calc} (nm)**	***f***	**Composition**	**Character**	**EDDM**
1	407.63	0.0001	HOMO→LUMO (90%) H-9→LUMO (8%)	d–d/LMCT	
2	403.55	0.0004	H-2→LUMO (96%)	d–d	
3	370.86	0.0004	H-8→LUMO (15%) H-1→LUMO (76%)	d–d/LMCT	
4	348.11	0.0001	H-6→LUMO (97%)	d–d	
5	270.49	0.0079	H-3→LUMO (97%)	LMCT	
6	269.69	0.0012	H-4→LUMO (89%) HOMO→L+1 (9%)	LMCT	
Complex 2					
Tr.	**E_{calc} (nm)**	***f***	**Composition**	**Character**	**EDDM**
1	411.49	0.0007	H-2→LUMO (27%) HOMO→LUMO (64%)	d–d/LMCT	
2	410.08	0.0005	H-2→LUMO (65%) HOMO→LUMO (27%)	d–d/LMCT	
3	372.56	0.0001	H-8→LUMO (13%) H-1→LUMO (73%)	d–d/LMCT	
4	353.07	0.0001	H-6→LUMO (88%)	d–d/LMCT	
5	273.74	0.0077	H-3→LUMO (92%)	LMCT	
6	270.27	0.0024	H-4→LUMO (83%)	d–d/LMCT	

In the EDDMs gray indicates a decrease in electron density, while blue-gray indicates an increase.

Table S5. Experimental and theoretical absorption spectra for for mono and bis 9-EtG adducts of complexes **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level



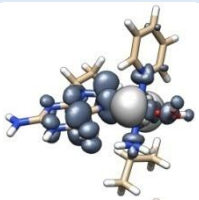
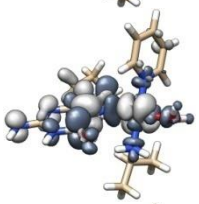
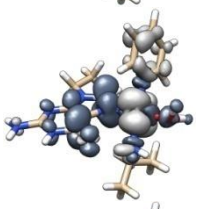
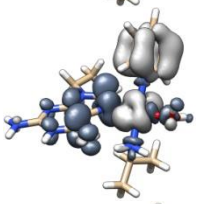
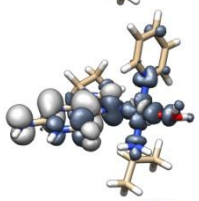
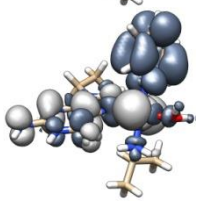
Singlet-singlet transitions are shown as vertical bars with heights equal to their oscillator strengths. The theoretical curves were obtained using GAUSSSUM 2.2. [32]

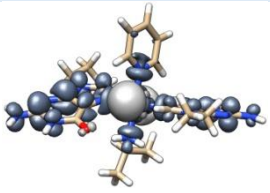
Table S6. Selected bond distances (Å) for the mono and bis 9-EtG adducts of complexes **1** and **2** optimized with the DFT method at the PBE1PBE:LANL08/6-31G** level using the PCM solvent (water) model.

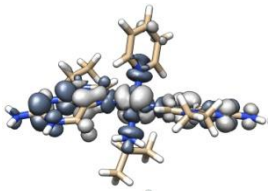
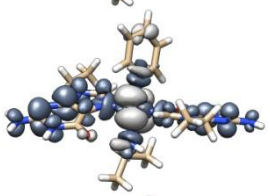
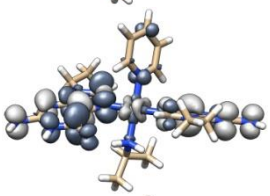
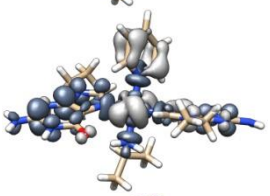
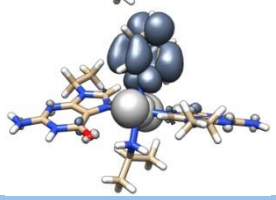
	Pt–O(H_2O)	**Pt–N(9EtG)**	**Pt–N(ma)**	**Pt–N(py)**
5	2.099	1.993	2.053	2.045
	Pt–N(9EtG)	**Pt–N(9EtG)**	**Pt–N(ma)**	**Pt–N(py)**
6	2.035	2.024	2.060	2.045
	Pt–O(H_2O)	**Pt–N(9EtG)**	**Pt–N(ipa)**	**Pt–N(py)**
3	2.100	1.993	2.053	2.046
	Pt–N(9EtG)	**Pt–N(9EtG)**	**Pt–N(ipa)**	**Pt–N(py)**
4	2.034	2.028	2.062	2.043

X-ray structural parameters are reported for comparison when available.

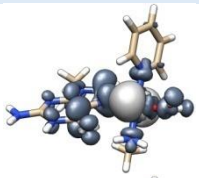
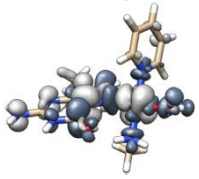
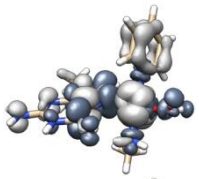
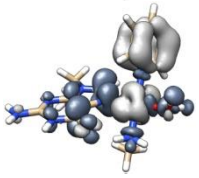
Table S7. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for mono and bis 9-EtG adducts of complexes **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level.

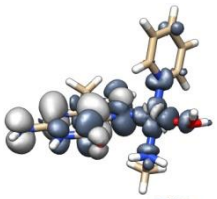
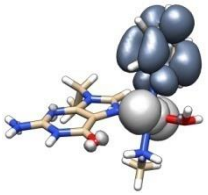
Complex 3					
Tr.	**E_{calc} (nm)**	***F***	**Composition**	**Character**	**EDDM**
1	342.85	0.0049	H-1→L+1 (42%) H-1→L+2 (41%)	MLCT	
2	292.01	0.0002	H-2→L+1 (26%) H-2→L+2 (25%) HOMO→L+1 (11%)	d–d/LC	
3	282.91	0.0000	H-3→L+1 (33%) H-3→L+2 (32%)	MLCT	
4	273.07	0.0007	H-5→L+1 (25%) H-5→L+2 (24%) H-4→L+1 (8%) H-4→L+2 (8%)	MLCT	
5	248.41	0.1776	HOMO→L+1 (45%) HOMO→L+2 (39%)	LC	
6	241.29	0.0022	H-1→LUMO (91%) HOMO→LUMO (4%)	MLCT	

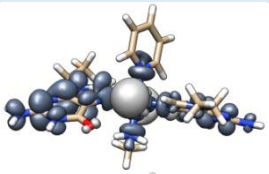
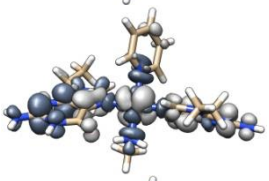
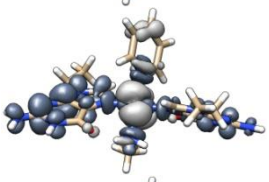
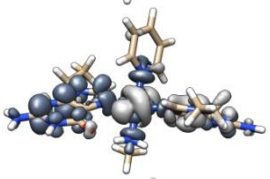
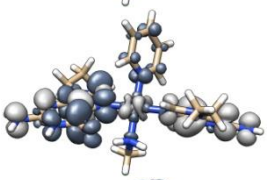
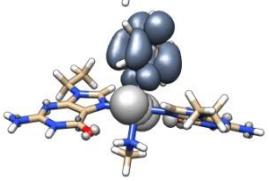
Complex 4					
Tr.	**E_{calc} (nm)**	***F***	**Composition**	**Character**	**EDDM**
1	301.70	0.0004	H-2→L+4 (19%) H-2→L+5 (62%) H-2→L+6 (11%)	MLCT	

2	266.07	0.0008	H-3→L+4 (11%) H-3→L+5 (36%) HOMO→L+5 (17%)	d-d/LC	
3	254.14	0.0005	H-4→L+4 (17%) H-4→L+5 (55%) H-4→L+6 (10%)	MLCT	
4	248.04	0.2898	H-1→L+1 (33%) H-1→L+2 (14%) HOMO→L+1 (29%)	LC	
5	247.39	0.0045	H-5→L+4 (11%) H-5→L+5 (37%) H-5→L+6 (7%)	MLCT	
6	245.99	0.0165	H-2→LUMO (80%) HOMO→L+2 (5%)	MLCT	

Complex 5

Tr.	E_{calc} (nm)	*F*	Composition	Character	EDDM
1	342.50	0.0052	H-1→L+1 (26%) H-1→L+2 (57%) H-1→L+6 (11%)	MLCT	
2	290.92	0.0005	H-2→L+1 (17%) H-2→L+2 (35%) HOMO→L+2 (12%) H-2→L+6 (7%) HOMO→L+1 (7%)	d–d/LC	
3	281.99	0.0000	H-3→L+1 (19%) H-3→L+2 (42%) H-3→L+6 (8%)	MLCT	
4	271.91	0.0007	H-5→L+1 (15%) H-5→L+2 (33%) H-4→L+2 (9%) H-3→L+2 (8%)	MLCT	

5	247.78	0.1722	HOMO→L+1 (63%) HOMO→L+2 (20%) HOMO→L+4 (7%)	LMCT	
6	241.00	0.0022	H-1→LUMO (92%) HOMO→LUMO (3%)	MLCT	

Complex 6					
Tr.	**E_{calc} (nm)**	***F***	**Composition**	**Character**	**EDDM**
1	300.39	0.0004	H-2→L+4 (58%) H-2→L+5 (30%)	MLCT	
2	263.95	0.0009	H-3→L+4 (33%) H-3→L+5 (17%) HOMO→L+4 (15%) HOMO→L+5 (7%)	MLCT	
3	252.90	0.0002	H-4→L+4 (49%) H-4→L+5 (25%)	MLCT	
4	248.32	0.0397	H-5→L+4 (35%) H-5→L+5 (18%)	MLCT	
5	247.69	0.2211	H-1→L+1 (43%) HOMO→L+1 (22%)	LC	
6	245.77	0.0148	H-2→LUMO (85%) HOMO→L+2 (3%)	MLCT	

In the EDDMs gray indicates a decrease in electron density, while blue-gray indicates an increase.