Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Synthesis and Hydrogen Evolving Catalysis of a Panchromatic Photochemical Molecular Device

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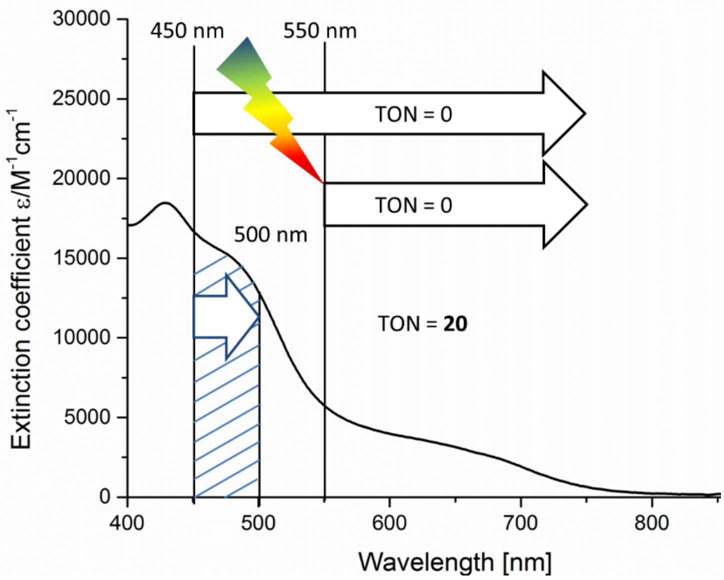

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Experimental Part

Materials and Devices

The synthesis of **Ostpphz** is described elsewhere.[7] The syntheses of the sacrificial electron donors BIH and BNAH were performed following literature procedures with minor variations.[10] Acetonitrile was purchased from VWR (HPLC grade) and purified with a MBraun MB-SPS-800 solvent drying system. Triethylamine was purchased from Carl Roth (spectroscopic grade). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer, UV-Vis spectra with a Jasco V-670 Spectrophotometer. ESI mass spectra were recorded with a Bruker solariX hybrid 7T FT-ICR. Chromatograms were on a Bruker Scion SQ gaschromatograph with a Restek ShinCarbon ST column with different mixtures of hydrogen and argon as reference.

Photocatalytical measurements

Photocatalytic experiments were carried out in a home-built air-cooling apparatus for maintaining 25 °C under constant irradiation of a Schlenk-vessel (ESI S9). All samples were prepared under inert conditions, dried and degassed (1 min per 1 mL) acetonitrile and degassed demineralized water was used. Concentration of the mixtures was 1.08×10^{-5} mol/L for **OsPt** and 1.08×10^{-2} mol/L for the electron donors in 10 mL catalytic mixtures. In addition the samples were prepared in schlenk-tubes with a headspace-solution ratio of 11/10 in the dark under argon stream. As light sources two blue LED lights (each 470 nm ± 15 nm, P = 35 mW ± 5 mW) were used. After specific time, 100 µL samples were drawn from the headspace and injected immediately into the GC apparatus. Hydrogen measurements and irradiation experiments were performed several times.

For the excitation with a broad band light source, some changes of the conditions above were made. Due to a different reactor geometry, 20 mL of the catalytic mixtures were used and the headspace-solution ratio was 11/20 (see ESI S8). The used light-source was a 150 W Xe lamp from LOT Oriel, with cut-off filters at > 450 nm, > 550 nm and < 500 nm purchased from Edmund optics.

UV-Vis measurements under catalytic conditions

The catalytic mixture was prepared as mentioned before and transferred to an UV-Vis cuvette. The sample was irradiated with a LED light stick (470 nm ± 15 nm, P = 35 mW ± 5 mW) in an apparatus with vents for remaining room temperature (25° C). After certain amounts of time an UV-Vis spectrum was measured with a mixture of acetonitrile: water (9:1) as a baseline.

Theoretical Section

To reduce the computational cost of the calculations without affecting the spectroscopic properties, the structure of the complexes were simplified by replacing the *tert*-butyl groups by methyl groups. The geometries of the singlet ground state were calculated by means of density functional theory (DFT) with the functional B3LYP. Harmonic vibrational frequencies were computed to confirm that the optimized structures correspond to minima on the potential energy surface. The 28-electron, 46-electron and 60-electron relativistic effective core potentials MWB were used with their basis sets for the ruthenium, iodine, osmium and platinum atoms, respectively. The 6-31G(d) basis set was employed for the ligands. The vertical excitation energies of the singlet and triplet excited states were obtained from time-dependent (TD) DFT calculations with the same functional, pseudopotential and basis set. The effects of the interaction with a solvent (acetonitrile, $\varepsilon = 35.688$, $n = 1.344$) on the geometries and excitation energies were taken into account by the polarizable continuum model (PCM). The nonequilibrium procedure of solvation was used for the calculation of the excitation energies. All the computations were performed with Gaussian 09[18].

Synthetic Procedures

[Os(tbbpy)$_2$(tpphz)PtI$_2$](PF$_6$)$_2$ (OsPt). [Os(tbbpy)$_2$(tpphz)](PF$_6$)$_2$ (76.0 mg, 54.2 µmol) and (DMSO)$_2$PtI$_2$ (50.0 mg, 82,26 µmol) were suspended in ethanol (100 mL) and heated at 85 °C for 18 h. The volume of the resulting black solution was concentrated to one third (ca. 30 mL) with the rotary evaporator and treated with a saturated solution of (NH$_4$)(PF$_6$) in water. The precipitate was washed with water (100 mL) and diethyl ether (20 mL). Yield was 78 % (78 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm]: 10.03 (s, 2H), 9.85 (d, *J* = 7.6 Hz, 2H), 9.79 (d, *J* = 7.6 Hz, 2H), 8.93 (s, 2H), 8.88 (s, 2H), 8.43 - 8.31 (m, 2H), 8.25 (d, *J* = 4.5 Hz, 2H), 8.18 – 8.08 (m, 2H), 7.75 (s, 2H), 7.67 (d, *J* = 5.5 Hz, 2H), 7.61 (d, *J* = 4.6 Hz, 2H), 7.32 (d, *J* = 4.9 Hz, 2H), 1.47 (s, 18H), 1.35 (s, 18HM) ^{13}C NMR (500 MHz, DMSO-d_6) δ [ppm]: 161.93, 161.41, 158.71, 158.39, 153.90, 153.39, 153.12, 151.64, 150.36, 149.31, 141.73, 138.12, 136.53, 134.12, 130.64, 129.03, 128.85, 128.67, 125.75, 125.63, 122.56, 122.44, 35.89, 35.74, 30.75, 30.59 MS (ESI): 780.11 ([M-2PF$_6$]$^{2+}$)

NMR Spectra

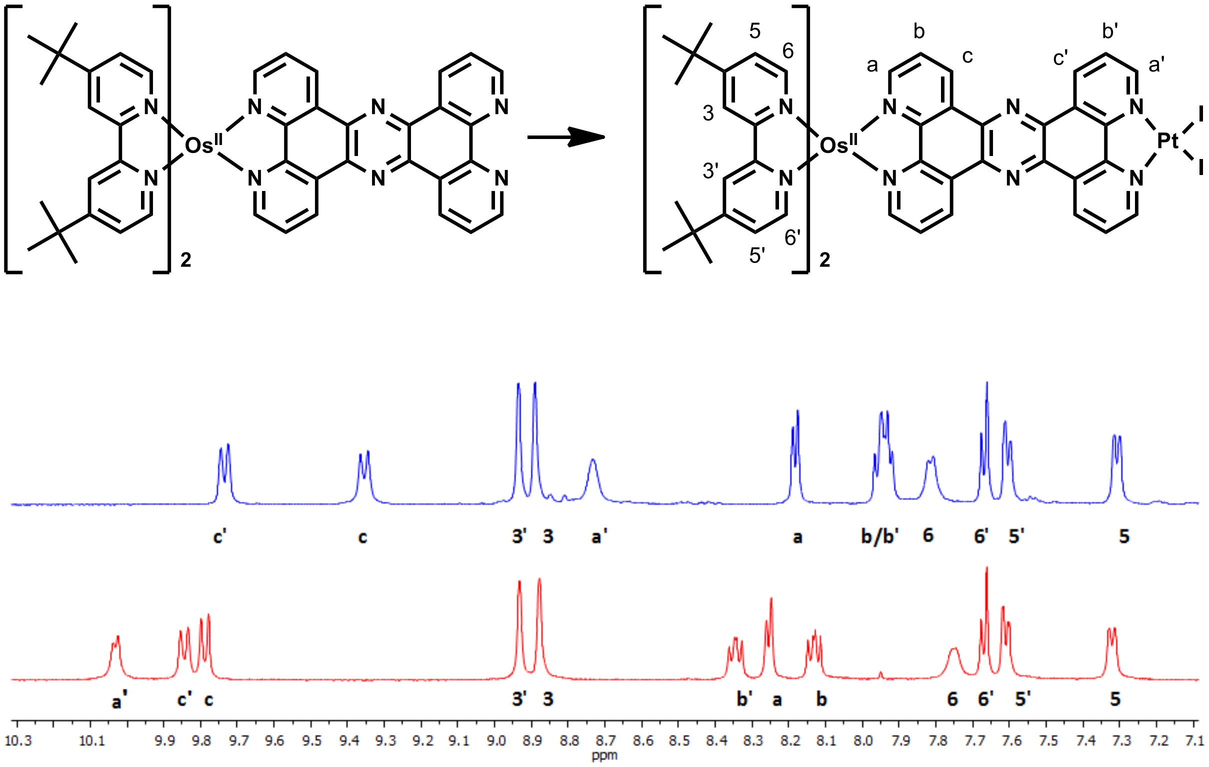


Figure S1. Structures and assignments of the ^{1}H NMR signals for **Ostpphz** and **OsPt** . ^{1}H NMR spectra of the aromatic regions of **Ostpphz** (blue) and **OsPt** (red) at the same concentrations (8 x 10^{-4} mol/L) in DMSO-d6.

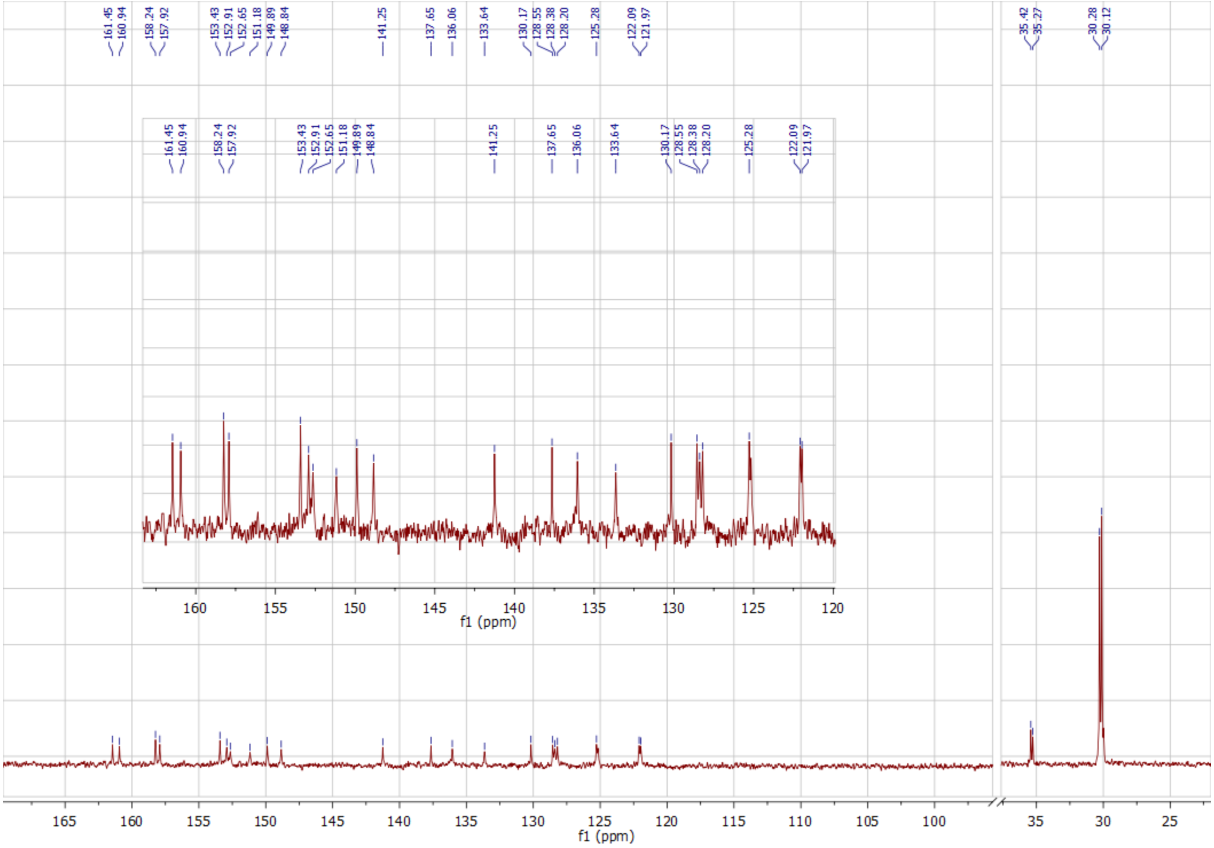


Figure S2. ^{13}C NMR spectrum of **OsPt** in DMSO-d6.

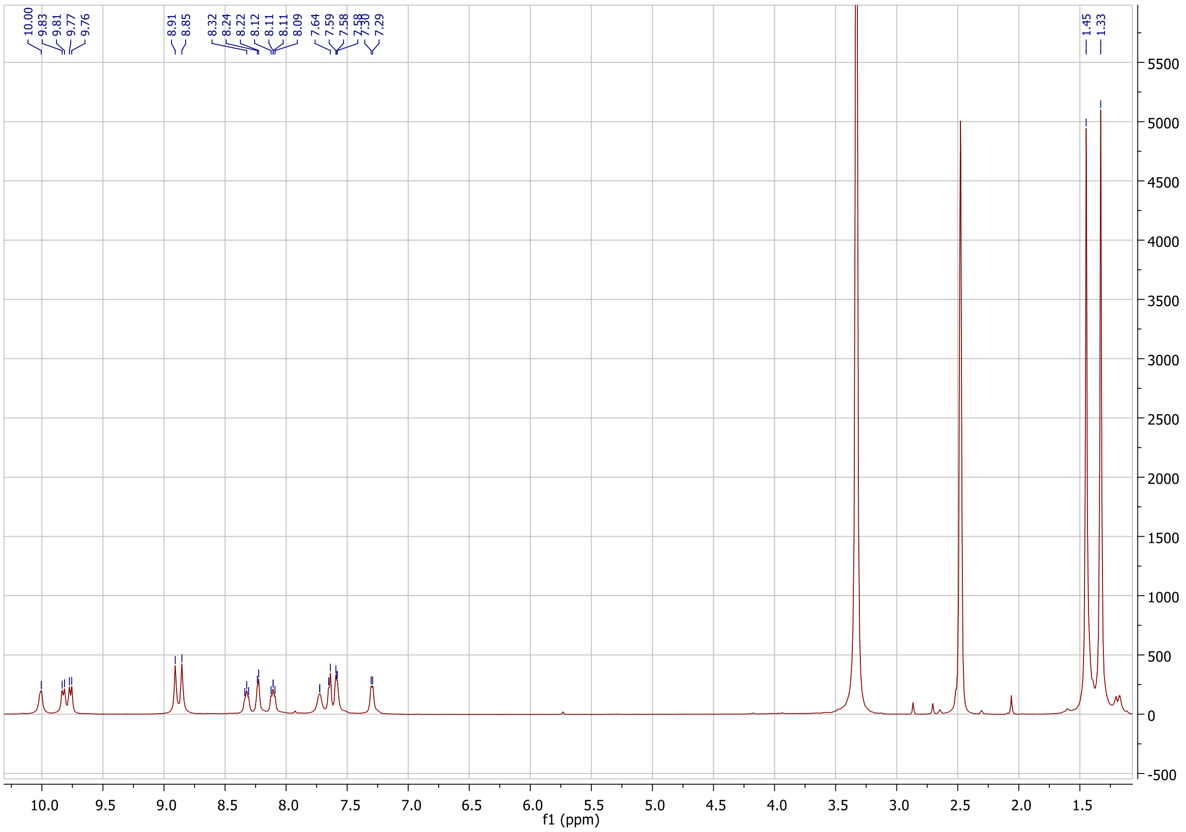


Figure S3. ^{1}H NMR spectrum of **OsPt** in DMSO-d6 at a concentration of 8 x 10^{-4} mol/L.

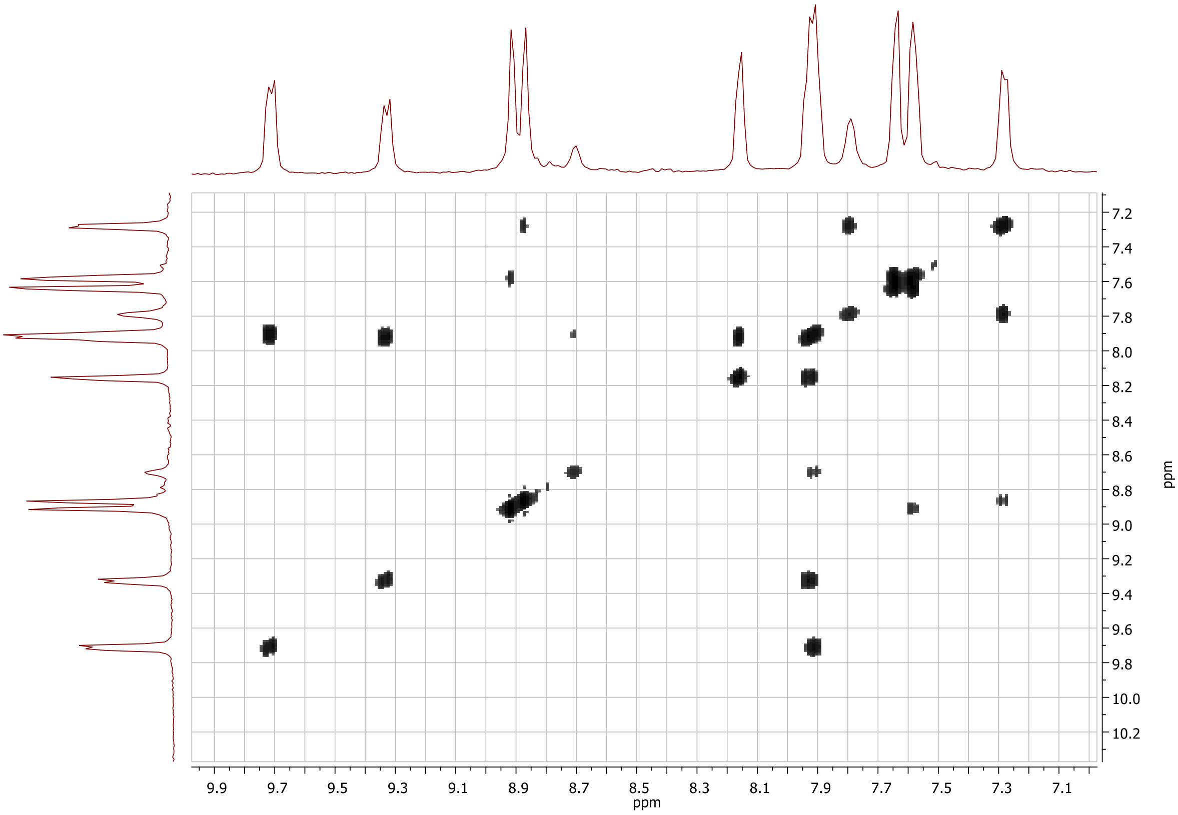
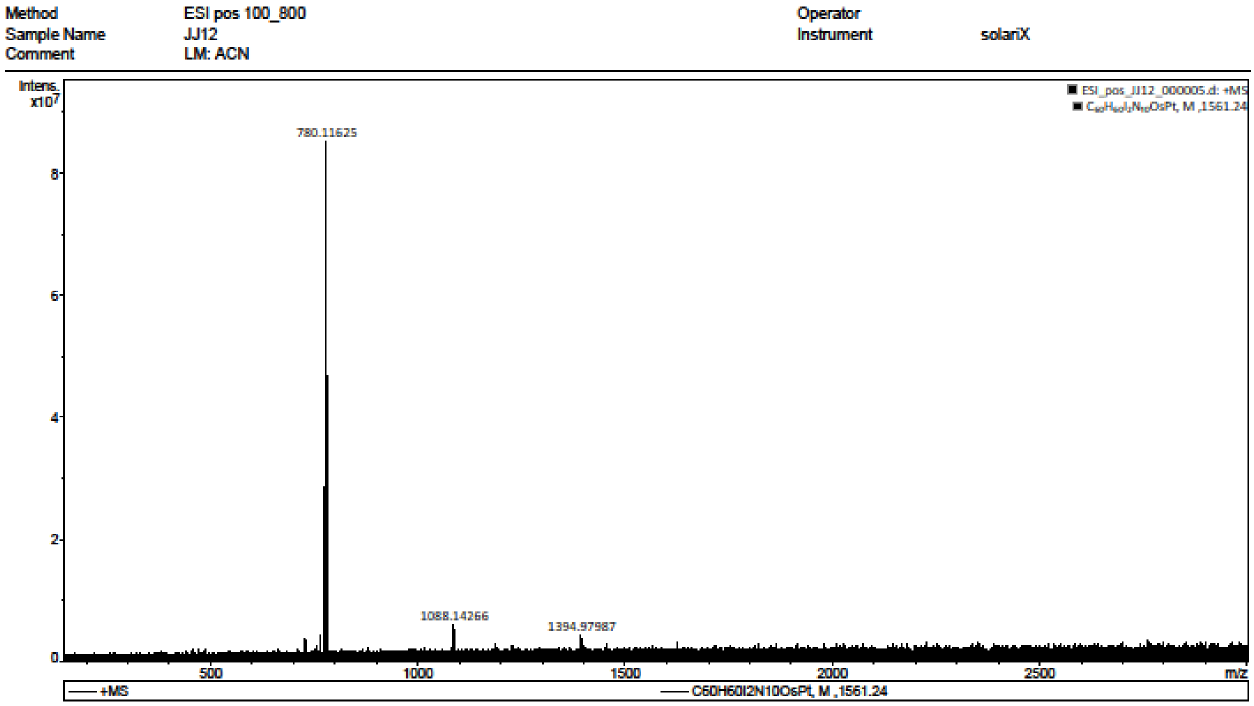
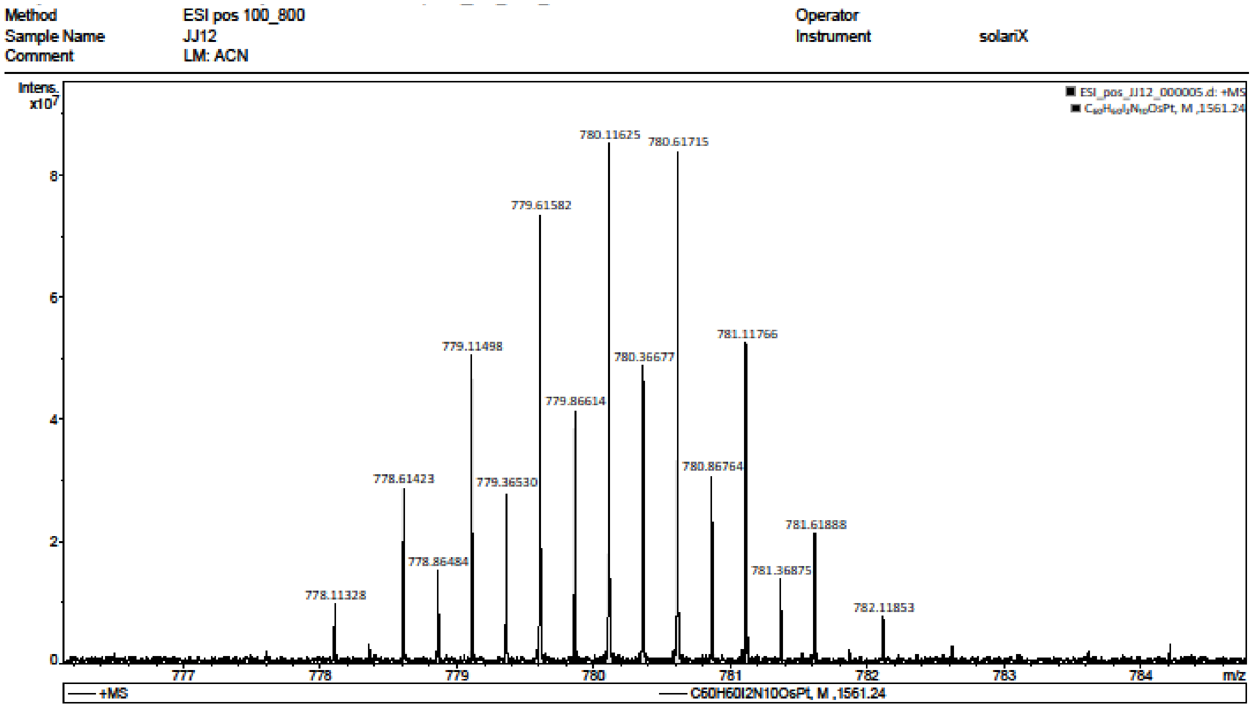


Figure S4. H-H COSY spectrum of **OsPt** in DMSO-d6 at a concentration of 8 x 10^{-4} mol/L.

Mass Spectrometry

MS: ESI – positive mode





Photocatalytic Activity

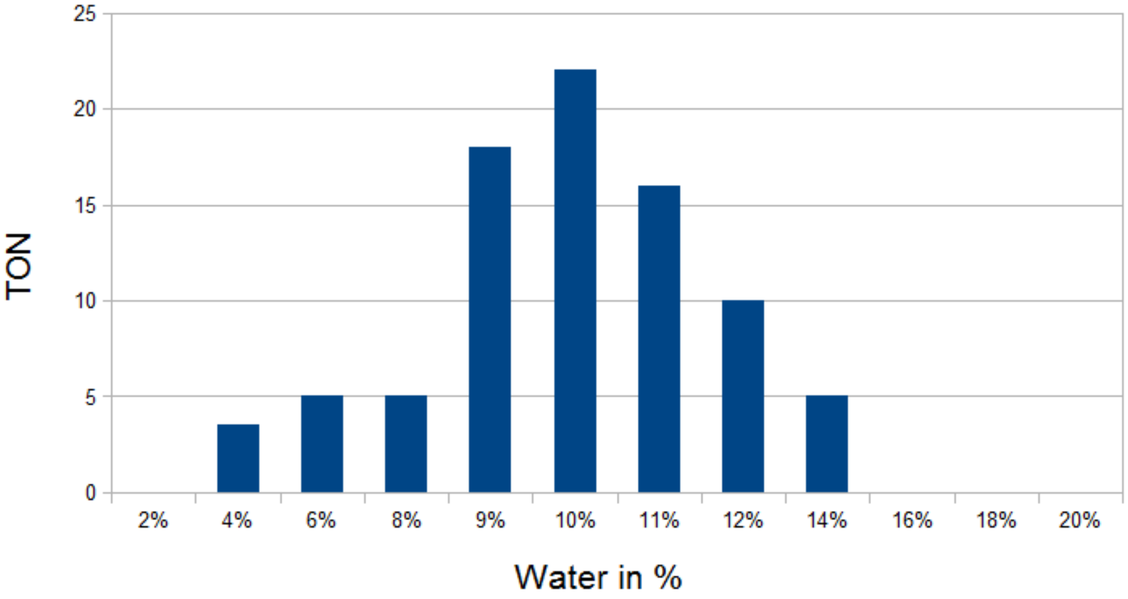


Figure S5. Photo catalytic activity of **OsPt** in relation with water content (BNAH as e⁻donor).

Absorption Spectra

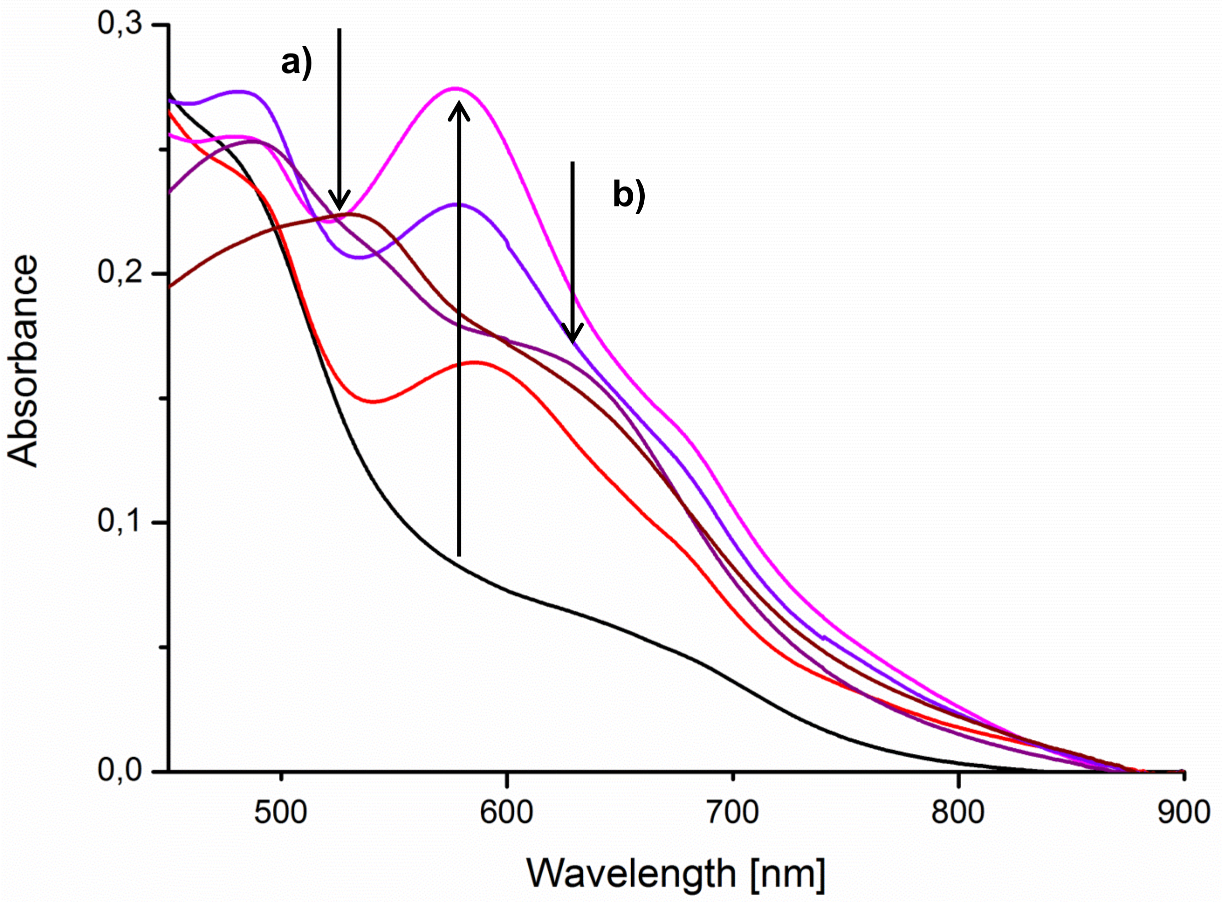


Figure S6. UV-Vis in the catalytic mixture with irradiation at 470 nm. Spectra at different times of irradiation. Starting with the black spectrum without irradiation a band emerges at 590 nm (orange spectrum, 15 min; violet, 45 min) with a maximum intensity after 2h (pink). After completion of the catalysis two bands appear, one at 520 nm (a) and a second at 640 nm (b).

Cyclic voltammetry

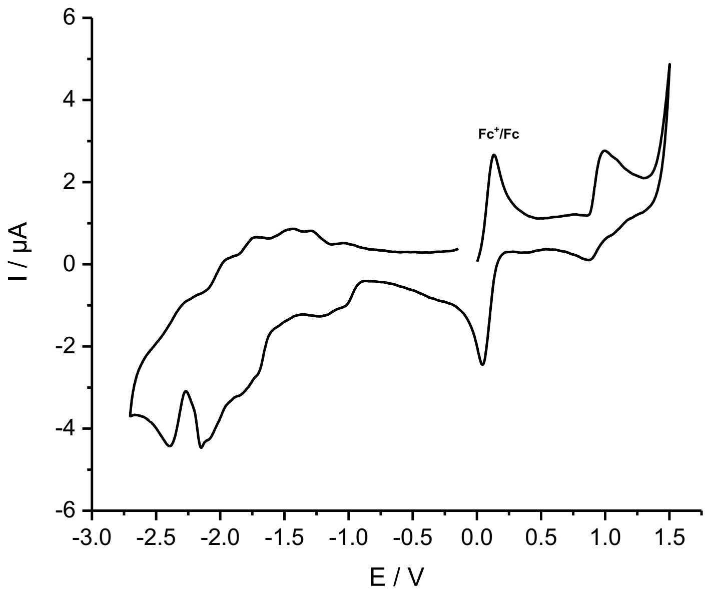


Figure S7: Cyclic voltammogram of RuPt in MeCN containing *n*Bu_4NPF_6 as electrolyte with a glassy carbon electrode as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. Scan rate: 100 mV s^{-1}. All data are referenced against Fc^+/Fc.

Spectroelectrochemical Data

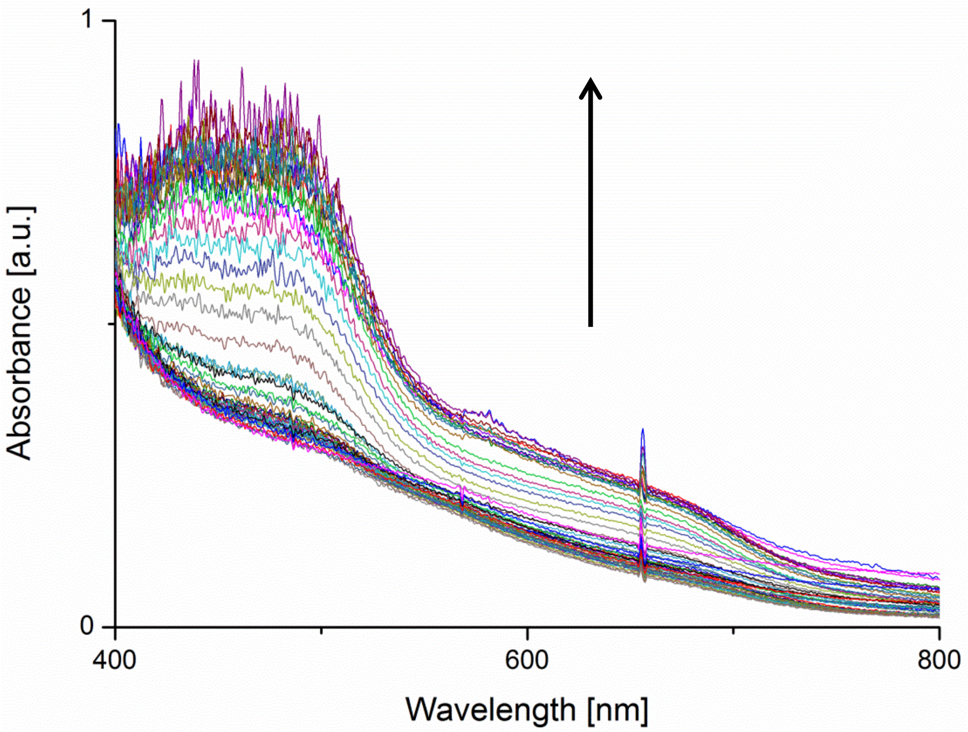


Figure S8. Spectroelectrochemistry of **Ostpphz** (reduction).

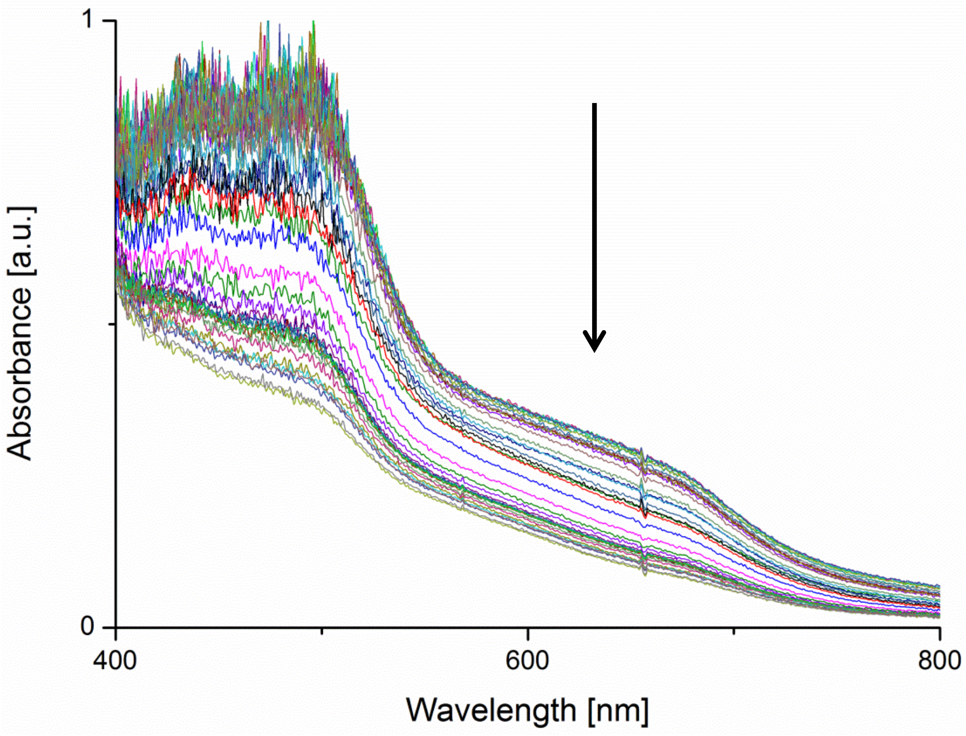


Figure S9. Spectroelectrochemistry of **Ostpphz** (re-oxidation).

Irradiation Setup

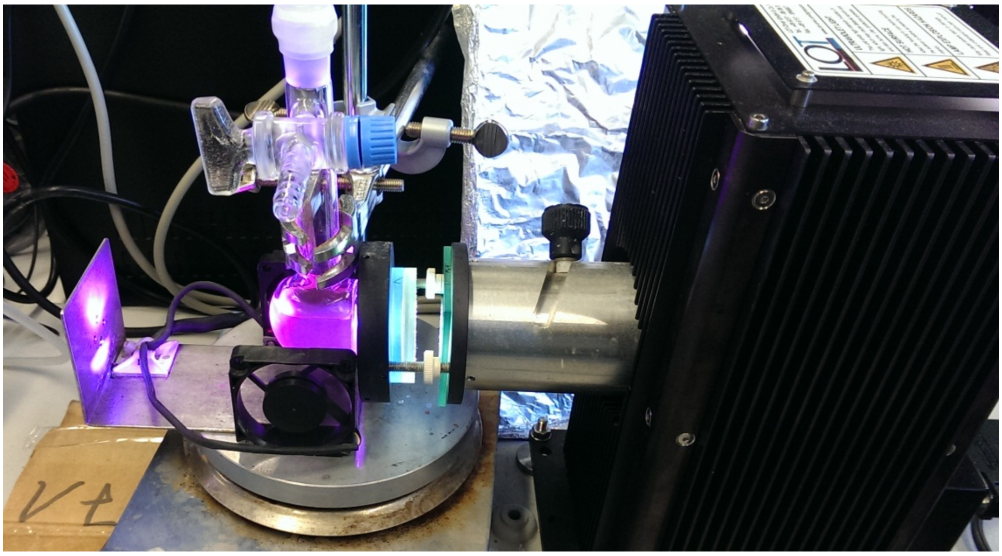


Figure S10. Setting for irradiation with a 150 W Xenon lamp with different cut-off filters.

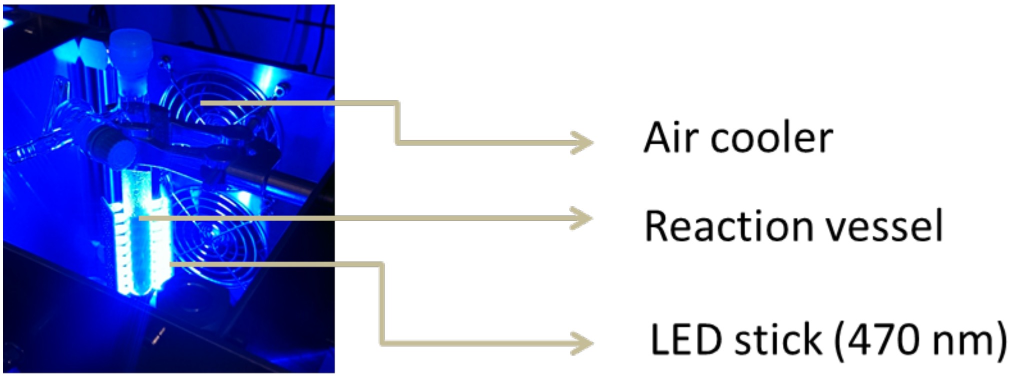


Figure S11. Apparatus for irradiation with blue light (470 nm).

DFT Calculations

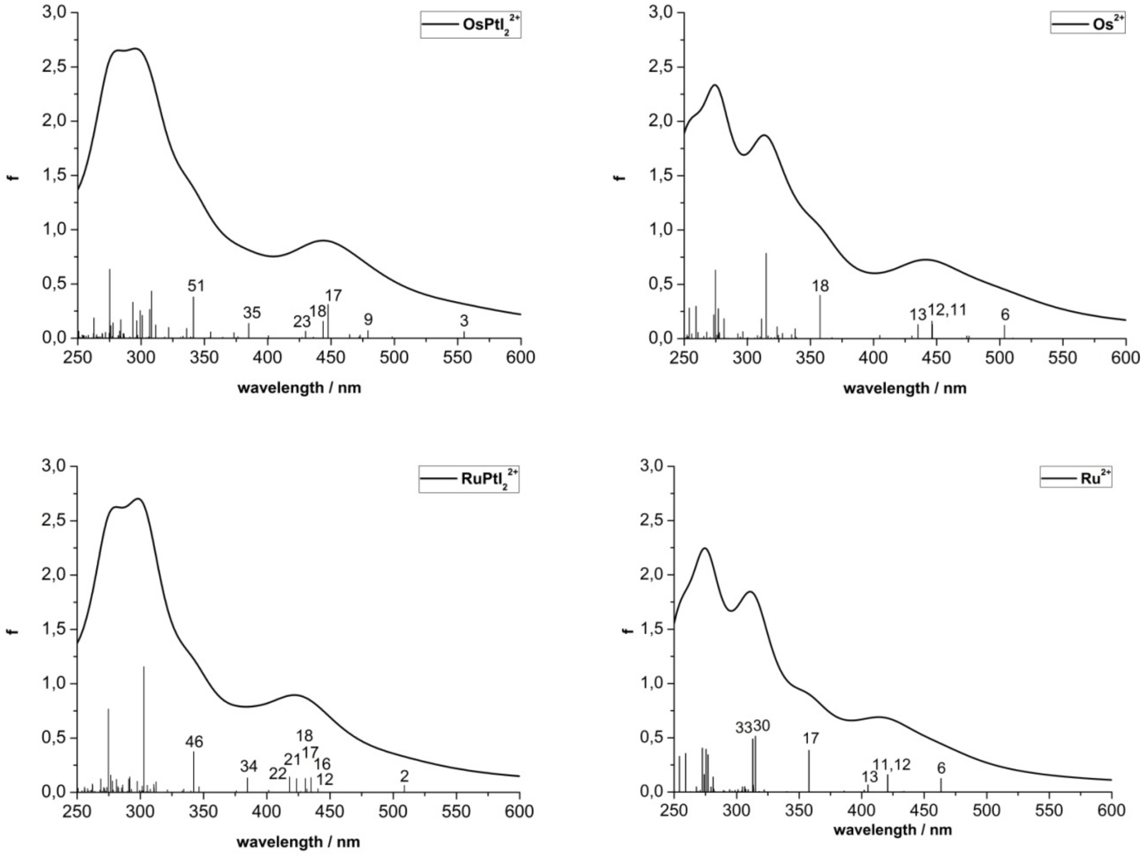


Figure S12. Calculated absorption spectra of **OsPt**, **Ostpphz**, **RuPt** and **Rutpphz**

Table S1. Calculated singlet excited state properties of **OsPt**

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S3	218 ->221	93	2.23	555	0.061	0.000
S8	219 ->224 219 ->226 219 ->221	79 9 8	2.49	498	0.014	0.000
S9	218 ->224 219 ->223 218 ->226	60 22 10	2.59	479	0.071	0.000
S10	219 ->223 218 ->226 218 ->224	68 13 12	2.62	472	0.030	0.000
S11	219 ->226 218 ->227 218 ->223 219 ->224	42 32 15 8	2.63	472	0.013	0.000
S15	218 ->223 219 ->226 218 ->227	78 8 5	2.67	464	0.035	0.000

S17	219 ->227 218 ->226 218 ->224	46 29 14	2.77	447	0.312	0.000
S18	218 ->227 219 ->226	60 34	2.79	443	0.157	0.000
S21	218 ->222 215 ->225	82 9	2.84	436	0.011	0.000
S23	215 ->221	88	2.88	429	0.065	0.000
S31	216 ->225	94	3.10	400	0.025	0.000
S35	215 ->222 217 ->223	68 21	3.22	384	0.138	0.000
S38	215 ->223	93	3.29	376	0.015	0.000
S39	220 ->228	84	3.32	373	0.053	0.000
S41	220 ->229	96	3.40	364	0.010	0.000
S44	219 ->228	90	3.49	354	0.059	0.000
S51	209 ->221 212 ->221 210 ->223	61 21 9	3.63	341	0.381	0.000

Table S2. Calculated triplet excited state properties of **OsPt**

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
T1	220 ->221 220 ->224 220 ->226	58 26 9	1.96	633	0.000	2.000
T2	217 ->225 213 ->225 208 ->225	62 20 8	2.11	586	0.000	2.000
T3	218 ->221 218 ->224 218 ->226	34 28 20	2.12	585	0.000	2.000
T4	220 ->221 220 ->224 220 ->226	33 31 9	2.12	585	0.000	2.000
T5	213 ->225 217 ->225 214 ->225	61 19 13	2.14	580	0.000	2.000
T6	218 ->221 220 ->223 218 ->224 218 ->226	49 12 12 11	2.20	563	0.000	2.000
T7	219 ->221 220 ->224 219 ->224 220 ->226	56 14 11 9	2.20	562	0.000	2.000
T8	220 ->226 219 ->221 220 ->224	57 21 12	2.22	558	0.000	2.000
T9	220 ->227	85	2.24	553	0.000	2.000
T10	215 ->225 205 ->225	85 11	2.30	538	0.000	2.000

Table S3. Calculated singlet excited state properties of **Ostpphz**

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S6	202 ->205 202 ->206	80 14	2.46	503	0.124	0.000
S8	203 ->206 202 ->209 203 ->208	41 31 19	2.61	475	0.025	0.000
S9	204 ->207 202 ->206 202 ->208	47 24 21	2.62	473	0.026	0.000
S11	203 ->207 203 ->209 202 ->208 202 ->206	30 28 19 13	2.78	446	0.132	0.000
S12	202 ->209 203 ->208	49 41	2.78	446	0.163	0.000
S13	203 ->207 203 ->209	60 30	2.85	435	0.130	0.000
S14	202 ->207	92	2.88	430	0.026	0.000
S15	202 ->208 203 ->209 203 ->207	47 26 5	3.06	404	0.031	0.000
S16	204 ->211	97	3.38	367	0.010	0.000
S18	200 ->205 201 ->207	85 10	3.47	357	0.400	0.000

Table S4. Calculated singlet excited state properties of **RuPt**

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S2	218 ->221	95	2.44	508	0.065	0.000
S12	219 ->223 218 ->224	70 21	2.81	440	0.034	0.000
S16	218 ->224 218 ->226 219 ->223	39 32 16	2.85	434	0.137	0.000
S17	218 ->223 219 ->226 218 ->227	56 22 14	2.87	431	0.032	0.000
S18	215 ->221 218 ->226	81 7	2.88	430	0.129	0.000
S21	219 ->227 218 ->226 218 ->224 219 ->223 215 ->221	39 23 19 7 5	2.93	423	0.128	0.000
S22	218 ->227 219 ->226	53 42	2.97	418	0.144	0.000
S29	216 ->225	96	3.09	401	0.021	0.000
S34	215 ->222 217 ->223	72 22	3.22	384	0.134	0.000
S35	215 ->223	94	3.30	375	0.016	0.000
S45	220 ->228	88	3.58	346	0.052	0.000
S46	210 ->221 212 ->221	61 23	3.62	342	0.376	0.000

	209 ->223	9				

Table S5. Calculated singlet excited state properties of **Rutpphz**

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S6	203 ->205	82	2.68	463	0.126	0.000
	203 ->206	11				
S11	203 ->206	34	2.95	420	0.160	0.000
	202 ->209	25				
	202 ->207	18				
	203 ->205	7				
	203 ->208	6				
	204 ->207	5				
S12	202 ->208	47	2.95	420	0.158	0.000
	203 ->209	39				
	202 ->206	5				
	203 ->207	5				
S13	202 ->207	66	3.06	404	0.067	0.000
	202 ->209	28				
S14	203 ->207	83	3.09	401	0.018	0.000
	203 ->209	12				
S17	200 ->205	86	3.47	357	0.386	0.000
	201 ->207	10				
S25	202 ->211	90	3.85	322	0.021	0.000
S30	204 ->214	44	3.94	315	0.533	0.000
	201 ->207	32				
S31	204 ->215	74	3.96	313	0.025	0.000
	201 ->206	7				
S32	201 ->206	42	3.96	313	0.074	0.000
	200 ->207	14				
	195 ->205	13				
	204 ->215	12				
S33	201 ->207	41	3.96	312	0.474	0.000
	204 ->214	19				
	202 ->213	7				
	200 ->205	5				
	202 ->214	5				

Table S6. Orbitals of **OsPt**

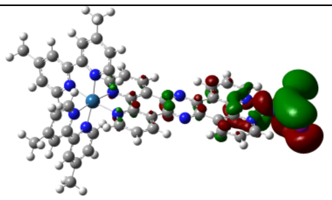
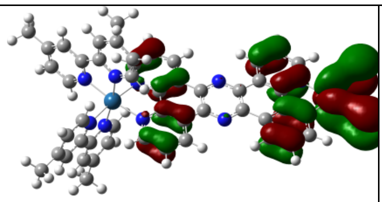
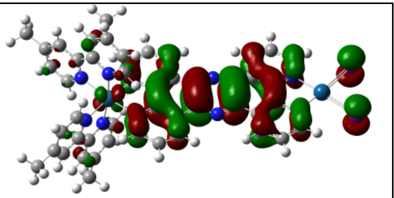
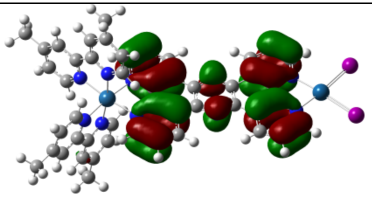
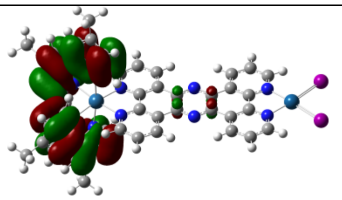
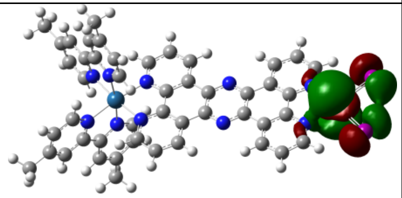
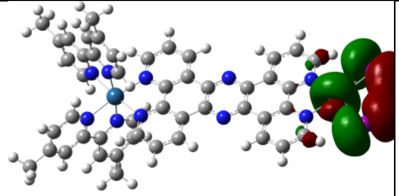
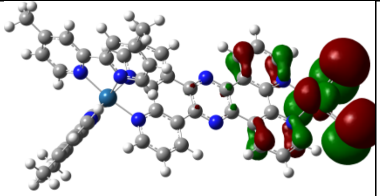
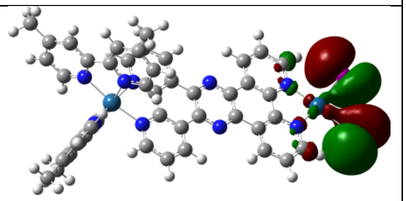
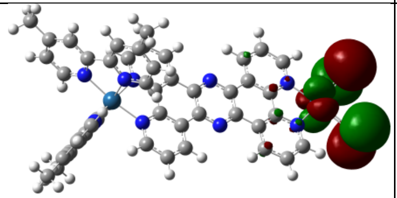
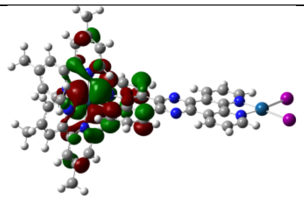
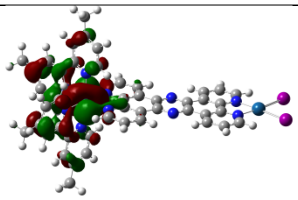
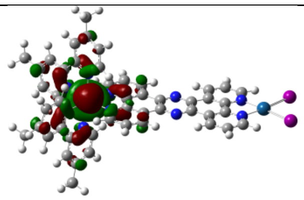
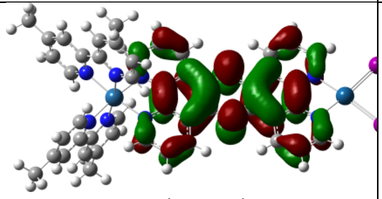
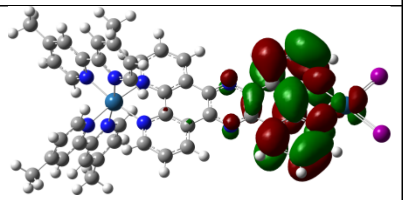
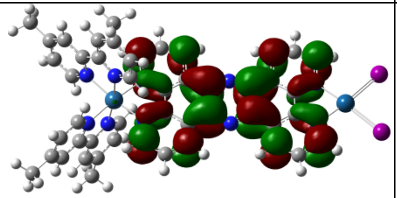
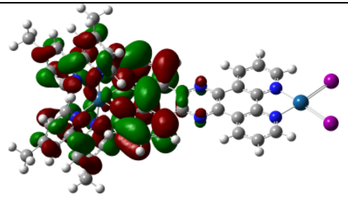
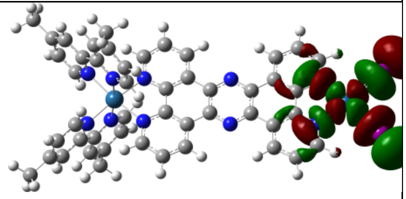
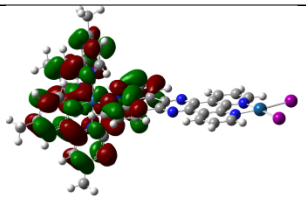
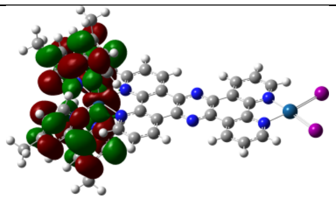
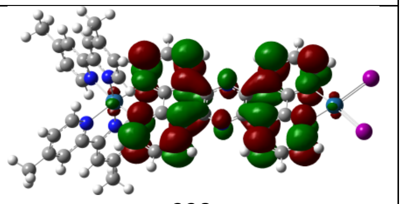
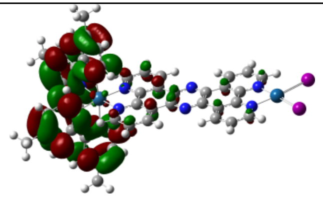
 205	 208	 209
 210	 212	 213
 214	 215	 216
 217	 218	 219
 220 (HOMO)	 221 (LUMO)	 222
 223	 224	 225
 226	 227	 228
 229		

Table S7. Orbitals of **Ostpphz**

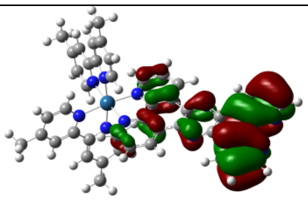
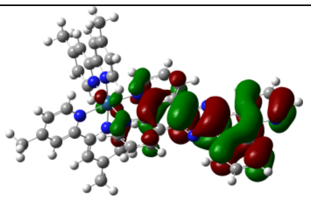
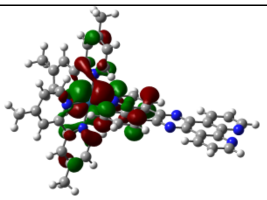
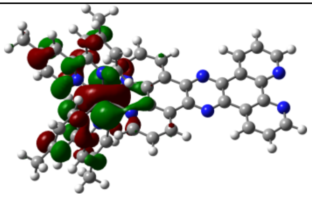
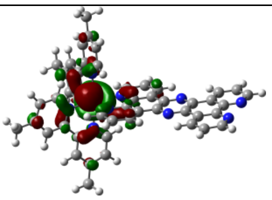
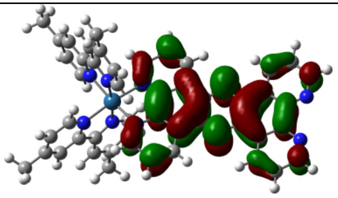
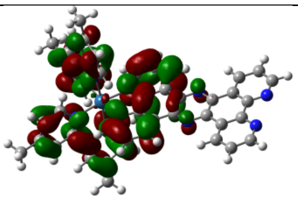
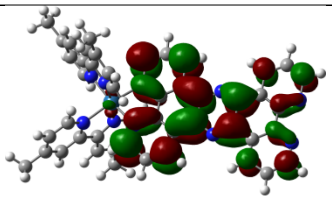
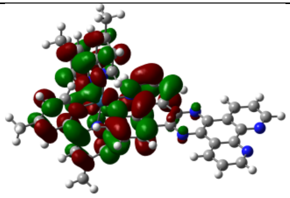
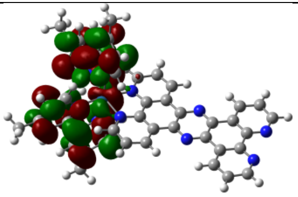
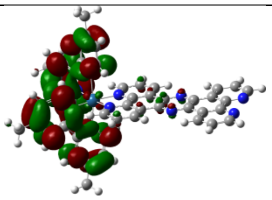
 200	 201	 202
 203	 204	 205 (HOMO)
 206 (LUMO)	 207	 208
 209	 211	

Table S8. Orbitals of **RuPt**

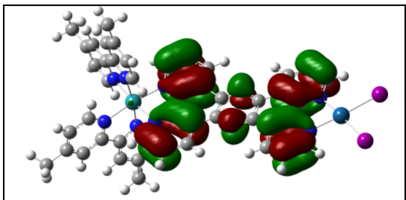
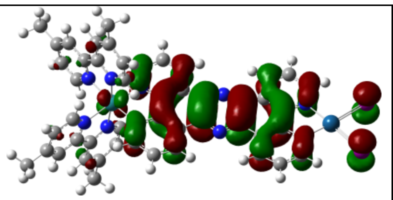
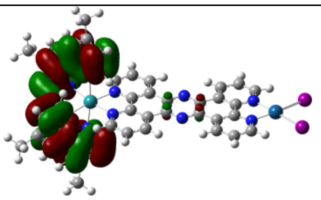
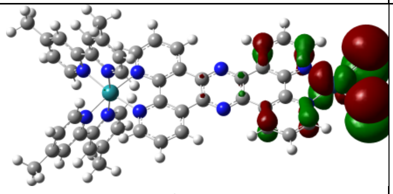
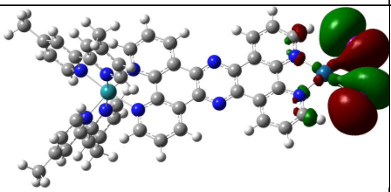
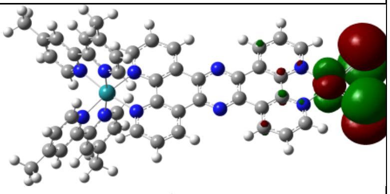
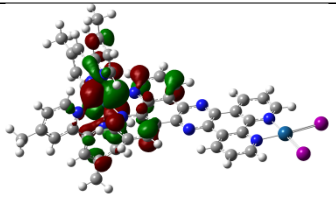
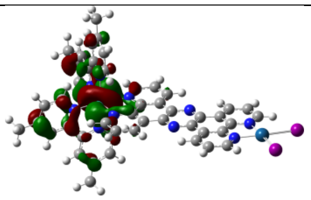
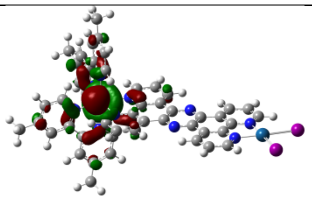
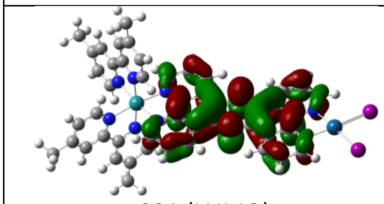
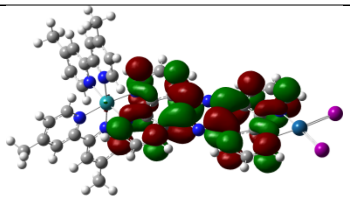
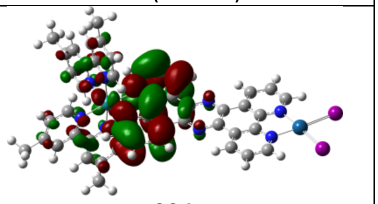
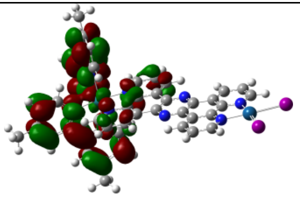
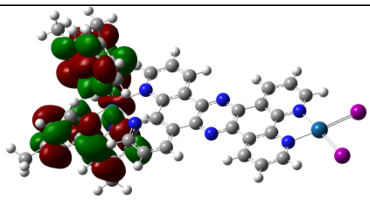
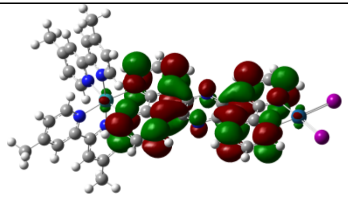
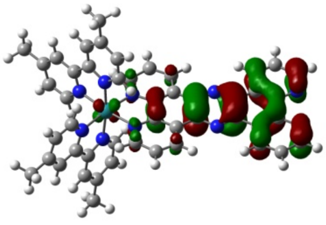
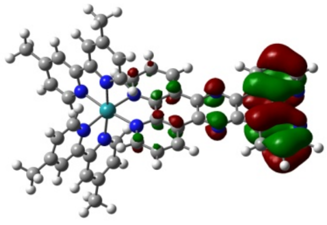
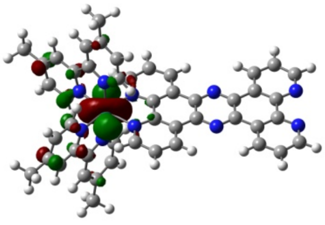
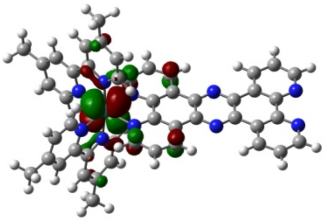
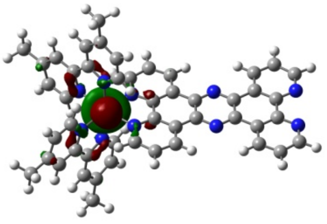
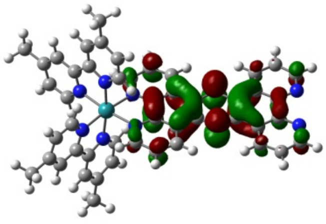
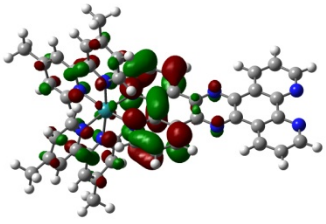
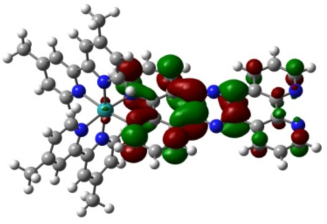
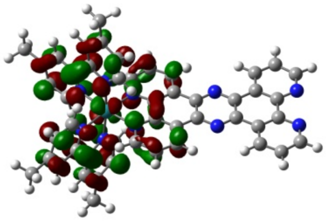
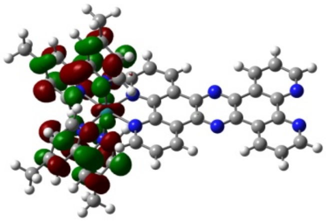
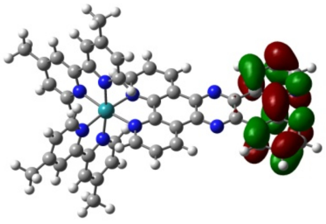
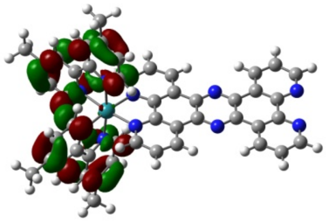
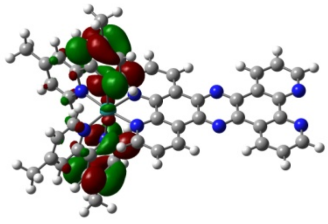
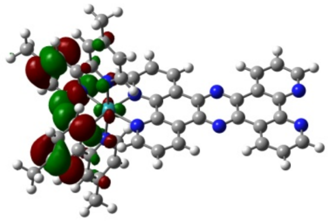
 209	 210	 212
 215	 216	 217
 218	 219	 220 (HOMO)
 221 (LUMO)	 223	 224
 226	 227	 228

Table S9. Orbitals of **Rutpphz**

 200	 201	 202
 203	 204 (HOMO)	 205 (LUMO)
 206	 207	 208
 209	 210	 211
 213	 214	