Electronic Supplementary Information

Mechanism of Action of the Curcumin *cis*-Diammineplatinum(II) Complex as Photocytotoxic Agent

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Table of Contents

- **Table S1:** Vertical excitation energies, ΔE (eV), wavelength λ (nm), oscillator strengths (f) and main configuration (%) for curcumin and Platicur complex computed in water …. S3
- **Figure S1:** Energetic diagram of the highest occupied molecular orbitals (from H to H-3) and the lowest unoccupied molecular orbitals (from L to L+2) involved in the electronic transitions of Platicur ……… S4
- **Figure S2:** Electron Density Difference Maps EDDMs between the excited singlet and ground states for Platicur complex (Purple and yellow colors represent a decrease and an increase in charge density, respectively). Natural Transition Orbitals NTOs for the corresponding states ……… S5
- **Figure S3:** TDDFT singlet excited states Sn (with n = 1-10) energy from relaxed scan calculation along the Pt-O distance reaction coordinate, going from 2.0 to 3.0 Å, accounting for the detachment of the curcumin ligand ……… S6
- **Figure S4:** Optimized structures (with selected geometric parameters) of ground and lowest singlet excited states (S_1 and S_2) and their adiabatic energy gaps ……… S7
- **Figure S5**: Optimized structures and selected geometric parameters of the triplet excited states (T_1 – T_4) lying below the energy of S_1 ……… S8

- **Figure S6**: Energy profile for the conversion of $ADD_{(1)}$ in $ADD_{(4)}$ and the optimized structure of the involved transition state …………………………………………………………………………………S9
- **Figure S7:** Photophysical properties of curcumin: a) excited states adiabatic energies, b) SOC and $\Delta E(S_m-T_n)$, c) vertical electron affinity VEA and ionization potential VIP (Type I photoreactions), d) Molecular Orbitals counter plot ……………………………………………… S10
- **Figure S8:** Potential energy surface and a cut out of the optimized structures of all the stationary points intercepted along the GS curcumin release ………………………………….. S11
- **References** ……………………………………………………………………………………………………….. S12

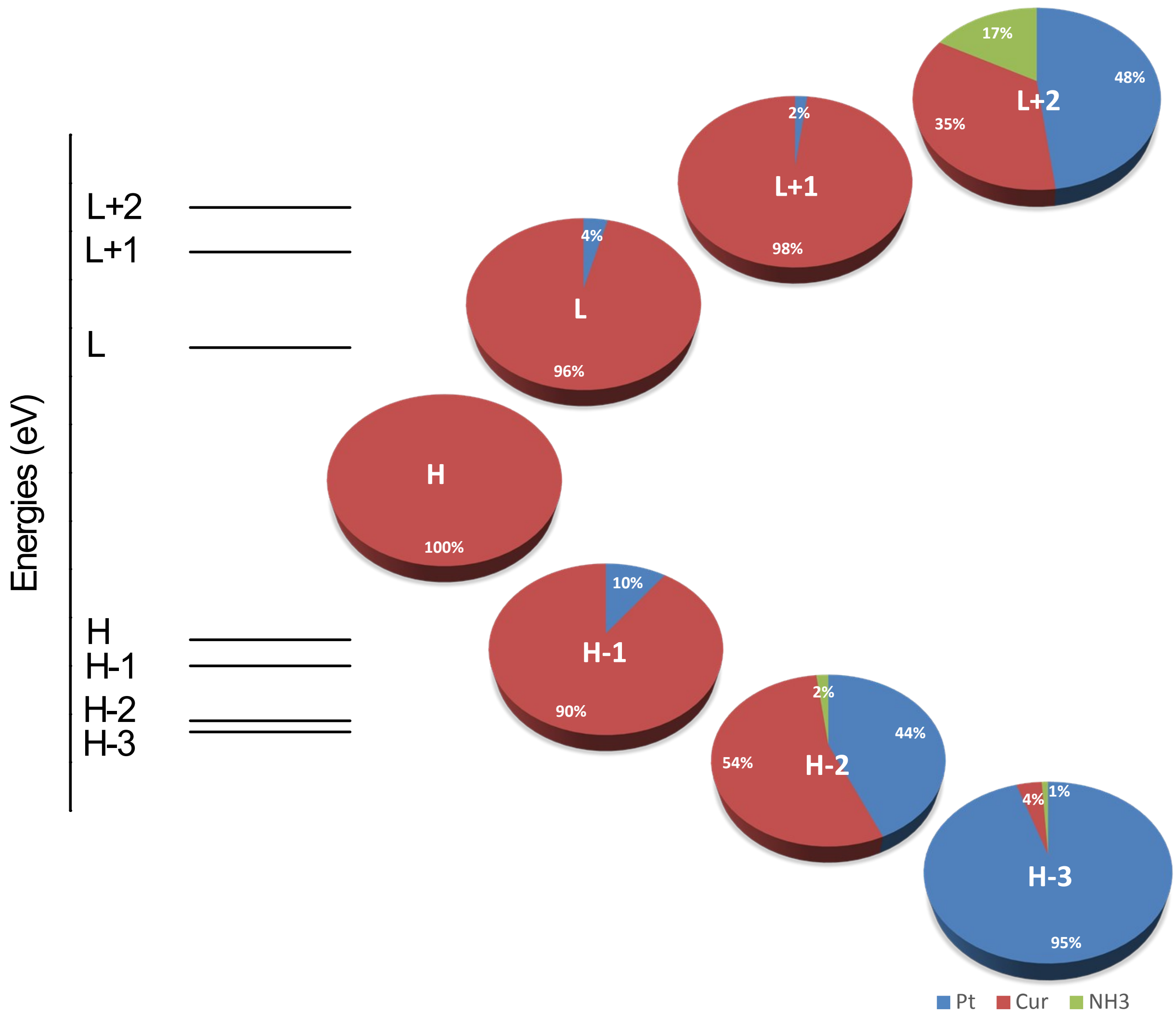
Table S1

Vertical excitation energies, ΔE (eV), wavelength λ (nm), oscillator strengths (f) and main configuration (%) for curcumin (HCur) and Platicur complex computed in water.

	λ	ΔE	Main Configuration, %	f^{a}	$\lambda^{exp,b}$	Assignment
HCur						
S_1	452	2.74	H→L, *99*	1.051	430	$^1\pi\pi^*$
S_2	385	3.22	H-1→L, *93*	0.143		$^1\pi\pi^*$
S_3	334	3.71	H→L+1, *69*	0.169	358	$^1\pi\pi^*$
S_4	309	4.01	H-1→L+1, *54*	0.268		$^1\pi\pi^*$
Platicur						
S_1	473		H→L, *99*	0.902	460	^{1}LC/^{1}LMCT
S_2	411		H-1→L, *96*	0.334	435	^{1}LC/^{1}MLCT
S_3	330		H→L+1, *48*; H-4→L, *23*	0.468	385	^{1}LC/^{1}MLCT
S_4	319		H-2→L+1, *82*	0.235		^{1}MLCT

a. Only transitions with oscillator strength greater than 0.1 were included, b. experimental spectrum from ref. [1]

Figure S1



Energetic diagram of the highest occupied molecular orbitals (from H to H-3) and the lowest unoccupied molecular orbitals (from L to L+2) involved in the electronic transitions of **Platicur**. The pie charts represent the percentage of participation of each portion of the complex, platinum (■ Pt), curcumin (■ Cur) and ammonia (■ NH_3) ligands, in the reported molecular orbitals.

Figure S2

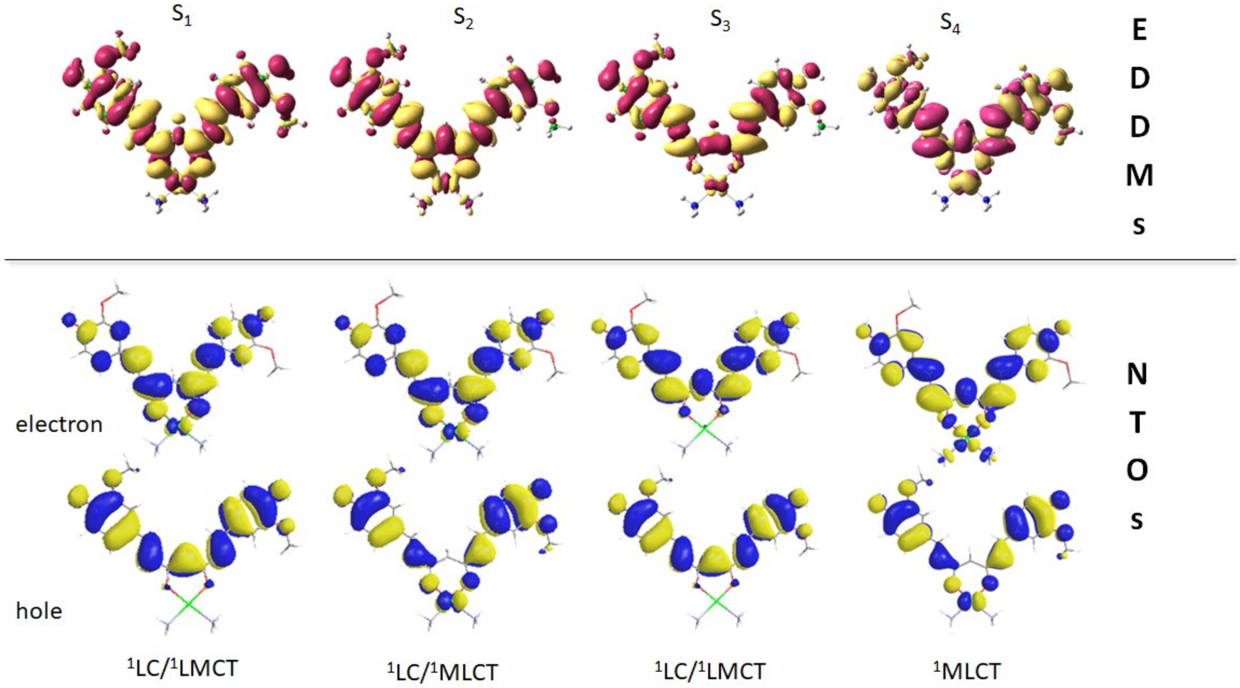
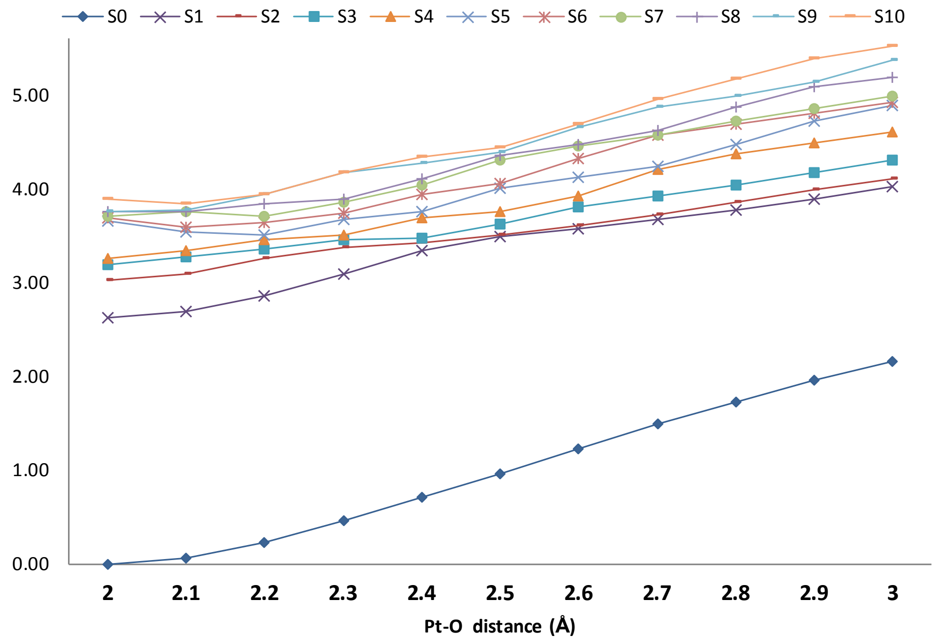
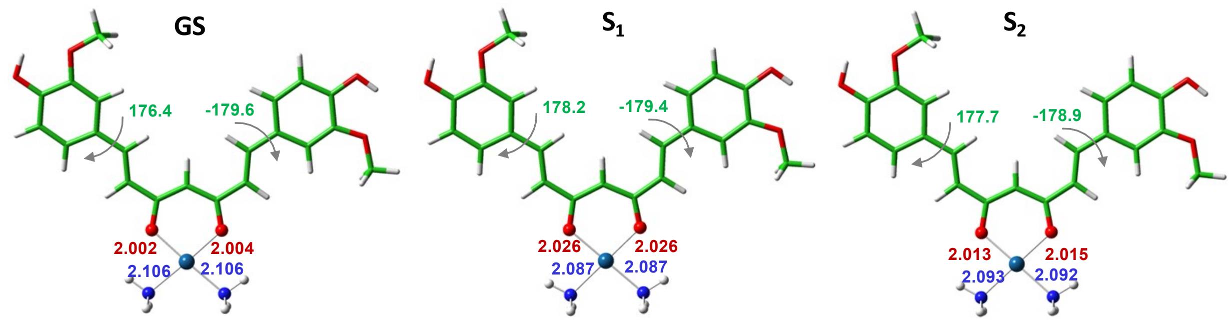

S1
S2
S3
S4
EDDMs
NTOs
electron
hole
1LC/1LMCT
1LC/1MLCT
1LC/1LMCT
1MLCT

Figure S3



S0
S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
0.00
1.00
2.00
3.00
4.00
5.00
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3
Pt-O distance (Å)

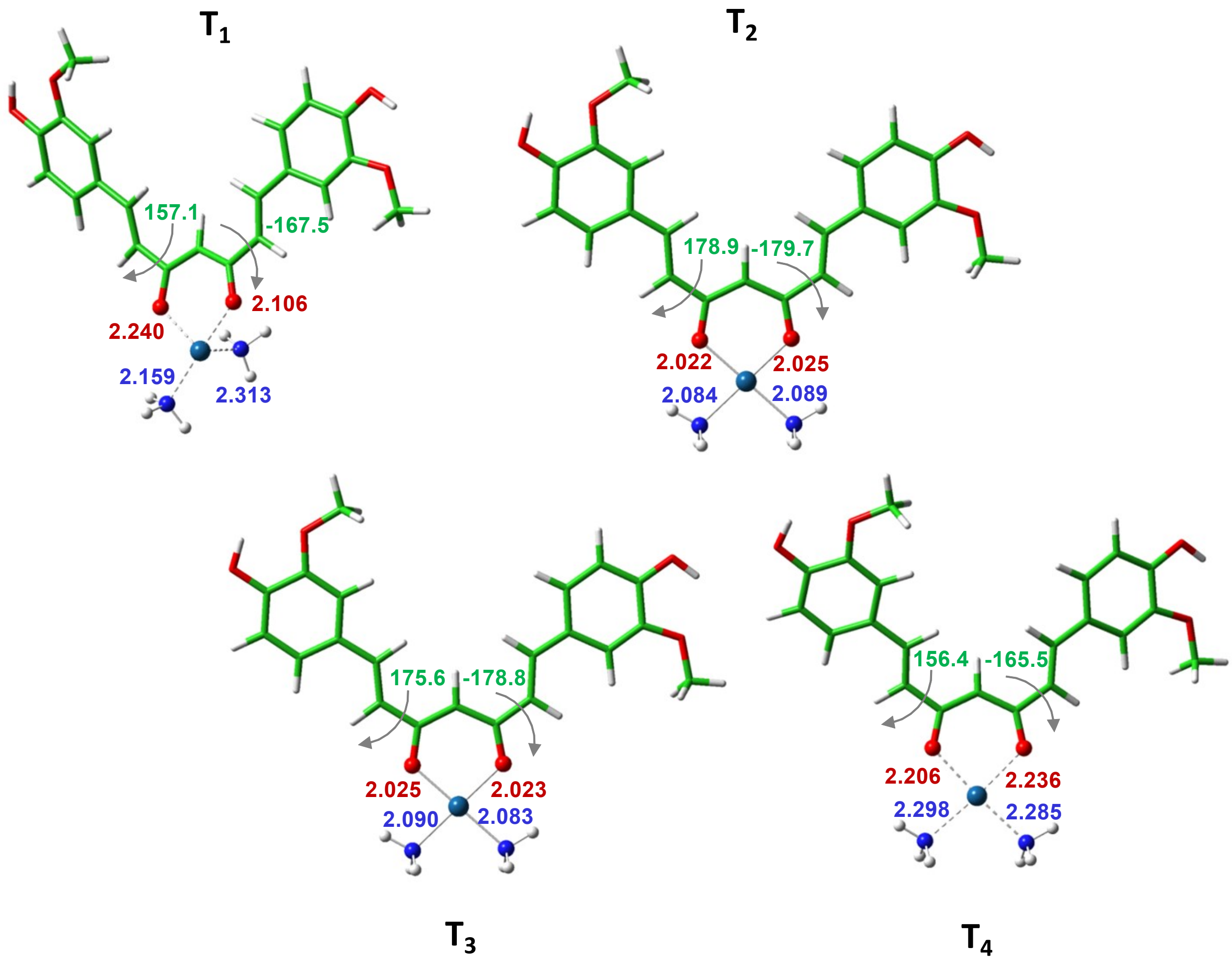
Figure S4



ΔE^a (eV)	0.0	2.42	2.87

[a]Adiabatic energies

Figure S5



T_1
157.1
-167.5
2.240
2.106
2.159
2.313
T_2
178.9
-179.7
2.022
2.025
2.084
2.089
175.6
-178.8
2.025
2.023
2.090
2.083
156.4
-165.5
2.206
2.236
2.298
2.285
T_3
T_4

Figure S6

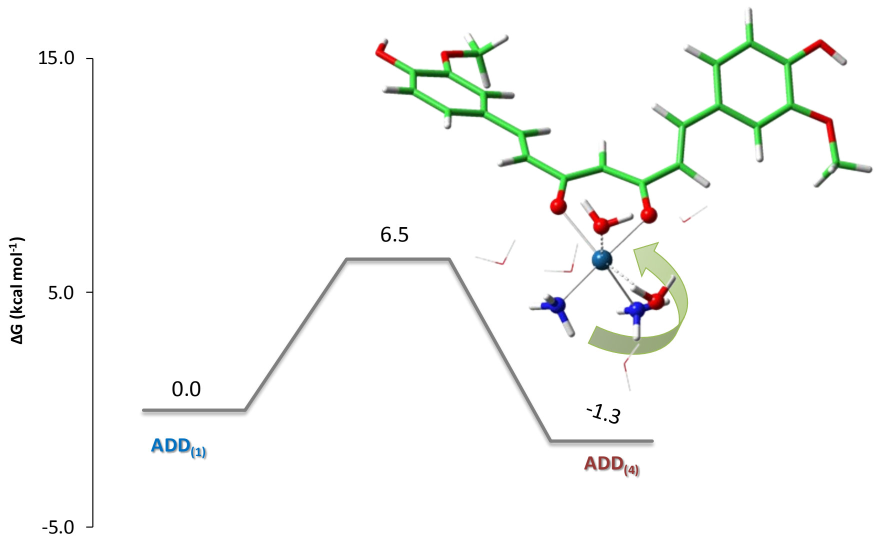
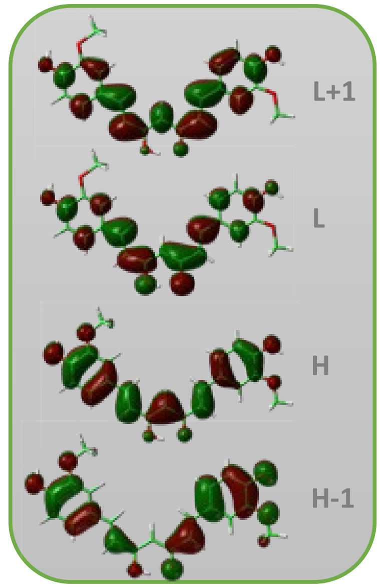


Figure S7

a)	ΔE (eV)	Main Configuration, %	Character
S_1	2.45	H→L, 99	$^1\pi\pi^*$
S_2	2.97	H-1→L, 93	$^1\pi\pi^*$
T_1	**1.61**[a]	H→L, 47;	$^3\pi\pi^*$
		H→L+1, 47	$^3\pi\pi^*$
T_2	2.08	H→L, 51;	$^3\pi\pi^*$
		H→L+1, 48	
T_3	2.74	H-1→L, 76	$^3\pi\pi^*$
T_4	2.87	H→L+1, 49	$^3\pi\pi^*$

b)	m,n	SOC (cm^{-1})	ΔE S_m-T_n(eV)
	1,1	$5.4 \cdot 10^{-3}$	0.85
	1,2	$5.4 \cdot 10^{-3}$	0.37
	2,3	$5.2 \cdot 10^{-2}$	0.23
	2,4	$5.2 \cdot 10^{-2}$	0.11

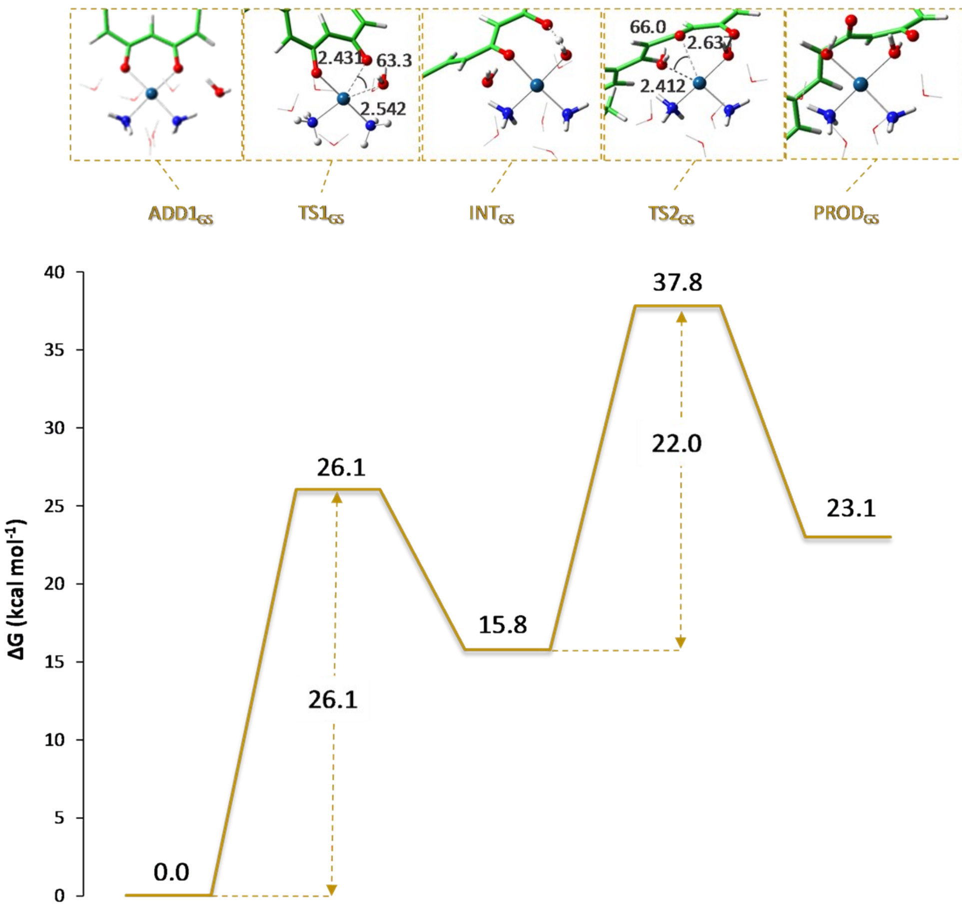
d)



c)	[b] Photoprocess	Requirement	VEA	VIP	VEA(T_1)	VIP(T_1)
1.	$^3Ps + {}^3O_2 \rightarrow Ps^{(+)\cdot} + O_2^{(-)\cdot}$	VEA ($^3O_2$) + VIP (^3Ps) < 0	-2.83	5.67	-4.76	3.74
2.	$Ps^{(-)\cdot} + {}^3O_2 \rightarrow {}^1Ps + O_2^{\cdot(-)}$	VEA ($^3O_2$) + VEA (^1Ps) <0				
3.	$^3Ps + {}^1Ps \rightarrow Ps^{(+)\cdot} + Ps^{(-)\cdot}$	VEA (^3PS) + VIP (^1Ps) < 0				
4.	$^3Ps + {}^3Ps \rightarrow Ps^{(+)\cdot} + Ps^{(-)\cdot}$	VEA (^3PS) + VIP (^3Ps) < 0			**VEA($^3O_2$)**	**-3.16**

[a] sufficient energy to promote the molecular oxygen transition ($^3\Sigma_g^- \rightarrow {}^1\Delta_g$); [b] computed in water B3LYP/6-311+G**.

Figure S8



66.0
2.637
2.431
63.3
2.412
2.542
ADD1$_{GS}$
TS1$_{GS}$
INT$_{GS}$
TS2$_{GS}$
PROD$_{GS}$
ΔG (kcal mol^{-1})
40
35
30
25
20
15
10
5
0
0.0
26.1
26.1
15.8
37.8
22.0
23.1

References

[1] Mitra, K.; Gautam, S.; Kondaiah, P.; Chakravarty. A. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 13989-13993.