Ultrafast photoinduced charge transport in Pt(II) donor-acceptor assembly bearing naphthalimide electron acceptor and phenothiazine electron donor Supplementary Information

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S1. ADDITIONAL FIGURES: EXPERIMENTAL SECTION

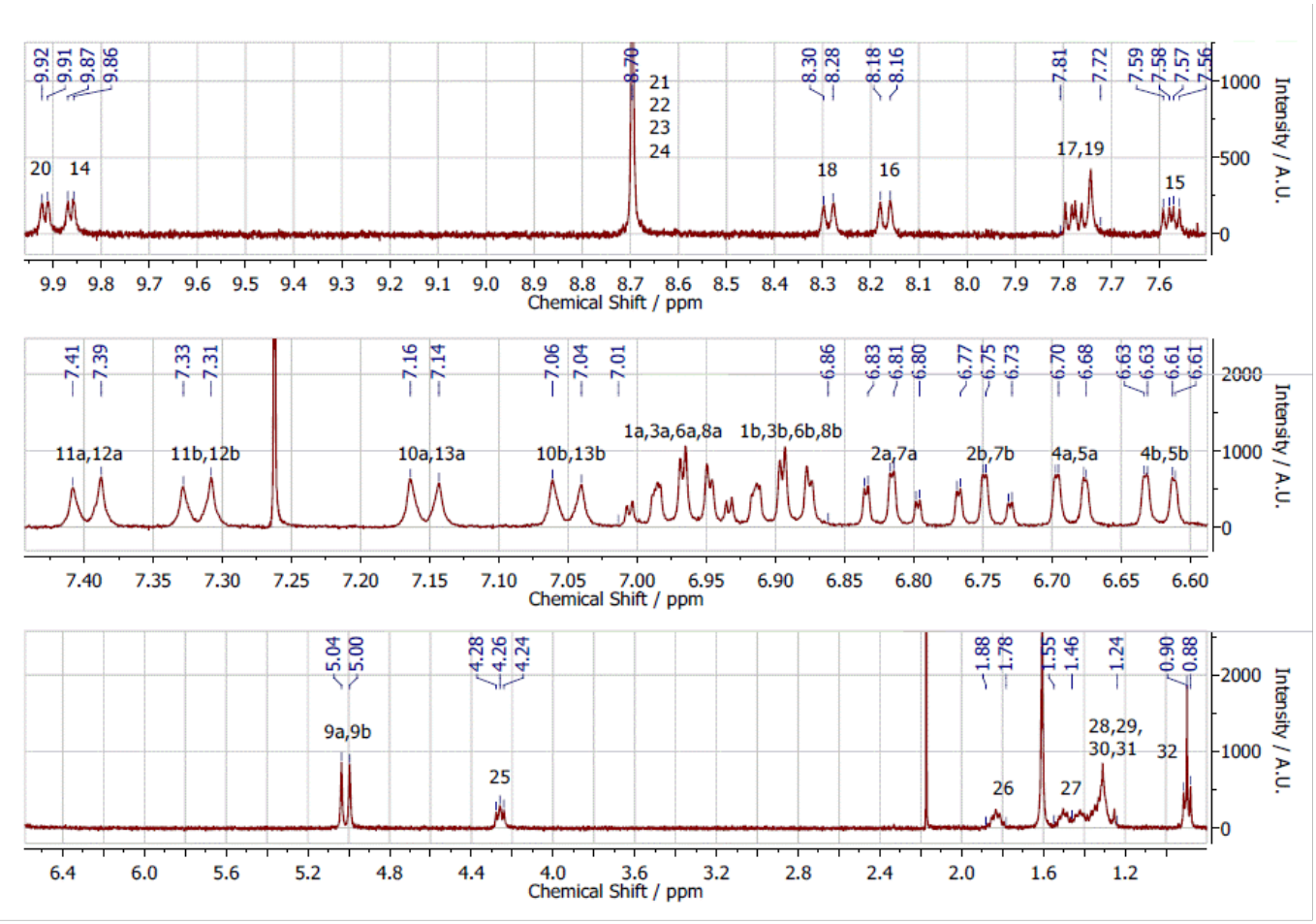


FIG. S1. The ^{1}H NMR spectrum of **1** in $CDCl_3$.

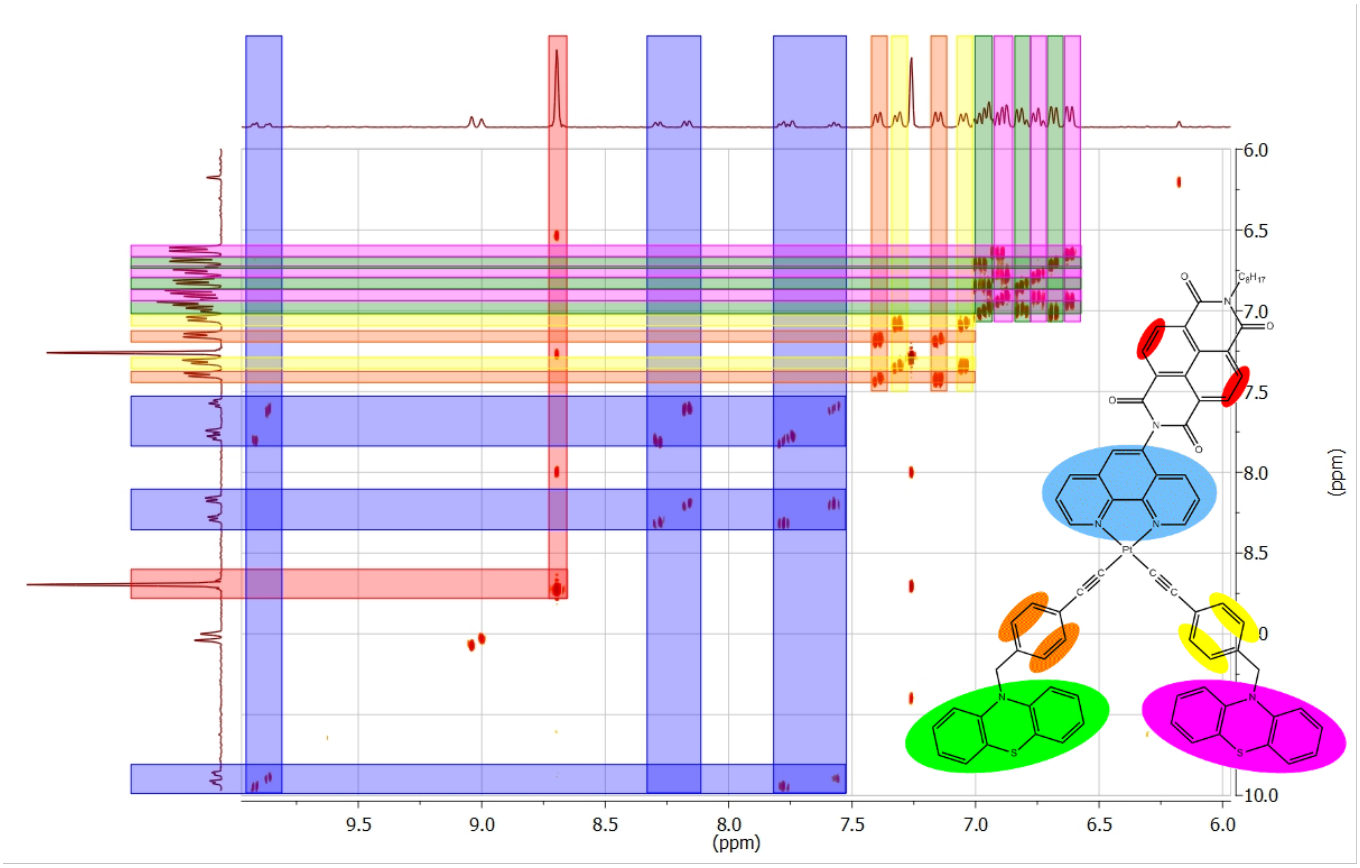


FIG. S2. COSY ^{1}H NMR spectrum of **1** in $CDCl_3$. The signals in the NMR are coloured and correspond to the highlighted protons on the complex.

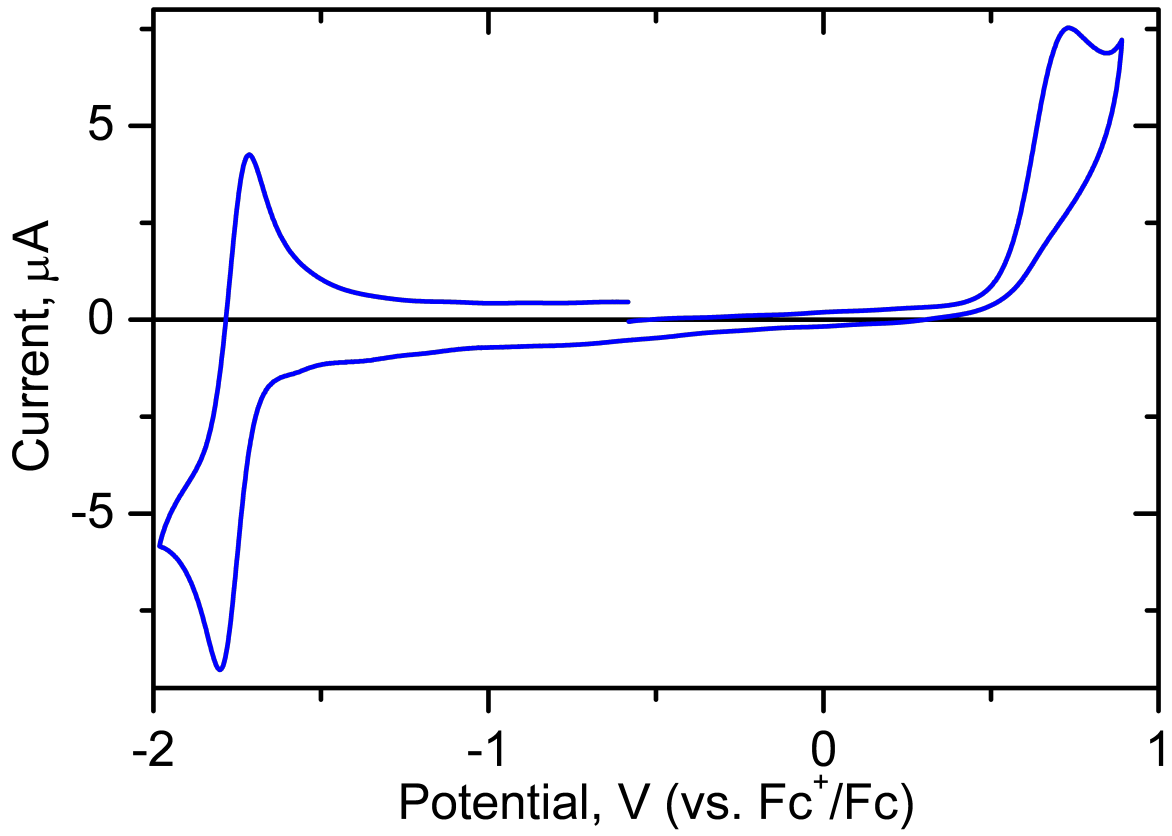


FIG. S3. Cyclic voltammogram of a 1.5 mM CH_2Cl_2 solution of (phen)Pt(C≡C−C_6H_4−CH_3)$_2$ recorded at 100 mVs^{-1} with 0.2 M [NBu_4][PF_6] as supporting electrolyte. All potentials are quoted against the Fc^+/Fc internal reference.

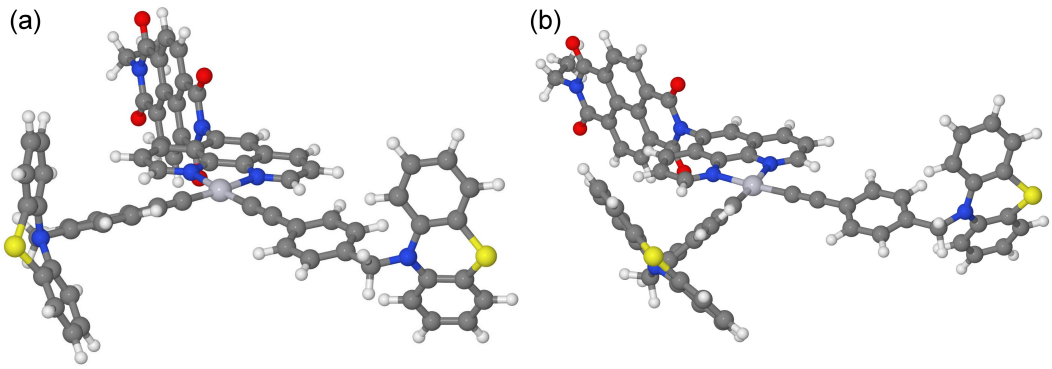


FIG. S4. Structure for the alternative conformation of [1]. Panel (a): Singlet ground (S_0) state. Panel (b): First excited Triplet (T_1) state

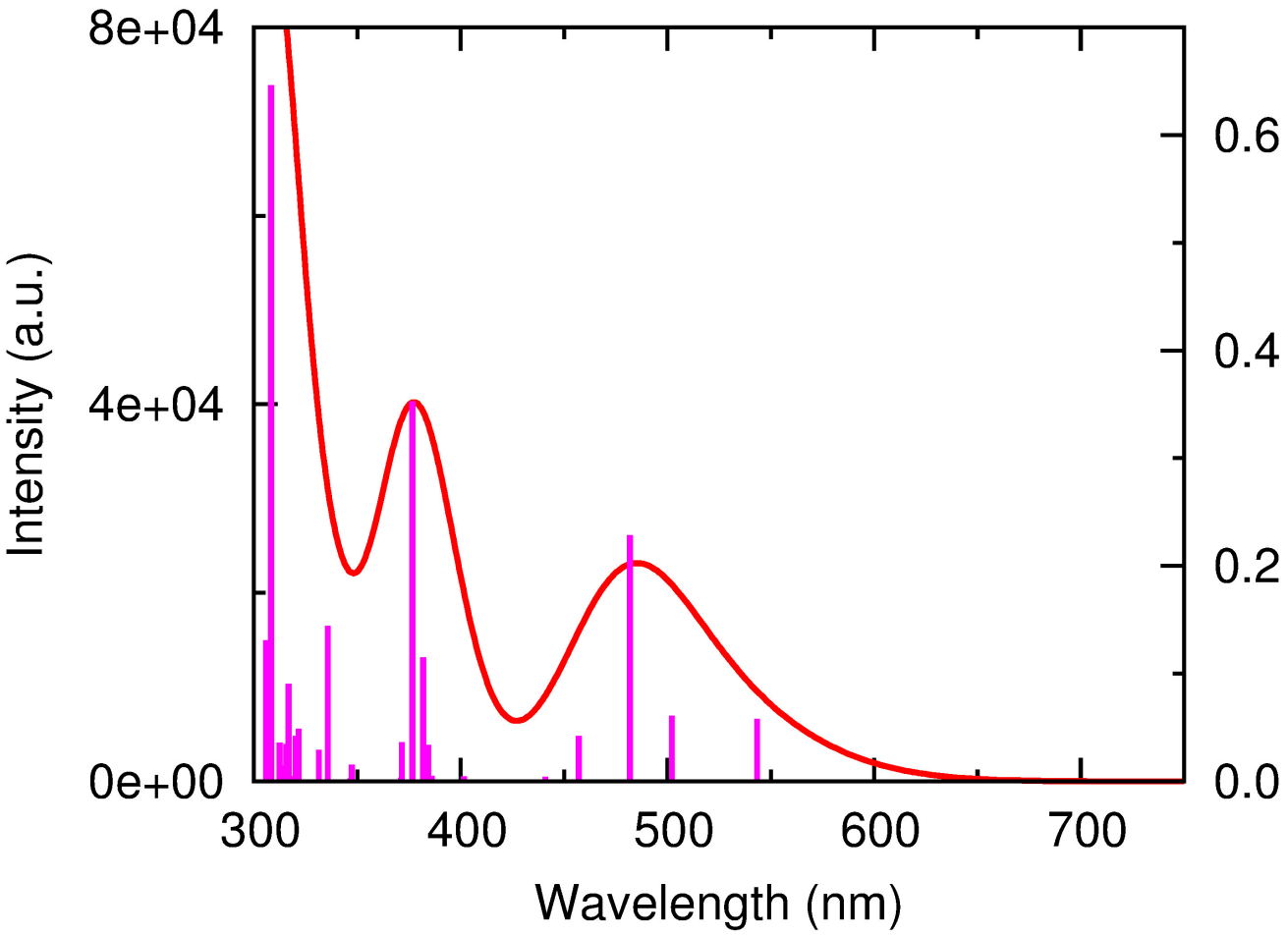


FIG. S5. UV-VIS spectrum for the ground singlet (S_0).

S2. ANALYTICAL DATA FOR 1

^{1}H NMR ($CDCl_3$, Figure S1): 0.90 (t, J = 7.03 Hz, 3H, H_{32}), 1.24 – 1.46 (m, 8H, H_{28--31}), 1.46 – 1.55 (m, 2H, H_{27}), 1.78 – 1.88 (m, 2H, H_{26}), 4.26 (t, J = 7.68, 2H, H_{25}), 5.00 (s, 2H, H_{9b}), 5.04 (s, 2H, H_{9a}), 6.62 (dd, J = 0.85, 8.15 Hz, 2H, $H_{4b,5b}$), 6.69 (dd, J = 0.85, 8.07 Hz, 2H, $H_{4a,5a}$), 6.75 (dt, J = 1.06, 7.37 Hz, 2H, $H_{2b,7b}$), 6.82 (dt, J = 1.08, 7.46 Hz, 2H, $H_{2a,7a}$), 6.86 – 7.01 (m, 8H, $H_{1,3,6,8}$), 7.05 (d, J = 8.29 Hz, 2H, $H_{10b,13b}$), 7.15 (d, J = 8.24 Hz, 2H, $H_{10a,13a}$), 7.32 (d, J = 8.13 Hz, 2H, $H_{11b,12b}$), 7.40 (d, J = 8.20 Hz, 2H, $H_{11a,12a}$), 7.58 (dd, J = 5.10, 8.38 Hz, 1H, H_{15}), 7.72 – 7.81 (m, 2H, $H_{19,17}$), 8.17 (d, J = 8.37 Hz, 1H, H_{16}), 8.29 (d, J = 8.12 Hz, 1H, H_{18}), 8.70 (s, 4H, H_{21--24}), 9.86 (d, J = 5.02 Hz, 1H, H_{14}), 9.92 (d, J = 5.02 Hz, 1H, H_{20}). MALDI-MS: m/z = 1376 (M^+), 1178 (M^+ –PTZ).

From the COSY ^{1}H NMR spectrum (Figure S2), spin-spin coupling allowed the specific assignment of the NMR peaks. H_{14} and H_{20} on phenanthroline (highlighted in blue) were strongly deshielded by the close proximity of nitrogen and appear as doublets at 9.86 and 9.92 ppm in the spectrum. Protons 14 and 20 could be seen to be spin-spin coupled with the doublet of doublets at 7.75 and 7.58 ppm, which were assigned to H_{15} and H_{19}. These were also spin-spin coupled with the peaks at 8.17 and 8.29 ppm which were assigned as protons 16 and 18. H_{17} occurred as a singlet at approximately 7.72 ppm and did not have any spin-spin coupling with other nuclei. Four doublets were observed at 7.05, 7.15, 7.32 and 7.40 ppm. The doublet at 7.05 ppm was coupled to the one at 7.32 ppm, while the one at 7.15 ppm was coupled to that at 7.40 ppm. These protons were assigned to the benzyl fragment of the acetylide ligand. Protons 21 – 24 on the naphthalene diimide were all magnetically equivalent which resulted in a singlet observed at 8.70 ppm corresponding to 4H. Two doublets and two triplets could clearly be seen upfield between 6.62 and 6.82 ppm with the second pair of doublets and triplets overlapping between 6.86 and 7.01 ppm. These were all assigned to the two phenothiazine moieties and although the peaks relating to the individual phenothiazines could be determined, it was difficult to identify which phenothiazine was which.

The synthesis of compound **2**, $((COOEt)_2bpy)Pt(C{\equiv}C–PTZ)_2$ was performed in the following way. N–(4–ethynylbenzyl)–phenothiazine (200 mg, 0.64 mmol), CuI (12 mg, 0.06 mmol), $Pt((COOEt)_2bpy)Cl_2$ (185 mg, 0.33 mmol) and diisopropylamine (6 ml, 4.33 g, 42.89 mmol) were sonicated in degassed CH_2Cl_2 (30 ml) in the dark for 7 hrs. A colour change from orange to red was observed. The reaction was stirred for 3 days, diluted with CH_2Cl_2 (20 ml) and washed with H_2O (50 ml) and acetic acid (2 ml). The organic layer was dried with $MgSO_4$, filtered and reduced in volume. The product precipitated on addition of diethyl ether, dried under vacuum and purified by column chromatography (alumina / CH_2Cl_2). The product was precipitated on addition of hexane, filtered and dried under vacuum. Yield = 99 mg, 0.09 mmol (28%). ^{1}H NMR ($CDCl_3$): 1.46 (t, J = 7.28 Hz, 6H, H_5), 4.49 (q, J = 7.13 Hz, 4H, H_4), 5.07 (s, 4H, H_8), 6.66 (d, J = 8.17 Hz, 4H, H_{12}), 6.86 (dt, J = 0.86, 7.47 Hz, 4H, H_{10}), 6.98 (dt, J = 1.48, 7.91 Hz, 4H, H_{11}), 7.08 (dd, J = 1.47, 7.53 Hz, 4H, H_9), 7.20 (d, J = 8.19 Hz, 4H, H_6 or H_7), 7.46 (d, J = 8.17 Hz, 4H, H_7 or H_6), 8.11 (dd, J = 1.49, 5.69 Hz, 2H, H_2), 8.66 (s, 2H, H_3), 9.98 (d, J = 5.67, 2H, H_1). RMM $PtC_{58}H_{44}N_4O_4S_2$ = 1120.20 g mol^{-1}. Elemental analysis: measured / % (calculated for $PtC_{58}H_{44}N_4O_4S_2{\bullet}(CH_2Cl_2)_{0.25}$ / %) C 61.12 (61.29), H 3.94 (3.93), N 4.96 (4.91). MALDI mass spectrometry: m/z = 1120 (M^+), 922 (M^+ –PTZ), 724 (M^+ –2x PTZ).

S2.1. Cyclic Voltammetry

Cyclic voltammograms were recorded using an Autolab Potentiostat 100 using General Purpose Electrochemical Software (GPES) version 4.9. Analyte solutions were prepared using dry reagent grade dichloromethane to give a concentration of 1.50 mmoldm^{-3}. $[N^nBu_4][PF_6]$ was employed as supporting electrolyte, being recrystallised and oven dried prior to use. The concentration of electrolyte in solution was 0.2 moldm^{-3}. Solutions were degassed with solvent saturated nitrogen, with a positive pressure of N_2 being maintained during the measurements. The working electrode was a Platinum disc, the counter electrode a Platinum wire and a Ag/AgCl reference electrode which was chemically isolated from the analyte solution by an electrolyte containing bridge tube tipped with a porous frit. All potentials are quoted against the ferrocinium-ferrocene couple, employed in each experiment as an internal standard.

S2.2. Spectroscopic Studies

In-house facilities were used for CHN and EI MS analysis. The following instruments were used: absorption spectra, a Cary 50 Bio UV-Visible spectrophotometer; ^{1}H NMR spectra (presented as δ in ppm and J in Hz), a Bruker 250 MHz spectrometer.

Ground state FTIR data were obtained on N_2-purged Spectrum One FTIR spectrometer (Perkin Elmer).

S2.3. Electronic Transient Absorption Spectroscopy

Picosecond Transient Absorption experiments were performed at B.I. Stepanov Institute of Physics, Minsk, on pump-probe spectrometer based on a home-made original fs Ti:Sapph pulsed oscillator and regenerative amplifier system operated at 10 Hz repetition rate.[A. P. Blokhin, Gelin, M.; Buganov, O.; Dubovskii, V.; Tikhomirov, S.; Tolstorozhev, G. B. *J. Appl. Spectrosc.* 2003, **70**, 70-78.] Ti:Sapph master oscillator was synchronously pumped with doubled output of home-made mode-locked picosecond pulsed Nd:YAG laser. The regenerative amplifier was pumped with ns Q-switched Nd:YAG laser LS-2134 (LOTIS TII). The pulse width and energy of Ti:Sapph system after the amplifier were ca. 150 fs and 0.5 mJ, respectively, tuneable over the spectral range 760 – 820 nm. The fundamental output of Ti:Sapph system (790 nm output wavelength was set for present study) was split into two beams in the ratio 1:4. The more intense beam was passed through a controlled delay line and after frequency doubling (to provide 395 nm radiation) was utilised for sample pumping. The energy of 395 nm pump pulses was ca. 40 μJ, being focused to 500 μm x 500 μm spot on the sample. The second beam of the fundamental frequency was used for generation of a femtosecond supercontinuum (by focusing into 1 cm pathlength cell filled with water), which served as the probe radiation. The continuum probe light was split with a beam splitter into two pulses (reference and signal) and the signal was focused on the sample by mirror optics. The spectra of both pulses were recorded for each laser flash by spectrometer equipped with CCD camera and transferred to the computer. All the measurements were performed in quartz cells with 1 mm path. The pump beam was polarized at "magic angle" with respect to the probe. The time resolution of the setup is limited by the pump and probe pulse duration and estimated as ca. 0.2 ps.

S2.4. Picosecond Time-Resolved IR spectroscopy

The studies of compound **2** were performed in the Laser for Science Facility, Rutherford Appleton Laboratory, on the PIRATE setup which was described in detail elsewhere. *[M. Towrie, D. C. Grills, J. Dyer, J. A. Weinstein, P. Matousek, R. Barton, P. D. Bailey, N. Subramaniam, W. M. Kwok, C. Ma, D. Phillips, A. W. Parker and M. W. George Appl. Spec. 2003,* ***57****, 367 – 380].* The estimate of time resolution of TRIR setup is ca. 0.4 ps for these experiments. Briefly, part of the output from a 1 kHz, 800 nm, 150 fs, 1 mJ Ti:Sapphire oscillator/regenerative amplifier was used to pump a white light continuum seeded BBO OPA. The signal and idler produced by this OPA were difference frequency mixed in a type I $AgGaS_2$ crystal to generate tuneable mid-infrared pulses (ca. 150 cm^{-1} FWHM, 0.1 μJ). Second harmonic generation of the residual 800 nm light provided 400 nm pulses, which were used to excite the sample (typical excitation energy 3 μJ, focus 150 x 150 μm^2). All measurements were carried out at magic angle polarization. Changes in infrared absorption were recorded by normalising the outputs from a pair of 64-element HgCdTe linear array detectors on a shot-by-shot basis. A solution of **2** in CH_2Cl_2 was flown through IR Harrick cell (100-500 μm pathlength) over the course of the experiment to supply fresh sample solution into the photoexcited volume. The sample cell was mounted on a 2D-translational stage which was raster-scanned in x and y directions during irradiation. The FTIR spectra recorded before and after TRIR experiments confirm the absence of the photodegradation.

The studies of compound **1** were performed in the Laser for Science Facility, Rutherford Appleton Laboratory, on both PIRATE and ULTRA setups. The ULTRA setup has been described in detail previously.[G. Greetham, P. Burgos, Q. Cao, I. Clark, P. Codd, R. Farrow, M. W. George, M. Kogimtzis, P. Matousek, A. W. Parker, M. Pollard, D. Robinson, Z.-J. Xin and M. Towrie, *Appl. Spectrosc.* 2010, **64**, 1311–1319.] Briefly, a 65 MHz Ti:Sapphire oscillator synchronously seeded a pair of regenerative amplifiers (Thales) operating at 10 kHz repetition rate. One amplifier was configured to produce 40 fs duration pulses with broad bandwidth. Second harmonic generation of part of the 800 nm output from the femtosecond amplifier produced pulses of ∼50 fs at 400-nm for sample excitation. Approximately 0.4 mJ of the 50-fs, broadband output pulse train pumped a TOPAS OPA, and difference frequency mixing of the signal and idler components generated mid-IR pulses with ∼400 cm^{-1} bandwidth and ∼50 fs pulse duration at the output of the OPA to be used as a probe beam. All measurements were carried out at magic angle polarization. The 400 nm pump beam energies were ∼2 μJ per pulse, and the pump and IR probe beam diameters at the sample were, respectively, ∼100 and 70 μm. The IR radiation transmitted by the solution was dispersed by a grating onto a pair of 128-element HgCdTe array detectors (IR Associates), providing broad (i.e. ∼400 cm^{-1}) spectral coverage with every laser pulse. The overall instrument response time was ∼200 fs. A reference spectrum of the laser pulse was accumulated on a third, 64-element array detector and used to remove the effects of laser fluctuations from transient absorption data. The sample solution was flown through IR Harrick cell (100-500 μm pathlength) over the course of the experiment to supply fresh sample solution into the photoexcited volume. The sample cell was mounted on a 2D-translational stage which was raster-scanned in x and y directions during irradiation. The FTIR spectra recorded before and after TRIR experiments confirm the absence of the photodegradation.

S2.5. Flash-photolysis data for 1

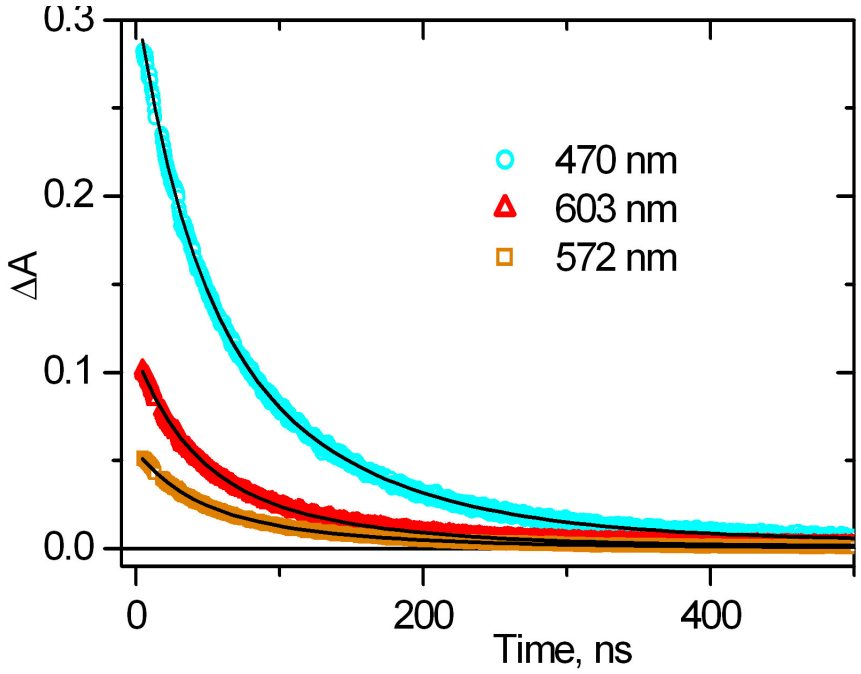
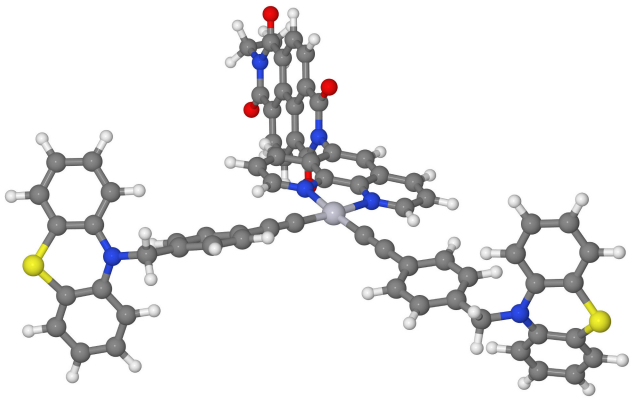


FIG. S6. Representative transient absorption decay traces, obtained for **1** in CH_2Cl_2 by nanosecond flash photolysis. The black solid lines represent the fitting curves. The decay times yielded by the fit: τ_1=36±4 ns and τ_2=107±11 ns.

S3. COMPOUND 1 (^{1}A)

S3.1. General Information



SMILES	:	CCN1C(=O)c2ccc3c4c2c(ccc4C(=O)N(C3=O)c5cc6ccc[n+]7c6c8c5ccc[n+]8[Pt]7(C#Cc9ccc(cc9)CN2c3ccccc3Sc3c2cccc3)C#Cc2ccc(cc2)CN2c3ccccc3Sc3c2cccc3)C1=O
Formula	:	$C_{70}H_{44}N_6O_4PtS_2$
Charge	:	0
Multiplicity	:	1
Dipole	:	17.8606 Debye
Energy	:	-4240.07831238 a.u.
Number of imaginary frequencies	:	0

S3.2. Cartesian Co-ordinates (XYZ format)

127

C	-3.52740860	-1.32355094	-0.00757718
C	-4.18698120	-0.08536840	-0.14615865
C	-3.44292712	1.07014632	-0.24409337
C	-2.04401946	1.00100672	-0.20372093
N	-1.39766717	-0.15430555	-0.07558342
C	-2.11670804	-1.30929804	0.02022404
C	-1.38271809	-2.53188419	0.15022071
C	-2.07004285	-3.75698042	0.25710303
C	-3.50126958	-3.75202608	0.23420925
C	-4.19679499	-2.59253764	0.10710230
N	-0.02166045	-2.45546818	0.16426453
C	0.68421841	-3.57730532	0.28338662
C	0.07586904	-4.83577728	0.39444387
C	-1.29886425	-4.93142605	0.38207546
Pt	0.71473128	-0.46023408	-0.00365658
C	1.20057237	1.42985499	-0.15874270
C	2.61240792	-0.93183190	0.06812989
C	3.78712988	-1.26456082	0.11425300
C	1.46162260	2.61930823	-0.25796625
C	5.16370630	-1.63483274	0.17461936
C	1.77022612	4.00684261	-0.38241220
C	5.57822657	-2.96001482	-0.04844945
C	6.15862751	-0.67800516	0.46227735
C	7.49711943	-1.03865623	0.52259600
C	7.90284443	-2.36059117	0.29912040

C	6.92313099	-3.31279349	0.01288257
C	3.00541067	4.43119335	-0.91349649
C	3.30080009	5.78140116	-1.03742290
C	2.38551831	6.76379681	-0.63852042
C	1.16184771	6.35043907	-0.10911173
C	0.85658002	4.99853039	0.01709837
C	9.39078808	-2.68728590	0.37962368
C	2.77418661	8.22977066	-0.80360019
N	9.80028534	-4.07338667	0.15803915
N	1.81103396	9.24475193	-0.37906694
C	9.77081108	-4.97511959	1.24534702
C	10.00957966	-4.51955748	-1.16625428
C	10.79911137	-5.65457439	-1.43042648
S	11.69004345	-6.44340944	-0.10266966
C	10.53568172	-6.15670156	1.22551966
C	8.98286915	-5.60740805	3.46147871
C	8.99190998	-4.72209883	2.38529110
C	10.48803234	-7.05952072	2.28502107
C	9.72119045	-6.78508568	3.41559601
C	9.45105743	-3.84458256	-2.26288199
C	9.67741776	-4.28023863	-3.56705427
C	10.43636608	-5.41981077	-3.81109738
C	10.98540688	-6.11109257	-2.73305154
C	1.78752375	9.63662624	0.97837824
C	1.22402942	10.86688709	1.36608350
S	0.68745911	12.02726364	0.12322199
C	0.13649037	10.87683392	-1.12246060
C	0.80052549	9.64581585	-1.28136265
C	2.32273555	9.22579765	3.31852150
C	1.73706341	10.43120956	3.69018364
C	1.17679513	11.24328518	2.70624924
C	2.33311152	8.82383728	1.98427022
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C	-1.22183383	10.45889759	-3.08078885
C	-0.55410647	9.25326443	-3.26706886
C	0.43098298	8.84210110	-2.37120581
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C	-8.45243359	-2.76342821	0.05290585
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C	-6.30552292	-2.48095894	1.32237542
C	-6.26043367	-2.82857060	-1.16959262
C	-7.74111080	-2.90037847	-1.16187048
C	-9.87017727	-2.83431506	0.03721680
C	-10.58769417	-2.69771481	1.24691069
C	-9.91232586	-2.49571490	2.43635821
C	-8.50955582	-2.42423153	2.45412421
C	-8.42254353	-3.10261178	-2.34872675
C	-9.82523727	-3.17609191	-2.36142683
C	-10.54341602	-3.04392195	-1.18737543
N	-12.69690895	-2.95932412	0.00373563
C	-12.07349014	-2.76991463	1.24299061
C	-12.02858543	-3.12259793	-1.21563840
O	-5.59152317	-2.93081737	-2.17700577
O	-5.67174339	-2.30237103	2.34203815
O	-12.64605522	-3.31748009	-2.24722695
O	-12.72819042	-2.66888881	2.26501727
C	-14.17604542	-3.02423859	-0.01425739
C	-14.70201302	-4.44574213	0.17508793
H	-14.52682209	-2.37336016	0.78338724
H	-14.49501038	-2.61882997	-0.97184300
H	-14.38157654	-4.85721922	1.13427901
H	-15.79461956	-4.43577909	0.15695104
H	-14.35465717	-5.10167122	-0.62555718
H	-10.47911453	-2.39343333	3.35237885

H	-7.98023510	-2.26591969	3.38468671
H	-10.35842705	-3.33621883	-3.28927588
H	-7.85967493	-3.20444798	-3.26739550
H	-4.02970886	-4.69348669	0.31899884
H	-1.79161906	-5.89249229	0.46673644
H	0.69881362	-5.71515417	0.48876092
H	1.76027167	-3.46123934	0.29059586
H	-1.42533076	1.88604629	-0.27585059
H	-3.92028213	2.03488541	-0.35167378
H	-5.26776981	-0.04585627	-0.17636302
H	0.90635395	7.88296747	-2.52092862
H	-0.80541611	8.61181450	-4.10377359
H	-1.99874318	10.77511692	-3.76625633
H	-1.38097990	12.20897102	-1.83407450
H	0.72030056	12.18994331	2.97223663
H	1.71332467	10.74027634	4.72813463
H	2.76308894	8.57727051	4.06693554
H	3.70267487	8.41588688	-0.25686666
H	3.00361919	8.42130756	-1.85548735
H	4.25991488	6.07812071	-1.45149302
H	0.43537807	7.08854771	0.20965184
H	-0.09882327	4.70024538	0.43256342
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H	4.83491945	-3.71564674	-0.27403602
H	5.86574173	0.35020399	0.63829917
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H	9.93061352	-2.07077980	-0.34443793
H	9.76731205	-2.39162278	1.36274314
H	8.82603645	-2.97742844	-2.10247707
H	9.23919106	-3.72765493	-4.39000177
H	10.60203743	-5.77051163	-4.82253551
H	11.58537579	-6.99846411	-2.89999747
H	11.07651234	-7.96834040	2.23001575
H	9.70502186	-7.48326540	4.24368286
H	8.37831116	-5.37369871	4.33013296
H	8.37891579	-3.83318758	2.43427300
H	2.76189637	7.86458111	1.73069859

S3.3. TD-DFT Calculations

Table with most important transitions ($f > 0.04$)

No.	Energy (cm^{-1})	Wave length (nm)	Osc. Strength	Major contributions
7	18402	543.41	0.06	H-2→L+1 (98%)
11	19918	502.06	0.06	H-3→L+1 (52%), H-2→L+2 (47%)
12	20754	481.83	0.23	H-3→L+1 (47%), H-2→L+2 (52%)
16	21877	457.10	0.04	H-3→L+2 (98%)
25	26184	381.91	0.12	H-16→LUMO (13%), H-15→LUMO (12%), H-14→LUMO (14%), H-13→LUMO (12%), H-9→LUMO (25%)
26	26552	376.62	0.35	H-21→LUMO (14%), H-16→LUMO (19%), H-15→LUMO (55%)
28	26905	371.67	0.04	H-21→LUMO (63%), H-8→L+1 (16%)
50	29778	335.82	0.14	H-2→L+5 (95%)
56	31085	321.70	0.05	H-16→L+1 (10%), H-3→L+5 (72%)
57	31224	320.26	0.04	H-26→LUMO (45%), H-22→LUMO (47%)
61	31563	316.83	0.09	H-16→L+1 (28%), H-3→L+5 (21%)
64	32009	312.41	0.04	H-17→L+1 (22%), H-14→L+1 (14%), H-13→L+1 (14%), H-11→L+1 (22%), H-9→L+1 (17%)
65	32441	308.25	0.65	H-2→L+7 (84%)
69	32669	306.10	0.06	H-1→L+14 (50%), H-1→L+15 (27%)
70	32681	305.99	0.13	HOMO→L+14 (31%), HOMO→L+15 (47%)
84	34121	293.08	0.11	H-16→L+1 (10%), H-15→L+2 (16%), H-14→L+2 (17%), H-11→L+2 (17%)
90	34650	288.60	0.06	H-28→LUMO (83%)
92	34956	286.08	0.15	H-11→L+2 (12%), H-2→L+8 (31%), H-2→L+18 (16%)

S3.4. Molecular Orbitals

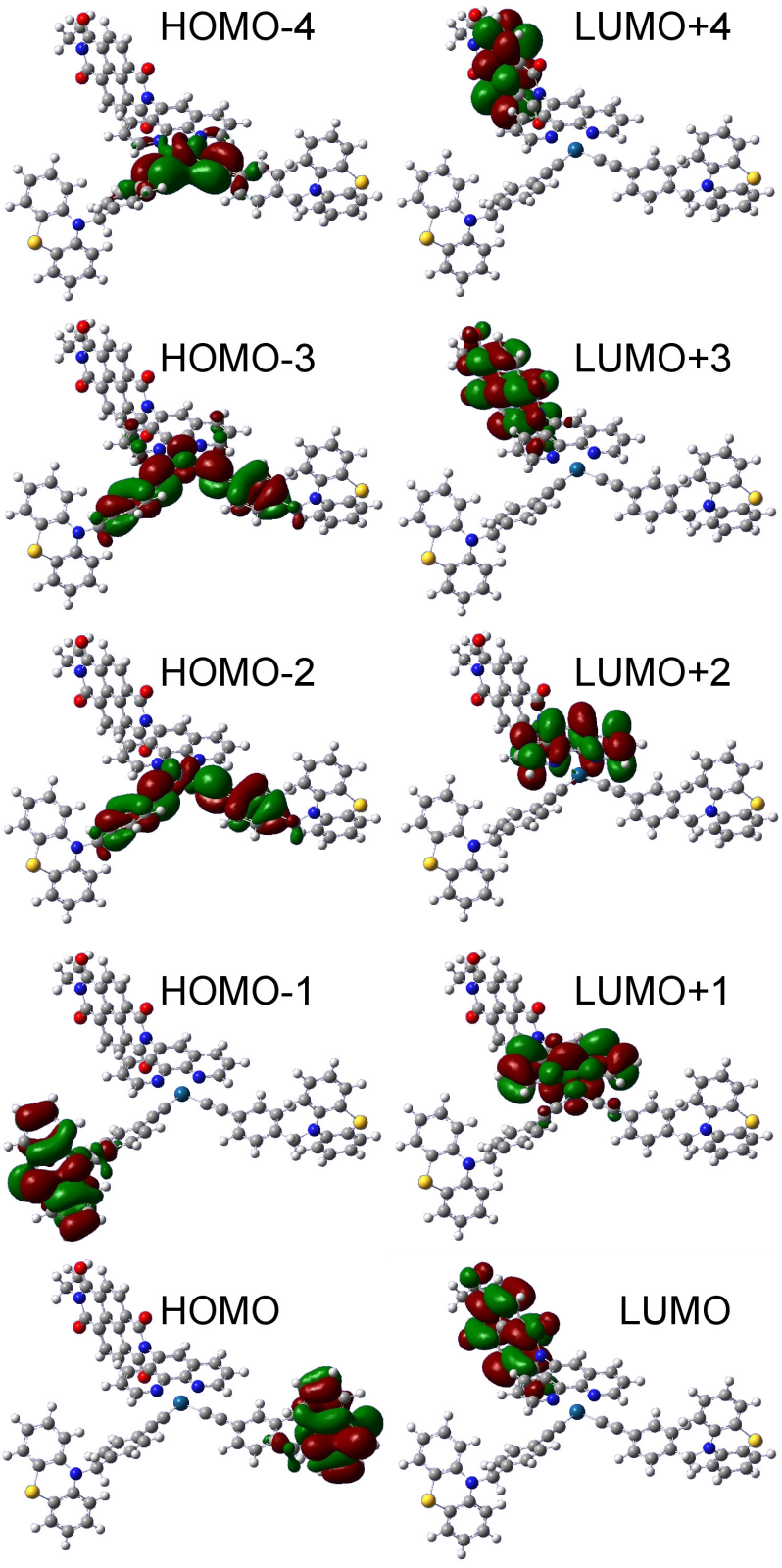


FIG. S7. Frontier orbitals Singlet state [**1**]

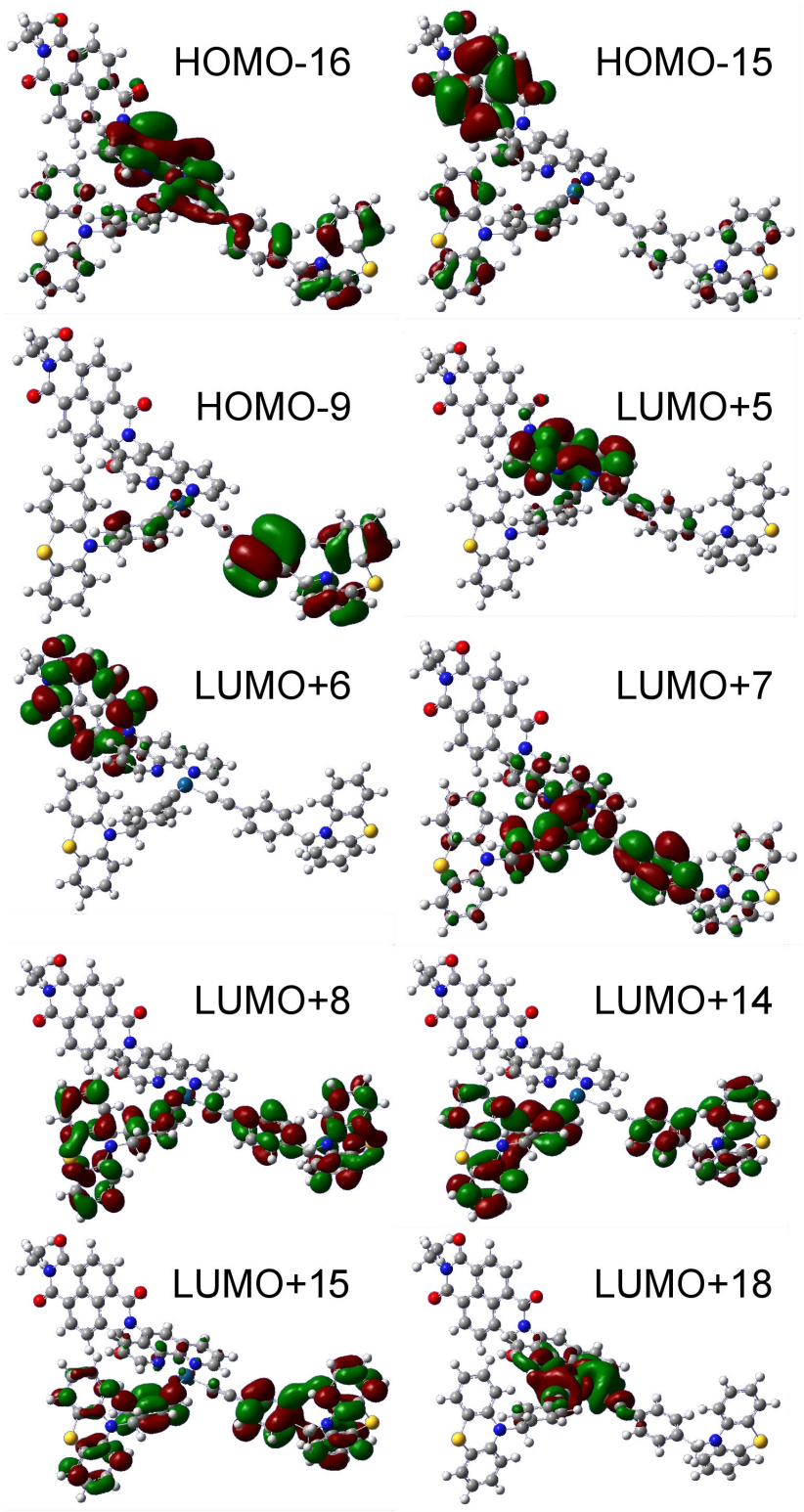
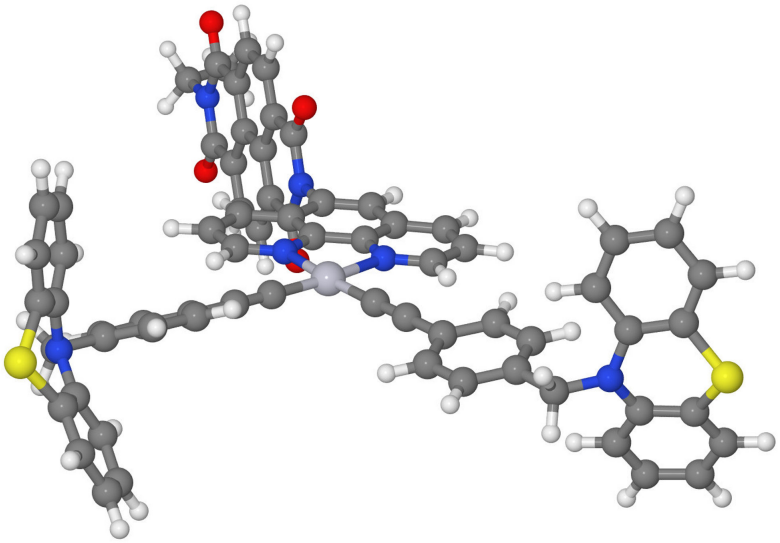


FIG. S8. Selected other orbitals Singlet state [**1**]

S4. COMPOUND 1 (^{1}A) ALTERNATIVE ISOMER

S4.1. General Information



SMILES	:	CCN1C(=O)c2ccc3c4c2c(ccc4C(=O)N(C3=O)c5cc6ccc[n+]7c6c8c5ccc[n+]8[Pt]7(C#Cc9ccc(cc9)CN2c3ccccc3Sc3c2cccc3)C#Cc2ccc(cc2)CN2c3ccccc3Sc3c2cccc3)C1=O
Formula	:	$C_{70}H_{44}N_6O_4PtS_2$
Charge	:	0
Multiplicity	:	1
Dipole	:	20.1566 Debye
Energy	:	-4240.07819211 a.u.
Number of imaginary frequencies	:	0

S4.2. Cartesian Co-ordinates (XYZ format)

127

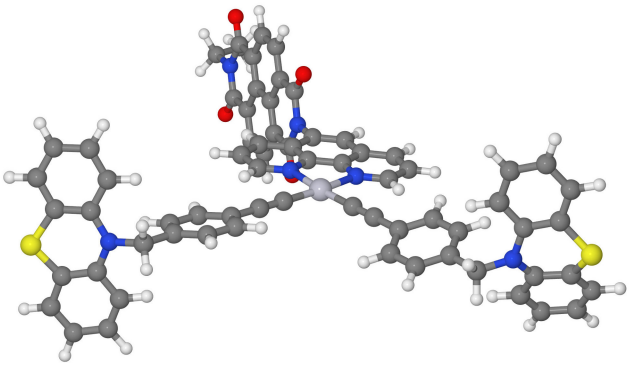
C	4.41990376	-0.45382598	-0.15056005
C	4.87201023	0.87679851	-0.26111439
C	3.95209217	1.89620662	-0.37537399
C	2.58285594	1.59882736	-0.38105991
N	2.13052273	0.35227379	-0.27775320
C	3.02561164	-0.67036206	-0.16218074
C	2.49796629	-1.99679089	-0.05013813
C	3.37330985	-3.09401512	0.07078807
C	4.78481340	-2.85608196	0.07787866
C	5.28447819	-1.59778595	-0.02796252
N	1.14258182	-2.14308405	-0.06567105
C	0.62669057	-3.36543179	0.03659693
C	1.42947662	-4.50843716	0.16046800
C	2.80137229	-4.37893295	0.17814550
Pt	0.09621671	-0.29389092	-0.26596114
C	-0.68782353	1.49081051	-0.44658574
C	-1.70140743	-1.06866980	-0.23870555
C	-2.80530047	-1.59178853	-0.21422783
C	-1.14163482	2.62011862	-0.55377525
C	-4.09918785	-2.19258404	-0.18890567

C	-1.67916572	3.93702674	-0.66734689
C	-4.27881432	-3.52925158	0.20966323
C	-5.24567366	-1.46230817	-0.56334412
C	-6.50325680	-2.04833627	-0.53733969
C	-6.67464495	-3.38019753	-0.13877273
C	-5.54373121	-4.10883856	0.23359200
C	-2.97338986	4.23572969	-0.20438787
C	-3.49553442	5.52128172	-0.31074157
C	-2.75086927	6.55444002	-0.88261306
C	-1.46238029	6.26342010	-1.34804666
C	-0.93322939	4.98466301	-1.24445391
C	-8.08490372	-3.96208906	-0.13121425
C	-3.26965857	7.98204041	-1.02559316
N	-8.24737358	-5.35468054	0.28419098
N	-4.61148357	8.27716255	-0.52547038
C	-8.07056522	-6.37708044	-0.67487955
C	-8.36125469	-5.64619350	1.66216946
C	-8.93507290	-6.85457468	2.10045838
S	-9.68709850	-7.95860052	0.91956848
C	-8.61484623	-7.65953159	-0.47311240
C	-7.20512247	-7.15941620	-2.81290531
C	-7.35974932	-6.15068722	-1.86392844
C	-8.41889000	-8.67635059	-1.40452278
C	-7.72353935	-8.42990875	-2.58660054
C	-7.91966343	-4.74192619	2.64072633
C	-8.05156231	-5.02939034	3.99788690
C	-8.59400654	-6.23989916	4.41570997
C	-9.02364540	-7.15565491	3.45745015
C	-4.77603388	8.59257984	0.84199989
C	-5.90979433	9.29653072	1.28970063
S	-7.07048702	9.95178223	0.10542870
C	-6.95129442	8.68315983	-1.14182901
C	-5.72159386	8.03590679	-1.36578166
C	-3.97698307	8.55862904	3.14226246
C	-5.11617184	9.22927094	3.57435393
C	-6.08719969	9.58529282	2.64062643
C	-3.81533504	8.22830486	1.79814172
C	-8.05459976	8.42663193	-1.95224106
C	-7.94888353	7.56122780	-3.03916621
C	-6.73177767	6.93667078	-3.28974700
C	-5.63715458	7.15563154	-2.45565581
N	6.71419764	-1.39696276	-0.01917515
C	9.51143646	-1.07553411	0.00333534
C	8.84749222	-1.25688624	-1.23226511
C	7.37494135	-1.42375040	-1.26821232
C	7.33036947	-1.21029305	1.23902416
C	8.80356312	-1.04588747	1.22745585
C	10.92206192	-0.91665369	0.01492215
C	11.63629150	-0.94628137	-1.20398259
C	10.96427536	-1.12617779	-2.39885092
C	9.56811619	-1.28025258	-2.41298032
C	9.48156834	-0.86454266	2.41963553
C	10.87767696	-0.70980752	2.42890978
C	11.59229660	-0.73471028	1.24553394
N	13.73216152	-0.58378273	0.03679499
C	13.11485672	-0.78257310	-1.20397973
C	13.07032681	-0.56852984	1.27046955
O	6.66296244	-1.18841815	2.25246215
O	6.74365234	-1.57430649	-2.29378843
O	13.68688488	-0.42322421	2.31070113
O	13.76875210	-0.81590980	-2.23096037
C	15.20242691	-0.40861464	0.04787390
C	15.94927406	-1.73523605	0.17224185
H	15.46396446	0.09610675	-0.87942535

H	15.43265343	0.24434167	0.88669193
H	15.71927071	-2.39398718	-0.66747779
H	17.02605247	-1.54880130	0.17362140
H	15.69117260	-2.24418712	1.10301483
H	11.52844715	-1.14592481	-3.32195711
H	9.04114342	-1.41977572	-3.34787130
H	11.40863705	-0.56934375	3.36120963
H	8.92132092	-0.84453446	3.34530663
H	5.45791292	-3.69951773	0.16858204
H	3.44228530	-5.24717569	0.27263868
H	0.95586520	-5.47775793	0.24014901
H	-0.45368269	-3.42649746	0.01751911
H	1.83013308	2.37142181	-0.46915686
H	4.26803350	2.92723656	-0.46110949
H	5.93225431	1.09262574	-0.25548270
H	-4.71535349	6.62665033	-2.65277267
H	-6.62713146	6.25788689	-4.12815714
H	-8.80662823	7.38141012	-3.67585444
H	-8.99194908	8.92869091	-1.74118817
H	-6.98047113	10.11361599	2.95399427
H	-5.25308704	9.47392082	4.62069988
H	-3.20980024	8.26987553	3.85127759
H	-2.57916784	8.66341782	-0.52070504
H	-3.24901795	8.26422310	-2.08190370
H	-4.49544907	5.71747208	0.05788160
H	-0.86401474	7.05016518	-1.79791462
H	0.06563620	4.78169918	-1.61259687
H	-3.56820011	3.44826341	0.24290931
H	-3.41539669	-4.11361885	0.50521380
H	-5.13489580	-0.43035752	-0.87433082
H	-7.36778831	-1.46055698	-0.83132577
H	-5.64640522	-5.14106178	0.54681444
H	-8.71791553	-3.35398269	0.52082658
H	-8.51373863	-3.87082648	-1.13291490
H	-7.45984983	-3.80899739	2.34658861
H	-7.70956230	-4.30246973	4.72537661
H	-8.68420219	-6.47369766	5.46957827
H	-9.45539570	-8.10287094	3.76015282
H	-8.83715534	-9.65732574	-1.20966780
H	-7.59239817	-9.22104836	-3.31485534
H	-6.65977383	-6.94502163	-3.72466040
H	-6.91353273	-5.18416071	-2.05110884
H	-2.93788934	7.67321825	1.49766064

S5. COMPOUND 1 (^{3}A)

S5.1. General Information



SMILES	:	CCN1C(=O)c2ccc3c4c2c(ccc4C(=O)N(C3=O)c5cc6ccc[n+]7c6c8c5ccc[n+]8[Pt]7(C#Cc9ccc(cc9)CN2c3ccccc3Sc3c2cccc3)C#Cc2ccc(cc2)CN2c3ccccc3Sc3c2cccc3)C1=O
Formula	:	$C_{70}H_{44}N_6O_4PtS_2^3$
Charge	:	0
Multiplicity	:	3
Dipole	:	20.1566 Debye
Energy	:	-4240.03211474 a.u.
Number of imaginary frequencies	:	0

S5.2. Cartesian Co-ordinates (XYZ format)

127

C	3.48651838	-1.47319078	-0.00844088
C	4.18767166	-0.25386605	0.08722270
C	3.48342991	0.92908823	0.14488345
C	2.08294892	0.90623540	0.10572561
N	1.39721906	-0.22972849	0.01657343
C	2.07770681	-1.41127789	-0.03850215
C	1.30454159	-2.61199975	-0.12889072
C	1.95425534	-3.86091614	-0.19046338
C	3.38476491	-3.90152812	-0.16480720
C	4.12237167	-2.76375508	-0.07819197
N	-0.05359326	-2.49235916	-0.15173878
C	-0.79567873	-3.59378505	-0.23435575
C	-0.22706631	-4.87392521	-0.29831597
C	1.14403617	-5.01262856	-0.27685010
Pt	-0.72281593	-0.46970236	-0.05519190
C	-1.14754152	1.43822658	0.02646816
C	-2.63535500	-0.88319629	-0.12348045
C	-3.81931663	-1.18224776	-0.16568843
C	-1.36893809	2.63930273	0.07095255
C	-5.20368195	-1.52338469	-0.22058691
C	-1.63051867	4.03883457	0.12163530
C	-5.65721464	-2.80627823	0.13502818
C	-6.16725826	-0.58132219	-0.63540488
C	-7.51284027	-0.91577202	-0.69058931
C	-7.95724964	-2.19577599	-0.33559906
C	-7.00894117	-3.13276815	0.07826369

C	-2.93744731	4.52744627	0.33037066
C	-3.19095135	5.88987494	0.37912694
C	-2.15486240	6.81937695	0.22245978
C	-0.85826385	6.34761095	0.01450479
C	-0.59884548	4.98167515	-0.03519170
C	-9.45060921	-2.49575830	-0.42109400
C	-2.50680709	8.29620647	0.29183206
N	-9.90276146	-3.83554482	-0.04927439
N	-1.37778854	9.23697281	0.09558287
C	-9.87058353	-4.86050320	-1.02135968
C	-10.15660763	-4.11666298	1.31198955
C	-10.98417282	-5.19229269	1.68557584
S	-11.86425781	-6.10928869	0.43512323
C	-10.66883564	-6.01176453	-0.88417929
C	-9.04250145	-5.77206898	-3.12242579
C	-9.05518436	-4.76456308	-2.15977001
C	-10.61881351	-7.03549051	-1.82724571
C	-9.81474400	-6.91709518	-2.95905256
C	-9.60591888	-3.33139420	2.33673739
C	-9.87586212	-3.60455990	3.67630076
C	-10.67229557	-4.68799877	4.03133297
C	-11.21460724	-5.48733759	3.02712059
C	-1.10241663	9.66373444	-1.20236361
C	-0.29316190	10.79898262	-1.46947062
S	0.43571803	11.76212692	-0.21859932
C	0.17654130	10.79404068	1.20238209
C	-0.67727786	9.66021824	1.22372937
C	-1.40714359	9.39955807	-3.59861827
C	-0.62832868	10.54068756	-3.84687662
C	-0.07383704	11.22857285	-2.78834224
C	-1.64114451	8.96924305	-2.30941248
C	0.83474261	11.21773529	2.36824155
C	0.67367792	10.52627182	3.55020046
C	-0.14629546	9.38733101	3.57929373
C	-0.80743587	8.96222210	2.44610786
N	5.55747128	-2.83434486	-0.05488218
C	8.33275604	-3.00129557	-0.02034595
C	7.66909933	-2.82289577	-1.25986850
C	6.21983719	-2.72915578	-1.30439579
C	6.17125654	-3.00605893	1.21245837
C	7.62199306	-3.09463024	1.20220876
C	9.76386261	-3.08490753	-0.00232385
C	10.48103046	-2.99088454	-1.21885705
C	9.79015636	-2.81733727	-2.43443251
C	8.41302967	-2.73318243	-2.45515943
C	8.32015324	-3.27098608	2.41526961
C	9.69738674	-3.35594153	2.42854333
C	10.43421459	-3.26335216	1.23125589
N	12.55888939	-3.23356795	0.03430712
C	11.93852043	-3.07299662	-1.21654558
C	11.89095974	-3.35197711	1.26513493
O	5.46889496	-3.06409216	2.22027636
O	5.55467272	-2.56394029	-2.32594848
O	12.53543663	-3.51929069	2.30325651
O	12.62205887	-3.00625110	-2.24101353
C	14.03122330	-3.30382514	0.05551532
C	14.55463314	-4.73323584	-0.08577029
H	14.38863373	-2.68579531	-0.76550418
H	14.35430431	-2.87326312	1.00112367
H	14.22836304	-5.17434835	-1.02998126
H	15.64811230	-4.73272562	-0.06908043
H	14.20151901	-5.35841513	0.73696285
H	10.36651802	-2.75082660	-3.34827805
H	7.87685919	-2.59802771	-3.38590527

H	10.23834705	-3.49320865	3.35609221
H	7.74883032	-3.33876467	3.33228469
H	3.88197255	-4.86207962	-0.21630044
H	1.60605264	-5.99143696	-0.32530764
H	-0.87744546	-5.73597860	-0.36401021
H	-1.86737347	-3.44396496	-0.24987514
H	1.49528039	1.81390309	0.14617167
H	3.99357986	1.88022006	0.21914147
H	5.26926899	-0.25513169	0.11509200
H	-1.40040863	8.06211185	2.49657965
H	-0.25746703	8.82354641	4.49674511
H	1.18769956	10.85426998	4.44438028
H	1.47577679	12.08983040	2.32391214
H	0.54199517	12.10260391	-2.96266413
H	-0.45178580	10.87328339	-4.86156464
H	-1.82417059	8.83831882	-4.42509747
H	-3.25978756	8.54750156	-0.45433775
H	-2.95610619	8.53999519	1.25388718
H	-4.20683002	6.23587132	0.54120851
H	-0.03391561	7.03969431	-0.11157916
H	0.41437158	4.63566780	-0.19930451
H	-3.75032759	3.82238674	0.45379183
H	-4.93873262	-3.54927754	0.46064991
H	-5.84448290	0.41461813	-0.91465288
H	-8.23177147	-0.16937988	-1.01537514
H	-7.32396793	-4.13052607	0.36013293
H	-9.99318218	-1.78487837	0.20821646
H	-9.79258060	-2.31136632	-1.44326818
H	-8.95264816	-2.50548649	2.09283590
H	-9.44176769	-2.97050524	4.44062042
H	-10.87174702	-4.91307688	5.07200480
H	-11.84297085	-6.33365345	3.28041935
H	-11.23367310	-7.91649580	-1.68224394
H	-9.79595280	-7.70952320	-3.69738579
H	-8.40845203	-5.65919352	-3.99415445
H	-8.41602039	-3.90350580	-2.29551220
H	-2.21504426	8.06809235	-2.15788722

S5.3. TD-DFT Calculations

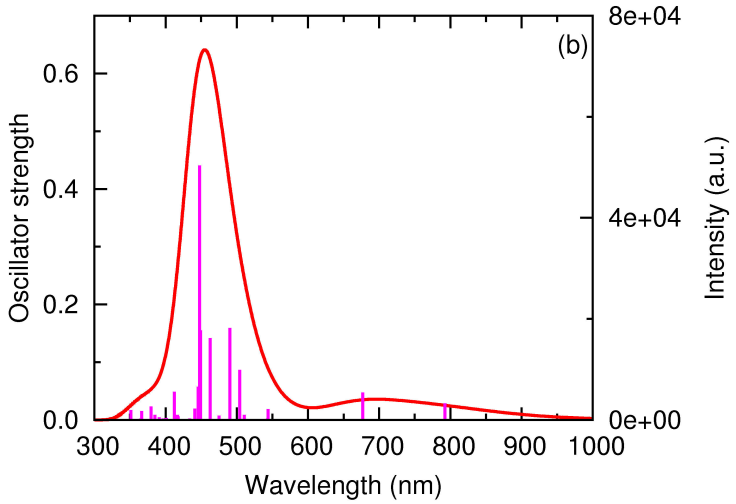


FIG. S9. Simulated UV-VIS spectrum for the ^{3}[NDI^{-}-Pt-(PTZ)$^{+}$] state of [**1**]

Table with most important transitions ($f > 0.04$)

No.	Energy (cm^{-1})	Wave length (nm)	Osc. Strength	Major contribs
15	14776	676.76	0.05	HOMO(α)→L+5(α) (95%)
35	19833	504.22	0.09	H-2(α)→LUMO(α) (48%), H-1(β)→L+1(β) (26%), H-1(β)→L+2(β) (23%)
38	20395	490.30	0.16	H-27(β)→LUMO(β) (14%), H-25(β)→LUMO(β) (78%)
46	21614	462.66	0.14	H-3(α)→LUMO(α) (22%), H-2(β)→L+1(β) (11%), HOMO(β)→L+3(β) (43%)
47	21615	462.64	0.11	H-3(α)→LUMO(α) (17%), HOMO(β)→L+3(β) (57%)
48	22269	449.05	0.16	H-1(β)→L+1(β) (15%), H-1(β)→L+2(β) (25%), H-1(β)→L+3(β) (25%)
49	22329	447.85	0.44	H-2(α)→L+1(α) (37%), HOMO(α)→L+14(α) (33%)
50	22444	445.55	0.06	H-2(α)→L+1(α) (10%), H-1(β)→L+1(β) (26%), H-1(β)→L+2(β) (27%), H-1(β)→L+3(β) (13%)
61	24246	412.44	0.05	H-3(α)→L+1(α) (38%), H-2(β)→L+3(β) (36%)

S5.4. Molecular Orbitals

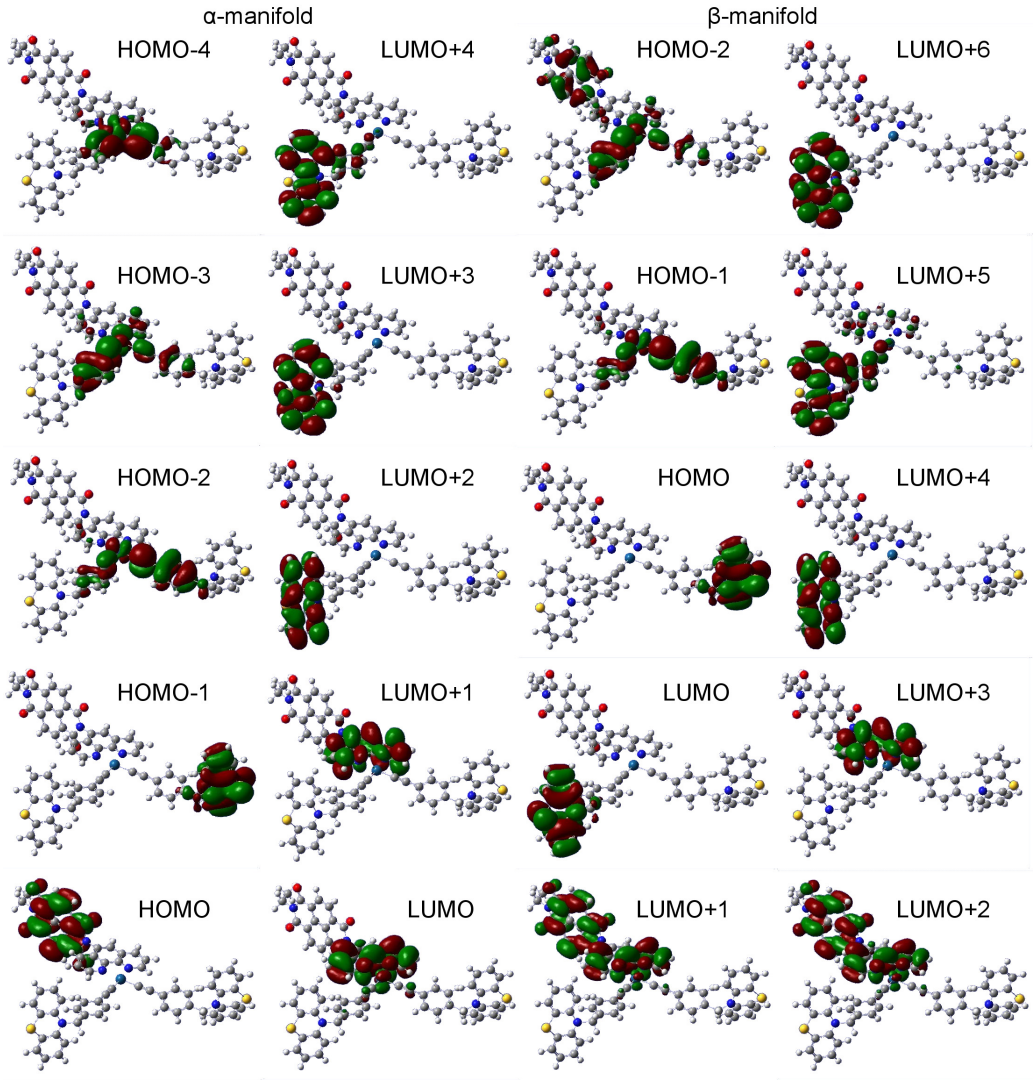
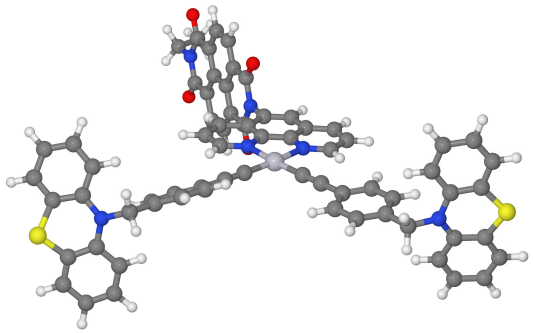


FIG. S10. Frontier orbitals for the triplet state of [**1**].

S6. COMPOUND 1 (T_2)

S6.1. General Information



SMILES	:	CCN1C(=O)c2ccc3c4c2c(ccc4C(=O)N(C3=O)c5cc6ccc[n+]7c6c8c5ccc[n+]8[Pt]7(C#Cc9ccc(cc9)CN2c3ccccc3Sc3c2cccc3)C#Cc2ccc(cc2)CN2c3ccccc3Sc3c2cccc3)C1=O
Formula	:	$C_{70}H_{44}N_6O_4PtS_2^3$
Charge	:	0
Multiplicity	:	3
Dipole	:	0.0000 Debye
Energy	:	-4240.03168957 a.u.
Number of imaginary frequencies	:	0

S6.2. Cartesian Co-ordinates (XYZ format)

127

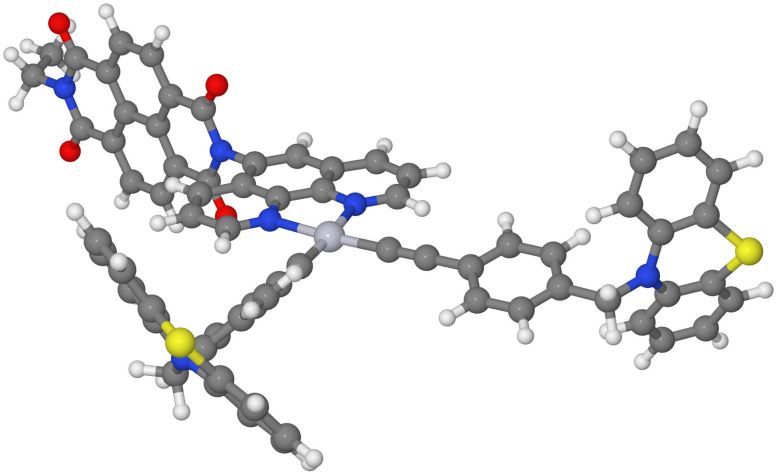
C	3.51561379	-1.53534341	0.03161843
C	4.23418903	-0.32618085	0.12894249
C	3.54666877	0.86503643	0.21228832
C	2.14532161	0.86093897	0.19820766
N	1.44376910	-0.26525635	0.10740048
C	2.10741043	-1.45476890	0.02584101
C	1.31695986	-2.64430547	-0.06550156
C	1.94911301	-3.90089107	-0.15249543
C	3.37889385	-3.96043754	-0.14907411
C	4.13285351	-2.83352518	-0.06085272
N	-0.03979959	-2.50735831	-0.06294632
C	-0.79689103	-3.59845161	-0.14489520
C	-0.24639820	-4.88480043	-0.23405053
C	1.12294912	-5.04111528	-0.23844507
Pt	-0.68081468	-0.47700787	0.07272349
C	-2.59865713	-0.85826850	0.02952719
C	-1.07605588	1.43730974	0.19835587
C	-1.28068173	2.63913369	0.27986166
C	-3.78955674	-1.13091230	-0.00231800
C	-1.51720941	4.04247761	0.38387439
C	-5.18249893	-1.42669964	-0.04401404
C	-0.56724226	4.97947264	-0.06069363
C	-2.71409464	4.53854132	0.93991715
C	-2.93852019	5.90399408	1.04451144
C	-1.98739874	6.83148193	0.60064954
C	-0.80133587	6.34715223	0.04641467
C	-6.13976288	-0.39416009	-0.13570444
C	-7.49598360	-0.67943549	-0.17737028

C	-7.95337820	-2.00252676	-0.13091873
C	-7.01589537	-3.03204346	-0.03908426
C	-5.65391254	-2.75076389	0.00408313
C	-2.29814529	8.31791210	0.74716443
C	-9.45324898	-2.23923230	-0.19095203
N	-1.29697084	9.27619648	0.28136757
N	-9.88585377	-3.65192533	-0.06789485
C	-0.24556759	9.64198589	1.15175045
C	-1.28825545	9.64456940	-1.08271921
C	-0.67739719	10.84059048	-1.50436985
S	-0.05722812	11.99358368	-0.29400930
C	0.47111946	10.83761978	0.95644349
C	1.14058840	9.21446896	3.10801482
C	0.11402308	8.83751774	2.24423885
C	1.52539480	11.18708324	1.79684186
C	1.85913050	10.38425064	2.88568139
C	-1.89531612	8.84240055	-2.06152034
C	-1.89791322	9.22187805	-3.40239143
C	-1.26546335	10.39216137	-3.80814481
C	-0.64453119	11.19268417	-2.85153174
C	-10.13709831	-4.14688540	1.21050215
C	-10.86237335	-5.34761953	1.42796302
S	-11.50314617	-6.31903124	0.13584784
C	-10.75556469	-5.61827040	-1.26935673
C	-10.04025459	-4.39236736	-1.23842573
C	-9.94566059	-3.90411496	3.62075853
C	-10.68837738	-5.07816362	3.82138300
C	-11.13651752	-5.79332542	2.73105454
C	-9.67505264	-3.44668460	2.34817767
C	-10.92951965	-6.31608582	-2.47555113
C	-10.39108658	-5.82859468	-3.64750385
C	-9.65665817	-4.63266611	-3.62630105
C	-9.48373032	-3.92930579	-2.45275593
N	5.56677103	-2.92697597	-0.05547143
C	8.33660698	-3.16645551	-0.05363283
C	7.66295862	-2.97457981	-1.28574538
C	6.21600199	-2.84458232	-1.31356442
C	6.19124603	-3.10854506	1.20514953
C	7.63874722	-3.23455620	1.17803860
C	9.76476479	-3.29203701	-0.05290451
C	10.46917248	-3.22467375	-1.27863598
C	9.76873779	-3.03431630	-2.48616385
C	8.39446259	-2.91009688	-2.49027824
C	8.34654713	-3.42529631	2.38329768
C	9.72070408	-3.55060768	2.37987733
C	10.44480991	-3.48571539	1.17306602
N	12.55386066	-3.52968574	-0.05058987
C	11.92324734	-3.35364318	-1.29424441
C	11.89831448	-3.62028909	1.18916130
O	5.49906921	-3.14593768	2.22112870
O	5.54244184	-2.67032170	-2.32802820
O	12.55019665	-3.80362654	2.21994591
O	12.59558487	-3.31387830	-2.32747555
C	14.02295780	-3.65132475	-0.04826825
C	14.49328518	-5.09883261	-0.19195917
H	14.39089870	-3.04872608	-0.87598622
H	14.37366867	-3.22972822	0.89147234
H	14.13771343	-5.53068590	-1.12984943
H	15.58620644	-5.13729906	-0.19103898
H	14.13000965	-5.70874214	0.63781947
H	10.33532810	-2.98745918	-3.40731716
H	7.85105419	-2.76239014	-3.41487670
H	10.26890278	-3.69952154	3.30132198
H	7.78511047	-3.47204995	3.30770779

H	3.86276388	-4.92681026	-0.21706934
H	1.57135808	-6.02504492	-0.30651805
H	-0.90865815	-5.73791027	-0.29838234
H	-1.86660981	-3.43510294	-0.13943389
H	1.57030082	1.77555895	0.26114494
H	4.07010508	1.80874240	0.28843370
H	5.31602716	-0.34171468	0.13815092
H	-8.88332939	-3.03287697	-2.46850467
H	-9.20789433	-4.25647306	-4.53684616
H	-10.52458858	-6.37338305	-4.57309437
H	-11.48584080	-7.24550009	-2.47127175
H	-11.69834518	-6.70943499	2.86747909
H	-10.89843082	-5.42908096	4.82343483
H	-9.56742668	-3.35072803	4.47084904
H	-9.96154404	-1.68356860	0.59637266
H	-9.86618137	-1.86314809	-1.12631667
H	-8.20857239	0.13633071	-0.24719146
H	-7.33610439	-4.06672096	0.00095257
H	-4.94218302	-3.56406951	0.07676468
H	-5.80301428	0.63453746	-0.17366695
H	0.36026552	4.62593269	-0.49544847
H	-3.46287704	3.83799219	1.29019606
H	-3.86926198	6.25636482	1.47934055
H	-0.04806924	7.04157114	-0.30646998
H	-3.22936749	8.54072475	0.21897653
H	-2.49188781	8.53881359	1.80050278
H	-2.36167932	7.90833187	-1.78149903
H	-2.38518214	8.58258343	-4.12938833
H	-1.25138831	10.68264675	-4.85162306
H	-0.15018457	12.11202240	-3.14427304
H	2.06831050	12.10612774	1.60752106
H	2.66831231	10.67272663	3.54554796
H	1.38401115	8.57370567	3.94754887
H	-0.40139517	7.90392685	2.42066264
H	-9.07040977	-2.56072760	2.23136973

S7. COMPOUND 1 (^{3}A) ALTERNATIVE ISOMER

S7.1. General Information



SMILES	:	CCN1C(=O)c2ccc3c4c2c(ccc4C(=O)N(C3=O)c5cc6ccc[n+]7c6c8c5ccc[n+]8[Pt]7(C#Cc9ccc(cc9)CN2c3ccccc3Sc3c2cccc3)C#Cc2ccc(cc2)CN2c3ccccc3Sc3c2cccc3)C1=O
Formula	:	$C_{70}H_{44}N_6O_4PtS_2^3$
Charge	:	0
Multiplicity	:	3
Dipole	:	20.1566 Debye
Energy	:	-4240.03204222 a.u.
Number of imaginary frequencies	:	0

S7.2. Cartesian Co-ordinates (XYZ format)

127

C	4.29369545	-0.47953382	-0.12131557
C	4.71770954	0.85762227	-0.26181817
C	3.77792335	1.85262322	-0.42182925
C	2.41589952	1.52438641	-0.44464067
N	1.98935235	0.27118018	-0.31561187
C	2.90544677	-0.72732586	-0.15439130
C	2.40696597	-2.06199026	-0.01808607
C	3.30768871	-3.13208246	0.15300822
C	4.71229029	-2.85932827	0.18291070
C	5.18958330	-1.59398246	0.05111460
N	1.05599523	-2.24333906	-0.06070015
C	0.56738335	-3.47444963	0.06515498
C	1.39575934	-4.59220934	0.24069847
C	2.76326609	-4.42692089	0.28495702
Pt	-0.02672619	-0.42725217	-0.33839157
C	-0.84424335	1.33156884	-0.59803224
C	-1.80580711	-1.24800467	-0.34176326
C	-2.89870930	-1.79440594	-0.34325060
C	-1.31212044	2.44971299	-0.75315672
C	-4.17980766	-2.42243290	-0.35517806
C	-1.85276341	3.75715828	-0.92331612
C	-4.35691643	-3.73829341	0.10855444

C	-5.31626558	-1.74090803	-0.83697283
C	-6.56121111	-2.35350442	-0.85193807
C	-6.72992516	-3.66476798	-0.38916978
C	-5.60940361	-4.34486866	0.09076257
C	-2.95081496	4.19484663	-0.16114141
C	-3.47411990	5.47376251	-0.32261440
C	-2.92087984	6.35877705	-1.24938989
C	-1.82664120	5.93384075	-2.01312590
C	-1.30182159	4.65962601	-1.85658586
C	-8.12650585	-4.27714396	-0.43449301
C	-3.45322108	7.76180744	-1.48877823
N	-8.28728771	-5.65239763	0.03512951
N	-4.46874619	8.23966503	-0.51939148
C	-8.03425694	-6.71364403	-0.86290354
C	-8.48259163	-5.88396549	1.41523314
C	-9.06595421	-7.08100605	1.87157130
S	-9.72658920	-8.24874306	0.69732928
C	-8.57176208	-7.99484539	-0.63723552
C	-7.02184010	-7.57590055	-2.90311599
C	-7.25182104	-6.52836657	-2.01331043
C	-8.30150414	-9.04905605	-1.50640500
C	-7.53517818	-8.84377956	-2.65189576
C	-8.11512470	-4.92996740	2.37692261
C	-8.32734776	-5.15897751	3.73503709
C	-8.87834740	-6.35846663	4.17307758
C	-9.23492718	-7.32290411	3.23275256
C	-4.01524019	8.87353325	0.63622761
C	-4.86921263	9.66110802	1.45163691
S	-6.55221033	9.91715240	1.09598196
C	-6.85025835	8.75904751	-0.16697499
C	-5.81384373	8.05299473	-0.83242637
C	-2.18995500	9.40371227	2.14986205
C	-3.04023409	10.19940758	2.93354130
C	-4.36897755	10.32070446	2.58587480
C	-2.66227293	8.75575924	1.02771664
C	-8.19257164	8.57839203	-0.53763735
C	-8.52587318	7.69664526	-1.54391885
C	-7.51385975	6.96983337	-2.19028258
C	-6.18966532	7.14143133	-1.84565532
N	6.60596704	-1.35244882	0.07818096
C	9.35476780	-0.93902141	0.13640113
C	8.72412872	-1.20139015	-1.10537398
C	7.28815842	-1.41677320	-1.16379333
C	7.18442726	-1.08136714	1.34428227
C	8.62284565	-0.87442088	1.34842145
C	10.77264690	-0.72872108	0.16674040
C	11.51080894	-0.79060560	-1.03926206
C	10.85294914	-1.05498564	-2.25682926
C	9.48798084	-1.25453711	-2.29017663
C	9.28792286	-0.60818380	2.56375098
C	10.65330315	-0.41054723	2.58989382
C	11.41000652	-0.46641493	1.40280020
N	13.54011822	-0.30983126	0.22527258
C	12.95562744	-0.58118743	-1.02392399
C	12.85340118	-0.25386575	1.45020509
O	6.46186686	-1.03346360	2.33862686
O	6.64986324	-1.64054573	-2.19106674
O	13.47122669	-0.03218164	2.49433041
O	13.65749073	-0.63085288	-2.03683567
C	14.99635029	-0.08193782	0.25718415
C	15.79020882	-1.36915684	0.48112941
H	15.26604080	0.36931750	-0.69529361
H	15.18788147	0.62599969	1.06105435
H	15.60141563	-2.08680129	-0.32009634

H	16.86111450	-1.14785516	0.49514511
H	15.52456856	-1.82761300	1.43588388
H	11.44406033	-1.09653175	-3.16268778
H	8.97716808	-1.45700514	-3.22294855
H	11.16940022	-0.20824906	3.51966524
H	8.70153427	-0.56482482	3.47270274
H	5.40282917	-3.68341303	0.31130877
H	3.42327905	-5.27566338	0.41901940
H	0.94506186	-5.57088137	0.33813182
H	-0.51024753	-3.56402421	0.02306094
H	1.64875722	2.27735114	-0.56972241
H	4.07287931	2.88771391	-0.53140903
H	5.77365637	1.09277105	-0.24359363
H	-5.44230032	6.53893805	-2.33849859
H	-7.76886797	6.25526333	-2.96246886
H	-9.56273174	7.55835915	-1.82168615
H	-8.96260071	9.13469410	-0.01703047
H	-5.04264069	10.91891003	3.18726492
H	-2.66146159	10.70556736	3.81200266
H	-1.15110445	9.28336716	2.42963457
H	-2.63889098	8.48551846	-1.47360718
H	-3.89910483	7.84415388	-2.47933149
H	-4.31766796	5.77163744	0.28921843
H	-1.37940240	6.60700130	-2.73753500
H	-0.45554054	4.34816217	-2.45679474
H	-3.39185691	3.52209902	0.56405044
H	-3.50126934	-4.28525162	0.48667046
H	-5.20702362	-0.72594059	-1.20021629
H	-7.41790581	-1.80388880	-1.23073936
H	-5.71020699	-5.36041403	0.45502034
H	-8.80789566	-3.65375352	0.15113950
H	-8.49731255	-4.24090719	-1.46262431
H	-7.64990902	-4.00412178	2.06906104
H	-8.04045582	-4.39544725	4.44873571
H	-9.03029919	-6.54687500	5.22893572
H	-9.67131901	-8.26288700	3.55096030
H	-8.71667099	-10.02759838	-1.29356217
H	-7.34550095	-9.66454315	-3.33291650
H	-6.42163754	-7.39355516	-3.78694820
H	-6.80811548	-5.56368113	-2.21534777
H	-1.98908329	8.12419605	0.46906835

S7.3. TD-DFT Calculations

Table with most important transitions for alternative Triplet state ($f > 0.04$)

No.	Energy (cm^{-1})	Wave length (nm)	Osc. Strength	Major contributions
15	14774	676.88	0.05	HOMO(α)→L+5(α) (97%)
35	19957	501.08	0.09	H-2(α)→LUMO(α) (48%), H-1(β)→L+1(β) (26%), H-1(β)→L+2(β) (22%)
37	20383	490.62	0.16	H-26(β)→LUMO(β) (16%), H-25(β)→LUMO(β) (76%)
47	21880	457.03	0.22	H-3(α)→LUMO(α) (37%), H-3(β)→L+1(β) (17%), H-3(β)→L+2(β) (18%)
48	22342	447.59	0.62	H-2(α)→L+1(α) (11%), HOMO(α)→L+14(α) (47%), H-2(β)→L+1(β) (10%), H-1(β)→L+3(β) (13%)

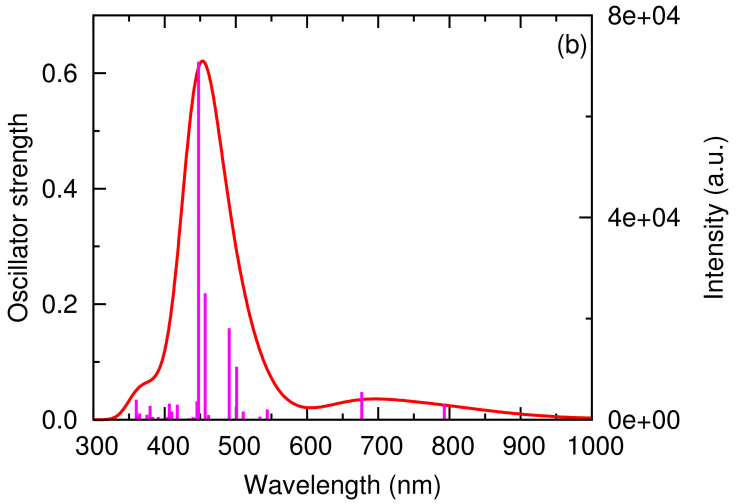
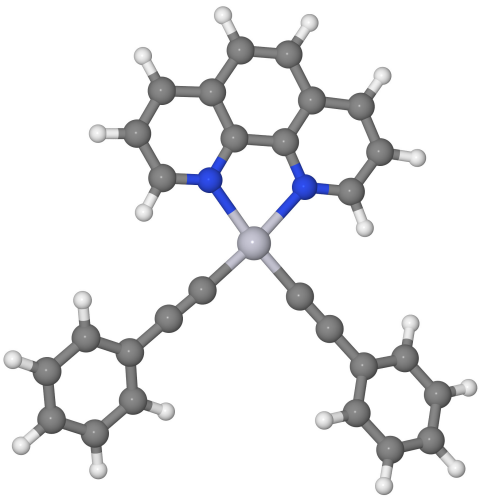


FIG. S11. Simulated UV-VIS spectrum for the alternative ^{3}[NDI^{-}-Pt-(PTZ)$^{+}$] state of [**1**]

S8. CHROMOPHORIC CORE, (phen)PT(-CC-Ph)$_2$ (S_0)

S8.1. General Information



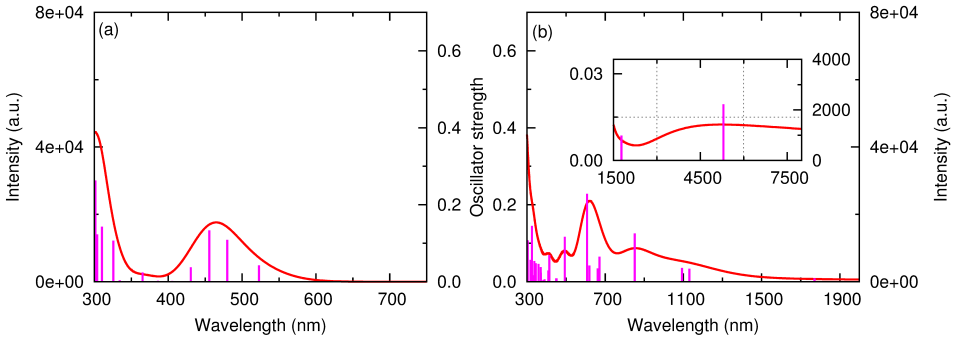


FIG. S12. UV-VIS spectra for the lowest singlet [Panel (a)] and triplet states [Panel (b)] for the Chromophoric Core, (phen)Pt(-CC-Ph)$_2$

SMILES	: c1ccc(cc1)C#C[Pt]2([n+]3cccc4c3c5[n+]2cccc5cc4)C#Cc6ccccc6	
Formula	: $C_{28}H_{18}N_2Pt$	
Charge	: 0	
Multiplicity	: 1	
Dipole	: 0.0000	Debye
Energy	: -1306.99762925	a.u.
Number of imaginary frequencies	: 0	

S8.2. Cartesian Co-ordinates (XYZ format)

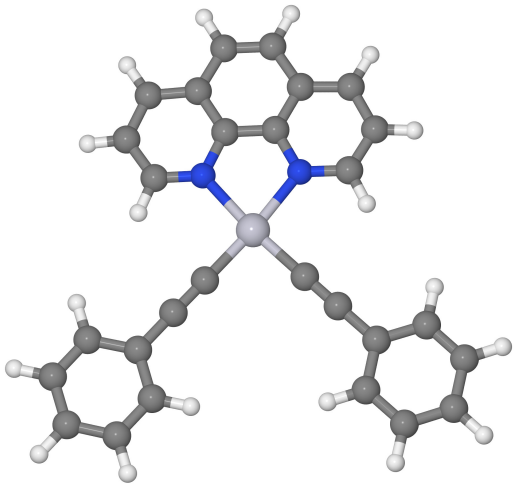
49

C	0.00000000	4.40913820	1.42078400
C	0.00000000	4.34544611	2.83011293
C	0.00000000	3.11547899	3.45208502
C	0.00000000	1.94655001	2.67741299
N	0.00000000	1.97786903	1.34744096

C	0.00000000	3.18709302	0.71570700
C	0.00000000	3.18706298	-0.71590900
C	0.00000000	4.40907812	-1.42102897
C	0.00000000	5.63757706	-0.68029702
C	0.00000000	5.63760519	0.68000799
N	0.00000000	1.97781205	-1.34759700
C	0.00000000	1.94643700	-2.67756796
C	0.00000000	3.11533308	-3.45228100
C	0.00000000	4.34532595	-2.83035493
Pt	0.00000000	0.32147199	-0.00004800
C	0.00000000	-1.06524396	1.38211703
C	0.00000000	-1.06528401	-1.38216603
C	0.00000000	-1.90299499	-2.27166605
C	0.00000000	-1.90287805	2.27169299
C	0.00000000	-2.88747406	-3.30545497
C	0.00000000	-2.88720989	3.30562997
C	0.00000000	-2.58330011	-4.60784006
C	0.00000000	-4.19412899	-3.05003500
C	0.00000000	-5.15244579	-4.05780220
C	0.00000000	-4.83556318	-5.34263897
C	0.00000000	-3.54689193	-5.61075020
C	0.00000000	-4.19412804	3.05043888
C	0.00000000	-5.15229607	4.05835676
C	0.00000000	-4.83499384	5.34312105
C	0.00000000	-3.54605603	5.61101007
C	0.00000000	-2.58261490	4.60794497
H	0.00000000	0.96266103	-3.12875104
H	0.00000000	3.03142810	-4.53085518
H	0.00000000	5.26115084	-3.40944910
H	0.00000000	6.57117081	-1.23025799
H	0.00000000	6.57122278	1.22993696
H	0.00000000	5.26129723	3.40917301
H	0.00000000	3.03162003	4.53066206
H	0.00000000	0.96279299	3.12863207
H	0.00000000	-4.44459915	2.05370212
H	0.00000000	-1.58335102	4.82088900
H	0.00000000	-3.28998995	6.60612392
H	0.00000000	-5.58404684	6.12658119
H	0.00000000	-6.15165520	3.83999109
H	0.00000000	-1.58424699	-4.82096577
H	0.00000000	-4.44428205	-2.05324197
H	0.00000000	-6.15159512	-3.83925796
H	0.00000000	-5.58473396	-6.12597799
H	0.00000000	-3.29114604	-6.60591984

S9. CHROMOPHORIC CORE, (phen)PT(-CC-Ph)$_2$ (T_1)

S9.1. General Information



SMILES	:	c1ccc(cc1)C#C[Pt]2([n+]3cccc4c3c5[n+]2cccc5cc4)C#Cc6ccccc6
Formula	:	$C_{28}H_{18}N_2Pt^3$
Charge	:	0
Multiplicity	:	3
Dipole	:	0.0000 Debye
Energy	:	-1306.91640793 a.u.
Number of imaginary frequencies	:	0

S9.2. Cartesian Co-ordinates (XYZ format)

49

C	0.00000000	-4.43768311	1.39463997
C	0.00000000	-4.39358282	2.78516698
C	0.00000000	-3.14496708	3.43526912
C	0.00000000	-1.98245203	2.68507099
N	0.00000000	-1.97980297	1.33739102
C	0.00000000	-3.20406508	0.67518598
C	0.00000000	-3.18479490	-0.72134697
C	0.00000000	-4.39813089	-1.47191000
C	0.00000000	-5.63532686	-0.73364300
C	0.00000000	-5.65426493	0.62501597
N	0.00000000	-1.94123495	-1.35136199
C	0.00000000	-1.90999496	-2.70409012
C	0.00000000	-3.05096507	-3.47990894
C	0.00000000	-4.31944180	-2.86100006
Pt	0.00000000	-0.34205699	0.00768000
C	0.00000000	1.01319695	1.38096797
C	0.00000000	1.05018604	-1.35874295
C	0.00000000	1.91906905	-2.22838902
C	0.00000000	1.87551200	2.26788712
C	0.00000000	2.91953206	-3.23006606
C	0.00000000	2.86393690	3.26743889
C	0.00000000	4.28886509	-2.87958097
C	0.00000000	2.57480788	-4.60061979
C	0.00000000	3.56179905	-5.57608080

C	0.00000000	4.91087294	-5.21309090
C	0.00000000	5.26835108	-3.86256909
C	0.00000000	2.51086998	4.63999510
C	0.00000000	3.49367595	5.61599922
C	0.00000000	4.84470320	5.25361681
C	0.00000000	5.21107388	3.90379095
C	0.00000000	4.23784781	2.91820908
H	0.00000000	-0.92361301	-3.14843297
H	0.00000000	-2.95671606	-4.55786991
H	0.00000000	-5.22541285	-3.45568705
H	0.00000000	-6.56411886	-1.29377198
H	0.00000000	-6.59797812	1.15960002
H	0.00000000	-5.31477404	3.35626698
H	0.00000000	-3.07679105	4.51510715
H	0.00000000	-1.00886297	3.15722704
H	0.00000000	1.46318495	4.91346121
H	0.00000000	4.51178885	1.87068295
H	0.00000000	6.25871181	3.62726998
H	0.00000000	5.60974884	6.02109718
H	0.00000000	3.21421909	6.66285515
H	0.00000000	4.56240511	-1.83159900
H	0.00000000	1.52844095	-4.88044691
H	0.00000000	3.28247690	-6.62337494
H	0.00000000	5.67872620	-5.97793198
H	0.00000000	6.31450796	-3.57898688