Supplementary Materials: 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$Å^{-3}$	

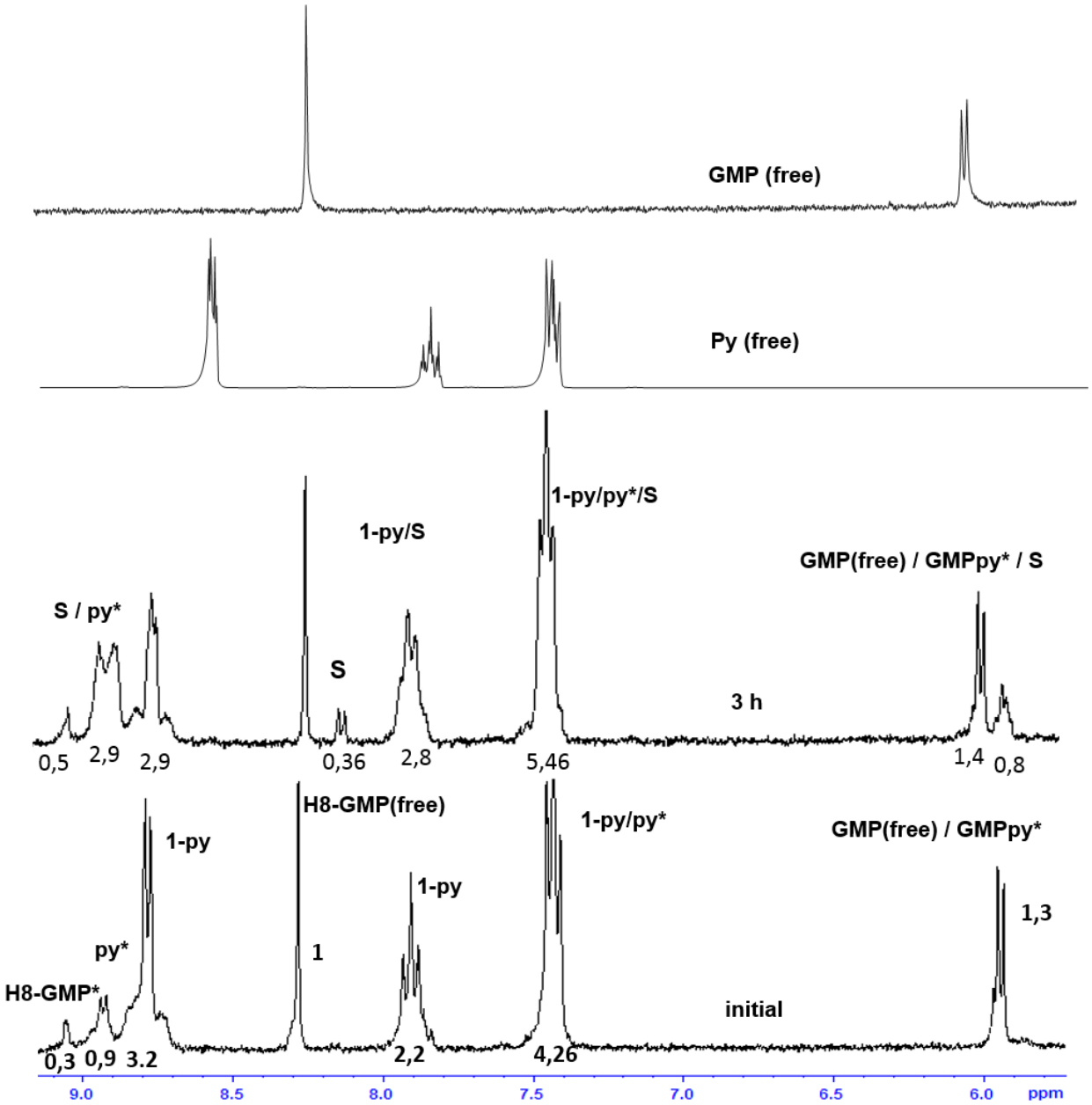


Figure S1. Progress of the reaction between complex **1** and 5′-GMP at 37 °C monitored by ^{1}H NMR (acetone-d_6 and D_2O in a ratio 2:1) showing changes in the aromatic area and showing above the ^{1}H NMR (acetone-d_6 and D_2O in a ratio 2:1) of non coordinated 5′-GMP and pyridine. Labels: H8-GMP(free) and GMP(free), free nucleotide; H8-GMP* and GMPpy*, nucleotide adduct; 1-py, pyridine ligand complex 1; py*, pyridine signal adducts; S, speciation. The numbers at the base of the signals stand for the integrals

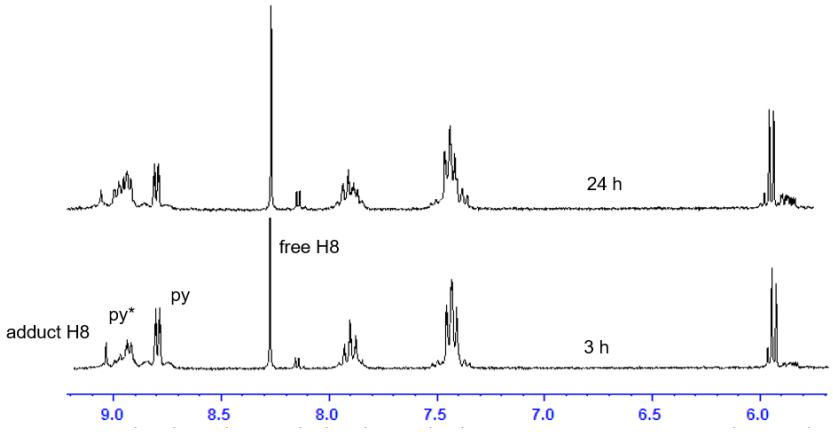


Figure S2. Progress of the reaction between complex **2** and 5′-GMP at 37 °C monitored by ^{1}H NMR showing changes in the aromatic area. Labels: free H8, free nucleotide; adduct H8, nucleotide adduct; **py**, pyridine ligand complex **1**; py*, pyridine signal adducts.

Table S2a. 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–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 S2b. Selected bond distances (Å) for complex **2** optimized with the DFT method at the PBE1PBE:ECP/6-31G** level using different ECPs for the Pt atom and the PCM solvent (water) model.

		6-31G PCM (water)**					
Complex **2**	X-ray	LANL2DZ	Δ	LANL08	Δ	SDD	Δ
Pt–I(2)	2.596	2.706	0.110	2.687	0.091	2.692	0.096
Pt–I(3)	2.592	2.706	0.114	2.687	0.095	2.692	0.100
Pt–N(8)	2.067	2.068	0.001	2.065	-0.002	2.070	0.003
Pt–N(20)	2.025	2.032	0.007	2.030	0.005	2.037	0.012

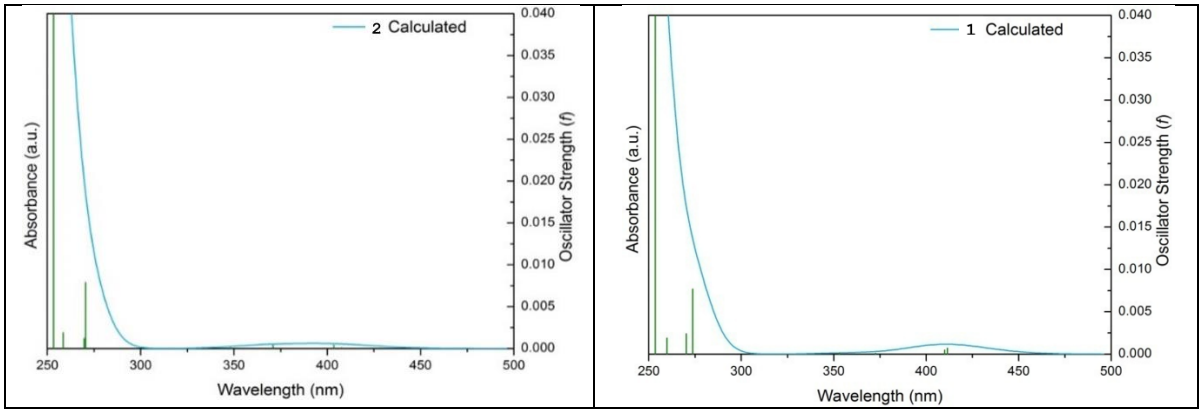
Table S2c. Selected bond distances (Å) for complex **2** optimized with the DFT method at the PBE1PBE:LANL08/BS level using different basis sets (BS) for the non-Pt atoms and the PCM solvent (water) model.

		LANL08 PCM (water)					
Complex **2**	X-ray	6-31G**	Δ	6-31+G**	Δ	6-311G**	Δ
Pt–I(2)	2.596	2.687	0.091	2.683	0.087	2.682	0.086
Pt–I(3)	2.592	2.687	0.095	2.683	0.091	2.682	0.090
Pt–N(8)	2.067	2.065	-0.002	2.064	-0.003	2.065	-0.002
Pt–N(20)	2.025	2.030	0.005	2.030	0.005	2.032	0.007
						6-311+G**	Δ
						2.685	0.089
						2.685	0.093
						2.064	-0.003
						2.032	0.007

Table S2d. Selected bond distances (Å) for complex **2** optimized with the DFT method using different functionals, the LANL08/6-31G** ECP/basis set and the PCM solvent (water) model.

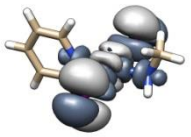
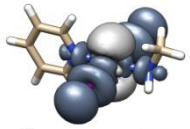
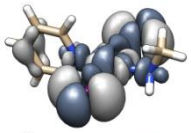
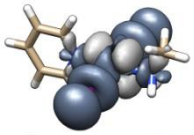
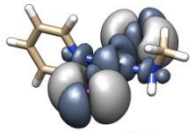
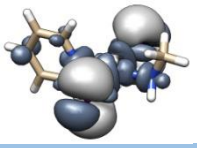
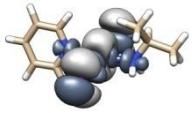
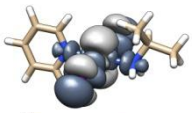
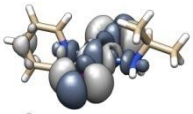
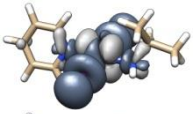
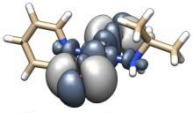
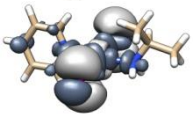
		LANL08/6-31G PCM (water)**					
Complex **2**	X-ray	PBE1PBE	Δ	LC-wPBE	Δ		
Pt–I(2)	2.596	2.687	0.091	2.664	0.068		
Pt–I(3)	2.592	2.687	0.095	2.664	0.072		
Pt–N(8)	2.067	2.065	-0.002	2.059	-0.008		
Pt–N(20)	2.025	2.030	0.005	2.032	0.007		
		B3LYP	Δ	CAM-B3LYP	Δ	M062X	Δ
		2.739	0.143	2.707	0.111	2.707	0.111
		2.739	0.147	2.707	0.115	2.707	0.115
		2.090	0.023	2.074	0.007	2.072	0.005
		2.056	0.031	2.046	0.021	2.046	0.021

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



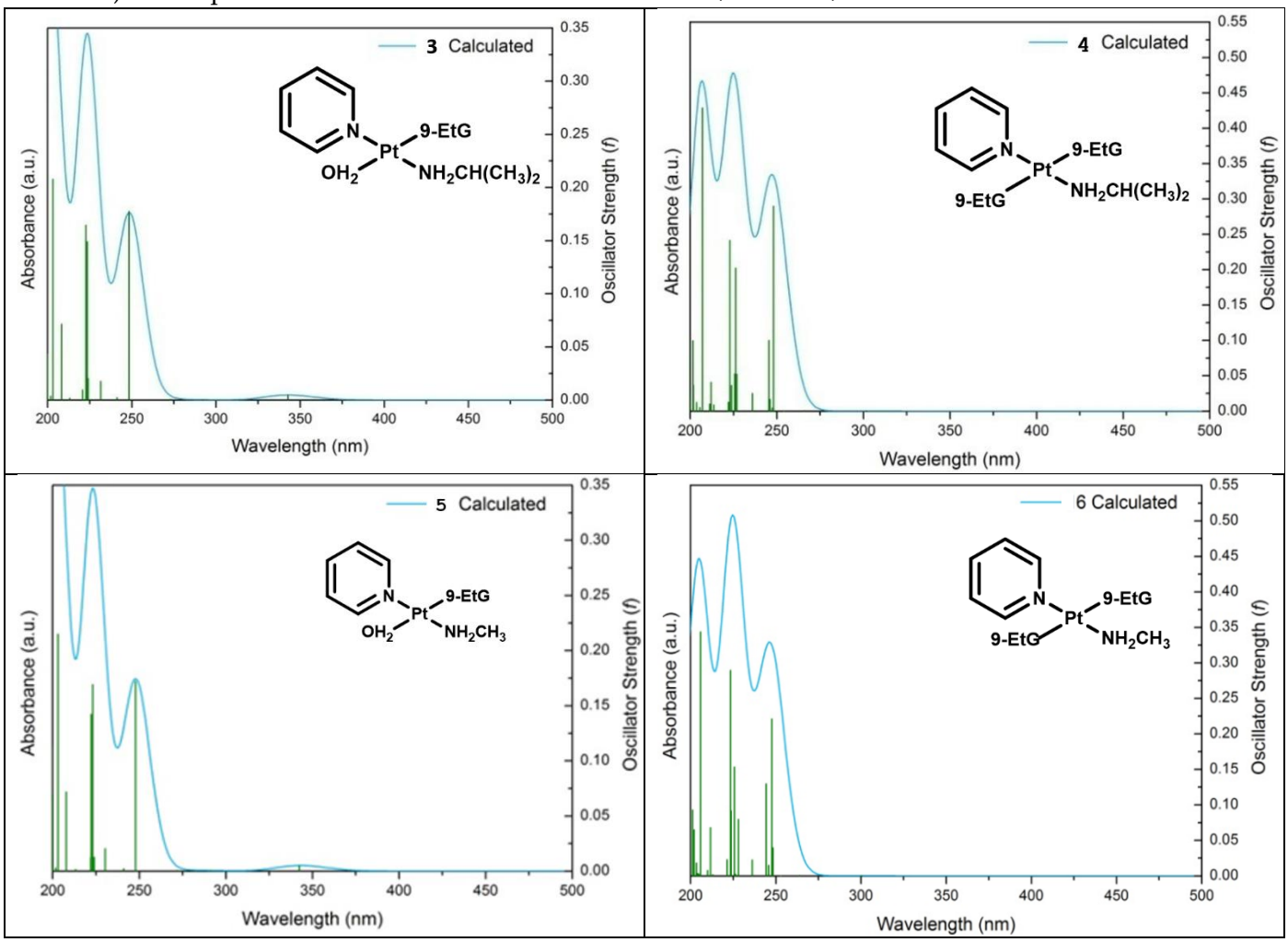
Singlet-singlet transitions are shown as vertical bars with heights equal to their oscillator strengths. The theoretical curves were obtained using GAUSSSUM 2.2.[32]

Table S4. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for complexes **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	

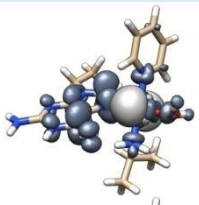
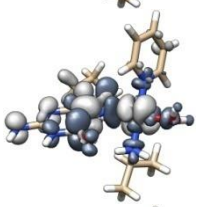
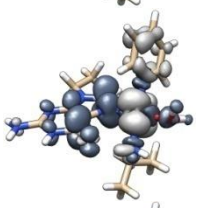
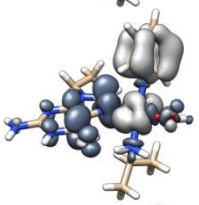
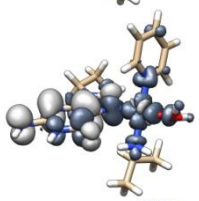
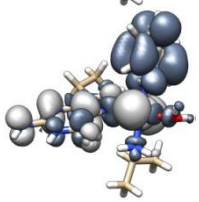
In the EDDMs gray indicates a decrease in electron density, while blue-gray indicates an increase.

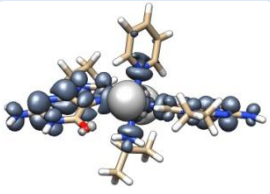
Table S5. Experimental and theoretical absorption spectra for mono and bis 9-EtG adducts (complexes **3** to **6**) of complexes **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level

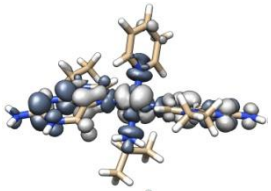
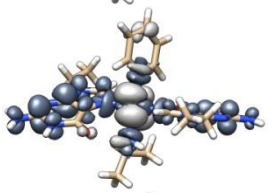
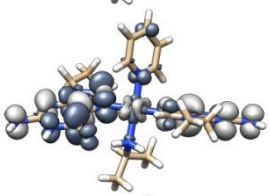
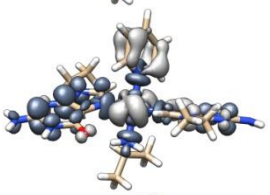
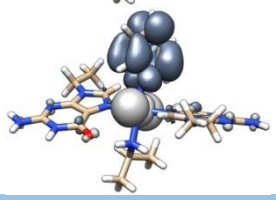


Singlet-singlet transitions are shown as vertical bars with heights equal to their oscillator strengths. The theoretical curves were obtained using GAUSSSUM 2.2. [32]

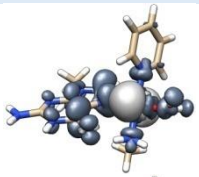
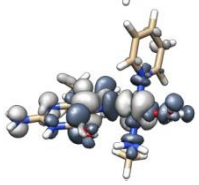
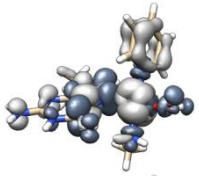
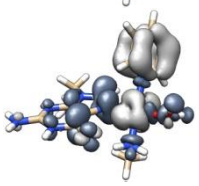
Table S6. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for mono and bis 9-EtG adducts of complexes **1** and **2** in water at the CAM-B3LYP/LANL08/6-31G** level. In the EDDMs gray indicates a decrease in electron density, while blue-gray indicates an increase.

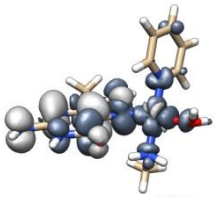
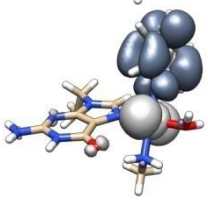
Complex 3					
Tr.	**E_{calc} (nm)**	***F***	**Composition**	**Character**	**EDDM**
1	342.85	0.0049	H-1→L+1 (42%) H-1→L+2 (41%)	MLCT	
2	292.01	0.0002	H-2→L+1 (26%) H-2→L+2 (25%) HOMO→L+1 (11%)	d–d/LC	
3	282.91	0.0000	H-3→L+1 (33%) H-3→L+2 (32%)	MLCT	
4	273.07	0.0007	H-5→L+1 (25%) H-5→L+2 (24%) H-4→L+1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

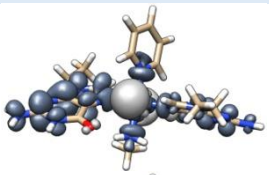
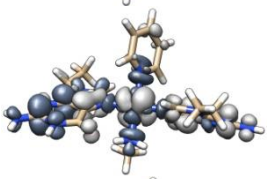
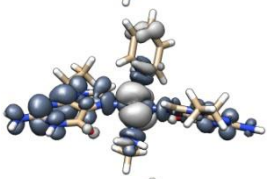
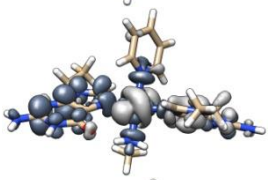
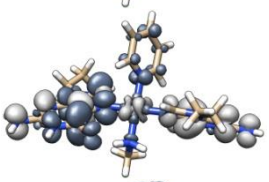
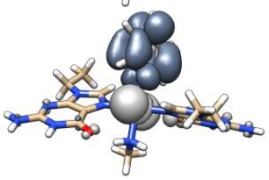
Tr.	E_{calc} (nm)	*F*	Composition	Character	EDDM
1	300.39	0.0004	H-2→L+4 (58%) H-2→L+5 (30%)	MLCT	
2	263.95	0.0009	H-3→L+4 (33%) H-3→L+5 (17%) HOMO→L+4 (15%) HOMO→L+5 (7%)	MLCT	
3	252.90	0.0002	H-4→L+4 (49%) H-4→L+5 (25%)	MLCT	
4	248.32	0.0397	H-5→L+4 (35%) H-5→L+5 (18%)	MLCT	
5	247.69	0.2211	H-1→L+1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

Table S7. Selected frontier molecular orbitals for complexes **3** to **6** (9-EtG adducts).

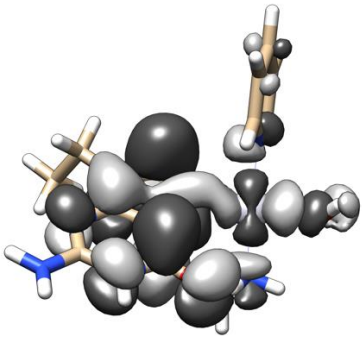
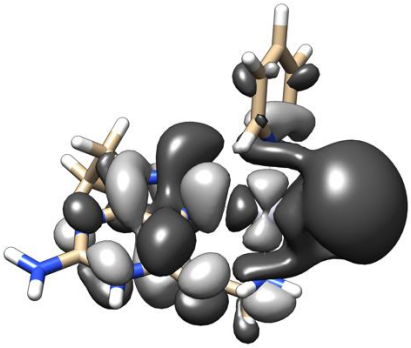
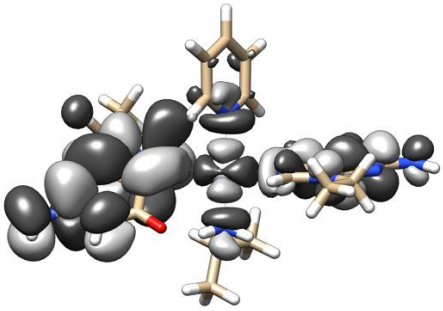
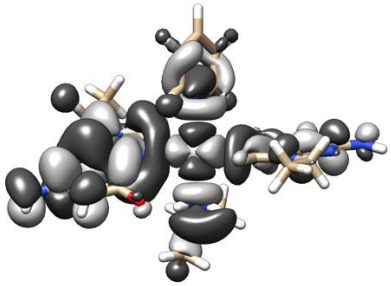
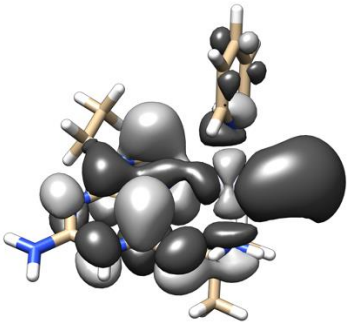
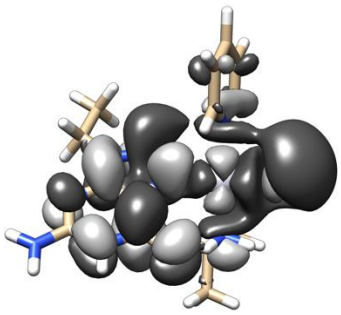
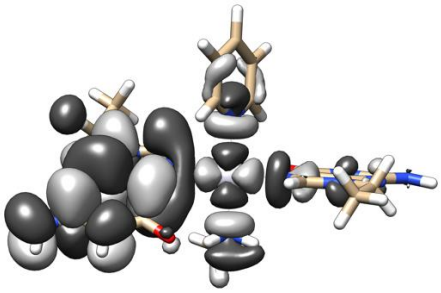
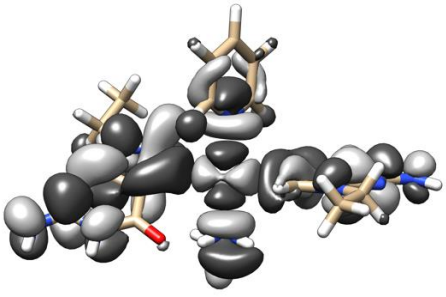
 3 – LUMO+1	 3 – LUMO+2
 4 – LUMO+4	 4 – LUMO+5
 5 – LUMO+1	 5 – LUMO+2
 6 – LUMO+4	 6 – LUMO+5

Table S8. 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.