Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Triplet state structure-property relationships in a series of platinum acetylides: effect of chromophore length and electronic properties

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Electronic Supporting Information

Contents

Linear spectroscopy data

Ground state absorption spectra of these compounds dissolved methyl-THF, emission and excitation spectra collected from methyl-THF glass at 77 K were collected by Abigail Shelton from Kirk Schanze's group, Department of Chemistry, University of Florida, Gainesville FL. Emission spectra(10 nm ex/em bandwidth) were obtained by exciting the sample at the ground state spectrum absorption maximum while excitation spectra(10 nm ex/em bandwidth) were obtained by monitoring emission intensity at the emission maximum. The spectra have been converted to transition dipole moment representation and corrected for inner filter effects. (Angulo, Grampp, & Rosspeintner, 2006)

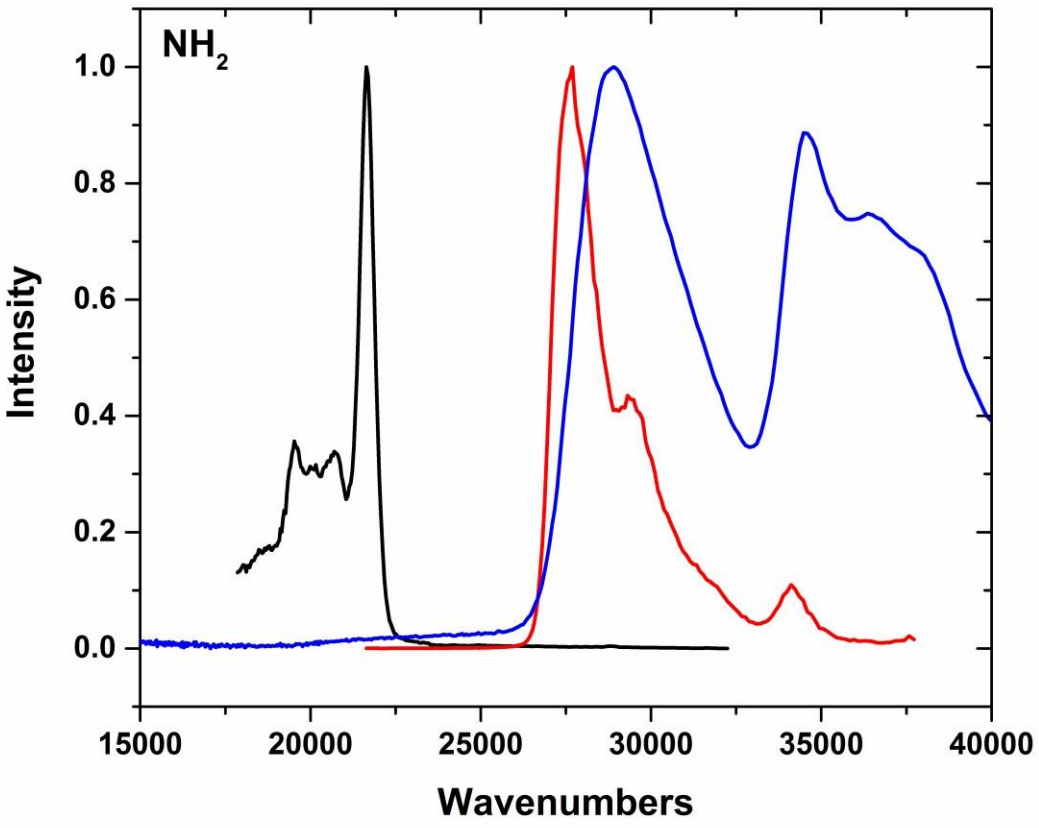


Fig S1 Emission(black line), excitation(red line) and absorption(blue line) spectra for **NH_2.**

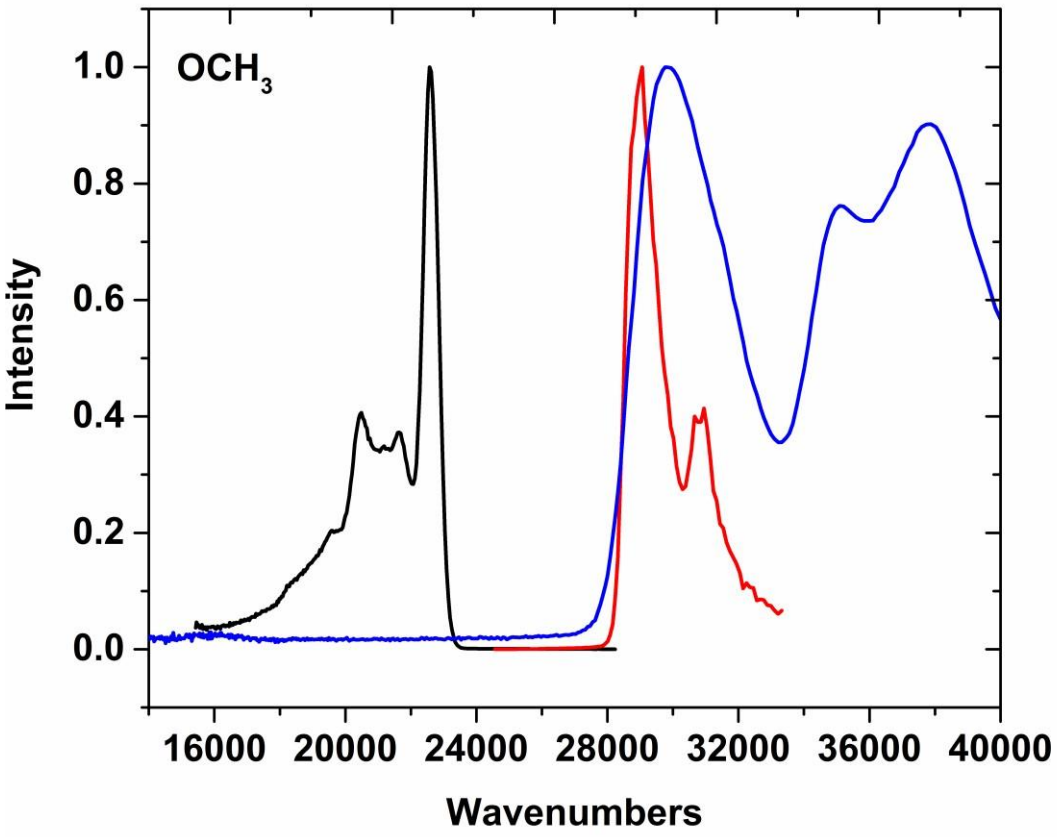


Fig S2 Emission(black line), excitation(red line) and absorption(blue line) spectra for **OCH_3.**

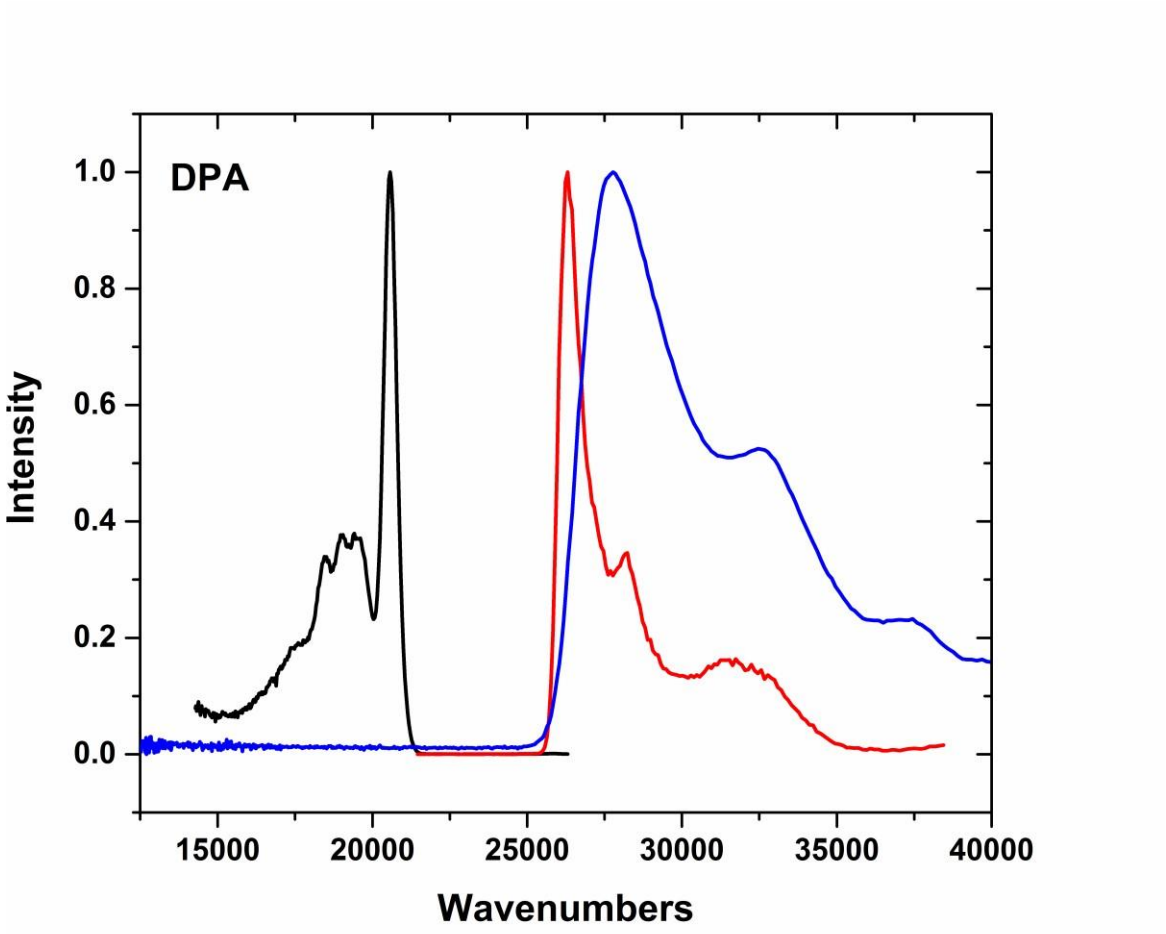


Fig S3 Emission(black line), excitation(red line) and absorption(blue line) spectra for **DPA**.

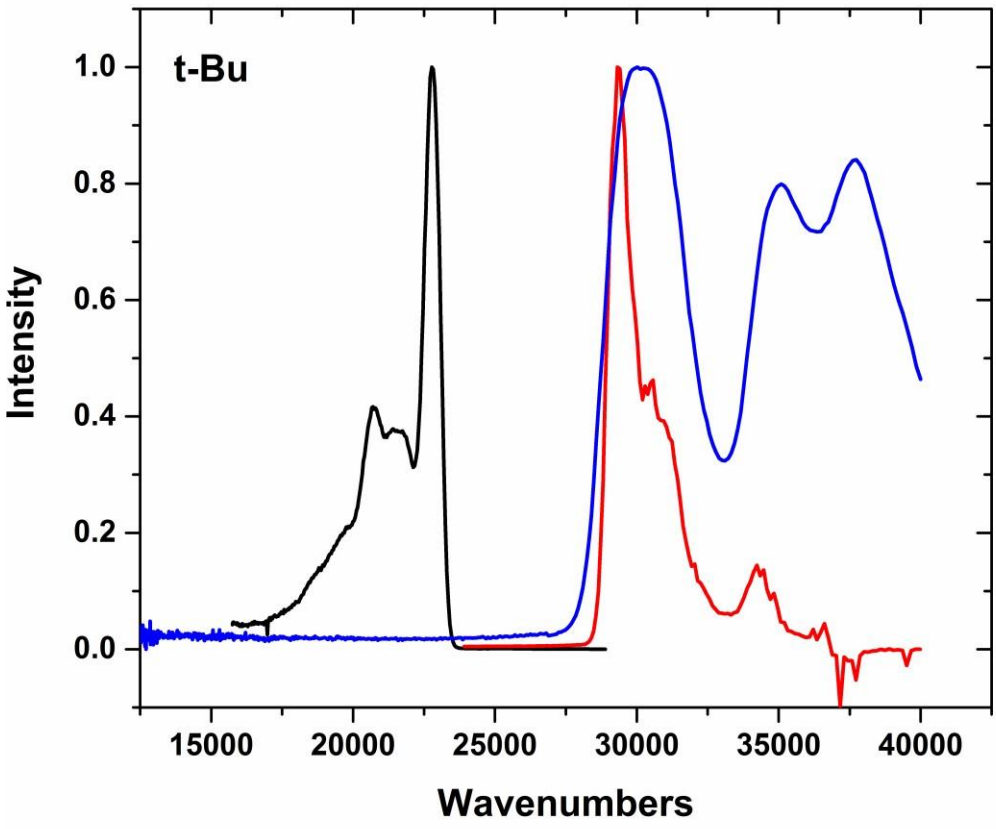


Fig S4 Emission(black line), excitation(red line) and absorption(blue line) spectra for **t-Bu.**

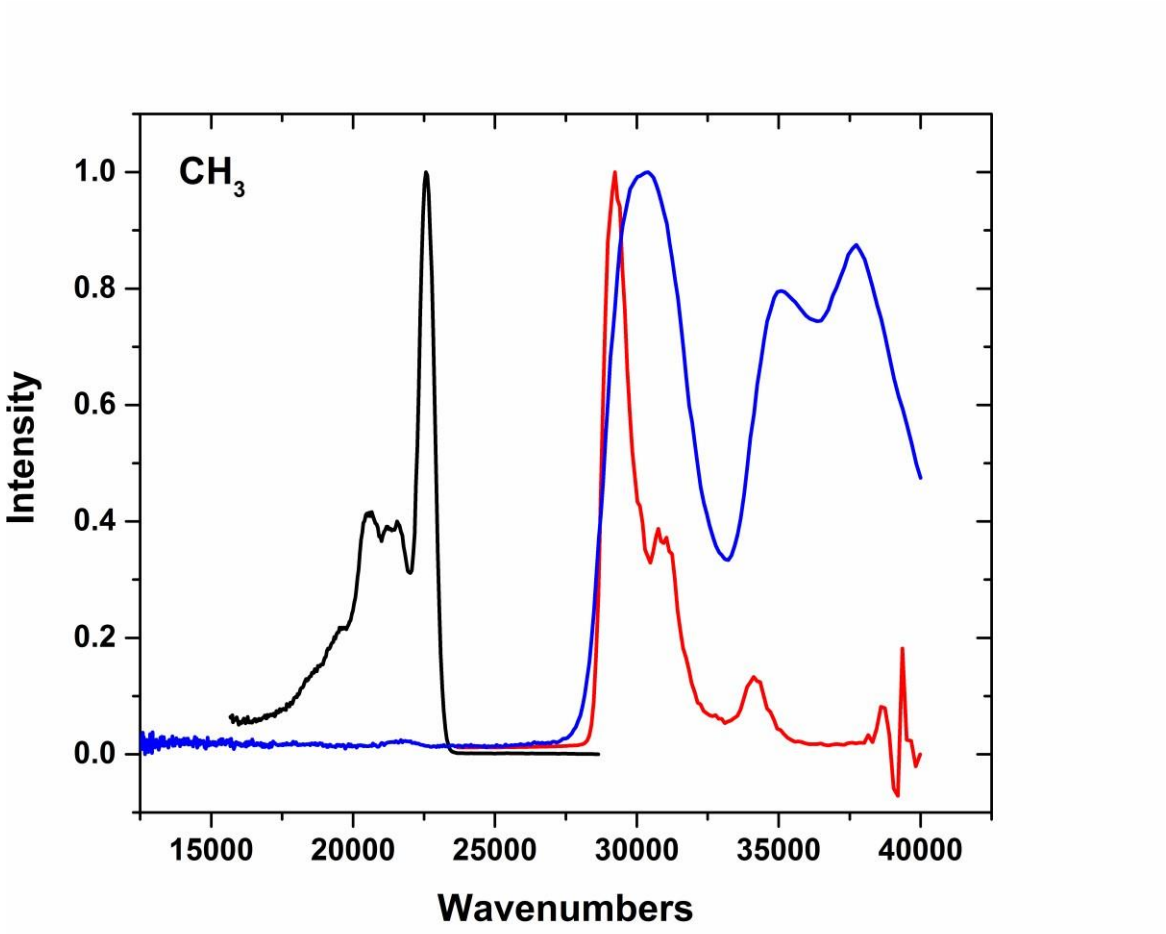


Fig S5 Emission(black line), excitation(red line) and absorption(blue line) spectra for **CH_3.**

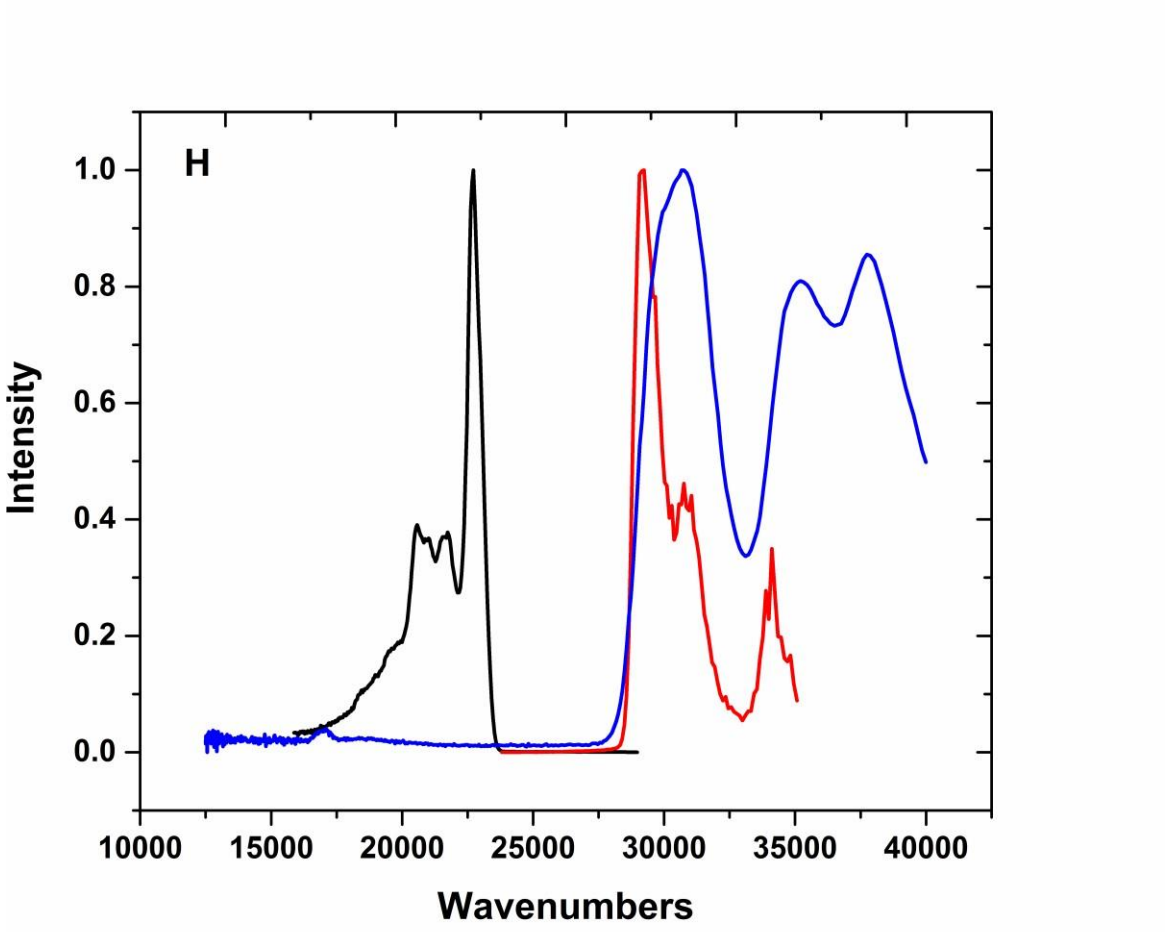


Fig S6 Emission(black line), excitation(red line) and absorption(blue line) spectra for **H.**

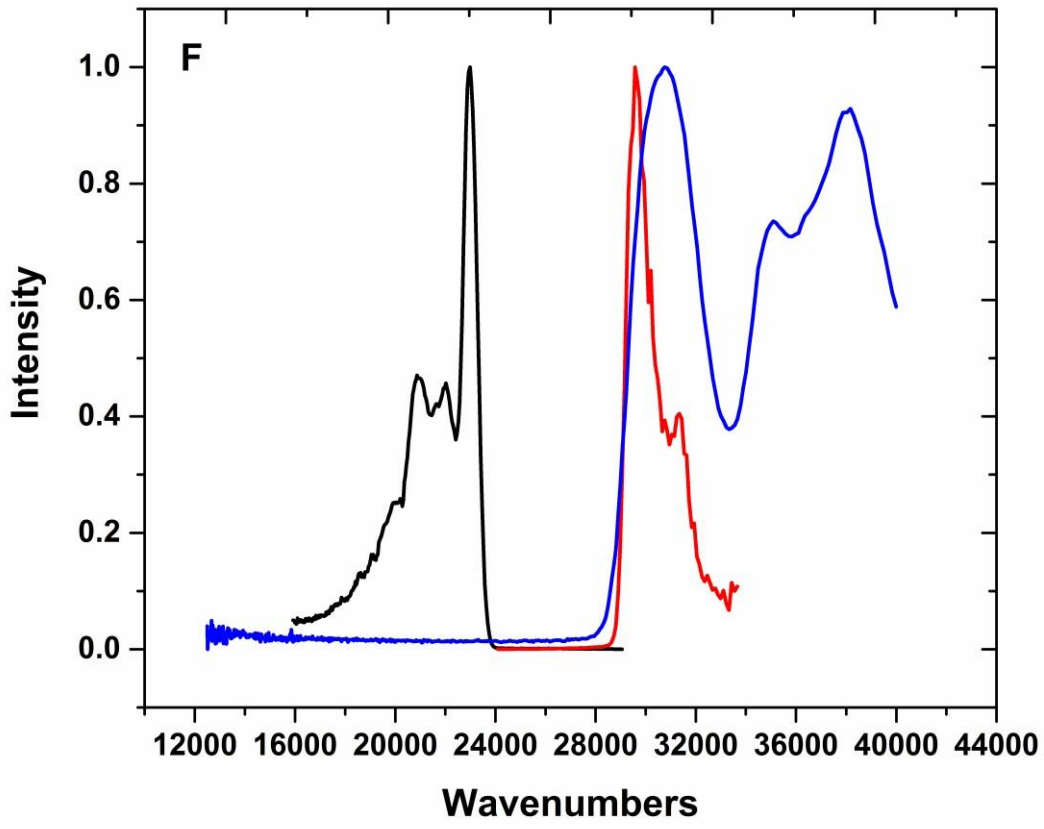


Fig S7 Emission(black line), excitation(red line) and absorption(blue line) spectra for **F**.

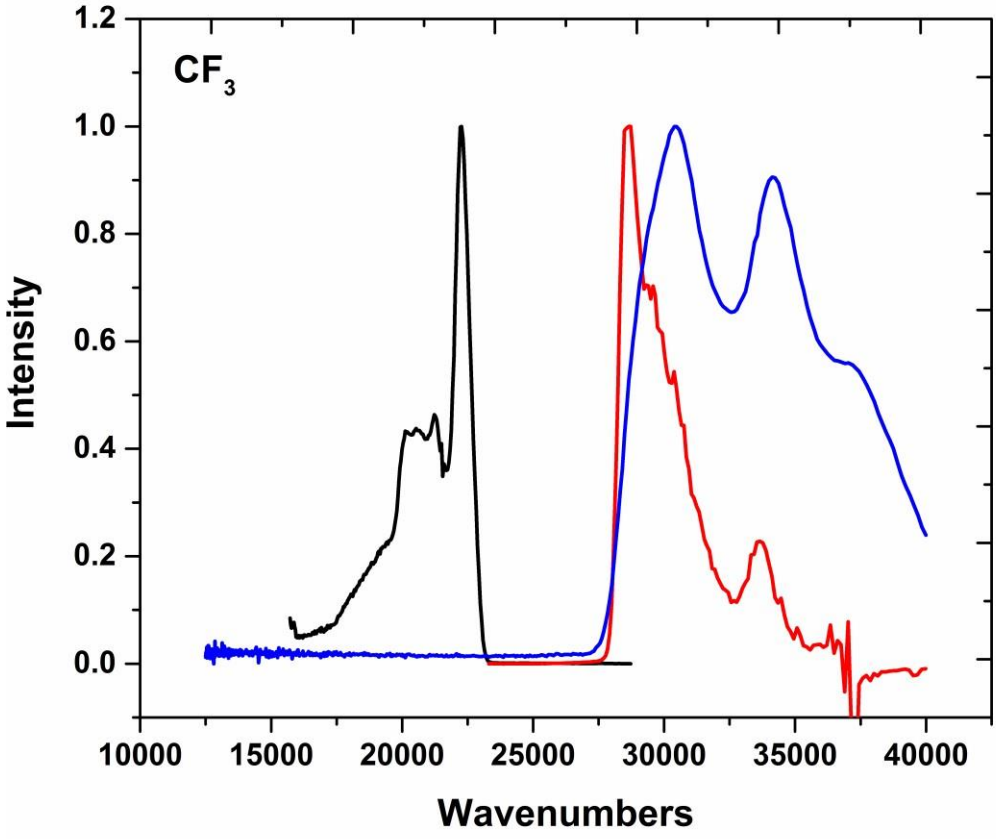


Fig S8 Emission(black line), excitation(red line) and absorption(blue line) spectra for CF_3.

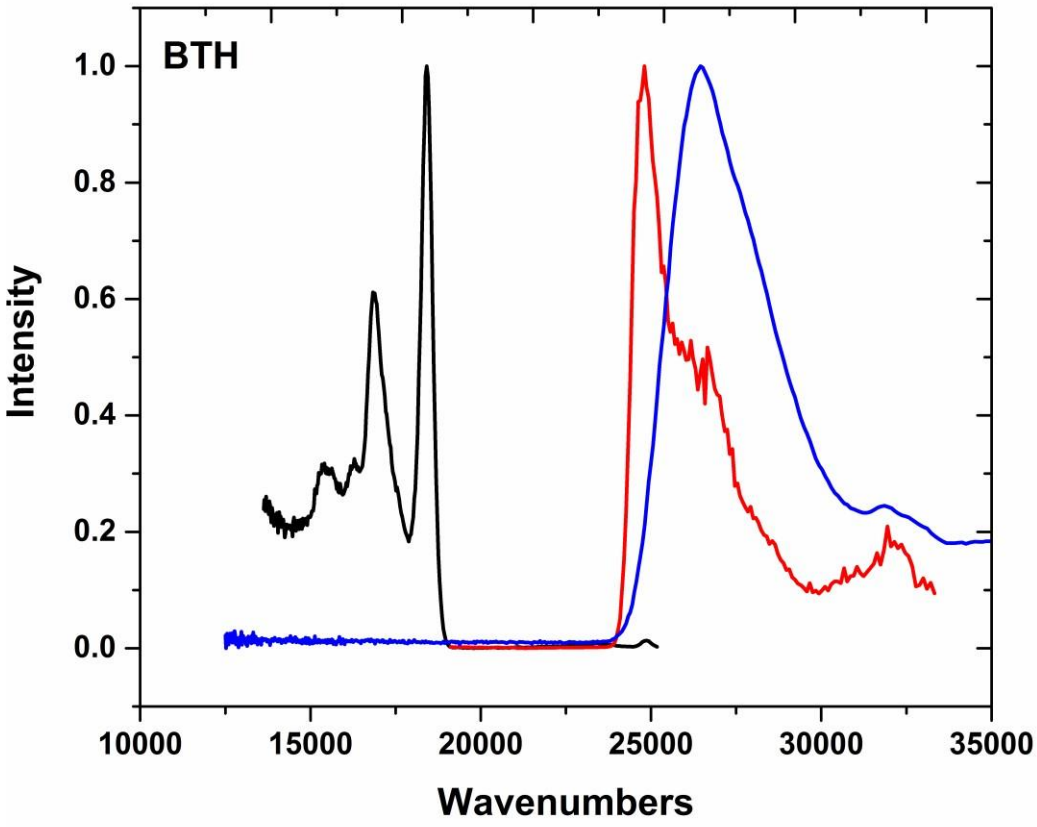


Fig S9 Emission(black line), excitation(red line) and absorption(blue line) spectra for **BTH**.

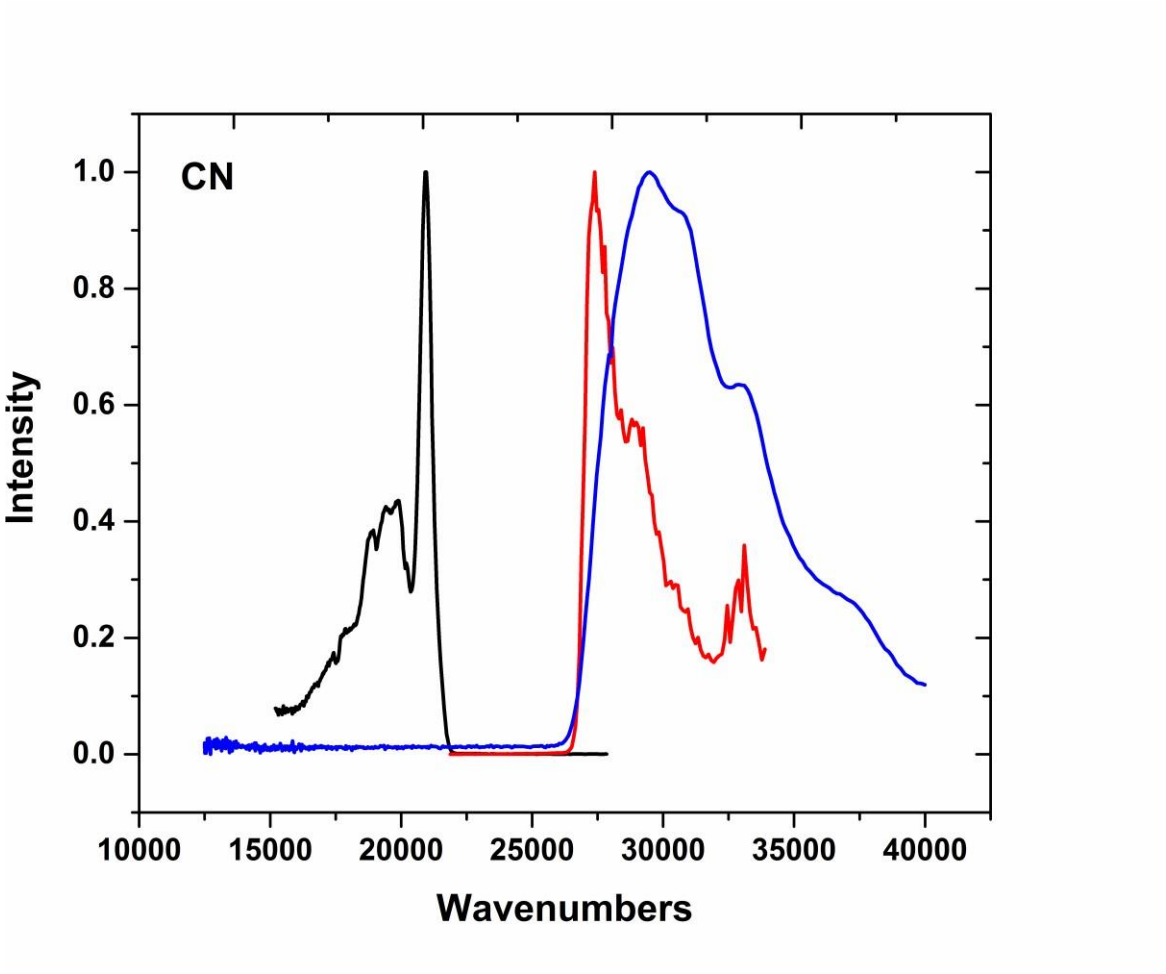


Fig S10 Emission(black line), excitation(red line) and absorption(blue line) spectra for **CN**.

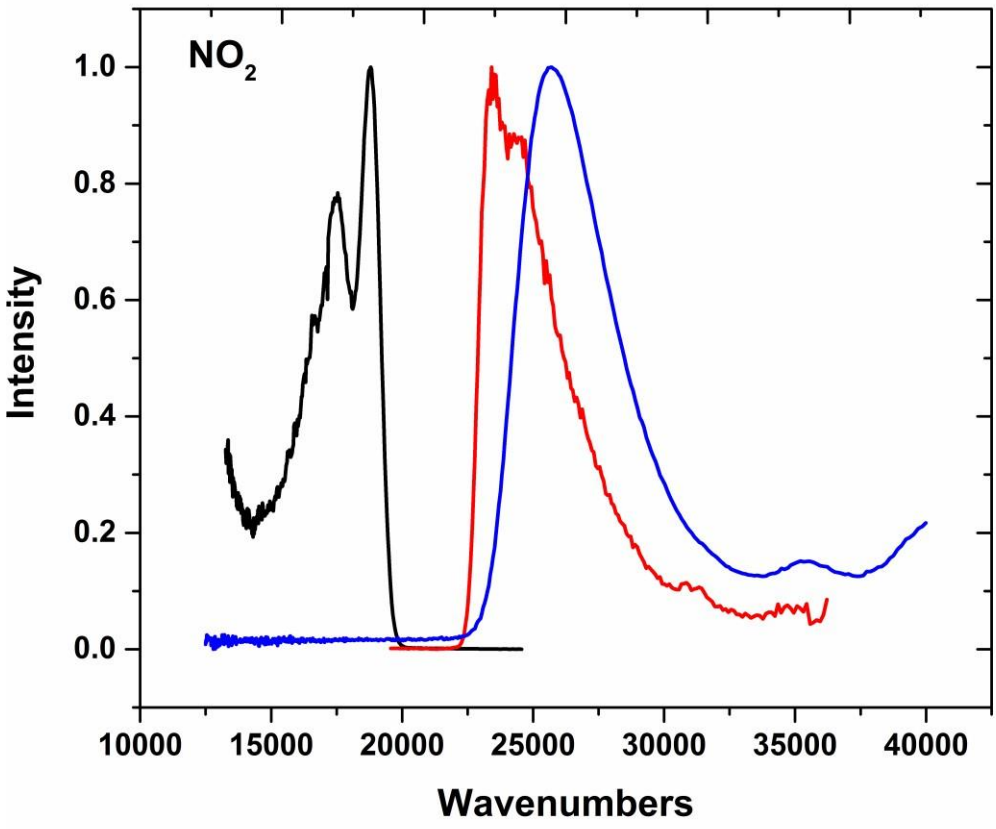


Fig S11 Emission(black line), excitation(red line) and absorption(blue line) spectra for NO_2.

Computational Chemistry Figures

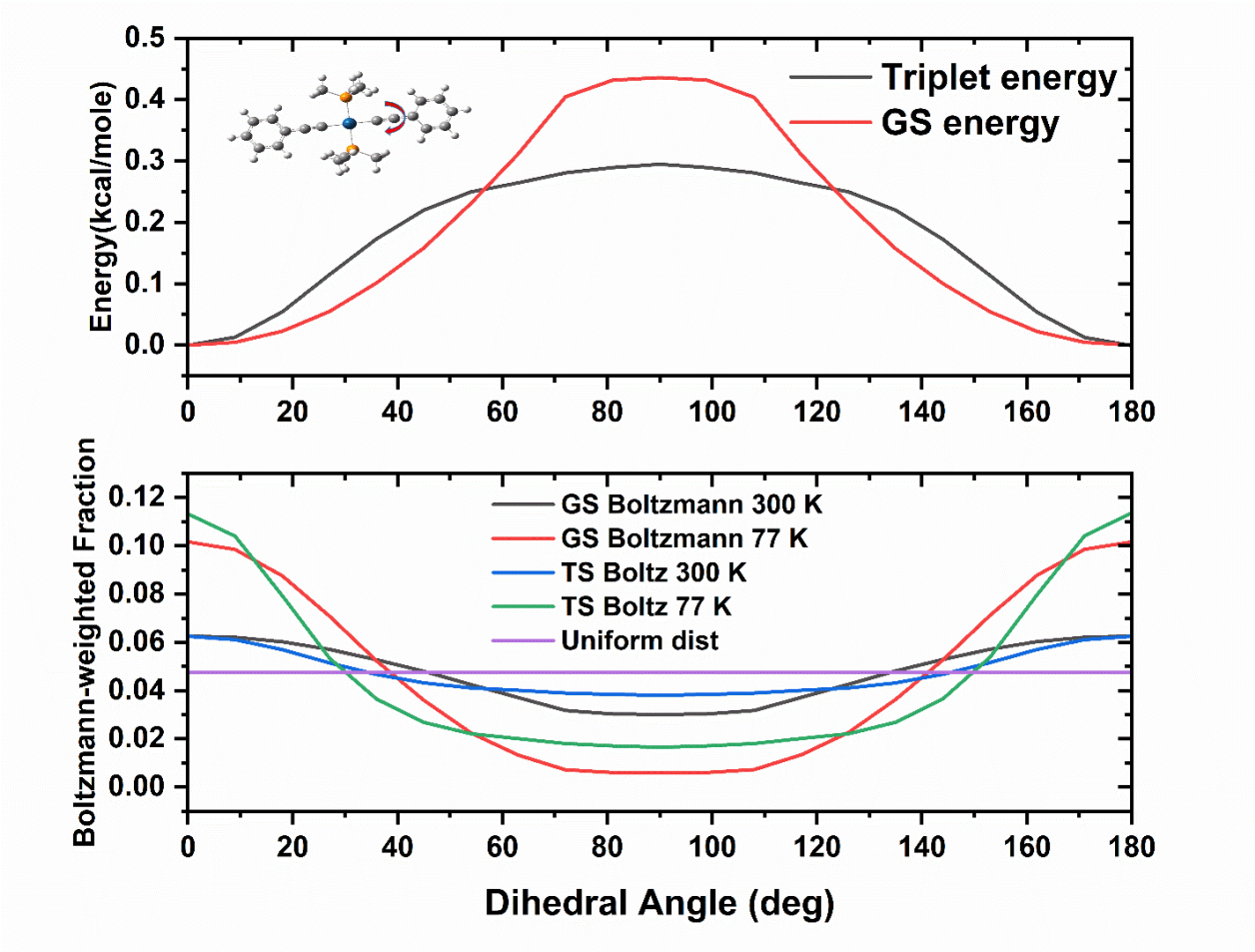


Fig S12 Upper panel: PES scan of the **H** ground and triplet state; Lower panel: Boltzmann-weighted dihedral angle distribution for chromophore **H**.

Triplet state absorption spectra

The samples were dissolved in benzene and deoxygenated by three successive freeze-pump-thaw cycles.Nanosecond transient absorption measurements were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width of ~5 ns). Pulse fluences of up to 1 mJ cm-2 at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus was published earlier. (Rogers, Cooper, Fleitz, Glass, & McLean, 2002)

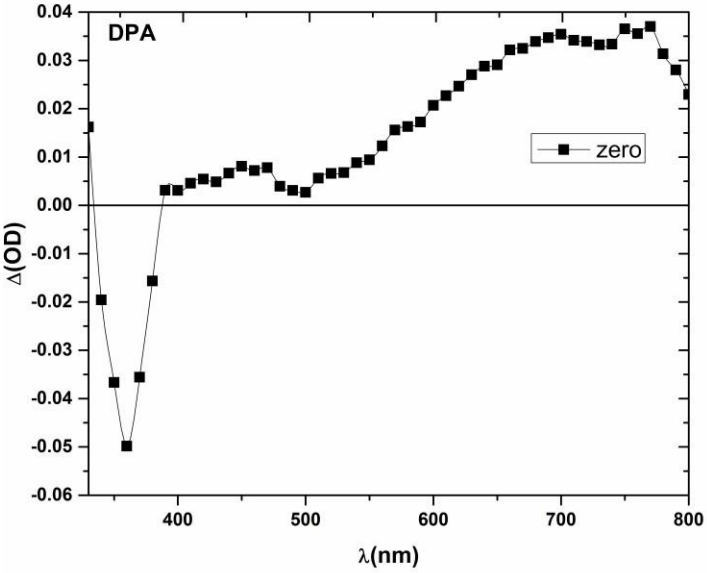


Fig S13 Triplet state absorption spectrum of **DPA**.

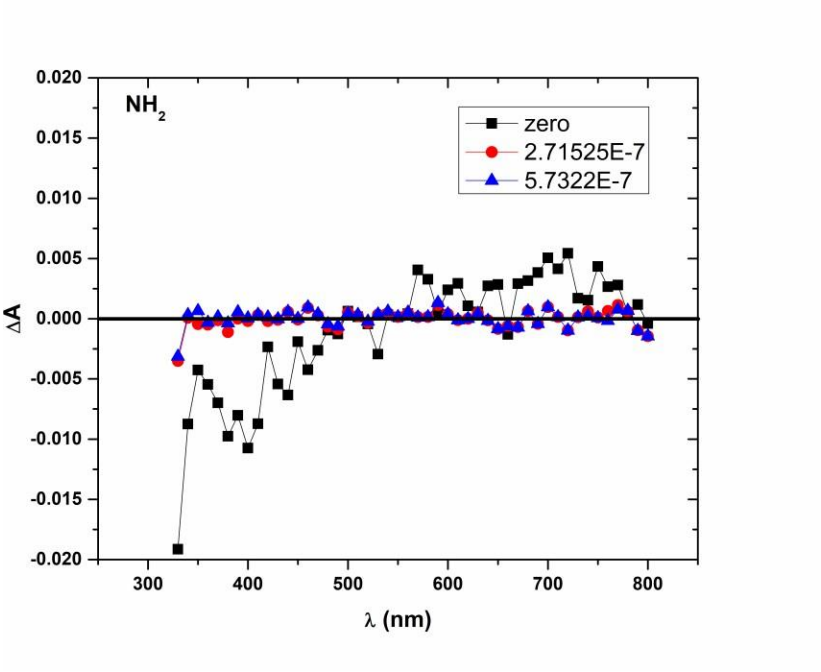


Fig S14 Triplet state absorption spectrum of NH_2.

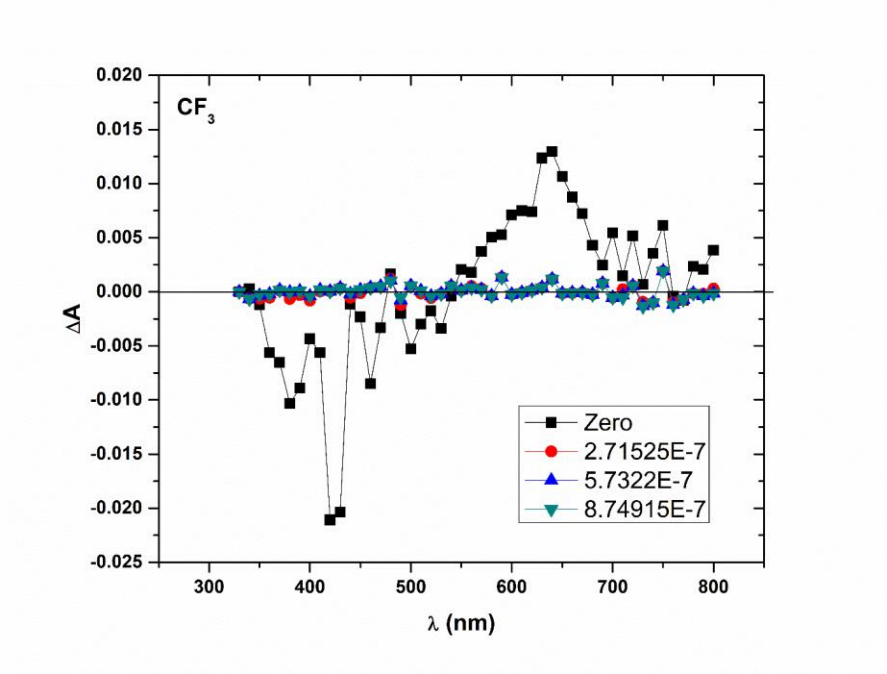


Fig S15 Triplet state absorption spectrum of CF_3.

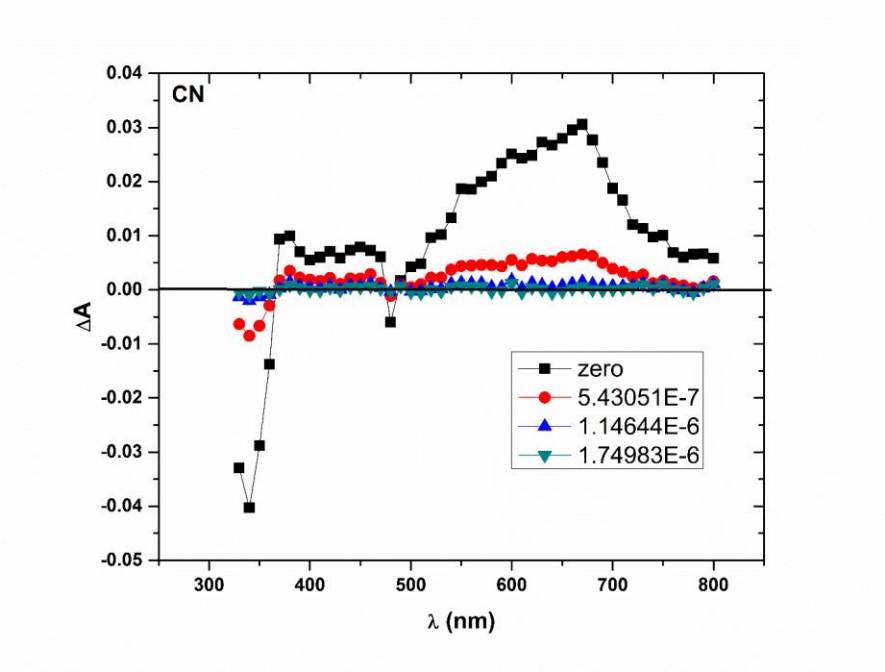


Fig S16 Triplet state absorption spectrum of **CN**.

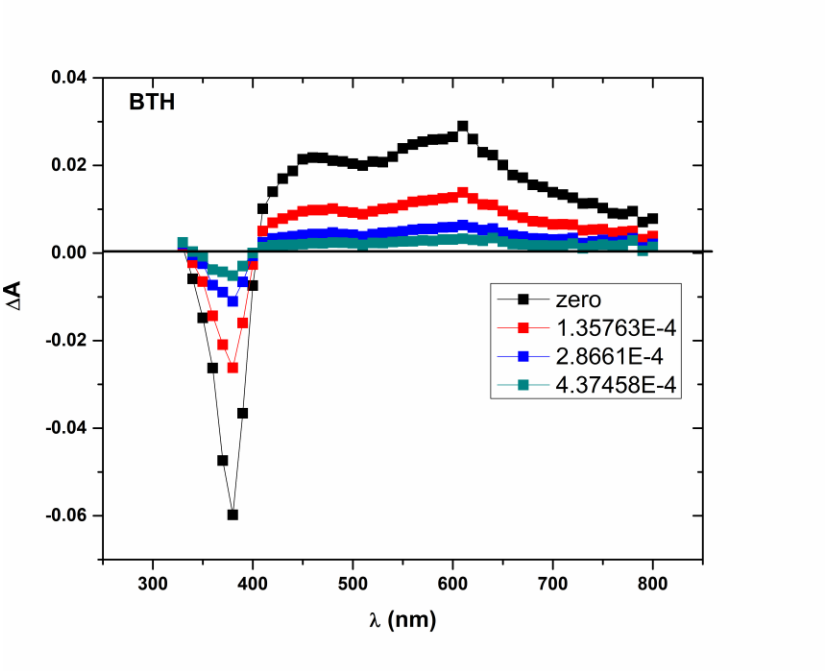


Fig S17 Triplet state absorption spectrum of **BTH**.

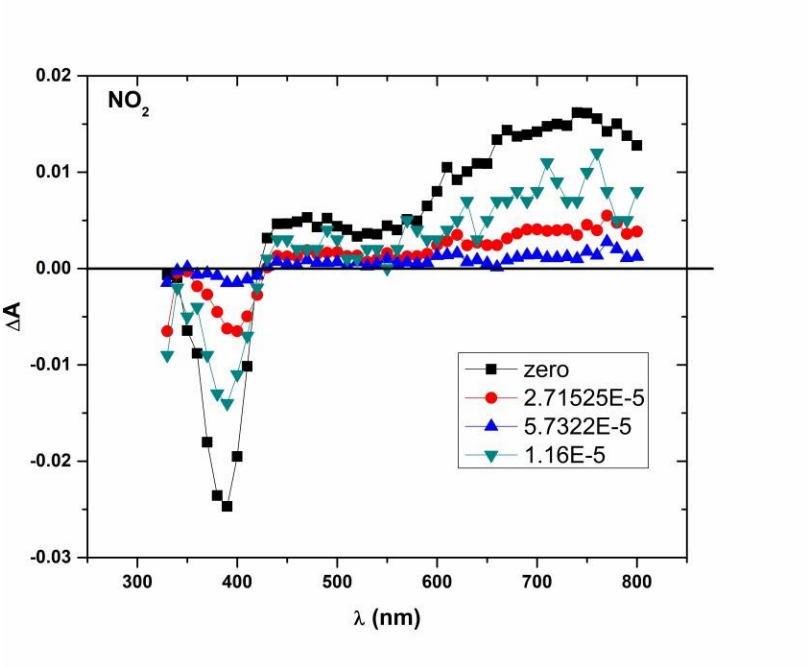
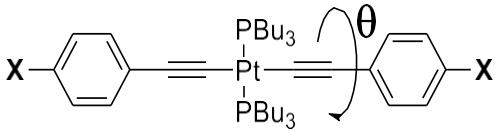


Fig S18 Triplet state absorption spectrum of **NO_2**.

Computational chemistry data tables

Calculations were done using Gaussian 09W, Version 7.0. (Frisch, G.W., Schlegel, & G. E. Scuseria) The chromophores were modeled as trans-$Pt(PMe_3)_2(C{\equiv}C\text{-Phenyl-X})_2$ in THF through use of PCM. We performed DFT energy minimizations for the ground state using B3LYP/6-311g(2d,p) and TDDFT calculations using CAM-B3LYP/6-311g(2d,p). The basis set for the central Pt atom was SDD.



For all calculations the angle θ between the phenyl rings was 90 deg.

Table S1 Calculated ground(S_0) and triplet state(T_1) energies.

Ligand	$E(S_0)$[a]	$E(S_0)$ (T_1)[b]	ΔE[c]	$E(T_1)$[d]	E_H[e]	E_L	EA[f]
NH_2	-1768.39606	-1768.38113	0.406	-1768.29393	-5.02898	-0.82288	0.52572
OCH_3	-1886.75848	-1886.74509	0.364	-1886.65584	-5.24776	-0.90479	0.69933
DPA	-2692.81217	-2692.80075	0.311	-2692.71997	-5.02898	-1.13472	1.0656
t-Bu	-1972.24079	-1972.22657	0.387	-1972.13716	-5.39770	-1.01581	0.93825
CH_3	-1736.29960	-1736.28546	0.385	-1736.19653	-5.41021	-1.00683	0.94396
H	-1657.64252	-1657.62853	0.381	-1657.53809	-5.50681	-1.06833	1.0555
F	-1856.17748	-1856.16331	0.386	-1856.07291	-5.51661	-1.06234	1.0672
BTH	-3100.89742	-3100.88432	0.357	-3100.81590	-5.55770	-1.99461	2.1165
CF_3	-2331.94370	-2331.93050	0.359	-2331.84314	-5.73865	-1.45283	1.6972
CN	-1842.18888	-1842.17698	0.324	-1842.09610	-5.83362	-1.84876	2.1693
NO_2	-2066.78035	-2066.77052	0.267	-2066.70045	-5.93240	-2.67572	2.8232

[a]Energy(relaxed S_0 geometry, perpendicular conformation(au).
[b]Energy(ground state, relaxed T_1 geometry(au).
[c]E(S_0, relaxed T_1 geometry) – E(relaxed S_0 geometry, perpendicular conformation)(eV).
[d]E(relaxed T_1 geometry)(au).
[e]HOMO, LUMO energies, relaxed S_0 geometry, perpendicular conformation(eV).
[f]Ligand electron affinity(- E(LUMO)(eV).

Table S2 Summary of TDDFT Calculations for θ = 90 deg.

X	ΔE^a	ΔE_1 [b]	ΔE_2	ΔE_3	ΔE_4	ΔE_5
NH_2	3.99	2.84	2.94	3.71	3.74	3.92
OCH_3	4.07	2.90	3.01	3.90	3.91	3.97
DPA[c]	3.76	2.67	2.75	3.14	3.14	3.47
t-Bu	4.09	2.90	3.00	3.96	4.22	4.29
CH_3	4.10	2.89	2.99	3.97	4.22	4.24
H	4.12	2.92	3.03	3.99	4.22	4.33
F	4.14	2.92	3.04	3.99	4.09	4.11
BTH	3.53	2.34	2.39	3.21	3.27	3.83
CF_3	4.06	2.81	2.91	4.01	4.11	4.30
CN	3.88	2.60	2.68	3.96	3.98	4.28
NO_2	3.53	2.46	2.53	2.74	2.75	3.39

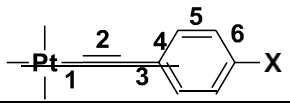
[a]Transition energy in for the $S_0 \rightarrow S_1$ transition(eV) for state 1.

[b]Transition energy for the $S_0 \rightarrow T_1$ transition(eV), and $S_0 \rightarrow T_2$, T_3, T_4 and T_5 states in columns 4-7.

[c]Additional $S_0 \rightarrow T_n$ transitions(eV) for DPA. State 6: 3.59;State 7: 3.69; State 8: 3.70,

[d]Additional $S_0 \rightarrow T_n$ transitions(eV) for NO_2. State 6: 3.39; State 7: 3.80.

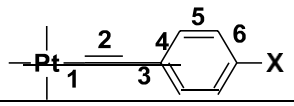
Table S3 Selected bond lengths from equilibrium ground state geometry



Ligand	1[a]	2	3	4	5	6
NH_2	2.0077	1.2459	1.4330	1.4229	1.4000	1.4189
OCH_3	2.0070	1.2454	1.4330	1.4193	1.4055	1.4105
DPA	2.0144	1.2432	1.4361	1.4213	1.4014	1.4143
t-Bu	2.0062	1.2454	1.4332	1.4230	1.3999	1.4182
CH_3	2.0062	1.2453	1.4335	1.4214	1.4039	1.4129
H	2.0050	1.2454	1.4332	1.4236	1.4037	1.4102
F	2.0043	1.2451	1.4326	1.4240	1.4033	1.3994
BTH	2.0074	1.2439	1.4314	1.4226	1.3989	1.4160
CF_3	2.0023	1.2450	1.4299	1.4240	1.3990	1.4105
CN	2.0037	1.2447	1.4298	1.4244	1.3982	1.4175
NO_2	1.9997	1.2447	1.4287	1.4252	1.3974	1.4090

[a]Ground state bond length 1(Å). The other bonds are labeled 2-6.

Table S4 Selected bond lengths from equilibrium T_1 state geometry.



Ligand	1 [a]	2	3	4	5	6
NH_2	1.9817	1.2799	1.3725	1.4816	1.3758	1.4431
OCH_3	1.9795	1.2820	1.3708	1.4772	1.3712	1.4466
DPA	1.9932	1.2712	1.3806	1.4775	1.3705	1.4566
t-Bu	1.9778	1.2837	1.3703	1.4811	1.3807	1.4401
CH_3	1.9778	1.2835	1.3704	1.4777	1.3749	1.4506
H	1.9754	1.2852	1.3701	1.4805	1.3796	1.4387
F	1.9750	1.2847	1.3696	1.4836	1.3790	1.4271
BTH	1.9934	1.2607	1.3962	1.4576	1.3708	1.4667
CF_3	1.9740	1.2817	1.3736	1.4750	1.3746	1.4439
CN	1.9800	1.2757	1.3770	1.4747	1.3703	1.4592
NO_2	1.9757	1.2695	1.3867	1.4605	1.3755	1.4433

[a]Triplet state bond length 1(Å). The other bonds are labeled 2-6.

Table S5 Electron central platinum atom population change upon excitation to the S_1 state.

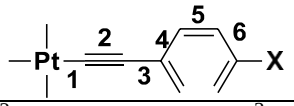
Ligand	d[1]	π^*[2]	$\Delta\rho$[3]
NH2	0.11	0.50	0.39
OCH3	0.15	0.47	0.32
DPA	0.06	0.36	0.30
t-Bu	0.17	0.43	0.26
CH3	0.17	0.43	0.26
H	0.19	0.42	0.23
F	0.18	0.43	0.25
BTH	0.14	0.06	-0.08
CF3	0.21	0.24	0.03
CN	0.19	0.15	-0.04
NO2	0.21	0.05	-0.16

[1]Ground state electron density of d orbital on Pt atom.

[2]S_1 state electron density of π^* orbital on Pt atom.

[3]Calculated from population analysis of S_1 state when platinum complex is in an out-of-plane conformation. Change in population is defined as population(π^* orbital, platinum atom) – population(d orbital, platinum atom).

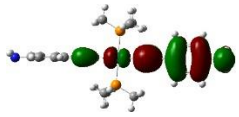
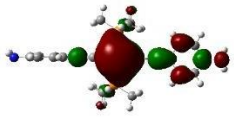
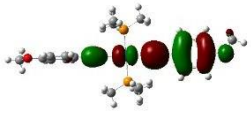
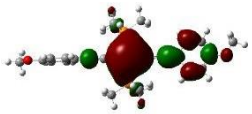
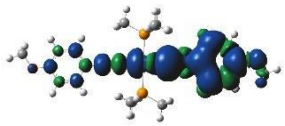
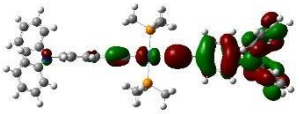
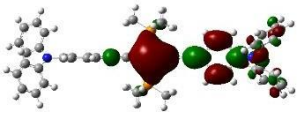
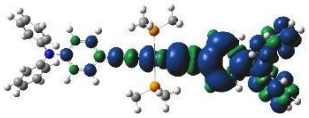
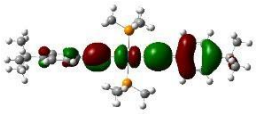
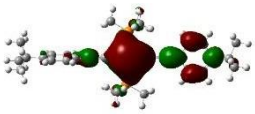
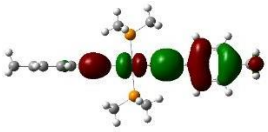
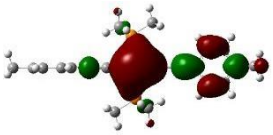
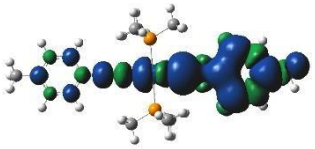
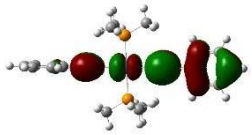
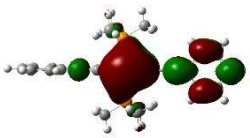
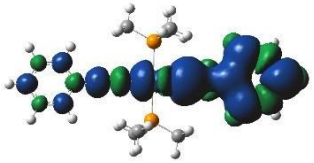
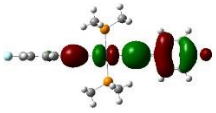
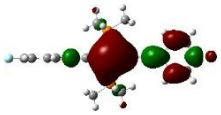
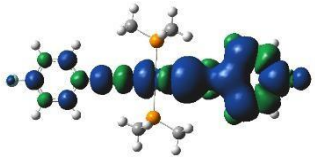
Table S6 Summary of spin density data

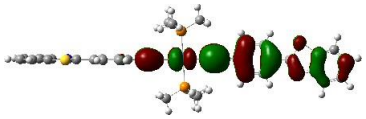
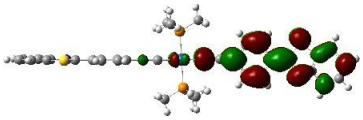
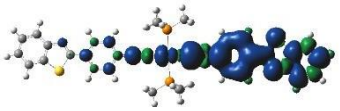
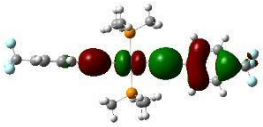
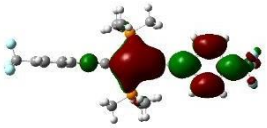
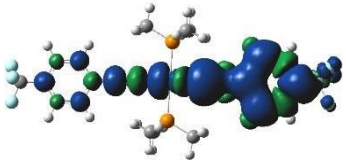
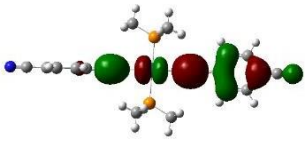
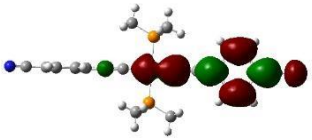
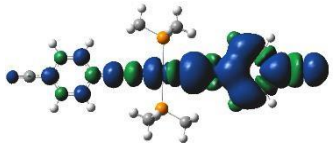
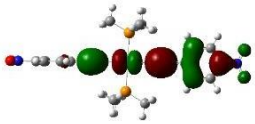
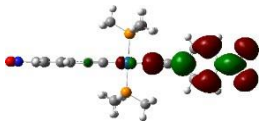
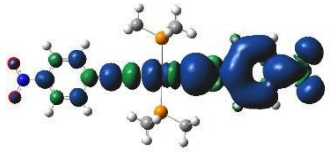


Ligand	Pt[1]	CC[2]	Phenyl[3]	End Cap(X)[4]	Remainder[5]
NH_2	0.24079	0.47223	0.95941	0.19662	0.13095
OCH_3	0.21824	0.53472	1.0377	0.10705	0.10230
DPA	0.14693	0.39034	1.0701	0.33764	0.055008
t-Bu	0.20722	0.56586	1.1312	0.0028490	0.092854
CH_3	0.20448	0.56052	1.1330	0.011192	0.090758
H	0.21530	0.59700	1.1275	-0.036182	0.096352
F	0.21529	0.58816	1.0630	0.039800	0.093796
BTH	0.10496	0.31934	0.90661	0.63572	0.033368
CF_3	0.19391	0.58325	1.1109	0.032180	0.079750
CN	0.16647	0.51310	1.0977	0.15673	0.065982
NO_2	0.18419	0.44802	0.80913	0.48414	0.074516

[1]Spin density on central platinum atom
[2]Spin density on acetylene bond
[3]Spin density on phenyl ring
[4]Spin density on end cap
[5]Remainder spin density on the rest of the molecule(Remainder = 2-(SD(Pt)+SD(CC)+SD(Phenyl)+SD(X))

Table S7 HOMO, LUMO and T_1 state Spin Density images

Ligand	HOMO	LUMO	Spin Density
NH_2			
OCH_3			
DPA			
t-Bu			
CH_3			
H			
F			

BTH			
CF_3			
CN			
NO_2			

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