Effect of a Peripheral Substituent on the Ultrafast Dynamics and the rate of Intersystem Crossing in charge-transfer states of Platinum(II) acetylides

Supplementary Information

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General information

All reagents were purchased from Sigma Aldrich and used without further purification, unless otherwise stated. HPLC-grade solvents were purchased and used as is, unless otherwise stated. Spectroscopy grade solvents were used in all spectroscopic experiments.

1 Synthetic Procedure for *trans*-{4-ethynyl-N-(p-methyl-benzoate)-1,8-naphthalimide}$Pt(PBu_3)_2Cl$

1.1 *cis*-$Pt(PBu_3)_2Cl_2$

Tri-n-butylphosphine (0.51 ml, ρ = 0.81 g/mol, 2.041 mmol) was added to a suspension of $PtCl_2$ (307 mg, 1.154 mmol) in dry deaerated CH_2Cl_2 (20 ml) and stirred at room temperature for 50h. Reaction solution was filtered to remove unreacted solids and evaporated to dryness to give a waxy grey mass. Purification was carried out through thorough washing of crude material with small portions of hexane (3 × 20 ml) then redissolving into Et_2O. Ethereal solution was filtered and evaporated to yield waxy off-white product of yield = 456 mg, 67 %.

^1H NMR ($CDCl_3$, 250 MHz): 0.85-1.04 (m, 18H), 1.34-1.66 (m, 24H), 1.75-2.17 (m, 12H). ^{31}P NMR ($CDCl_3$, 250 MHz): 0.95 ($J_{Pt\text{-}P}$ = 3519 Hz). AP-MS: m/z = 670.2 (M^+, 95%), 635.2 (M^+-Cl, 100 %), 599.3 (M^+-2Cl, 32%). Anal. Calc. for $C_{24}H_{54}Cl_2P_2Pt$ (%): C 42.98, H 8.12. Found (%): C 42.49, H 8.21.

1.2 Synthesis of 4-bromo-*N*-(*p*-methylbenzoate)-1,8-naphthalimide

1.2.1 Method 1.

4-Bromo-1,8-naphthalic anhydride (1.0 g 3.609 mmol), methyl 4-aminobenzoate (702 mg, 4.644 mmol) and anhydrous $Zn(OAc)_2$ (505 mg, 2.752 mmol) were dissolved in anhydrous pyridine (10 ml). The resultant deep red-brown coloured mixture was stirred and heated to 125 °C for 2 days. The mixture was then cooled to room temperature and added to aqueous HCl (4 %, 100 ml).

A dark-brown precipitate was collected through filtration, washed with H_2O then redissolved in CH_2Cl_2 (400 ml). The organic layer was then washed with the following: 1 × 200 ml H_2O, 1 × 250 ml brine, 1 × 300 ml H_2O. The organic phase was removed and dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation. Crude solids were purified through column chromatography (SiO_2, gradient elution, $CH_2Cl_2$to 0.5 % MeOH:CH_2Cl_2). The product was isolated as a pale yellow solid. Yield = 240 mg, 16 %.

^{1}H NMR ($CDCl_3$, 400 MHz): 3.96 (s, 3H), 7.41 (d, *J* = 8.60 Hz, 2H), 7.91 (t, *J* = 7.92 Hz, 1H), 8.10 (d, *J* = 7.88 Hz, 1H), 8.23 (d, *J* = 8.60 Hz, 2H), 8.47 (d, *J* = 7.88 Hz, 1H), 8.66 (dd, *J* = 1.12, 8.52 Hz, 1H), 8.71 (dd, *J* = 1.12, 7.32 Hz, 1H). ES-MS: m/z = 412 (MH^+, 100%).

1.2.2 Method 2.

4-Bromo-1,8-naphthalic anhydride (1.021 g, 3.685 mmol) and methyl-4-aminobenzoate (1.366 g, 9.036 mmol) were dissolved in acetic acid (100 %, 60 ml) and refluxed for 41 hours. The orange-coloured solution which was cooled to room temperature and added to H_2O (250 ml). The resulting precipitate was collected through filtration, washed with H_2O and boiled in aqueous $NaHCO_3$ solution (20 %, 150 ml) for 1.5 hours. The suspension was cooled to room temperature and the crude solids were collected through filtration. Purification was performed by column chromatography (SiO_2, gradient elution, CH_2Cl_2 to 0.5 % MeOH: CH_2Cl_2) to yield a pale yellow solid. Yield = 310 mg, 21 %.

1H NMR (CDCl3, 250 MHz): 3.96 (s, 3H), 7.41 (d, *J* = 8.64 Hz, 2H), 7.91 (t, *J* = 7.94 Hz, 1H), 8.10 (d, *J* = 7.89 Hz, 1H), 8.23 (d, *J* = 8.59 Hz, 2H), 8.47 (d, *J* = 7.87 Hz, 1H), 8.66 (dd, *J* = 1.05, 8.59 Hz, 1H), 8.71 (dd, *J* = 1.09, 7.34 Hz, 1H). ES-MS: m/z = 412 (MH^+, 100%). Anal. Calc. for $C_{20}H_{12}NO_4Br$ (%): C 58.56, H 2.95, N 3.41. Found (%): C 57.88, H 2.80, N 3.31.

1.3 Synthesis of 4-ethynyl-*N*-(*p*-methylbenzoate)-1,8-naphthalimide

4-Bromo-N-(p-methylbenzoate)-1,8-naphthalimide (533 mg, 1.299 mmol), $Pd(PPh_3)_2Cl_2$ (47 mg, 0.066 mmol, 5.1 mol%), CuI (30 mg, 0.157 mmol, 12.1 mol%) and PPh_3 (24 mg, 0.091 mmol, 7.0 mol%) were dissolved in dry, deaerated THF (20 ml). Trimethylsilylacetylene (0.82 ml, ρ = 0.695 g/ml, 5.803 mmol) was added and the solution stirred at room temperature for 5 minutes, then deaerated Et_3N (15 ml) was added, and a colour change from yellow to dark brown was observed. The reaction mixture was heated to 70 °C for 24 hours then cooled to room temperature and the solvent removed by rotary evaporation, The crude residue was redissolved in CH_2Cl_2 (150 ml) and washed with H_2O (2 × 100 ml). The organic phase was removed, dried over $MgSO_4$, filtered and then evaporated to dryness.

Removal of the trimethylsilyl protecting group was carried out by adding the solids to a suspension of K_2CO_3 (545 mg, 3.943 mmol) in deaerated 1:3 (v/v) MeOH/CH_2Cl_2 (40 ml) and stirring vigorously for 19 hours at room temperature. The reaction was quenched by addition of H_2O (50 ml) and the organic solvents then removed by rotary evaporation. An additional aliquot of H_2O (100 ml) was added to the resultant aqueous suspension and extracted with 2 × 100 ml portions of CH_2Cl_2. The organic phases were combined and washed with 1 × 100 ml H_2O dried over $MgSO_4$, then filtered and reduced in volume. The product was purified through column chromatography (SiO_2, 0.25 % MeOH:CH_2Cl_2) which yielded a pale yellow solid. Yield = 246 mg, 53 %.

^{1}H NMR ($CDCl_3$, 400 MHz): 3.78 (s, 1H), 3.96 (s, 3H), 7.41 (d, *J* = 8.52 Hz, 2H), 7.88 (t, *J* = 7.80 Hz, 1H), 7.99 (d, *J* = 7.56 Hz, 1H), 8.23 (d, *J* = 8.52 Hz, 2H), 8.58 (d, *J* = 7.60 Hz, 1H), 8.68 (dd, *J* = 1.04, 7.32 Hz, 1H), 8.75 (dd, *J* = 1.04, 8.44 Hz, 1H). ESMS: m/z = 356 (MH^+, 100%).

1.4 Synthesis of *trans*-{4-ethynyl-*N*-(*p*-methylbenzoate)-1,8-naphthalimide}$Pt(PBu_3)_2Cl$

4-ethynyl-N-(*p*-methylbenzoate)-1,8-naphthalimide (77 mg, 0.216 mmol) and cis-$Pt(PBu_3)_2Cl_2$ (173 mg, 0.258 mmol) were dissolved in deaerated $^iPr_2NH$ (25 ml) and heated to 90 °C in the dark for 16 hour. The solution was allowed to cool to room temperature and the solvent was removed to give a yellow-orange residue. Purification was carried out through column chromatography (SiO_2, 0.2 % MeOH:CH_2Cl_2). A distinct yellow band was collected which, after removal of the solvent, yielded the product as a yellow oil. Yield = 97 mg, 45 %.

^{1}H NMR ($CDCl_3$, 400 MHz): 0.91 (t, *J* = 7.24 Hz, 18H), 1.37-1.48 (m, 12H), 1.57-1.66 (m, 12H), 1.96-2.08 (m, 12H), 3.96 (s, 3H), 7.40 (d, *J* = 8.56 Hz, 2H), 7.63 (d, *J* = 7.72 Hz, 1H), 7.72 (t, *J* = 7.80 Hz, 1H), 8.22 (d, *J* = 8.60 Hz, 2H), 8.49 (d, *J* = 7.76 Hz, 1H), 8.62 (dd, *J* = 1.12, 7.22 Hz, 1H), 8.80 (dd, *J* = 1.16, 8.34 Hz, 1H). 31P NMR ($CDCl_3$, 101 MHz): 7.87 ($J_{Pt\text{-}P}$ = 2335 Hz). ES-MS: m/z = 954 (MH^+-Cl, 14%), 599 ($Pt(PBu_3)_2^+$, 100%).

2 Cyclic Voltammetry

Cyclic voltammograms were recorded using an Autolab Potentiostat 100 using GPE software. Analyte solutions were prepared using N_2-saturated dry CH_2Cl_2 obtained from a Grubbs solvent purification column having a typical concentration of 1.65 mmol dm^{-3}. Measurements were performed at room temperature under a positive pressure of solvent saturated N_2. $[N^nBu_4][PF_6]$ was used as a supporting electrolyte, being recrystallised from ethanol and oven dried prior to use, with a typical solution concentration of 0.2 mol dm^{-3}. The working electrode was either a platinum or glassy carbon disc. Platinum wire was utilised as the counter electrode. The reference electrode was Ag/AgCl, being chemically isolated from the analyte solution by an electrolyte containing bridge tube tipped with a porous frit. Ferrocene was utilised as an internal reference, with all potentials being quoted relative to the Fc/Fc^+ couple.

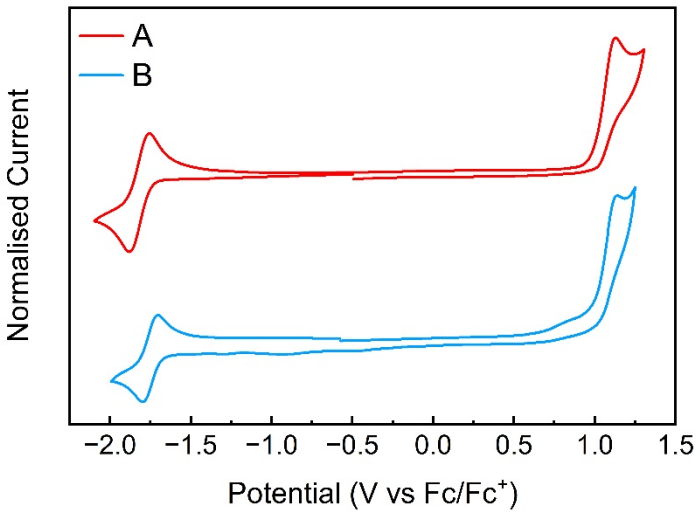


Figure S1: Cyclic voltammograms for complexes A (Cl-Pt-NAP) and B (Cl-Pt-NAP-PhCOOMe) in f CH_2Cl_2 solution recorded at room temperature at a scan rate of 100 mV s^{-1}. Solutions contained 0.2 mol dm^{-3} $[N^nBu_4][PF_6]$ as the supporting electrolyte. All potentials are shown against the Fc/Fc^+ couple.

3 Ultrafast Transient Absorption: Comparison of the data for compounds A and B

3.1 Comparison of UV-visible TA DAS components between complex A and B

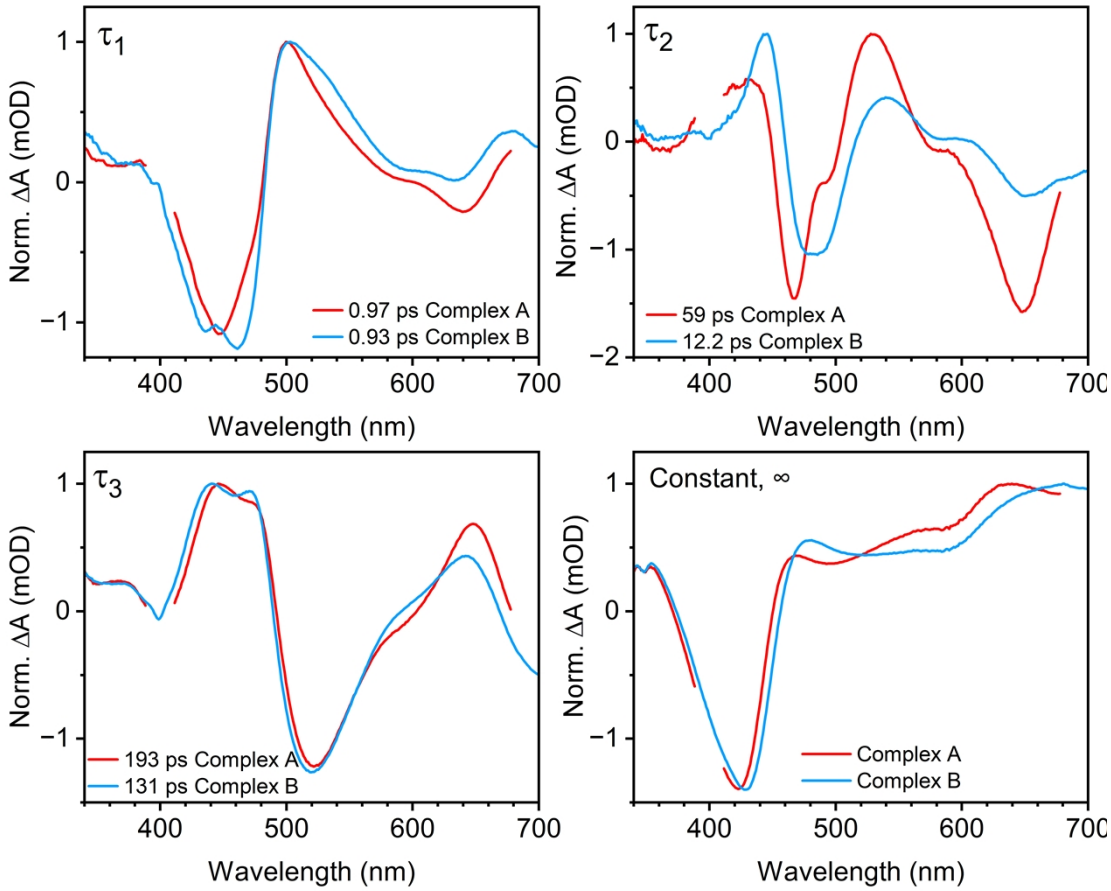


Figure S2: Comparison of DAS components obtained from GLA of TA measurements in traces from UV-visible for complex A (Cl-Pt-NAP) and B (Cl-Pt-NAP-PhCOOMe) showing the different rates of decay of the naphthalimide anion, NAP, and growth of the triplet state localised on the naphthalimide, ^{3}NAP. Excitation wavelength was 400 nm recorded in solution of CH_2Cl_2.

4 Near-Infrared Transient Absorption

4.1 Decay associated Spectra of the NIR components

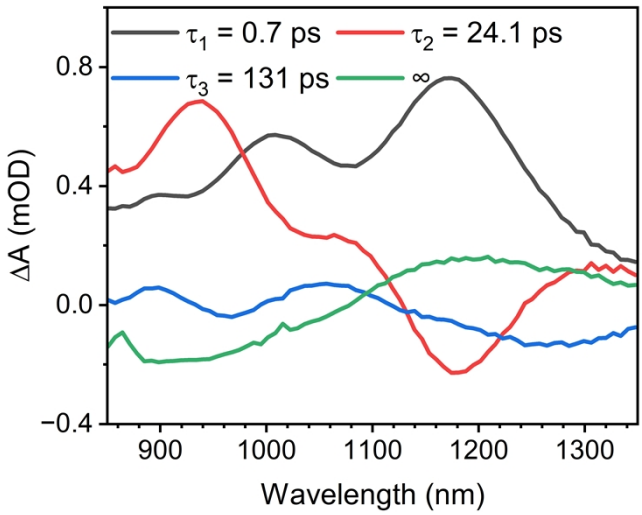


Figure S3: DAS for the TA in the NIR region for complex **B** (Cl-Pt-NAP-PhCOOMe**)** in CH_2Cl_2 after excitation with a 400 nm pump. DAS components were obtained from global lifetime analysis using a parallel model of four components.

5 Picosecond Time-Resolved Infrared Spectroscopy

5.1 Decay-Associated TRIR Spectra for complex B

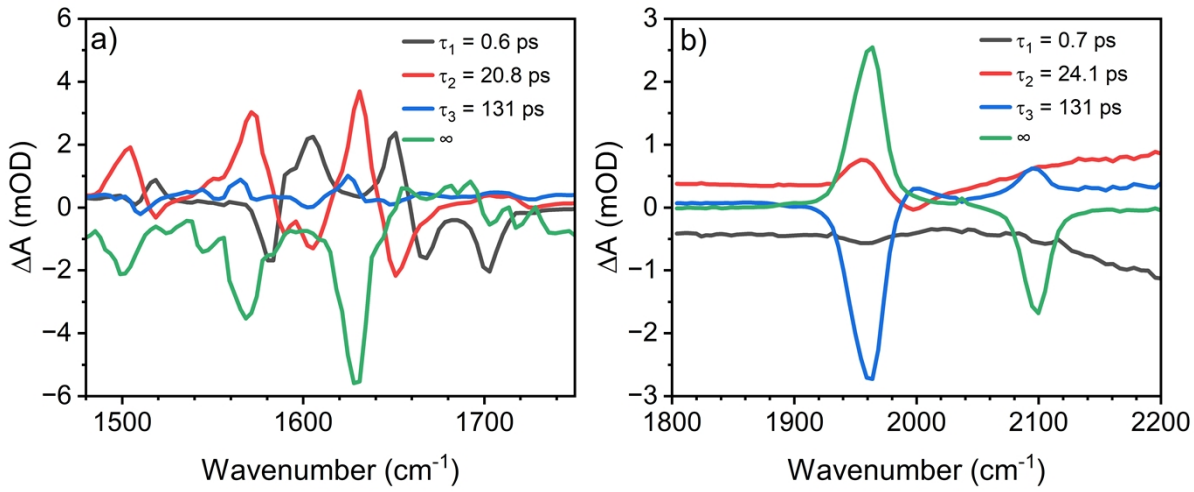
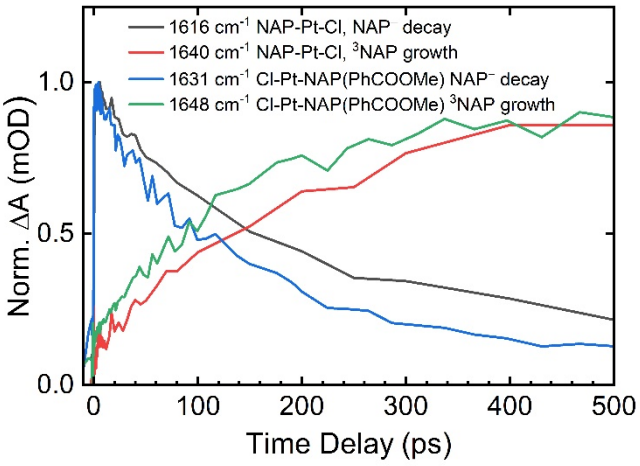


Figure S4: DAS components for the carbonyl region (a) and acetylide regions (b) from TRIR measurements for complex B (Cl-Pt-NAP-Ph-COOMe) in solution of CH_2Cl_2 with a pump wavelength of 400 nm and mid-IR probe.



5.2 Comparison of kinetic behaviour in TRIR data between complex A and B

Figure S5. Comparison of kinetic traces from TRIR measurements acquired from 400 nm excitation in solution of CH_2Cl_2. The kinetic traces show different rates of decay of the naphthalimide anion, NAP, and growth of the triplet state localised on the naphthalimide, ^{3}NAP in each complex.

Table S1. Comparison of spectral positions of the naphthalimide anion and triplet naphthalimide for complex **A** (Cl-Pt-NAP) and **B** (Cl-Pt-NAP-PhCOOMe) acquired after photoexcitation with pump wavelength of 400 nm in solution of CH_2Cl_2.

Spectral Feature	**A (cm^{-1})**	**B (cm^{-1})**
NAP^-	1567, 1616	1566, 1630
^3NAP	1594,1640, 1960	1602, 1650, 1969

5.3 Time-resolved Infrared Spectroscopy Performed under Excitation at 420 nm

TRIR measurements at excitation of 420 nm were performed at the Lord Porter Laboratory at the University of Sheffield. The experimental set-up is as described previously.[1] The pump pulses were generated from the second OPA (TOPAS, Light Conversion) pumped from a Ti:Sapphire amplifier (Spectra Physics Spitfire ACE PA-40) with an 800 nm fundamental, repetition rate of 10 kHz and a pulse duration of 40 fs. The excitation range covered was 410-460 nm with a FWHM of 10 nm. All other experimental details are described in the main text.

Samples were measured in solution in a flow-through IR cell (Harrick Scientific) with two 2 mm CaF_2 windows and PTFE spacer (650 µm). The cell was rastered.

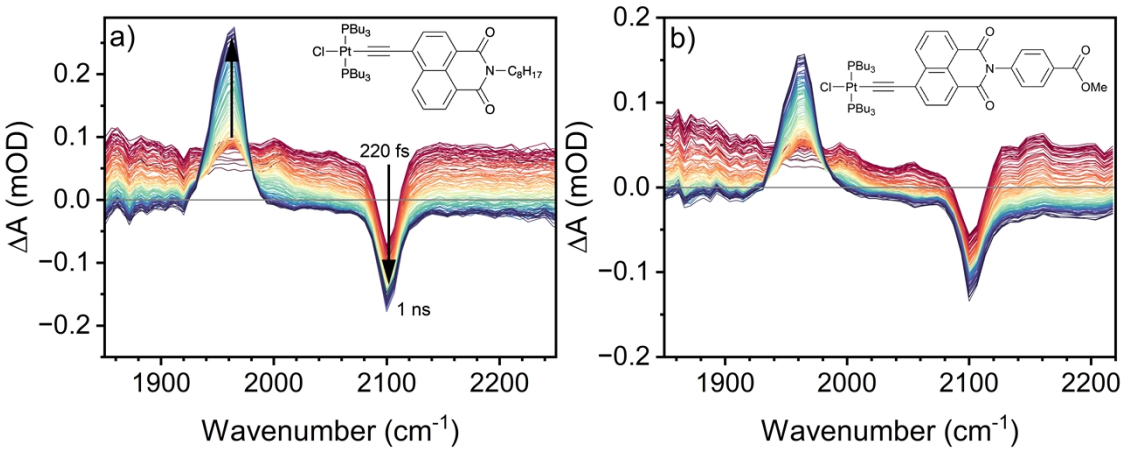


Figure S6: TRIR spectra of a) Complex A (Cl-Pt-NAP) b) Complex B (Cl-Pt-NAP-PhCOOMe) following photoexcitation with 420 nm pump in solution of CH_2Cl_2. Time delays change exponentially with an initial and final time delay of 220 fs and 1 ns, respectively.

6 Density Functional Theory

Calculations were performed using Gaussian 16, revision C.01.[2] The solvent, dichloromethane, was simulated using the conductor-like polarisable continuum model (CPCM) using the parameters as implemented in Gaussian 16.[3–6] All calculations utilized the PBE0 functional.[7] The Karlsruhe basis set, def2-SVP, was employed for all atoms except Pt.[8] For Pt, the Dirac-Hartree-Fock basis set, dhf-SVP, was used instead.[9–11] Basis sets were obtained from the Basis Set Exchange.[12–14] Frequency calculations within the harmonic approximation were performed to confirm the minimum energy had been found, where the optimized structure show zero imaginary frequencies. Restricted space anharmonic frequency calculations were performed for the acetylide (C≡C) and carbonyl (C=O) vibrational modes. Ground to excited state transition energies were determined for the first 15 singlet and first 15 triplet states using Time-Dependent DFT within the Tann-Dancoff Approximation,[15] in line with previous work on Pt(II) D-B-A complexes.[16] Molecular orbital contribution analysis was performed using Multiwfn. to determine the percentage contribution of the Pt centre to each MO.[17,18]

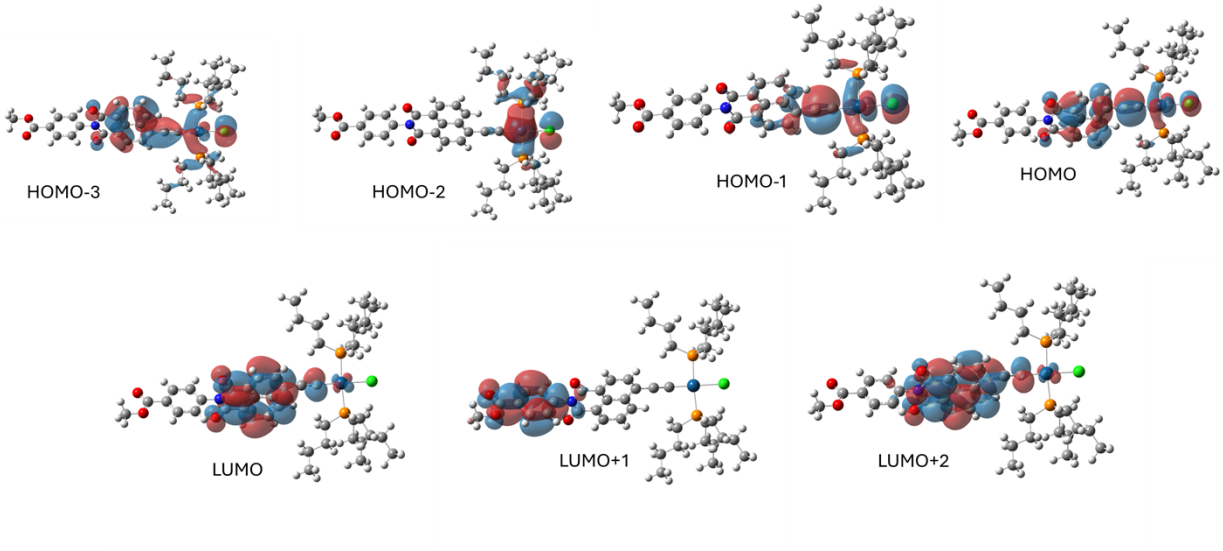


Figure S7 – HOMO−3, HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 obtained from by TD-DFT calculations at the the singlet ground state optimised geometry for Complex **B**.

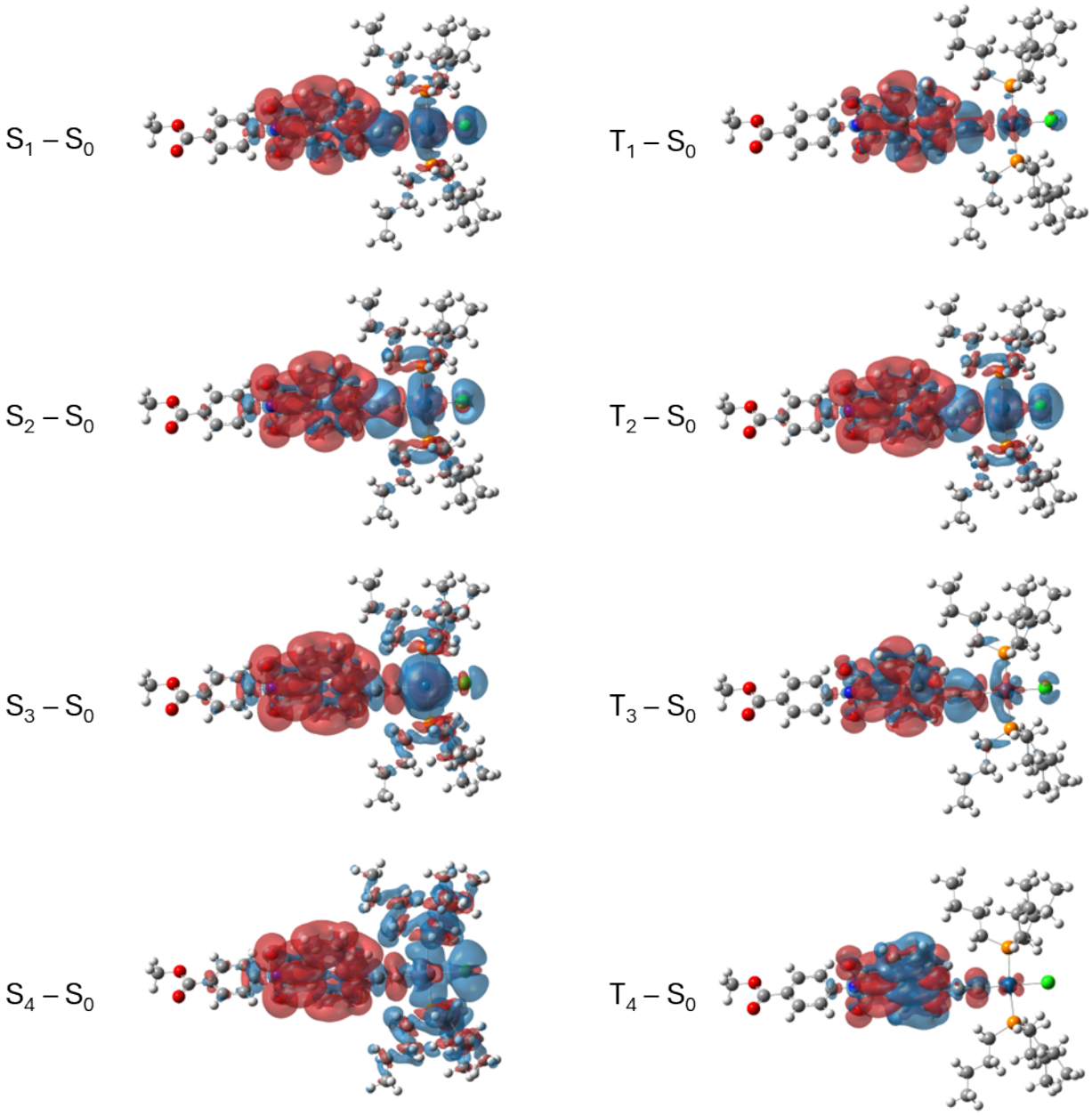


Figure S8 – Charge density difference surfaces obtained by TD-DFT for the first four singlet and triplet excited states of Complex **B**.

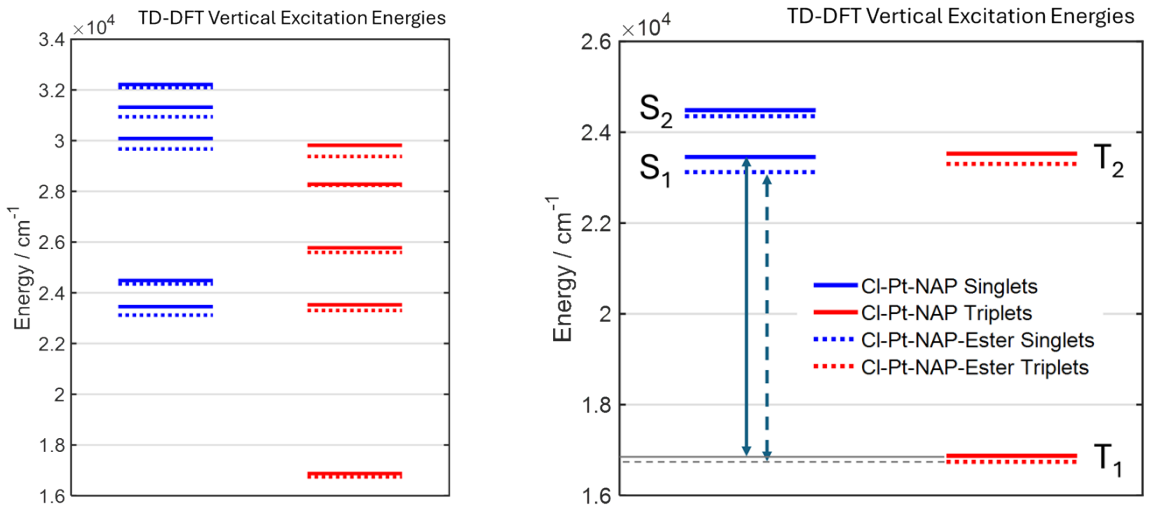


Figure S9. Left) Simulated energy level diagram for the $S_1 - S_5$ and $T_1 - T_5$ excited states of compounds A (solid lines) and B (dashed lines). Right) Energy level diagram focusing on S_1, S_2, T_1, and T_2, illustrating the predicted reduction in singlet – triplet energy gap upon addition of the ester group to NAP.

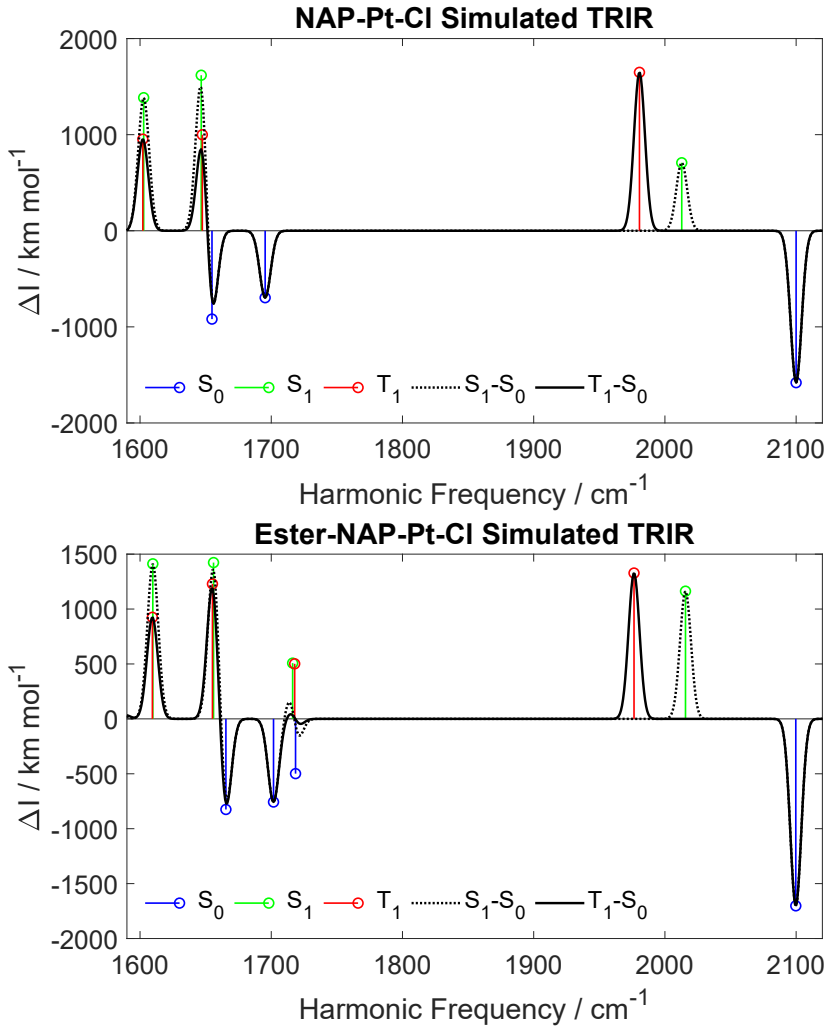


Figure S10. Simulated TRIR spectra of the first singlet and triplet excited states of complexes **A** and **B**. The vibrational frequencies are calculated using the harmonic approximation and scaled to match experimental values of the singlet ground state. Frequencies of the carbonyl modes are scaled by 0.936 and frequencies of the acetylide group are scaled by 0.955.

Table S2. Largest contributing molecular orbital transitions to the vertical electronic excitations of complexes A and B, obtained from TD-DFT calculations performed at the optimized singlet ground state geometry.

Complex	Transition	Main Components (%)
A	$S_0 \rightarrow S_1$	HOMO−1 → LUMO (28) HOMO → LUMO (63)
	$S_0 \rightarrow S_2$	HOMO−1 → LUMO (63) HOMO → LUMO (28)
	$S_0 \rightarrow T_1$	HOMO−4 → LUMO (16) HOMO−1 → LUMO (12) HOMO → LUMO (66)
	$S_0 \rightarrow T_2$	HOMO−1 → LUMO (67) HOMO → LUMO (18)
B	$S_0 \rightarrow S_1$	HOMO−1 → LUMO (25) HOMO → LUMO (65)
	$S_0 \rightarrow S_2$	HOMO−1 → LUMO (64) HOMO → LUMO (25)
	$S_0 \rightarrow T_1$	HOMO−4 → LUMO (16) HOMO−1 → LUMO (13) HOMO → LUMO (66)
	$S_0 \rightarrow T_2$	HOMO−1 → LUMO (67) HOMO → LUMO (14)

Table S3. Energies and percentage contribution from the Pt centre for the molecular orbitals of complexes A and B from HOMO−5 to LUMO+5.

Complex	Molecular Orbital	Energy / eV	Percentage Pt Contribution
A	HOMO−5	-7.58022	0.04
	HOMO−4	-7.25055	9.74
	HOMO−3	-6.93506	78.2
	HOMO−2	-6.93004	22.7
	HOMO−1	-6.39427	34.5
	HOMO	-6.03006	15.3
	LUMO	-2.53354	1.45
	LUMO+1	-0.87972	3.56
	LUMO+2	-0.75021	0.00457
	LUMO+3	-0.29052	31.57
	LUMO+4	-0.19402	48.6
	LUMO+5	0.23482	4.14
B	HOMO−5	-7.61103	0.0306
	HOMO−4	-7.25075	10.6
	HOMO−3	-6.94571	63.5
	HOMO−2	-6.94381	36.5
	HOMO−1	-6.44475	32.2
	HOMO	-6.0442	17.7
	LUMO	-2.5878	1.59
	LUMO+1	-1.52683	0.00945
	LUMO+2	-0.97907	3.38
	LUMO+3	-0.78478	0.00581
	LUMO+4	-0.53144	0.02857
	LUMO+5	-0.30504	31.8

6.1 Optimized geometry, harmonic frequencies, and anharmonic corrections for Complex A

Route:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane) geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{46}H_{68}ClNO_4P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	9.030375 Debye
Energy	-3406.083221 Hartree
Number of imaginary frequencies	0

Table S4 – Atomic coordinates for the optimised geometry of the singlet ground state of $C_{46}H_{68}ClNO_4P_2Pt$.

Element	Position		
Pt	-3.21998	-0.01178	-0.08232
P	-3.15444	-2.36105	-0.17252
P	-3.51075	2.319644	0.008277
C	-4.14873	-2.93105	-1.61391
H	-4.95348	-2.18208	-1.69012
H	-3.49881	-2.7806	-2.49398
C	-1.47341	-3.09359	-0.31055
H	-1.02958	-2.99737	0.695662
H	-0.90704	-2.39162	-0.9434
C	-3.92229	-2.99814	1.37523
H	-3.52724	-2.34131	2.168888
H	-4.9901	-2.73625	1.28385
C	-1.95617	3.301525	0.007517
H	-1.57719	3.248561	-1.02821
H	-1.24465	2.707959	0.603595
C	-4.49271	2.812334	-1.46954
H	-4.06827	2.214461	-2.29394
H	-5.4958	2.389969	-1.28919
C	-4.45876	2.746875	1.528003
H	-5.13108	1.885141	1.668663
H	-3.72337	2.706176	2.350923
C	-4.56058	4.278589	-1.88322
H	-3.54634	4.649197	-2.10998
H	-4.93824	4.901003	-1.05628
C	-5.44714	4.486155	-3.10773
H	-6.46287	4.115649	-2.88327
H	-5.07376	3.856583	-3.93462
C	-5.51684	5.937208	-3.55733
H	-6.16364	6.055039	-4.44004
H	-5.9195	6.583887	-2.76098
H	-4.51892	6.322707	-3.82195
C	-1.97851	4.741366	0.509852
H	-2.70679	5.345541	-0.05486
H	-2.31129	4.76125	1.561628
C	-0.60534	5.400377	0.415341
H	-0.27057	5.386719	-0.63695
H	0.12727	4.788792	0.970977
C	-0.5883	6.827221	0.940995
H	0.413504	7.27539	0.857783
H	-1.28752	7.468714	0.380568
H	-0.88331	6.86632	2.002093
C	-5.26929	4.038644	1.580634

H	-4.63045	4.915467	1.388017
H	-6.02967	4.028072	0.781296
C	-5.96921	4.217732	2.924714
H	-6.60224	3.334746	3.122044
H	-5.21084	4.229044	3.727451
C	-6.81198	5.481495	2.997357
H	-7.60198	5.480385	2.229007
H	-7.30183	5.583364	3.977728
H	-6.19747	6.38218	2.837162
C	-3.72775	-4.45689	1.775072
H	-2.65239	-4.66759	1.904611
H	-4.07976	-5.13101	0.977894
C	-4.45689	-4.79589	3.071958
H	-4.1098	-4.11563	3.869647
H	-5.53334	-4.58511	2.944963
C	-4.26358	-6.23997	3.507644
H	-4.63412	-6.94163	2.742887
H	-3.19865	-6.46815	3.676018
H	-4.80157	-6.45398	4.443691
C	-1.31624	-4.5148	-0.84087
H	-1.89443	-5.22851	-0.23195
H	-1.72822	-4.57675	-1.86252
C	0.144738	-4.95442	-0.87105
H	0.72497	-4.23559	-1.47605
H	0.561668	-4.8919	0.149693
C	0.335971	-6.36003	-1.41897
H	1.398143	-6.64832	-1.42702
H	-0.20615	-7.10336	-0.81229
H	-0.03877	-6.44118	-2.45216
C	-4.75502	-4.33123	-1.61306
H	-5.43861	-4.43497	-0.75329
H	-3.97655	-5.10012	-1.48359
C	-5.52951	-4.61731	-2.89633
H	-6.3037	-3.84149	-3.03065
H	-4.84806	-4.51411	-3.75924
C	-6.17333	-5.99493	-2.91287
H	-5.41775	-6.7911	-2.81424
H	-6.88721	-6.11302	-2.08167
H	-6.7223	-6.17191	-3.85029
C	-1.30434	0.142862	-0.16686
C	-0.07647	0.250005	-0.22949
C	1.332194	0.377191	-0.31554
C	2.193773	-0.32408	0.603157
C	1.918598	1.182131	-1.29823
C	3.605797	-0.18643	0.47762
C	1.684747	-1.1491	1.633382

C	3.306992	1.308309	-1.4052
H	1.271813	1.717265	-1.99557
C	4.45628	-0.87937	1.375187
C	4.153844	0.635991	-0.53634
C	3.922907	-1.68183	2.369138
C	5.924362	-0.7554	1.260796
C	5.609987	0.78674	-0.67833
C	2.529807	-1.81527	2.499337
H	0.600787	-1.24465	1.72981
H	2.117112	-2.44693	3.288664
H	4.60562	-2.20203	3.044048
H	3.748136	1.939661	-2.17946
N	6.399848	0.07318	0.237647
O	6.70135	-1.32957	1.997172
O	6.136349	1.480458	-1.52628
Cl	-5.62494	-0.19776	0.012444
C	7.822185	0.205024	0.113029
C	8.514042	-0.59967	-0.79167
C	8.501952	1.137246	0.896981
C	9.893347	-0.47161	-0.91572
H	7.966505	-1.3247	-1.39691
C	9.880449	1.262489	0.773843
H	7.945718	1.760286	1.599957
C	10.58316	0.460853	-0.13229
H	10.44238	-1.09609	-1.62154
H	10.43333	1.98487	1.377266
C	12.05865	0.638676	-0.22557
O	12.68927	1.432038	0.433782
O	12.61721	-0.17483	-1.12025
C	14.02463	-0.07227	-1.27657
H	14.539	-0.29759	-0.33121
H	14.30312	-0.80519	-2.04173
H	14.30771	0.93966	-1.60055

Table S5 – Harmonic vibrational frequencies obtained from the optimised geometry of the singlet ground state of $C_{46}H_{68}ClNO_4P_2Pt$.

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	7.04	0.0567
2	9.12	0.2013
3	11.03	0.4268
4	11.94	0.2296
5	14.05	0.6008
6	15.83	0.848
7	20.31	0.6352
8	24.31	0.5592
9	25.31	0.1549
10	38.67	0.0338
11	38.96	0.0104
12	39.62	0.1003
13	40.97	0.0573
14	46.42	0.9075
15	49.25	0.0373
16	53.39	0.0154
17	54.32	0.0301
18	55.91	0.8084
19	59.07	0.8709
20	63.02	0.7509
21	65.18	0.0998
22	67.93	0.2428
23	72.89	0.1488
24	73.74	0.4614
25	76.11	0.0187
26	76.41	0.0482
27	79.2	0.0139
28	85.84	1.5967
29	88.63	3.7962
30	103.38	0.1728
31	107.04	4.3724
32	109.5	0.8053
33	114.03	0.0598
34	116.07	1.1971
35	126.94	5.3967
36	133.04	0.1391
37	134.48	4.1128
38	136.16	0.8371
39	139.74	3.195
40	142.38	1.6195
41	150.17	0.9556
42	151.43	5.1674

43	158.51	0.8457
44	163.66	5.6695
45	165.08	3.1812
46	167.75	1.6858
47	167.89	1.0558
48	170.28	0.111
49	172.34	9.1702
50	175.2	6.3736
51	178.91	0.3979
52	184.52	6.5299
53	202.26	2.7946
54	213.63	1.3557
55	218.76	0.1731
56	219.98	0.0692
57	222.72	0.8543
58	222.98	0.9562
59	225.76	2.657
60	234.23	0.2536
61	234.34	0.28
62	257.59	0.0725
63	258.07	0.0709
64	258.38	0.0591
65	258.42	0.0975
66	258.86	0.0073
67	259.19	0.1396
68	289.6	30.2909
69	299.94	35.6253
70	318.68	25.9837
71	329.49	6.311
72	333.82	0.8097
73	336.54	1.3121
74	339.66	8.4405
75	343.71	17.485
76	346.36	2.021
77	353.23	4.8444
78	375.81	9.4263
79	383.51	5.4903
80	390.86	75.9444
81	402.74	2.4069
82	403.37	0.0324
83	409.52	2.8661
84	410.19	3.0602
85	413.73	7.7763
86	415.69	20.2585
87	427.05	0.0722
88	433.37	14.2256

89	441.92	0.1153
90	459.74	7.9609
91	487.05	1.3806
92	500.21	20.5189
93	503.94	94.4675
94	523.14	41.4583
95	525.17	1.4731
96	531.2	6.7174
97	532.61	14.4435
98	546.62	3.64
99	565.7	1.7375
100	610.96	10.2489
101	638.55	0.5043
102	645.96	1.0413
103	682.6	16.8935
104	683.91	3.8688
105	690.37	34.8756
106	691.57	2.5986
107	701.68	4.1901
108	702.88	1.209
109	705.22	12.3999
110	722.58	26.3734
111	723.37	32.8001
112	723.42	8.237
113	723.76	31.3477
114	724.04	16.1272
115	755.74	0.2737
116	755.95	0.0869
117	761.29	3.3621
118	762.17	6.7449
119	762.79	1.6625
120	763.34	1.6565
121	763.99	8.9727
122	787.04	1.9889
123	787.83	43.0834
124	790.35	14.4906
125	791.19	38.8847
126	791.84	30.1877
127	794.99	94.1713
128	802.56	7.806
129	812.56	74.0445
130	832.84	50.3202
131	853.64	72.7026
132	864.02	0.9943
133	878.45	20.6465
134	884.29	4.1525

135	884.64	3.4247
136	886.88	5.9076
137	889.54	17.1546
138	895.02	24.9962
139	904.18	1.4471
140	904.64	7.3814
141	904.87	26.3604
142	905.28	36.5888
143	915.17	5.871
144	915.24	13.7141
145	915.5	7.556
146	915.72	8.8938
147	916.07	14.8121
148	916.35	3.3167
149	948.22	24.9416
150	986.66	0.0334
151	1009.35	1.5004
152	1016.89	0.098
153	1019.34	0.4567
154	1026.04	16.6438
155	1035.01	0.3323
156	1035.95	2.2486
157	1036.45	3.1589
158	1039.99	61.7013
159	1043.79	25.4066
160	1051.37	1.2584
161	1051.5	3.4242
162	1052.38	6.0296
163	1052.87	4.4464
164	1053.95	4.379
165	1054.67	1.7588
166	1074.15	2.0558
167	1075.01	5.9196
168	1076.54	6.6565
169	1078.04	13.7033
170	1089.19	30.6949
171	1089.66	1.3235
172	1089.74	0.6949
173	1089.93	3.1736
174	1090.36	3.5818
175	1092.6	4.8405
176	1093.09	0.5436
177	1112.84	20.2112
178	1116.41	11.0472
179	1116.82	1.0875
180	1117.43	44.4917

181	1117.59	27.9248
182	1120.97	131.7015
183	1124.36	12.2816
184	1152.9	45.3372
185	1158.45	10.4536
186	1162.14	8.6885
187	1169.28	2.753
188	1172.32	0.8782
189	1176.38	82.517
190	1212.94	8.1608
191	1213.04	2.0243
192	1213.59	4.2301
193	1216.15	2.0425
194	1216.63	3.2616
195	1217.17	3.8169
196	1218.07	3.2838
197	1222.13	79.9754
198	1229.77	1.7956
199	1230.38	3.5152
200	1230.54	0.943
201	1231.38	1.0675
202	1241.01	53.4041
203	1248.73	42.1516
204	1250	13.4113
205	1280.75	63.655
206	1289.87	0.7983
207	1290.23	4.9005
208	1293.8	15.8438
209	1294.18	6.739
210	1296.33	121.7015
211	1296.38	31.8916
212	1297.35	6.948
213	1299.3	169.3314
214	1301.92	446.861
215	1317.99	8.0989
216	1318.18	0.84
217	1318.75	4.7522
218	1319.17	3.1788
219	1319.94	0.6259
220	1320.31	1.5071
221	1320.88	0.6568
222	1321.56	1.1836
223	1321.94	2.6592
224	1322.49	1.0579
225	1325.83	31.9886
226	1326.61	4.4662

227	1344.54	639.2063
228	1375.43	11.0702
229	1380.81	0.2985
230	1381.02	0.2471
231	1381.87	0.255
232	1382.14	0.3787
233	1384.33	0.614
234	1384.54	0.2125
235	1398.29	0.1117
236	1398.38	0.029
237	1398.96	0.8913
238	1399.02	0.415
239	1399.42	17.9487
240	1401.01	19.3093
241	1401.18	4.435
242	1410.75	890.8617
243	1416.63	7.1498
244	1418.39	9.2079
245	1421.39	26.5707
246	1422.62	8.9051
247	1426.1	38.2068
248	1426.64	53.1818
249	1427.63	393.1827
250	1447.37	4.469
251	1447.66	2.1262
252	1449.14	1.416
253	1449.42	1.7017
254	1449.48	1.6445
255	1449.73	1.8189
256	1449.83	15.1533
257	1451.43	4.0575
258	1458.15	124.5639
259	1458.65	8.5971
260	1458.76	10.5609
261	1458.82	4.8182
262	1458.85	13.1074
263	1458.9	11.9758
264	1459.04	10.0872
265	1460.48	0.3031
266	1460.65	0.2004
267	1461.95	78.3206
268	1465.43	0.1977
269	1465.65	0.2486
270	1465.73	0.2583
271	1465.8	0.2143
272	1471.01	73.8537

273	1473.3	5.9705
274	1473.54	5.533
275	1476.84	15.8139
276	1477.11	14.3552
277	1477.18	15.1938
278	1477.31	16.0272
279	1492.98	44.9651
280	1508.11	60.7253
281	1559.65	20.2723
282	1580.53	248.8604
283	1637.01	9.9463
284	1657.17	1373.741
285	1663.66	5.5393
286	1693.62	27.8708
287	1697.15	29.4391
288	1778.98	824.8664
289	1817.74	757.0476
290	1835.67	498.557
291	2197.88	1702.422
292	3044.62	23.2842
293	3044.63	47.7577
294	3044.76	31.5737
295	3044.82	36.032
296	3045.01	36.152
297	3045.06	27.2861
298	3048.2	16.7681
299	3048.29	6.144
300	3048.29	19.7024
301	3048.34	26.8762
302	3048.38	77.7403
303	3048.46	27.3681
304	3057.38	22.6384
305	3057.71	3.9881
306	3059.59	26.645
307	3059.77	30.9938
308	3060.21	39.6737
309	3060.62	20.9228
310	3065.06	55.7023
311	3065.39	35.8142
312	3066.69	29.0463
313	3066.85	25.4504
314	3068.44	36.5858
315	3069.16	30.9122
316	3072.42	40.4817
317	3089.23	10.8718
318	3089.25	11.666

319	3089.63	11.2835
320	3089.71	10.9205
321	3090.04	10.5558
322	3090.13	11.5725
323	3115.3	7.5617
324	3115.5	7.4971
325	3116.23	18.966
326	3116.32	22.3488
327	3116.61	16.7405
328	3116.99	18.7356
329	3130.67	14.903
330	3130.85	15.2571
331	3132.73	5.1387
332	3133.3	10.8454
333	3133.53	5.1261
334	3133.68	3.5246
335	3138.35	43.3535
336	3138.43	54.8824
337	3138.44	24.9656
338	3138.45	74.2989
339	3138.48	80.0398
340	3138.52	80.952
341	3147.19	34.9942
342	3147.21	36.2483
343	3147.39	35.4141
344	3147.43	34.7821
345	3147.53	26.8782
346	3147.59	30.1387
347	3171.76	16.0675
348	3213.06	9.2427
349	3217.49	1.406
350	3225.87	4.6321
351	3226.43	1.059
352	3228.24	1.6114
353	3229.19	4.117
354	3237.97	2.9654
355	3239.01	3.6951
356	3240.02	1.5461
357	3248.07	0.3391

Table S6 – Anharmonic corrections for the vibrational frequencies of the acetylide and carbonyl groups obtained at the optimised geometry of the singlet ground state of $C_{46}H_{68}ClNO_4P_2Pt$.

Type	A	ν,A	B	ν,B	ω/ cm^{-1}	Δω / cm^{-1}	I / km mol^{-1}	ΔI / km mol^{-1}
Fundamental	288	1			1754.43	-24.56	2509.177	1929.964
Fundamental	289	1			1791.03	-26.72	245.5145	-285.934
Fundamental	290	1			1797.67	-38	200.4865	-149.592
Fundamental	291	1			2164.88	-32.98	4.8291	-1190.48
Overtone	288	2			3498.78	-59.21	3.2614	
Overtone	289	2			3574.37	-61.12	1.5287	
Overtone	290	2			3576.89	-94.45	3.3281	
Overtone	291	2			4311.59	-84.13	1.2697	
Combination	288	1	289	1	3527.92	-68.82	7.3777	
Combination	288	1	290	1	3552.1	-62.56	0.0098	
Combination	288	1	291	1	3919.15	-57.7	0.2954	
Combination	289	1	290	1	3588.64	-64.77	0.0054	
Combination	289	1	291	1	3955.7	-59.91	1.1449	
Combination	290	1	291	1	3962.57	-70.96	0.0066	

Table S7 – Transition wavelengths, extinction coefficients and oscillator strengths for the vertical electronic excitations between the optimised geometry of the singlet ground state of $C_{46}H_{68}ClNO_4P_2Pt$ and the first 15 singlet excited states.

Wavelength / nm	ε	Oscillator Strength
432.52	0.6812	1954476
410.66	0.2468	708110.4
337.01	0.0057	16354.25
323.2	0.0001	286.9167
311.59	0.0003	860.7501
304.65	0.0135	38733.75
304.15	0.0285	81771.26
302.54	0.073	209449.2
287.96	0.4099	1176072
280.4	0.0014	4016.834
277.28	0.0002	573.8334
275.25	0.0029	8320.584
273.85	0.0009	2582.25
272.39	0.0015	4303.75
271.45	0.0022	6312.167

Table S8 – Transition wavelengths, extinction coefficients and oscillator strengths for the vertical electronic excitations between the optimised geometry of the singlet ground state of $C_{46}H_{68}ClNO_4P_2Pt$ and the first 15 triplet excited states.

Wavelength / nm	ε	Oscillator Strength
597.36	0	0
429.15	0	0
390.74	0	0
354.16	0	0
340.4	0	0
334.55	0	0
328.85	0	0
328.38	0	0
324.68	0	0
311.64	0	0
310.09	0	0
303.98	0	0
297.77	0	0
296.67	0	0
291.59	0	0

6.2 S_1 excited state geometry optimisation

6.2.1 Optimized geometry and harmonic frequencies of the S_1 excited state, calculated by TD-DFT starting at the optimised S_0 geometry.

Route:	#p opt freq tda=(singlets,root=1)/genecp scrf=(cpcm,solvent=dichloromethane) density=current geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{46}H_{68}ClNO_4P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	22.311450 Debye
Energy	-3405.982989 Hartree
Number of imaginary frequencies	0

Table S9 – Atomic coordinates for the optimised geometry of the first triplet excited state of $C_{46}H_{68}ClNO_4P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure.

Element	Position		
Pt	3.20403	-0.11038	0.001905
P	3.431216	2.245043	-0.13109
P	3.221421	-2.48457	0.070276
C	4.44213	2.638451	-1.61706
H	5.140927	1.791198	-1.70292
H	3.74766	2.556002	-2.47157
C	1.851453	3.17465	-0.24088
H	1.448156	3.179143	0.786536
H	1.173114	2.531438	-0.82325
C	4.31338	2.812092	1.380865
H	3.866299	2.223043	2.199628
H	5.342042	2.430038	1.271389
C	1.566249	-3.27906	0.058235
H	1.193055	-3.16139	-0.97417
H	0.92932	-2.6278	0.677388
C	4.137792	-3.04223	-1.42503
H	3.786889	-2.37446	-2.23003
H	5.185519	-2.75192	-1.23838
C	4.115438	-3.03821	1.579421
H	4.869475	-2.25405	1.753163
H	3.382343	-2.95224	2.40066
C	4.025925	-4.49394	-1.87931
H	2.9724	-4.73438	-2.10119
H	4.33714	-5.18016	-1.07555
C	4.867575	-4.76694	-3.12258
H	5.922695	-4.52696	-2.90278
H	4.561918	-4.07243	-3.92482
C	4.758147	-6.20146	-3.61504
H	5.376322	-6.36744	-4.51034
H	5.08991	-6.91573	-2.84427
H	3.718492	-6.45693	-3.8762
C	1.434321	-4.72473	0.528134
H	2.089316	-5.39118	-0.05552
H	1.767762	-4.8042	1.576736
C	-0.00346	-5.22616	0.427546
H	-0.33846	-5.15171	-0.62215
H	-0.66271	-4.55143	1.001536
C	-0.1738	-6.65456	0.92046
H	-1.219	-6.98785	0.833193
H	0.448727	-7.35504	0.340667
H	0.119081	-6.75042	1.978457
C	4.792649	-4.40592	1.58673

H	4.068446	-5.20653	1.366922
H	5.550757	-4.44496	0.786173
C	5.469323	-4.69847	2.922687
H	6.18816	-3.89102	3.147374
H	4.712772	-4.66002	3.726139
C	6.179869	-6.04265	2.950255
H	6.966657	-6.09537	2.180482
H	6.655886	-6.22601	3.925471
H	5.477558	-6.87064	2.761674
C	4.295644	4.29301	1.745835
H	3.25466	4.629956	1.887106
H	4.709091	4.902226	0.926194
C	5.083378	4.573927	3.022226
H	4.674583	3.956908	3.841675
H	6.125762	4.237321	2.883316
C	5.065663	6.04027	3.424556
H	5.500508	6.676712	2.637025
H	4.037506	6.393699	3.604366
H	5.642116	6.211278	4.346355
C	1.859938	4.583315	-0.82661
H	2.557451	5.23398	-0.27504
H	2.225998	4.549142	-1.8668
C	0.471266	5.215818	-0.81188
H	-0.23118	4.559037	-1.35432
H	0.102756	5.253472	0.228451
C	0.44453	6.610523	-1.41703
H	-0.5681	7.040666	-1.39038
H	1.112345	7.296678	-0.87146
H	0.772931	6.596908	-2.46886
C	5.222591	3.949043	-1.66659
H	5.939944	3.981706	-0.82911
H	4.552195	4.81317	-1.53457
C	5.986592	4.106558	-2.97801
H	6.651439	3.235707	-3.11516
H	5.270928	4.074175	-3.81834
C	6.799252	5.390145	-3.04483
H	6.15429	6.277946	-2.94385
H	7.547862	5.432414	-2.23728
H	7.336631	5.47662	-4.00139
C	1.308735	-0.06255	-0.05491
C	0.059046	-0.092	-0.07362
C	-1.34471	-0.20705	-0.11126
C	-2.19377	0.843404	0.387134
C	-1.91789	-1.38168	-0.66305
C	-3.61067	0.661195	0.307519
C	-1.69033	2.031602	0.960187

C	-3.29027	-1.5363	-0.74945
H	-1.25226	-2.16521	-1.02943
C	-4.47882	1.670468	0.805061
C	-4.13825	-0.52392	-0.26284
C	-3.93943	2.846451	1.367199
C	-5.91899	1.504866	0.741034
C	-5.5907	-0.72708	-0.34363
C	-2.56331	3.016529	1.438503
H	-0.61097	2.168606	1.027187
H	-2.15204	3.931419	1.87282
H	-4.62826	3.607179	1.737895
H	-3.739	-2.43386	-1.17654
N	-6.38431	0.299807	0.165288
O	-6.73084	2.332306	1.142283
O	-6.09646	-1.73608	-0.81897
Cl	5.583223	-0.20132	0.115359
C	-7.80171	0.116035	0.106168
C	-8.46879	0.233877	-1.11369
C	-8.51163	-0.1831	1.27021
C	-9.8459	0.049993	-1.17252
H	-7.90218	0.469682	-2.01631
C	-9.88807	-0.36216	1.211953
H	-7.97836	-0.27304	2.218257
C	-10.5639	-0.24847	-0.00826
H	-10.3723	0.139954	-2.12364
H	-10.4608	-0.59568	2.111562
C	-12.0373	-0.45333	-0.01452
O	-12.6926	-0.71074	0.968972
O	-12.569	-0.32321	-1.23001
C	-13.9734	-0.50326	-1.32776
H	-14.5052	0.234561	-0.70968
H	-14.2286	-0.3641	-2.38412
H	-14.2612	-1.51222	-0.99852

Table S10 – Harmonic frequencies obtained for the optimised geometry of the first triplet excited state of $C_{46}H_{68}ClNO_4P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	5.07	0.3341
2	6.43	0.0465
3	8.73	0.1015
4	9.97	1.128
5	12.95	0.8512
6	15.71	1.0728
7	19.79	0.9516

8	25.94	0.6527
9	27.12	1.1205
10	36.8	0.0485
11	37.88	0.0455
12	39.26	0.263
13	41.3	0.186
14	48.68	0.939
15	49.45	0.5181
16	53.24	0.08
17	53.67	0.0584
18	55.04	0.5251
19	59.49	0.7003
20	64.24	0.6622
21	65.63	0.0333
22	67.43	0.5671
23	72.42	0.1379
24	73.38	0.503
25	76.23	0.0471
26	76.69	0.2175
27	80.25	0.051
28	86.47	2.9583
29	88.63	4.4631
30	101.83	0.2952
31	107.58	1.5337
32	112.11	0.0249
33	113.08	1.414
34	116.12	1.4104
35	125.78	0.1944
36	131.33	2.8527
37	132.54	0.5384
38	133.92	0.9481
39	137.67	2.698
40	141.3	1.7262
41	147.52	2.3948
42	150.67	0.5909
43	157.2	3.5364
44	161.8	12.9735
45	162.38	1.8307
46	165.8	1.1605
47	167.27	0.074
48	168.55	2.2211
49	169.67	0.1891
50	174.38	6.6267
51	176.47	1.4451
52	184.56	10.3561
53	204.05	15.9401

54	209.94	2.9191
55	214.31	6.8882
56	219.31	0.1718
57	219.92	1.1316
58	223	0.31
59	223.42	0.8243
60	233.01	0.6636
61	233.67	0.8296
62	256.6	0.0966
63	256.99	0.0586
64	257.37	0.1085
65	258.04	0.0902
66	258.22	0.0528
67	258.74	0.1404
68	285.56	12.843
69	300.96	27.4411
70	311.44	189.0963
71	321.23	30.2573
72	333.39	3.3772
73	335.55	13.5042
74	338.35	9.2257
75	342.85	0.5327
76	343.48	19.5851
77	351.34	51.5703
78	374.99	7.06
79	381.55	14.7436
80	392.69	59.6421
81	402.03	2.8838
82	403.77	0.0194
83	406.14	6.9209
84	409.34	2.1259
85	410.33	5.7069
86	413.94	4.1571
87	420.63	3.5539
88	426.01	1.8226
89	434.84	10.8985
90	451.13	7.1793
91	493.91	9.2366
92	498	13.305
93	502.74	80.575
94	516.47	118.3853
95	522.21	2.1018
96	529.07	3.9965
97	534.82	1.351
98	547.49	14.9246
99	561.04	12.8456

100	585.65	8.8925
101	634.57	7.465
102	643.76	4.867
103	653.94	0.526
104	681.57	19.7734
105	690.96	29.1507
106	692.39	14.7441
107	702.15	66.1158
108	702.61	6.8174
109	704.71	3.0981
110	723.21	43.2359
111	723.31	22.1096
112	724.04	13.047
113	724.2	25.9604
114	725.62	16.2974
115	740.14	27.2259
116	755.87	0.5753
117	755.95	0.7311
118	758.87	48.7305
119	762.09	2.839
120	762.95	6.5242
121	763.27	2.7444
122	764.21	3.606
123	778.49	75.4432
124	788.4	4.0183
125	788.99	49.8282
126	792.01	2.3536
127	792.69	43.99
128	795.81	39.068
129	799.29	6.8448
130	831.11	133.8157
131	840.1	55.8504
132	850.7	31.7924
133	860.88	2.1284
134	864.48	0.3083
135	876.04	22.5274
136	884.71	4.9552
137	884.91	4.2385
138	891.55	1.587
139	893.15	21.7678
140	904.75	5.9713
141	904.95	3.6013
142	905.63	17.8974
143	905.67	29.2004
144	915.52	7.0917
145	915.83	13.7678

146	915.88	12.5113
147	916.09	9.7456
148	916.39	2.4473
149	916.48	8.8746
150	944.73	9.5369
151	982.71	0.4222
152	996.18	0.3503
153	1005.89	0.7013
154	1016.28	1.076
155	1025.94	26.9987
156	1033.26	49.3134
157	1036.57	2.6539
158	1037.37	2.9281
159	1042.71	14.9827
160	1051.12	1.1531
161	1051.34	6.4634
162	1051.97	3.67
163	1052.35	4.2711
164	1053.24	7.5767
165	1053.94	0.3764
166	1075.22	0.2759
167	1075.76	8.2467
168	1076.68	4.9793
169	1077.88	0.5932
170	1088.4	18.2006
171	1089.28	0.9347
172	1089.75	0.8164
173	1090.13	0.7306
174	1090.41	1.4211
175	1092.66	6.8924
176	1093.08	0.6574
177	1113.69	19.6786
178	1116.15	10.4725
179	1116.47	1.7013
180	1117	41.0147
181	1117.22	35.9809
182	1120.57	137.9078
183	1123.65	78.7874
184	1132.49	95.5396
185	1148.94	71.184
186	1153.71	18.739
187	1162.13	17.1812
188	1172.31	0.8589
189	1176.65	56.4476
190	1198.81	332.5357
191	1213.44	1.0714

192	1213.71	1.5521
193	1216.09	0.4916
194	1216.27	5.1431
195	1216.79	2.6485
196	1217.31	0.8275
197	1221.01	97.5429
198	1223.87	69.6294
199	1229.96	1.984
200	1230.29	0.8994
201	1230.49	2.4048
202	1230.79	0.7128
203	1242.89	142.4999
204	1249.02	50.488
205	1249.08	230.3961
206	1256.34	1172.404
207	1290.7	0.5264
208	1290.98	0.1611
209	1294.2	4.7122
210	1294.58	1.098
211	1296.65	4.0335
212	1297.18	0.3129
213	1301.53	4.6711
214	1302.43	106.4274
215	1318.42	5.5377
216	1318.49	4.666
217	1318.59	0.7521
218	1319.24	3.773
219	1319.96	3.3051
220	1320.4	2.7097
221	1321.02	4.3024
222	1321.27	0.7404
223	1321.37	2.2826
224	1321.79	9.2063
225	1326.11	27.1215
226	1326.84	18.6626
227	1343.49	780.4847
228	1378.86	127.71
229	1381.24	0.4853
230	1381.35	0.0127
231	1381.88	0.1689
232	1382.19	0.3034
233	1384.49	0.477
234	1384.68	1.9959
235	1398.57	56.5197
236	1398.7	3.179
237	1398.79	14.168

238	1399.11	1.3246
239	1399.38	1.1976
240	1400.41	40.5507
241	1401.35	23.981
242	1401.47	3.8075
243	1419.21	48.6535
244	1420.12	27.7288
245	1420.42	22.7542
246	1421.28	11.917
247	1422.35	20.1759
248	1426.13	39.7378
249	1428.27	30.3817
250	1446.96	6.5578
251	1447.68	6.9231
252	1448.84	24.2232
253	1449.13	1.6137
254	1449.64	1.351
255	1449.65	14.2909
256	1449.66	2.3976
257	1449.72	2.1682
258	1452.02	8.9782
259	1458.27	129.2693
260	1458.69	7.9526
261	1458.72	11.6122
262	1458.83	9.3503
263	1458.97	9.9674
264	1458.99	11.2777
265	1459.1	10.2763
266	1459.95	1.5606
267	1460.22	2.4809
268	1465.32	0.1129
269	1465.34	0.7227
270	1465.52	0.4975
271	1465.75	0.4225
272	1467.74	357.1019
273	1470.93	37.7278
274	1473.16	7.6765
275	1473.44	6.5917
276	1476.78	13.1766
277	1476.94	16.4315
278	1477.01	19.5856
279	1477.24	16.9152
280	1486.02	1978.336
281	1553.65	342.6043
282	1560.45	92.7335
283	1572.82	996.7917

284	1590.3	492.8934
285	1646.62	308.3156
286	1661.2	18.4231
287	1695.22	86.8454
288	1719.48	1411.644
289	1768.91	1423.103
290	1833.3	507.6066
291	2109.89	1162.765
292	3045.06	30.6477
293	3045.67	46.3622
294	3045.69	37.6374
295	3045.72	19.134
296	3045.88	29.9782
297	3046.08	31.1037
298	3048.88	17.2297
299	3048.98	15.1914
300	3048.99	16.2422
301	3049.05	15.9722
302	3049.09	84.1423
303	3049.15	26.7381
304	3059.22	22.7567
305	3059.59	17.4087
306	3060.09	30.1235
307	3060.86	33.2701
308	3061.13	36.1033
309	3061.71	22.3856
310	3066.94	37.4138
311	3067.51	33.0397
312	3068.72	13.6597
313	3068.95	10.5494
314	3069.53	60.4698
315	3069.63	21.8311
316	3071.35	43.9977
317	3090.03	10.9038
318	3090.89	13.604
319	3090.97	12.0614
320	3090.99	8.0532
321	3091.08	13.7438
322	3091.19	5.5006
323	3117.32	9.0794
324	3117.64	11.4444
325	3118.1	17.1474
326	3118.23	18.0236
327	3118.88	17.4853
328	3119.81	14.9492
329	3132.77	11.6537

330	3133.18	9.8613
331	3135.26	3.7338
332	3136.13	3.4601
333	3136.26	4.3869
334	3136.49	0.2361
335	3139.09	62.8119
336	3139.34	45.4048
337	3139.41	43.4898
338	3139.43	60.6793
339	3139.47	66.6197
340	3139.52	78.4516
341	3148.41	34.4524
342	3148.45	37.752
343	3148.5	31.448
344	3148.51	29.3331
345	3148.93	27.2059
346	3149.15	28.1909
347	3170.14	16.812
348	3208.43	29.181
349	3211.71	9.7049
350	3227.14	1.5469
351	3228.25	5.1681
352	3229.42	2.0711
353	3237.7	6.5579
354	3239.77	2.0158
355	3242.31	0.681
356	3246.76	3.2365
357	3247.06	0.4455

6.3 T_1 excited state geometry optimisation

6.3.1 Optimized geometry and harmonic frequencies of the T_1 excited state, calculated by TD-DFT starting at the optimised S_0 geometry.

Route:	#p opt freq tda=(triplets,root=1)/genecp scrf=(cpcm,solvent=dichloromethane) density=current geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{46}H_{68}ClNO_4P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	14.326206 Debye
Energy	-3406.014299 Hartree
Number of imaginary frequencies	0

Table S11 – Atomic coordinates for the optimised geometry of the first triplet excited state of $C_{46}H_{68}ClNO_4P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure.

Element	Position		
Pt	3.203586	-0.09936	-0.03205
P	3.399919	2.249309	-0.14465
P	3.263867	-2.45842	0.052535
C	4.318166	2.688284	-1.67868
H	5.017229	1.848469	-1.81968
H	3.576146	2.616051	-2.49333
C	1.810974	3.173237	-0.14269
H	1.462676	3.14553	0.904493
H	1.107544	2.539096	-0.70544
C	4.36923	2.79754	1.321138
H	3.97368	2.193056	2.155067
H	5.388746	2.416948	1.141429
C	1.626502	-3.28036	0.195375
H	1.164345	-3.18298	-0.80246
H	1.034648	-2.62719	0.856123
C	4.056635	-3.03404	-1.50592
H	3.62153	-2.3911	-2.28987
H	5.109104	-2.7155	-1.41715
C	4.291301	-2.98069	1.487582
H	5.048617	-2.18567	1.578168
H	3.631542	-2.88497	2.367913

C	3.939465	-4.49686	-1.92102
H	2.876674	-4.7632	-2.05077
H	4.329648	-5.15966	-1.13221
C	4.68236	-4.78096	-3.22329
H	5.746346	-4.51459	-3.09585
H	4.297213	-4.11096	-4.01209
C	4.565145	-6.22813	-3.67541
H	5.111631	-6.40194	-4.61482
H	4.974485	-6.91786	-2.91968
H	3.513543	-6.51076	-3.84475
C	1.552461	-4.72004	0.69411
H	2.166493	-5.38723	0.068194
H	1.971202	-4.78078	1.713001
C	0.118153	-5.24066	0.718347
H	-0.30211	-5.18648	-0.30153
H	-0.50117	-4.56481	1.33406
C	0.006472	-6.66306	1.244375
H	-1.03788	-7.0103	1.247014
H	0.589327	-7.36522	0.626572
H	0.385157	-6.73889	2.276483
C	4.981634	-4.34135	1.464493
H	4.251145	-5.15338	1.320175
H	5.67149	-4.38885	0.604804
C	5.76965	-4.60153	2.744992
H	6.494993	-3.78255	2.894684
H	5.081521	-4.55497	3.607451
C	6.495895	-5.9376	2.739426
H	7.217208	-5.99756	1.908452
H	7.052766	-6.09704	3.675299
H	5.790259	-6.77631	2.624945
C	4.374836	4.271073	1.714412
H	3.345341	4.603115	1.931862
H	4.731132	4.896707	0.880448
C	5.246256	4.53086	2.939867
H	4.894419	3.897968	3.77358
H	6.277269	4.199036	2.725024
C	5.254452	5.989539	3.369566
H	5.634794	6.641209	2.566389
H	4.240338	6.337582	3.624291
H	5.891274	6.145252	4.253621
C	1.777272	4.596707	-0.68962
H	2.497823	5.238973	-0.15811
H	2.08918	4.593229	-1.74785

C	0.387078	5.217613	-0.58712
H	-0.33835	4.568114	-1.10785
H	0.073502	5.227911	0.471814
C	0.318229	6.626055	-1.15622
H	-0.69453	7.047325	-1.06615
H	1.009198	7.304654	-0.63038
H	0.590807	6.639991	-2.22388
C	5.085147	4.005611	-1.74904
H	5.850724	4.027693	-0.95496
H	4.418736	4.862388	-1.56039
C	5.769411	4.194538	-3.09978
H	6.430482	3.331474	-3.29306
H	5.005651	4.172693	-3.89711
C	6.568566	5.4852	-3.18989
H	5.925113	6.366159	-3.03386
H	7.363293	5.517945	-2.42716
H	7.04806	5.593964	-4.17459
C	1.297477	-0.07009	0.022622
C	0.046025	-0.10304	0.041984
C	-1.33598	-0.22349	0.025511
C	-2.21666	0.826089	0.515585
C	-1.92742	-1.43063	-0.50916
C	-3.63095	0.633692	0.42145
C	-1.74649	2.015318	1.080499
C	-3.27939	-1.60015	-0.58857
H	-1.25374	-2.21425	-0.86122
C	-4.5073	1.639998	0.880935
C	-4.15581	-0.56916	-0.13101
C	-4.00104	2.83222	1.43785
C	-5.962	1.467245	0.786924
C	-5.59376	-0.77535	-0.23544
C	-2.63334	3.008925	1.535152
H	-0.66909	2.164753	1.16647
H	-2.23023	3.92733	1.968716
H	-4.70733	3.588725	1.782304
H	-3.72115	-2.50891	-0.99856
N	-6.4105	0.265221	0.23133
O	-6.76126	2.310555	1.161501
O	-6.09397	-1.79231	-0.69933
Cl	5.605441	-0.17035	-0.12331
C	-7.82691	0.078142	0.128915
C	-8.46559	0.288943	-1.09296
C	-8.55748	-0.31523	1.250499

C	-9.83988	0.103087	-1.19666
H	-7.87985	0.597755	-1.96084
C	-9.93122	-0.49717	1.14684
H	-8.04373	-0.4771	2.199959
C	-10.5799	-0.291	-0.07569
H	-10.3464	0.264437	-2.14907
H	-10.5222	-0.80433	2.011765
C	-12.052	-0.5047	-0.13218
O	-12.7255	-0.84576	0.8124
O	-12.5564	-0.27967	-1.34468
C	-13.9566	-0.46157	-1.49104
H	-14.5095	0.21674	-0.82523
H	-14.1884	-0.2348	-2.53755
H	-14.2416	-1.49729	-1.25607

Table S12 – Harmonic frequencies obtained for the optimised geometry of the first triplet excited state of $C_{46}H_{68}ClNO_4P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	5.21	0.1397
2	8.52	0.5685
3	10.13	1.0229
4	12.1	0.4336
5	14.48	0.3363
6	16.86	0.1244
7	18.84	0.536
8	25.97	0.372
9	26.96	0.5186
10	37.07	0.041
11	39.1	0.0566
12	39.45	0.1954
13	41.6	0.1319
14	47.23	1.0231
15	50.02	0.1733
16	53.18	0.2116
17	53.95	0.0936
18	55.01	0.5435
19	58.45	0.5745
20	64.21	0.2303
21	65.62	0.3165
22	68.74	0.2608
23	72.82	0.1225
24	74.47	0.6268

25	76.27	0.123
26	77.14	0.1012
27	78.52	0.2411
28	85.7	0.1277
29	86.98	4.2514
30	97.98	1.0172
31	107.85	2.5203
32	111.83	1.4934
33	114.04	0.0367
34	115.14	1.014
35	126.63	6.7997
36	133.32	1.5282
37	134.61	3.0881
38	134.69	2.8949
39	138.38	2.9812
40	142.49	1.979
41	149.17	2.3044
42	151.76	4.9079
43	157.2	5.6532
44	161.25	9.0374
45	164.39	2.621
46	166.31	0.5391
47	167.29	1.8788
48	169.17	0.7772
49	169.99	0.4091
50	174.14	6.6081
51	177.7	1.4441
52	183.75	7.4591
53	201.6	5.005
54	210.21	1.0119
55	213.47	1.3895
56	220.18	0.211
57	221.29	0.7238
58	223.55	1.7642
59	225.07	1.047
60	233.46	0.0399
61	234.14	0.6209
62	257.27	0.062
63	257.51	0.1017
64	258.26	0.0924
65	258.64	0.0799
66	259.11	0.0111
67	259.38	0.1366
68	284.03	2.9502
69	296.46	37.5366
70	303.27	68.4827

71	319.58	28.4336
72	334.08	0.1829
73	335.46	4.6898
74	339.13	8.7968
75	342.96	0.3121
76	343.51	21.7583
77	351.36	16.7419
78	375.43	7.9528
79	382.6	20.3602
80	389.72	69.0951
81	399.5	17.1655
82	402.76	4.8691
83	403.48	0.0408
84	409.25	2.1981
85	409.97	4.6499
86	413.27	3.2167
87	416.42	38.2898
88	426.5	0.8436
89	432.07	4.7278
90	451.1	5.9316
91	484.96	3.5785
92	497.52	5.533
93	503.17	91.0584
94	518.88	128.7001
95	526.57	2.3415
96	528.95	1.3162
97	533.98	0.6603
98	542.8	24.5707
99	561.68	20.9266
100	567.16	3.8302
101	632.37	3.6518
102	639.34	0.2314
103	647.18	2.0916
104	679.48	22.8562
105	690.63	31.5424
106	691.93	9.2866
107	701	95.6583
108	703.69	6.8729
109	704.71	1.0625
110	723.2	37.9679
111	723.35	6.0859
112	723.51	31.3744
113	724.56	26.127
114	725.2	12.1172
115	744.13	8.8575
116	756.1	0.3056

117	756.29	0.6263
118	761.96	5.5534
119	762.82	3.2757
120	763.53	2.8198
121	764.16	10.7124
122	765.12	69.3253
123	787.66	62.2848
124	787.97	2.6037
125	791.05	32.4019
126	791.55	22.1156
127	792.2	34.3492
128	795.43	85.7433
129	799.44	29.3623
130	826.06	3.6024
131	828.79	122.6518
132	849.28	72.6645
133	863.23	1.6691
134	864.53	0.0968
135	875.16	28.81
136	884.77	5.0262
137	885.09	4.2869
138	892.17	27.1374
139	904.65	7.2159
140	904.77	1.3751
141	905.39	29.6604
142	905.47	27.5625
143	915.28	5.1648
144	915.44	14.2357
145	915.86	16.7008
146	916.13	3.3885
147	916.58	15.7363
148	916.64	2.2254
149	928.6	1.3185
150	941.33	9.5542
151	998.05	0.0814
152	1008.4	0.1752
153	1012.05	0.5233
154	1018.39	0.4829
155	1025.73	15.0318
156	1032.37	26.7441
157	1036.01	3.1025
158	1036.88	3.7928
159	1042.19	24.7295
160	1051.05	1.5009
161	1051.76	5.4972
162	1052.03	2.9992

163	1052.74	7.5281
164	1053.28	5.127
165	1054.14	0.7953
166	1074.36	3.0469
167	1075.81	4.5759
168	1076.51	6.7874
169	1077.84	7.8112
170	1089.19	0.8059
171	1089.7	0.2343
172	1089.73	0.9563
173	1089.76	1.5008
174	1090.12	8.0814
175	1092.23	6.2125
176	1092.62	0.3002
177	1113.66	19.6351
178	1116.36	9.9921
179	1116.67	1.5675
180	1117.17	41.8844
181	1117.49	34.7362
182	1118.89	17.3573
183	1120.77	129.5262
184	1123.89	49.4611
185	1146.65	5.7659
186	1154.29	2.3833
187	1162.18	23.8477
188	1172.34	0.8248
189	1176.53	40.3299
190	1200.84	262.4089
191	1212.82	2.7783
192	1213.98	1.4838
193	1216.13	1.9823
194	1216.47	2.9045
195	1216.8	3.0931
196	1217.71	2.3615
197	1221.88	111.14
198	1229.53	0.4086
199	1229.9	3.4383
200	1230.22	1.2309
201	1230.89	1.5213
202	1236.66	138.7382
203	1248.41	41.6466
204	1249.49	28.6494
205	1268.36	12.5015
206	1279.38	526.2875
207	1289.66	1.4175
208	1290.92	2.5094

209	1293.62	3.854
210	1294.92	5.4875
211	1296.31	5.5091
212	1296.99	1.9128
213	1301.06	7.0012
214	1305.58	58.2401
215	1317.72	4.1975
216	1318.35	5.3255
217	1318.58	3.2444
218	1319.17	3.2571
219	1319.52	1.0526
220	1320.63	0.6471
221	1321.03	0.2307
222	1321.59	1.1046
223	1321.81	3.8781
224	1322.51	3.4537
225	1325.57	26.655
226	1326.68	21.9567
227	1342.35	338.1223
228	1351.51	636.8078
229	1381.03	0.2851
230	1381.17	0.3118
231	1381.9	0.2812
232	1382.45	0.2541
233	1384.53	0.5538
234	1384.72	0.6437
235	1398.5	0.1228
236	1398.68	0.1675
237	1398.99	0.9001
238	1399.28	0.7311
239	1399.5	22.3265
240	1401.24	19.6655
241	1401.37	3.7437
242	1410.28	29.9665
243	1418.74	41.5889
244	1421.4	28.4879
245	1421.7	15.3361
246	1422.36	63.6647
247	1423.89	72.7559
248	1426.12	20.4081
249	1428.52	16.8573
250	1443.82	523.3022
251	1447.19	6.698
252	1447.47	2.5746
253	1449.18	0.5712
254	1449.28	1.9397

255	1449.56	1.8319
256	1449.76	1.7293
257	1449.9	14.8706
258	1451.69	3.892
259	1455.96	300.556
260	1458.26	99.306
261	1458.82	6.0028
262	1458.84	4.8218
263	1458.84	13.5639
264	1458.88	13.5966
265	1458.98	10.9264
266	1459.14	10.5354
267	1460.15	0.7926
268	1460.42	0.0955
269	1465.23	0.1037
270	1465.51	0.19
271	1465.8	0.1964
272	1465.82	0.2779
273	1470.93	97.0772
274	1473.27	7.445
275	1473.32	5.6536
276	1476.58	15.2463
277	1477.01	16.7391
278	1477.34	14.4303
279	1477.41	16.8954
280	1495.79	14.2032
281	1523.23	637.9312
282	1560.22	11.8225
283	1588.46	421.5484
284	1598.64	352.8215
285	1662.92	4.8754
286	1666.54	936.4107
287	1696.32	85.5136
288	1719.13	924.9162
289	1768.03	1228.798
290	1834.97	501.5201
291	2068.83	1327.865
292	3044.7	33.6284
293	3044.97	34.139
294	3045.09	36.4509
295	3045.28	35.2513
296	3045.37	35.5397
297	3045.42	27.2851
298	3048.49	19.6523
299	3048.57	17.8538
300	3048.63	23.0218

301	3048.68	17.1553
302	3048.74	82.871
303	3048.79	16.8582
304	3058.86	27.2865
305	3059.04	3.2589
306	3059.68	21.0904
307	3060.13	31.8295
308	3060.81	25.9719
309	3061.37	24.2212
310	3066.46	78.6596
311	3066.54	3.1116
312	3067.2	27.4554
313	3068.02	17.5059
314	3068.05	45.8475
315	3069.22	44.2705
316	3072.02	42.5333
317	3089.5	11.5975
318	3089.69	10.6454
319	3090.42	5.0521
320	3090.42	22.3966
321	3090.6	8.0727
322	3090.6	9.8032
323	3116.52	9.1604
324	3116.71	7.7407
325	3116.83	15.9299
326	3118.17	14.18
327	3118.47	22.8844
328	3119.01	16.0414
329	3131.85	12.9688
330	3132.11	13.9261
331	3133.72	8.3656
332	3134.91	4.4725
333	3135.14	0.6505
334	3135.4	3.0878
335	3138.83	39.5943
336	3138.87	69.4939
337	3138.92	43.9249
338	3138.93	8.8306
339	3138.95	122.845
340	3138.99	75.5585
341	3147.7	32.4742
342	3147.71	37.5761
343	3147.9	37.8499
344	3147.9	28.1475
345	3148.3	27.212
346	3148.36	29.8555

347	3171.16	16.3461
348	3212.57	9.3484
349	3215.43	17.2606
350	3226.16	10.178
351	3226.88	1.4355
352	3228.65	1.7879
353	3234.19	0.8303
354	3239.74	1.6421
355	3245.55	2.5852
356	3247.7	2.5912
357	3247.94	0.393

6.4 Optimized geometry, harmonic frequencies, and anharmonic corrections for Complex B

Route:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane) geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{39}H_{62}ClNO_2P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	7.349589 Debye
Energy	-2987.236996 Hartree
Number of imaginary frequencies	0

Table S13 – Atomic coordinates for the optimised geometry of the singlet ground state of $C_{39}H_{62}ClNO_2P_2Pt$.

Element	Position		
Pt	-1.65212	0.162732	-0.07498
P	-2.15982	-2.12942	0.026975
P	-1.35653	2.496373	-0.12226
C	-3.38113	-2.54412	-1.28722
H	-3.98507	-1.62758	-1.3846
H	-2.79158	-2.62945	-2.21709
C	-0.71947	-3.25731	-0.15544
H	-0.17114	-3.18982	0.800471
H	-0.06682	-2.76667	-0.89533
C	-2.92175	-2.44329	1.674222
H	-2.3173	-1.84249	2.374883
H	-3.90162	-1.9383	1.627666
C	0.387258	3.059401	-0.27368
H	0.665649	2.873667	-1.32583
H	0.97214	2.33084	0.309709
C	-2.28704	3.147684	-1.5722

H	-2.08371	2.421453	-2.37748
H	-3.34883	3.002822	-1.31006
C	-2.06206	3.220979	1.416806
H	-2.91199	2.560277	1.652459
H	-1.3027	3.043131	2.198691
C	-2.01437	4.560453	-2.07722
H	-0.95555	4.651894	-2.37386
H	-2.17487	5.299785	-1.27624
C	-2.89434	4.920053	-3.27093
H	-3.9547	4.828607	-2.97664
H	-2.73942	4.174655	-4.07087
C	-2.62938	6.31656	-3.81136
H	-3.27907	6.546491	-4.66954
H	-2.81027	7.084421	-3.04184
H	-1.58498	6.424792	-4.14604
C	0.755781	4.47761	0.149202
H	0.166459	5.221558	-0.41088
H	0.504383	4.623682	1.213562
C	2.241005	4.765682	-0.05023
H	2.496996	4.61945	-1.11443
H	2.83163	4.016445	0.506128
C	2.64324	6.165602	0.386752
H	3.718055	6.3434	0.230062
H	2.092736	6.934971	-0.17852
H	2.431469	6.327563	1.456073
C	-2.5286	4.673785	1.426158
H	-1.71128	5.354322	1.138202
H	-3.3237	4.80915	0.67334
C	-3.06645	5.090971	2.791841
H	-3.87846	4.402563	3.085198
H	-2.27244	4.958363	3.547891
C	-3.57114	6.525167	2.823861
H	-4.39099	6.676958	2.103271
H	-3.95018	6.796877	3.820834
H	-2.77023	7.237214	2.566838
C	-3.04266	-3.87011	2.198635
H	-2.0398	-4.32288	2.280829
H	-3.60814	-4.49983	1.493277
C	-3.72	-3.92035	3.565145
H	-3.15856	-3.28171	4.269754
H	-4.72448	-3.46864	3.485608
C	-3.83263	-5.32913	4.126532
H	-4.41851	-5.98067	3.458154
H	-2.83983	-5.79122	4.25026
H	-4.32594	-5.33259	5.110437
C	-0.9536	-4.71116	-0.552

H	-1.62534	-5.21201	0.163784
H	-1.46173	-4.75054	-1.53059
C	0.351923	-5.49607	-0.64232
H	1.029922	-4.98825	-1.35088
H	0.861503	-5.46192	0.336792
C	0.152953	-6.94258	-1.06719
H	1.110773	-7.48206	-1.12141
H	-0.49364	-7.48295	-0.35696
H	-0.32185	-7.00659	-2.05965
C	-4.30425	-3.74631	-1.11111
H	-4.9169	-3.60924	-0.20383
H	-3.72538	-4.67099	-0.95628
C	-5.2316	-3.93391	-2.30825
H	-5.80502	-3.0041	-2.46932
H	-4.62184	-4.07235	-3.21855
C	-6.18681	-5.10623	-2.14724
H	-5.63923	-6.05388	-2.01818
H	-6.83402	-4.97666	-1.26475
H	-6.84062	-5.21708	-3.0257
C	0.231697	-0.17707	-0.27862
C	1.436309	-0.40388	-0.42098
C	2.817231	-0.66883	-0.59941
C	3.783876	-0.24341	0.381281
C	3.273961	-1.34587	-1.73519
C	5.164077	-0.51644	0.160799
C	3.412634	0.438573	1.564107
C	4.633815	-1.60718	-1.93322
H	2.547178	-1.6714	-2.48153
C	6.121515	-0.09748	1.116881
C	5.581069	-1.20155	-1.0052
C	5.722951	0.571684	2.260737
C	7.55759	-0.37344	0.898912
C	7.006403	-1.489	-1.24418
C	4.361005	0.83937	2.485085
H	2.352307	0.638128	1.736016
H	4.0541	1.364074	3.392267
H	6.485342	0.881625	2.97833
H	4.97206	-2.13575	-2.82696
N	7.904684	-1.05045	-0.26618
O	8.422757	-0.03543	1.68654
O	7.400688	-2.0765	-2.23593
Cl	-4.01279	0.585974	0.170084
C	9.321079	-1.31001	-0.45802
H	9.880561	-0.36459	-0.48022
H	9.711061	-1.919	0.369277
H	9.440392	-1.84153	-1.40635

Table S14 – Harmonic vibrational frequencies obtained from the optimised geometry of the singlet ground state of $C_{39}H_{62}ClNO_2P_2Pt$.

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	6.43	0.0744
2	9.04	0.1168
3	10.1	0.3158
4	12.76	0.0656
5	15.35	0.7161
6	25.09	0.5636
7	34.68	0.2268
8	38.46	0.0074
9	38.86	0.0394
10	39.54	0.0275
11	40.53	0.0539
12	48.87	0.0149
13	50.24	0.0182
14	53.61	0.1278
15	58.68	0.0391
16	60.48	0.2266
17	65.09	0.3127
18	68.68	0.2644
19	73.2	0.4486
20	73.5	0.3332
21	74.53	0.2749
22	76.53	0.2754
23	77.67	0.0376
24	86.15	4.4815
25	88.84	1.7209
26	95.85	4.7739
27	104.77	1.3962
28	111.79	5.0715
29	114.28	0.1555
30	116.38	0.0906
31	133.74	0.927
32	134.58	2.431
33	137.45	0.1123
34	141.69	1.8496
35	144.27	1.3123
36	149.79	1.3586
37	157.18	2.4299
38	159.66	0.3166
39	163.61	1.5782

40	166.73	5.5364
41	169.02	0.5909
42	170.45	2.0538
43	173.38	4.6916
44	177.92	3.1617
45	178.94	3.0628
46	180.26	14.3587
47	219.79	0.1703
48	220.49	0.1826
49	223.36	1.0383
50	224.27	0.7338
51	225.39	1.7191
52	234.21	0.0828
53	234.65	0.2208
54	257.29	0.0509
55	257.31	0.1167
56	258.37	0.1499
57	258.63	0.0736
58	259.12	0.0218
59	259.36	0.2065
60	272.38	8.1225
61	283.91	0.4265
62	296.96	42.0627
63	321.55	5.2853
64	335.62	0.2649
65	337.28	0.7293
66	340.91	8.4696
67	343.76	18.8698
68	353.67	3.1978
69	371.46	24.5058
70	376.25	9.5495
71	383.9	2.9691
72	399.57	35.92
73	403.85	0.0401
74	409.57	1.2466
75	410.84	6.5082
76	414.47	51.1047
77	414.89	1.9234
78	428.17	17.6619
79	444.82	9.6154
80	460.34	7.6573
81	486.9	0.4832
82	503.88	97.6353
83	516.2	1.4996
84	523.82	37.0532
85	538.75	10.1951

86	553.71	3.5286
87	600.02	4.0986
88	609.51	10.7125
89	657.1	14.5316
90	682.32	5.4829
91	684.27	4.7592
92	690.66	32.9575
93	691.94	3.124
94	701.89	2.9775
95	703.57	1.4156
96	722.32	25.747
97	723.21	26.0129
98	723.49	13.3756
99	724	16.4504
100	755.9	0.2943
101	756.06	0.1071
102	759.93	1.1685
103	761.52	4.2059
104	762.42	8.6979
105	763.1	0.795
106	763.64	9.2392
107	786.68	40.8421
108	787.46	1.1136
109	790.47	6.6805
110	792.18	40.3059
111	794.92	91.4092
112	800.92	1.8978
113	811.69	62.139
114	833.64	12.6757
115	882.91	3.654
116	884.4	4.0684
117	884.93	3.2383
118	889.48	21.6737
119	904.18	3.4911
120	904.69	4.1312
121	904.9	29.9024
122	905.37	32.7524
123	907.68	5.0963
124	915.24	1.5288
125	915.27	13.7201
126	915.44	15.8793
127	915.82	6.375
128	916.04	15.8203
129	916.22	1.4942
130	985.1	0.0723
131	997.57	20.0483

132	1016.77	0.071
133	1033.85	0.2592
134	1036.25	1.7251
135	1036.87	2.2115
136	1051.6	1.7534
137	1051.89	2.969
138	1052.38	6.0826
139	1052.92	5.3418
140	1053.77	4.6913
141	1054.53	4.0944
142	1054.78	42.0888
143	1073.75	32.9458
144	1074.37	153.3281
145	1075.13	9.4022
146	1076.7	4.2873
147	1078.31	11.907
148	1089.39	0.7423
149	1089.81	0.2693
150	1089.89	0.3889
151	1090.25	81.9663
152	1090.45	4.437
153	1092.6	4.7635
154	1093.17	1.0569
155	1116.38	14.5759
156	1116.72	0.2149
157	1117.4	39.0142
158	1117.58	31.0496
159	1120.92	131.6223
160	1124.32	9.4418
161	1142.26	0.2117
162	1160.18	0.2397
163	1175.79	7.0744
164	1197.33	5.3888
165	1213.23	2.3871
166	1214.23	2.5745
167	1216.1	2.5192
168	1216.49	2.874
169	1217.37	3.0705
170	1218.26	4.1136
171	1229.68	1.2471
172	1229.98	2.4893
173	1230.42	2.6707
174	1231.38	0.7581
175	1248.98	47.0923
176	1250.01	8.044
177	1253.27	10.9036

178	1276.86	45.4895
179	1286.04	120.0943
180	1289.63	1.129
181	1290.81	0.2477
182	1293.33	3.791
183	1294.25	2.6642
184	1296.63	5.2417
185	1297.43	3.0654
186	1318.11	7.2749
187	1318.23	3.2842
188	1318.43	1.9415
189	1319.2	1.1683
190	1319.27	1.8357
191	1319.79	1.2846
192	1320.86	0.6706
193	1321.4	0.7978
194	1321.77	1.558
195	1322.13	3.2921
196	1325.94	32.3141
197	1326.76	7.3203
198	1338.24	356.6483
199	1374.44	0.2716
200	1380.91	0.3173
201	1381.02	0.1148
202	1381.74	0.3041
203	1382.1	0.2893
204	1384.26	0.8281
205	1384.45	0.1235
206	1397.89	229.369
207	1398.4	5.8626
208	1398.57	6.7511
209	1398.9	0.7684
210	1399.04	0.486
211	1401.09	22.3269
212	1401.2	0.1094
213	1416.89	7.6589
214	1417.17	133.2702
215	1419.06	40.4289
216	1422.03	29.1545
217	1422.7	4.1796
218	1426.34	30.1206
219	1426.93	5.6898
220	1432.62	605.4099
221	1447.29	4.2605
222	1447.5	1.8234
223	1449.29	1.6933

224	1449.33	1.6372
225	1449.42	1.8452
226	1449.58	1.7347
227	1456.44	17.0758
228	1458.65	9.0097
229	1458.7	7.5847
230	1458.75	10.0311
231	1458.77	11.1135
232	1458.88	9.6537
233	1458.89	11.2111
234	1460.24	0.4288
235	1460.5	0.3459
236	1463.22	99.6957
237	1465.39	0.1692
238	1465.52	0.2125
239	1465.58	0.2357
240	1465.87	0.2409
241	1467.96	87.0946
242	1473.3	5.5856
243	1473.44	5.3337
244	1476.79	15.2752
245	1477	14.3867
246	1477.13	15.4533
247	1477.41	15.8094
248	1503.82	95.0251
249	1509.43	29.5595
250	1581.05	221.9312
251	1637.78	9.879
252	1658.45	1159.384
253	1694.27	14.5362
254	1767.65	919.0558
255	1810.93	696.6807
256	2198.13	1580.809
257	3044.39	31.5851
258	3044.54	33.8112
259	3044.72	44.9941
260	3044.76	25.9688
261	3044.9	36.5352
262	3044.96	26.2751
263	3048.23	20.1249
264	3048.23	10.0292
265	3048.29	19.9578
266	3048.31	13.6237
267	3048.39	107.3191
268	3048.43	5.3593
269	3057.32	19.6622

270	3057.68	5.7144
271	3059.44	31.4887
272	3059.59	29.4345
273	3060.32	62.6899
274	3060.48	7.1995
275	3065.11	61.7491
276	3065.34	31.9851
277	3066.7	29.9122
278	3067.34	25.602
279	3069.26	29.7105
280	3069.65	20.3959
281	3083.35	44.4788
282	3089.06	10.6464
283	3089.14	11.7581
284	3089.62	10.3529
285	3089.83	13.6417
286	3089.97	5.6924
287	3089.97	14.5128
288	3115.06	7.7993
289	3115.64	8.8231
290	3116.25	18.5883
291	3116.3	21.7557
292	3116.47	17.8797
293	3117.06	19.5121
294	3130.48	15.593
295	3131.08	13.8949
296	3132.79	4.3412
297	3133.14	9.1118
298	3133.49	4.9956
299	3134.72	4.0112
300	3138.3	59.262
301	3138.33	47.758
302	3138.43	53.9657
303	3138.5	59.1009
304	3138.52	47.0882
305	3138.56	91.7482
306	3147.22	34.8894
307	3147.23	37.9326
308	3147.36	34.6765
309	3147.37	34.4666
310	3147.5	23.5866
311	3147.52	32.8227
312	3172.59	10.3312
313	3216.01	0.9998
314	3225.58	5.2849
315	3228.24	4.2827

316	3232.28	2.837
317	3237.89	2.6295
318	3238.57	3.3296

Table S15 – Vertical transition energies between the optimised geometry of the singlet ground state of $C_{39}H_{62}ClNO_2P_2Pt$ and the first 15 singlet excited states.

Wavelength / nm	ε	Oscillator Strength
426.35	0.6118	1681446
408.41	0.2562	704129.4
332.44	0.0043	11817.94
319.34	0	0
310.42	0.0003	824.5075
304.54	0.022	60463.88
300.15	0.0533	146487.5
283.99	0.3761	1033658
279.9	0.0019	5221.881
278.62	0.0001	274.8358
274.59	0.0169	46447.25
270.98	0.0002	549.6716
268.95	0.0121	33255.13
266.91	0.0138	37927.34
262.64	0.0108	29682.27

Table S16 – Transition wavelengths, extinction coefficients and oscillator strengths for the vertical electronic excitations between the optimised geometry of the singlet ground state of $C_{39}H_{62}ClNO_2P_2Pt$ and the first 15 triplet excited states.

Wavelength / nm	ε	Oscillator Strength
592.63	0	0
425.05	0	0
387.97	0	0
353.59	0	0
335.39	0	0
334.09	0	0
324.57	0	0
321.04	0	0
311.1	0	0
309.97	0	0
307.96	0	0
300.05	0	0
290.37	0	0
288.47	0	0
282.53	0	0

6.5 S_1 excited state geometry optimisation

Optimized geometry and harmonic frequencies of the S_1 excited state, calculated by TD-DFT starting at the optimised S_0 geometry.

Route:	#p opt freq tda=(singlets,root=1)/genecp scrf=(cpcm,solvent=dichloromethane) density=current geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{39}H_{62}ClNO_2P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	20.517533 Debye
Energy	-2987.135618 Hartree
Number of imaginary frequencies	0

Table S17 – Atomic coordinates for the optimised geometry of the first triplet excited state of $C_{39}H_{62}ClNO_2P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure.

Element	Position		
Pt	-1.64356	0.229796	-0.08999
P	-2.29663	-2.04526	0.023001
P	-1.19739	2.561493	-0.16624
C	-3.57872	-2.37479	-1.25413
H	-4.11998	-1.42058	-1.35262
H	-3.02147	-2.51632	-2.19681
C	-0.931	-3.2481	-0.2195
H	-0.32237	-3.19771	0.699863
H	-0.30184	-2.80682	-1.00886
C	-3.01593	-2.30104	1.696899
H	-2.35471	-1.73168	2.371827
H	-3.96888	-1.74523	1.680663
C	0.550698	3.006466	-0.50844
H	0.685597	2.843262	-1.5922
H	1.152365	2.224282	-0.02103
C	-2.22806	3.288568	-1.50576
H	-2.15796	2.56438	-2.33522
H	-3.2658	3.21679	-1.14021
C	-1.69726	3.284511	1.449418
H	-2.56398	2.677955	1.758112
H	-0.87966	3.031594	2.147173

C	-1.90484	4.688576	-2.01753
H	-0.87838	4.711276	-2.42116
H	-1.92897	5.420266	-1.19416
C	-2.87492	5.133614	-3.10815
H	-3.90314	5.110989	-2.70633
H	-2.85685	4.396377	-3.93005
C	-2.56618	6.519303	-3.65303
H	-3.28261	6.812707	-4.43528
H	-2.61092	7.281028	-2.85795
H	-1.55683	6.560736	-4.09331
C	1.059974	4.383417	-0.09324
H	0.456941	5.182351	-0.55399
H	0.950925	4.504159	0.998046
C	2.525622	4.584203	-0.46808
H	2.638173	4.463367	-1.55989
H	3.127957	3.77884	-0.01218
C	3.070141	5.938711	-0.0425
H	4.126743	6.054647	-0.32775
H	2.506587	6.762367	-0.51
H	3.003942	6.071566	1.049484
C	-2.05555	4.765498	1.535042
H	-1.2215	5.393703	1.183983
H	-2.90684	4.977415	0.866191
C	-2.42796	5.178608	2.955985
H	-3.25724	4.541908	3.311167
H	-1.57726	4.966916	3.627467
C	-2.81902	6.643756	3.069116
H	-3.69048	6.875565	2.435738
H	-3.07954	6.911565	4.104339
H	-1.99537	7.303484	2.751777
C	-3.19811	-3.71689	2.234129
H	-2.21956	-4.22362	2.285942
H	-3.82165	-4.31684	1.552258
C	-3.83072	-3.72111	3.622764
H	-3.21073	-3.11161	4.303561
H	-4.81059	-3.2145	3.573542
C	-4.00238	-5.11886	4.196503
H	-4.6463	-5.73952	3.552675
H	-3.03326	-5.63502	4.289776
H	-4.46124	-5.0896	5.196416
C	-1.26961	-4.69178	-0.57846
H	-1.92971	-5.14209	0.180024
H	-1.82897	-4.71648	-1.52902
C	-0.01627	-5.55065	-0.72112
H	0.650825	-5.09429	-1.47363
H	0.54518	-5.53002	0.229413
C	-0.31917	-6.98969	-1.10804

H	0.602789	-7.58335	-1.20156
H	-0.95657	-7.48086	-0.35514
H	-0.84826	-7.0419	-2.07329
C	-4.57769	-3.5068	-1.03055
H	-5.14868	-3.31607	-0.10602
H	-4.05932	-4.46762	-0.88202
C	-5.55426	-3.64169	-2.19519
H	-6.06718	-2.67613	-2.34933
H	-4.98562	-3.83184	-3.12249
C	-6.58193	-4.74322	-1.9879
H	-6.09702	-5.72511	-1.86492
H	-7.18907	-4.55975	-1.08675
H	-7.27035	-4.81717	-2.8434
C	0.189615	-0.23714	-0.20841
C	1.392256	-0.57379	-0.2682
C	2.739532	-0.96868	-0.37333
C	3.771898	-0.28171	0.357961
C	3.076272	-2.03436	-1.24782
C	5.126973	-0.69461	0.156831
C	3.507656	0.764688	1.269455
C	4.393482	-2.4096	-1.44321
H	2.27325	-2.54601	-1.78215
C	6.172903	-0.04732	0.865719
C	5.421491	-1.74764	-0.74499
C	5.872526	0.997741	1.762981
C	7.553483	-0.45659	0.66949
C	6.809577	-2.1782	-0.95921
C	4.555265	1.392438	1.956125
H	2.474457	1.069785	1.444049
H	4.328559	2.203654	2.652719
H	6.696478	1.479794	2.291611
H	4.66181	-3.22092	-2.12082
N	7.784548	-1.50266	-0.23621
O	8.511302	0.058916	1.243191
O	7.100261	-3.08578	-1.73464
Cl	-3.94086	0.793025	0.162657
C	9.170276	-1.8926	-0.41637
H	9.760659	-1.04326	-0.78834
H	9.604557	-2.20955	0.54217
H	9.196987	-2.71614	-1.13601

Table S18 – Harmonic frequencies obtained for the optimised geometry of the first triplet excited state of $C_{39}H_{62}ClNO_2P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	5.85	0.2987
2	11.2	0.9685
3	12.59	0.2968
4	15.28	0.4668
5	16.99	1.0296
6	25.86	0.2073
7	33.19	0.2175
8	38.59	0.0528
9	38.71	0.0185
10	40.23	0.0466
11	40.45	0.0039
12	48.73	0.176
13	51.72	0.288
14	54.18	0.0731
15	56.44	0.0816
16	62.28	0.2388
17	66.33	0.5143
18	67.47	0.3123
19	73.01	0.1655
20	73.22	0.2944
21	75.33	1.5765
22	76.65	0.0727
23	77.06	0.0655
24	82.26	1.4405
25	91.4	4.3725
26	95.51	1.8063
27	103.35	0.6642
28	112.38	3.9573
29	112.85	0.1288
30	116.61	0.8627
31	132.23	3.9928
32	134.65	2.7054
33	138.02	0.7631
34	141.15	0.2567
35	143.43	1.9923
36	147.58	3.1066
37	156.54	0.8327
38	158.2	1.1458
39	163.16	10.7563
40	164.73	5.8616
41	167.47	2.1348
42	167.83	2.2166

43	172.06	4.3218
44	177.02	2.1533
45	179.36	1.3829
46	182.56	10.0052
47	204.88	13.7373
48	217.89	0.3055
49	220.04	1.2118
50	221.88	1.0918
51	224.79	2.4848
52	233.45	0.0405
53	234.43	0.7129
54	256.9	0.1179
55	257.51	0.1169
56	258.03	0.3951
57	258.19	0.2541
58	258.77	0.2167
59	259.35	0.2083
60	264.67	4.0723
61	282.78	35.5135
62	300.58	62.3806
63	306.64	273.0134
64	334.53	0.4663
65	335.74	5.7078
66	340.07	8.5533
67	343.3	3.5235
68	349.31	33.6078
69	369.2	14.134
70	375.94	6.2281
71	382.26	15.516
72	396.54	40.7544
73	404.52	0.2466
74	409.99	0.5978
75	410.73	6.2722
76	413.43	5.2415
77	414.61	1.6686
78	416.93	41.3639
79	428.59	49.9125
80	454.21	1.7018
81	494.38	9.049
82	504.64	78.6894
83	513.68	8.402
84	518.15	146.32
85	539.36	6.298
86	552.95	13.2199
87	583.29	11.0234
88	595.4	97.9712
89	648.99	9.8382

90	654.47	10.4948
91	680	15.1109
92	690.56	30.2682
93	691.79	18.469
94	702.05	5.2863
95	703.42	5.2379
96	722.76	22.5774
97	723.33	21.5771
98	724.06	18.813
99	724.68	11.6411
100	739.96	44.5207
101	756.18	0.2808
102	756.45	2.3268
103	757.56	74.66
104	762.19	6.578
105	763.14	5.1144
106	763.98	2.9607
107	764.61	2.3472
108	778.6	62.1683
109	789.45	0.6645
110	792.66	1.8349
111	793.89	44.1699
112	796.55	7.5136
113	797.52	34.2713
114	830.02	1.3921
115	838.67	62.7912
116	859.67	0.4775
117	884.51	2.9089
118	885.6	5.6244
119	888.09	4.0998
120	903.85	14.8766
121	904.71	5.8942
122	904.99	5.3893
123	905.38	28.4135
124	906.34	15.2353
125	915.46	6.3036
126	915.7	7.8278
127	915.88	14.8409
128	916.15	10.3627
129	916.49	8.5757
130	916.75	4.3819
131	981.2	0.7959
132	991.2	29.4158
133	994.1	0.414
134	1037.17	3.2811
135	1038.11	6.0331
136	1043.03	0.329

137	1051.76	1.3548
138	1052.23	7.0591
139	1052.47	0.8911
140	1052.78	3.8468
141	1053.08	7.6731
142	1054.07	0.809
143	1065.67	339.3675
144	1075.15	3.3746
145	1076.85	5.3166
146	1077.56	7.4391
147	1079.15	0.7928
148	1088.06	110.2146
149	1089.37	1.7889
150	1089.78	12.613
151	1089.92	3.2836
152	1090.81	4.1215
153	1092.34	4.9754
154	1093.23	2.2579
155	1116.44	10.5336
156	1116.68	2.3081
157	1117.21	37.1248
158	1117.51	40.9481
159	1120.74	137.2347
160	1123.72	93.9931
161	1132.66	211.8607
162	1141.32	0.3088
163	1155.31	37.3502
164	1188.45	150.7696
165	1213.58	1.3682
166	1214.59	0.25
167	1216.72	1.5985
168	1217.28	4.6985
169	1217.68	3.5826
170	1218.44	1.2408
171	1230.09	2.4112
172	1230.25	4.465
173	1230.64	1.2167
174	1232.36	1.9592
175	1237.53	705.8247
176	1249.03	97.6971
177	1250.37	175.1554
178	1254.23	714.5655
179	1269.63	138.0815
180	1290.96	0.4195
181	1292.57	1.9194
182	1295.12	4.8869
183	1295.8	5.7675

184	1297.6	5.6094
185	1298.07	8.0632
186	1300.08	51.5291
187	1318.74	2.4445
188	1319.04	4.5502
189	1319.16	2.9531
190	1319.74	3.0165
191	1320.18	3.69
192	1321.39	0.0356
193	1321.43	2.1362
194	1322.33	0.9698
195	1322.87	3.4201
196	1323.28	10.4683
197	1326.6	27.6125
198	1327.67	35.019
199	1376.19	62.279
200	1381.18	0.415
201	1381.71	0.469
202	1382.13	0.368
203	1382.3	0.4172
204	1384.62	1.3713
205	1384.83	3.7129
206	1391.46	11.0092
207	1398.74	0.1004
208	1398.97	0.5158
209	1399.37	1.22
210	1399.39	0.2896
211	1401.53	20.5863
212	1401.61	5.1202
213	1408.14	9.436
214	1415.7	26.6903
215	1419.35	6.0815
216	1420.41	26.1074
217	1421.59	23.3069
218	1425.3	23.3802
219	1425.71	145.6291
220	1426.18	27.8875
221	1447.58	8.4585
222	1447.72	13.3437
223	1448.43	33.8311
224	1449.42	3.222
225	1449.43	2.3337
226	1449.75	1.8808
227	1450.38	3.4286
228	1454.62	16.0546
229	1458.65	9.2402
230	1458.84	9.0102

231	1458.89	8.137
232	1458.98	9.491
233	1459.05	11.976
234	1459.26	11.0629
235	1459.35	130.0241
236	1460.27	0.9831
237	1460.44	4.4637
238	1465.03	0.4229
239	1465.58	0.1087
240	1465.76	0.3896
241	1465.89	0.6348
242	1467.39	767.4753
243	1473.43	6.5838
244	1473.6	5.4389
245	1476.41	15.2684
246	1477	17.1922
247	1477.42	16.3623
248	1477.66	14.3865
249	1501.85	1240.516
250	1553.11	387.7361
251	1572.59	952.1165
252	1589.58	312.567
253	1649.05	327.0339
254	1712.04	1384.814
255	1758.89	1618.445
256	2106.9	707.6184
257	3045.72	28.7884
258	3045.78	46.2885
259	3045.79	21.1258
260	3045.85	36.4641
261	3045.97	27.0325
262	3046.04	31.4955
263	3048.4	26.6036
264	3048.99	13.1152
265	3049.01	12.5599
266	3049.05	44.3583
267	3049.1	44.6318
268	3049.23	36.7299
269	3059.92	26.3754
270	3060.25	43.4831
271	3060.43	15.5245
272	3061.89	25.4703
273	3062.02	38.9418
274	3062.55	30.4012
275	3067.8	53.0617
276	3068	18.2952
277	3068.89	27.7521

278	3069.62	10.4368
279	3070.4	21.4134
280	3072.5	18.3884
281	3078.98	79.9795
282	3091	15.4301
283	3091.04	9.2875
284	3091.14	15.1211
285	3091.18	9.9762
286	3091.26	8.0732
287	3091.36	4.9975
288	3117.33	6.7909
289	3118.52	11.8527
290	3118.92	31.6513
291	3119.31	17.1193
292	3119.5	20.4631
293	3119.55	5.7784
294	3132.84	12.9882
295	3134.26	8.4619
296	3135.4	3.4299
297	3136.58	2.3973
298	3137.35	2.29
299	3138.11	44.6336
300	3139.39	55.243
301	3139.43	57.3043
302	3139.57	44.0931
303	3139.58	13.2501
304	3139.6	134.48
305	3141.01	17.7245
306	3148.4	18.9191
307	3148.41	57.5517
308	3148.42	47.2596
309	3148.45	4.6403
310	3148.64	33.0457
311	3148.88	26.351
312	3165.27	14.1563
313	3207.05	28.67
314	3224.05	6.7467
315	3226.12	4.5508
316	3226.7	4.2892
317	3237.84	4.7106
318	3246.13	11.5839

6.6 T_1 excited state geometry optimisation

Optimized geometry and harmonic frequencies of the T_1 excited state, calculated by TD-DFT starting at the optimised S_0 geometry.

Route:	#p opt freq tda=(triplets,root=1)/genecp scrf=(cpcm,solvent=dichloromethane) density=current geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES:	Cl[Pt]([P](CCCC)(CCCC)CCCC)([P](CCCC)(CCCC)CCCC)C#CC1=CC=C(C(N2C3=CC=C(C(OC)=O)C=C3)=O)C4=C1C=CC=C4C2=O
Formula	$C_{39}H_{62}ClNO_2P_2Pt$
Charge	0
Multiplicity	Singlet
Dipole	11.880805 Debye
Energy	-2987.167659 Hartree
Number of imaginary frequencies	0

Table S19 – Atomic coordinates for the optimised geometry of the first triplet excited state of $C_{39}H_{62}ClNO_2P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure.

Element	Position		
Pt	-1.6399	0.207312	-0.06126
P	-2.263	-2.06321	0.041979
P	-1.24792	2.532911	-0.13891
C	-3.50538	-2.41503	-1.26915
H	-4.06605	-1.4714	-1.36553
H	-2.92263	-2.5291	-2.20013
C	-0.87348	-3.24972	-0.15354
H	-0.30586	-3.19615	0.791955
H	-0.21658	-2.79274	-0.91081
C	-3.02924	-2.33988	1.69269
H	-2.39515	-1.76673	2.39018
H	-3.98635	-1.79271	1.650328
C	0.51287	3.015984	-0.35208
H	0.745707	2.811598	-1.41195
H	1.085822	2.268778	0.218872
C	-2.19052	3.206964	-1.56947
H	-2.04023	2.465167	-2.37223
H	-3.25006	3.111792	-1.27813
C	-1.87847	3.293046	1.413919
H	-2.74948	2.671472	1.67731
H	-1.10615	3.08529	2.175383
C	-1.86926	4.602012	-2.09523

H	-0.8165	4.643721	-2.42276
H	-1.97409	5.354462	-1.29723
C	-2.76649	4.990172	-3.26696
H	-3.82093	4.948855	-2.94181
H	-2.66777	4.231861	-4.06362
C	-2.45496	6.368828	-3.82793
H	-3.11814	6.620407	-4.66952
H	-2.57928	7.150382	-3.06101
H	-1.41683	6.427223	-4.19306
C	0.95487	4.420334	0.046042
H	0.374582	5.184178	-0.49618
H	0.751294	4.581952	1.118315
C	2.441698	4.646155	-0.21341
H	2.649025	4.485046	-1.286
H	3.0229	3.875878	0.323716
C	2.916897	6.030471	0.199177
H	3.990949	6.163532	-0.00087
H	2.376017	6.819263	-0.34834
H	2.754593	6.205206	1.275096
C	-2.28026	4.765162	1.426216
H	-1.44157	5.406754	1.111816
H	-3.0889	4.931545	0.69437
C	-2.76105	5.212606	2.803531
H	-3.59461	4.562792	3.123187
H	-1.95312	5.048397	3.53826
C	-3.2	6.668128	2.840107
H	-4.03171	6.852957	2.141175
H	-3.53899	6.961329	3.845345
H	-2.37534	7.342168	2.557148
C	-3.21108	-3.76037	2.217103
H	-2.22865	-4.25618	2.296461
H	-3.80564	-4.36438	1.513216
C	-3.88632	-3.7807	3.585367
H	-3.29555	-3.16735	4.288405
H	-4.87033	-3.28563	3.508381
C	-4.05879	-5.18345	4.146634
H	-4.67451	-5.80843	3.479763
H	-3.08681	-5.68849	4.267543
H	-4.54907	-5.16548	5.131856
C	-1.17105	-4.69627	-0.5348
H	-1.85434	-5.16369	0.192326
H	-1.69021	-4.72349	-1.50795
C	0.10176	-5.53267	-0.63135
H	0.792814	-5.05692	-1.34957
H	0.62126	-5.51219	0.342845
C	-0.15842	-6.97282	-1.04442
H	0.776845	-7.55001	-1.10317

H	-0.81941	-7.48235	-0.32474
H	-0.6442	-7.02445	-2.03224
C	-4.48221	-3.57327	-1.08765
H	-5.08406	-3.40728	-0.17804
H	-3.94555	-4.52331	-0.93441
C	-5.42178	-3.71862	-2.28116
H	-5.95299	-2.76375	-2.44018
H	-4.82246	-3.88483	-3.1937
C	-6.42843	-4.84636	-2.11566
H	-5.92387	-5.8178	-1.98845
H	-7.06568	-4.68729	-1.23077
H	-7.08992	-4.9275	-2.99158
C	0.213282	-0.22065	-0.21535
C	1.424855	-0.51781	-0.30827
C	2.762502	-0.86153	-0.43619
C	3.791778	-0.26374	0.400606
C	3.155672	-1.82981	-1.43712
C	5.154558	-0.63503	0.175923
C	3.515344	0.652569	1.420212
C	4.460917	-2.17556	-1.63383
H	2.368946	-2.27753	-2.04827
C	6.177207	-0.06556	0.962391
C	5.486184	-1.58005	-0.83474
C	5.867291	0.865279	1.975982
C	7.58021	-0.43522	0.738096
C	6.873836	-1.9637	-1.07278
C	4.548187	1.212827	2.197638
H	2.476701	0.927579	1.615648
H	4.296128	1.92772	2.9846
H	6.683077	1.286524	2.564933
H	4.755333	-2.90018	-2.39353
N	7.840732	-1.35991	-0.26602
O	8.502906	0.033594	1.391605
O	7.188319	-2.77574	-1.93781
Cl	-3.97304	0.737495	0.171358
C	9.234434	-1.71072	-0.47135
H	9.818094	-0.8152	-0.72634
H	9.657368	-2.1423	0.446566
H	9.281615	-2.4379	-1.28709

Table S20 – Harmonic frequencies obtained for the optimised geometry of the first triplet excited state of $C_{39}H_{62}ClNO_2P_2Pt$, obtained by TD-DFT using the singlet ground state as the input structure

Mode	Harmonic frequency / cm^{-1}	IR intensity / km mol^{-1}
1	7.55	0.1225
2	9.05	0.2424
3	10.55	0.4176
4	13.46	0.0786
5	15.06	0.824
6	25.33	0.539
7	33.48	0.2079
8	38.13	0.0088
9	39.06	0.0455
10	39.86	0.026
11	40.16	0.054
12	47.85	0.0057
13	49.9	0.0312
14	53.67	0.1021
15	56.49	0.0871
16	60.9	0.2244
17	64.75	0.3206
18	68.12	0.3052
19	73.28	0.286
20	73.43	0.2034
21	74.89	0.1581
22	76.28	0.1099
23	76.88	0.1093
24	85.94	4.7986
25	90.29	1.3758
26	95.63	4.62
27	102.22	1.1645
28	112.22	3.7053
29	113.32	0.0738
30	115.55	0.4295
31	133.44	0.168
32	135.87	3.2451
33	137.33	0.0762
34	142.26	2.9185
35	143.37	2.632
36	147.48	2.2767
37	156.5	3.292
38	158.42	1.177
39	163.01	10.2852
40	163.73	1.6881
41	167.63	1.06
42	168.83	3.3681
43	170.76	2.6208

44	176.74	2.4543
45	177.68	2.2732
46	179.25	19.0912
47	210.67	0.6375
48	218.72	0.1256
49	219.63	0.0352
50	220.82	1.6014
51	224.83	1.5215
52	233.4	0.0434
53	234.12	0.5693
54	256.81	0.0742
55	257.59	0.0766
56	257.78	0.0884
57	258	0.0405
58	258.59	0.0735
59	259.09	0.1719
60	269.35	3.8622
61	282.21	1.6514
62	296.82	19.0253
63	301.43	55.6663
64	332.14	3.9521
65	334.33	0.4303
66	339.38	9.8314
67	342.1	2.5035
68	343.95	21.5985
69	368.96	23.8305
70	375.98	8.3123
71	383.05	12.3747
72	391.8	32.4784
73	404.11	0.054
74	409.08	2.3489
75	409.36	0.4969
76	410.48	7.1208
77	412.52	25.2281
78	414.38	34.5453
79	426.58	13.2591
80	450.89	15.943
81	488.59	6.2792
82	504.29	89.7877
83	519.69	12.1807
84	520.79	97.6414
85	537.4	7.2368
86	548.75	6.107
87	559.42	4.7699
88	590.01	82.0997
89	639.9	0.0993
90	649.31	56.6964

91	679.21	3.7322
92	690.57	33.2427
93	691.65	5.3921
94	702.05	3.0716
95	703.68	2.5017
96	722.72	38.825
97	722.93	6.8309
98	723.82	17.4032
99	724.62	17.4718
100	739.16	19.3342
101	755.92	0.6529
102	756	0.2005
103	761.74	6.0898
104	762.61	68.7423
105	762.77	3.6609
106	763.62	2.0153
107	764.1	7.969
108	788.24	2.6445
109	789.92	43.2564
110	791.33	8.8501
111	792.93	40.3979
112	795.74	82.1441
113	797.15	18.4488
114	824.81	4.2734
115	826.58	4.1248
116	858.43	0.4352
117	884.39	3.5027
118	885.07	4.1928
119	897.56	8.4061
120	904.37	6.6074
121	904.7	4.5378
122	905.14	30.8658
123	905.56	26.6142
124	915.08	7.054
125	915.31	9.5601
126	915.67	20.4249
127	915.79	9.3049
128	916.17	6.821
129	916.46	6.2749
130	922.8	2.2788
131	983.02	90.127
132	997.41	0.1594
133	1009.71	0.6134
134	1036.34	2.1374
135	1037.39	3.367
136	1049.36	9.6488
137	1051.67	1.3378

138	1052.11	3.6045
139	1052.39	4.7052
140	1052.94	7.1209
141	1053.68	6.2731
142	1054.45	0.5724
143	1067.69	90.3582
144	1074.36	2.8006
145	1075.81	5.8817
146	1077.2	5.8049
147	1078.87	9.8178
148	1089.61	0.8012
149	1089.86	1.43
150	1089.95	0.343
151	1090.57	2.917
152	1092.68	5.0108
153	1093.21	1.8288
154	1095.04	47.5499
155	1116.49	14.559
156	1116.78	1.3845
157	1117.43	31.3387
158	1117.59	39.1366
159	1120.87	132.6222
160	1122.89	37.444
161	1123.96	35.5101
162	1142.13	0.1859
163	1145.96	2.6506
164	1183.9	112.3896
165	1213.37	1.9625
166	1214.37	1.571
167	1216.23	3.3527
168	1216.85	3.0789
169	1216.95	1.8706
170	1218.46	2.8145
171	1229.65	0.3336
172	1230.28	2.1906
173	1230.44	3.4038
174	1231.89	1.4048
175	1248.95	37.0356
176	1250.34	26.4987
177	1254.38	3.4769
178	1277.4	74.137
179	1283.9	259.4014
180	1290.23	1.8362
181	1291.47	2.3892
182	1294.06	5.8947
183	1294.69	3.445
184	1297.1	5.0997

185	1297.82	2.636
186	1316.9	80.7658
187	1318.26	4.8273
188	1318.45	4.9505
189	1318.81	2.5708
190	1319.66	0.994
191	1319.87	3.1223
192	1320.46	1.0921
193	1320.81	0.8382
194	1321.48	0.5613
195	1322.15	1.6754
196	1322.71	3.0362
197	1325.86	25.5339
198	1326.94	18.1094
199	1343.91	192.7044
200	1380.8	0.254
201	1381.3	0.2988
202	1381.53	0.17
203	1382.32	0.1896
204	1384.13	0.4099
205	1384.66	0.2298
206	1396.72	3.7609
207	1398.43	0.0923
208	1398.77	0.3873
209	1398.94	0.4299
210	1399.26	0.5586
211	1401.18	16.3585
212	1401.41	7.1778
213	1416.59	30.8217
214	1417.82	51.9654
215	1419.7	45.7534
216	1421.4	28.4924
217	1422.02	10.6312
218	1424.03	49.4377
219	1425.81	27.3963
220	1426.84	9.1058
221	1446.02	301.9951
222	1447.42	6.3408
223	1447.56	0.6702
224	1449.27	2.0614
225	1449.36	1.821
226	1449.66	1.9407
227	1449.67	2.7935
228	1456.55	20.5751
229	1457.59	331.7529
230	1458.54	7.1635
231	1458.56	10.7715

232	1458.61	11.7501
233	1458.68	10.9333
234	1458.98	8.8903
235	1459.03	10.7142
236	1460.3	0.3686
237	1460.44	0.5274
238	1465.38	0.1784
239	1465.5	0.175
240	1465.68	0.1705
241	1465.81	0.2651
242	1468.98	34.6366
243	1473.41	9.6094
244	1473.41	1.7703
245	1476.9	15.2936
246	1476.92	14.3992
247	1477.1	16.2897
248	1477.65	15.3869
249	1497.93	14.1971
250	1529.88	549.4087
251	1589.07	264.1685
252	1593.33	332.5879
253	1668.82	814.4881
254	1711.36	953.0175
255	1759.78	999.3894
256	2073.17	1648.54
257	3044.82	33.4265
258	3044.84	25.7392
259	3045.12	46.7507
260	3045.14	22.534
261	3045.31	38.1529
262	3045.37	27.5678
263	3048.29	22.0418
264	3048.53	22.0645
265	3048.55	12.8621
266	3048.61	25.1129
267	3048.65	60.0378
268	3048.73	35.5453
269	3058.17	21.7145
270	3058.75	7.6029
271	3059.43	38.7892
272	3060.76	26.8895
273	3061.1	48.4571
274	3061.34	18.1008
275	3065.9	45.6526
276	3066.51	41.383
277	3068.03	23.7252
278	3068.66	19.2351

279	3069.57	25.8702
280	3069.81	30.356
281	3081.42	57.9207
282	3089.6	12.1087
283	3089.91	9.9844
284	3090.17	11.0534
285	3090.42	8.8948
286	3090.43	14.7856
287	3090.5	9.209
288	3116.12	8.5248
289	3117.08	9.9016
290	3117.26	20.5095
291	3117.56	20.6371
292	3117.83	17.7893
293	3118.27	15.2615
294	3131.69	13.4314
295	3132.59	11.0225
296	3134.14	1.8131
297	3134.31	7.5674
298	3134.5	4.8212
299	3137.39	8.119
300	3138.79	44.351
301	3138.82	64.2248
302	3138.85	28.9819
303	3138.91	67.4308
304	3138.91	51.9156
305	3138.94	96.0619
306	3147.66	35.0376
307	3147.69	36.5182
308	3147.79	34.6814
309	3147.85	33.1079
310	3147.93	26.0168
311	3148.11	28.6335
312	3169.75	11.3569
313	3212.91	15.1807
314	3221.6	9.6945
315	3225.51	3.3374
316	3229.75	3.1982
317	3244.83	2.6181
318	3248.87	3.4142

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