Benzoquinolateplatinum(II) Complexes as Building Blocks in the Synthesis of Pt–Ag Donor-Acceptor Extended Structures

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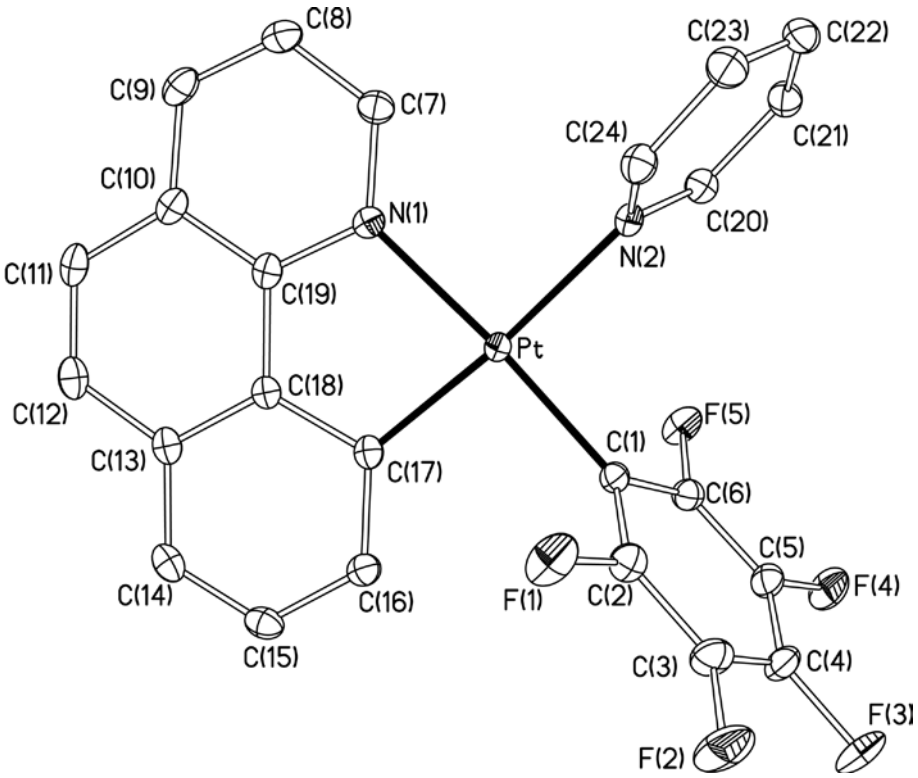

Figure S1. View of the molecular structure of [Pt(bzq)(C_6F_5)py] (**5**)

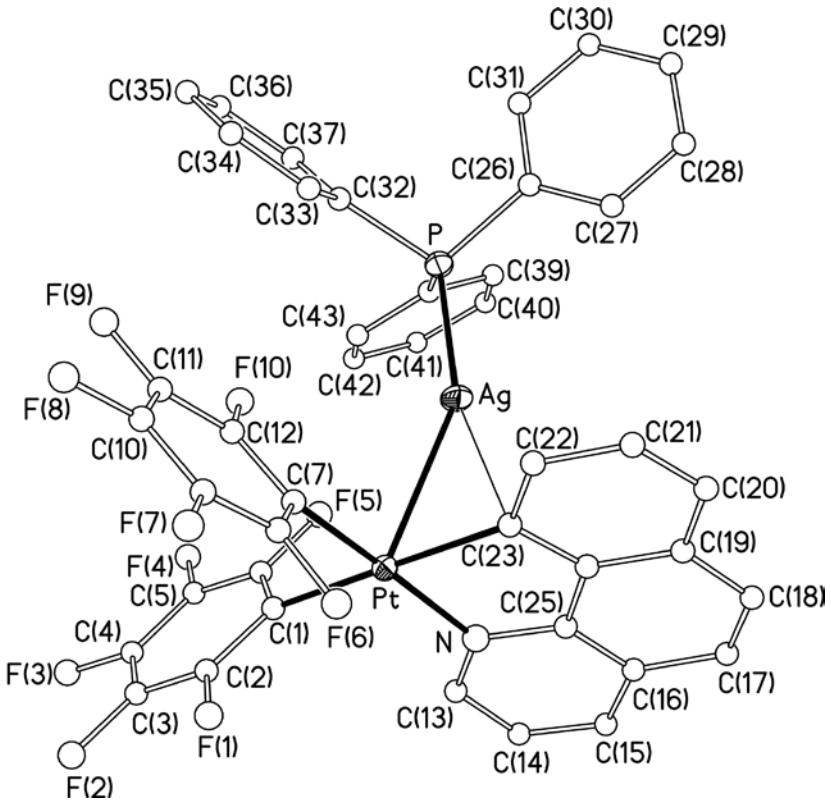

Figure S2. View of the molecular structure of [{Pt(bzq)(C_6F_5)$_2$}Ag(PPh_3)] (**3**)

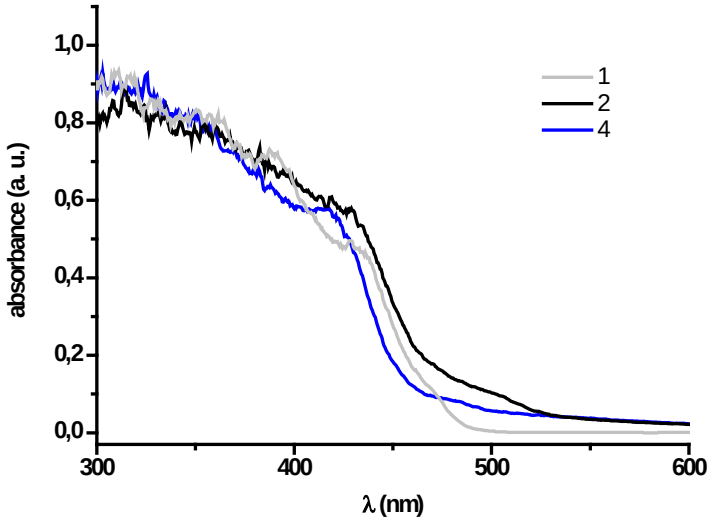

Figure S3. Normalized absorption spectra calculated from their reflectance diffuse spectra of **1**, **2** and **4** in solid state

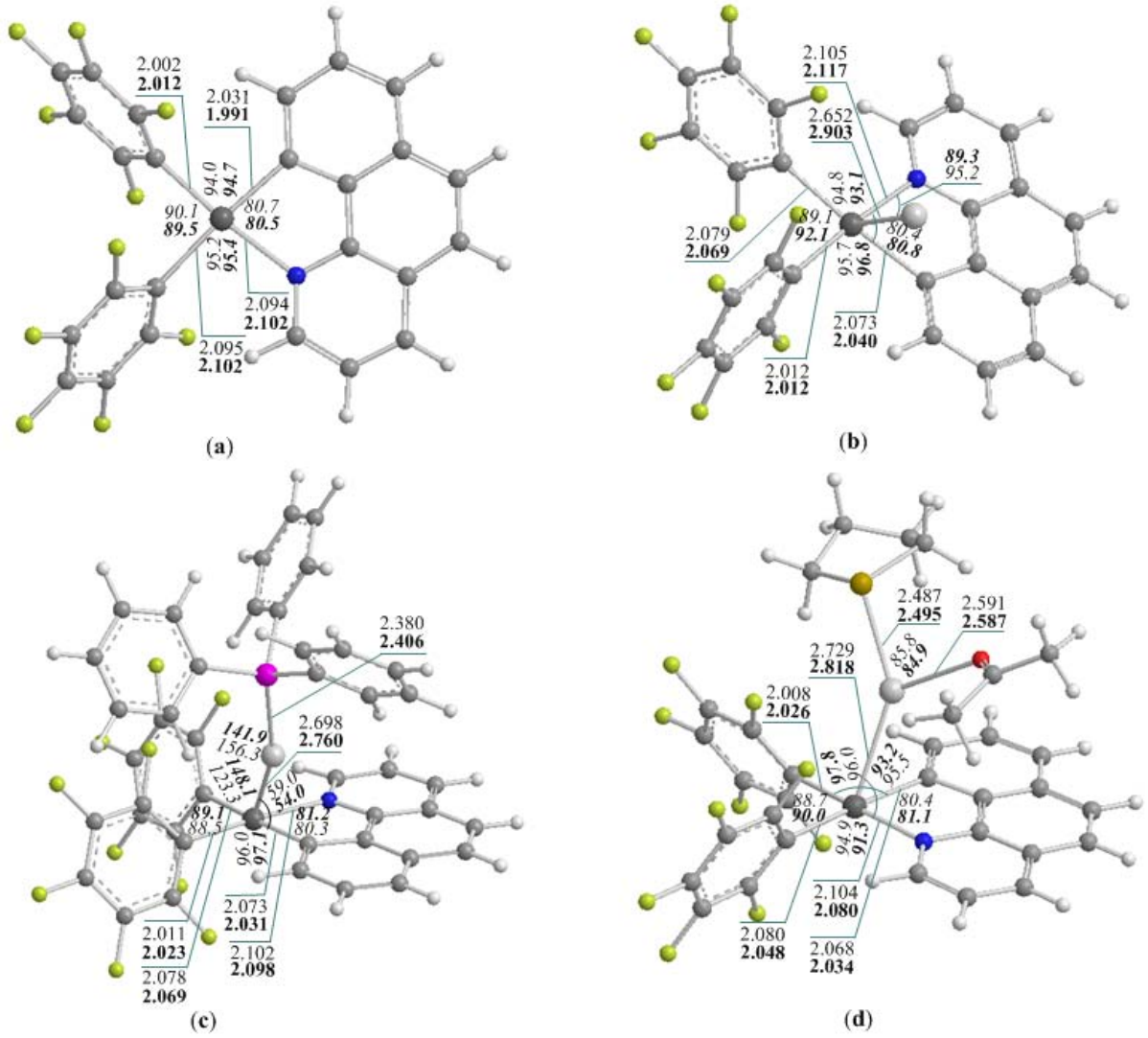

Figure S4. Optimized geometries along with selected structural parameters of **1 (a)**, **2 (b)**, **3 (c)** and **4' (d)** computed at the PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level (numbers in bold refer to structural parameters of the T_1 state).

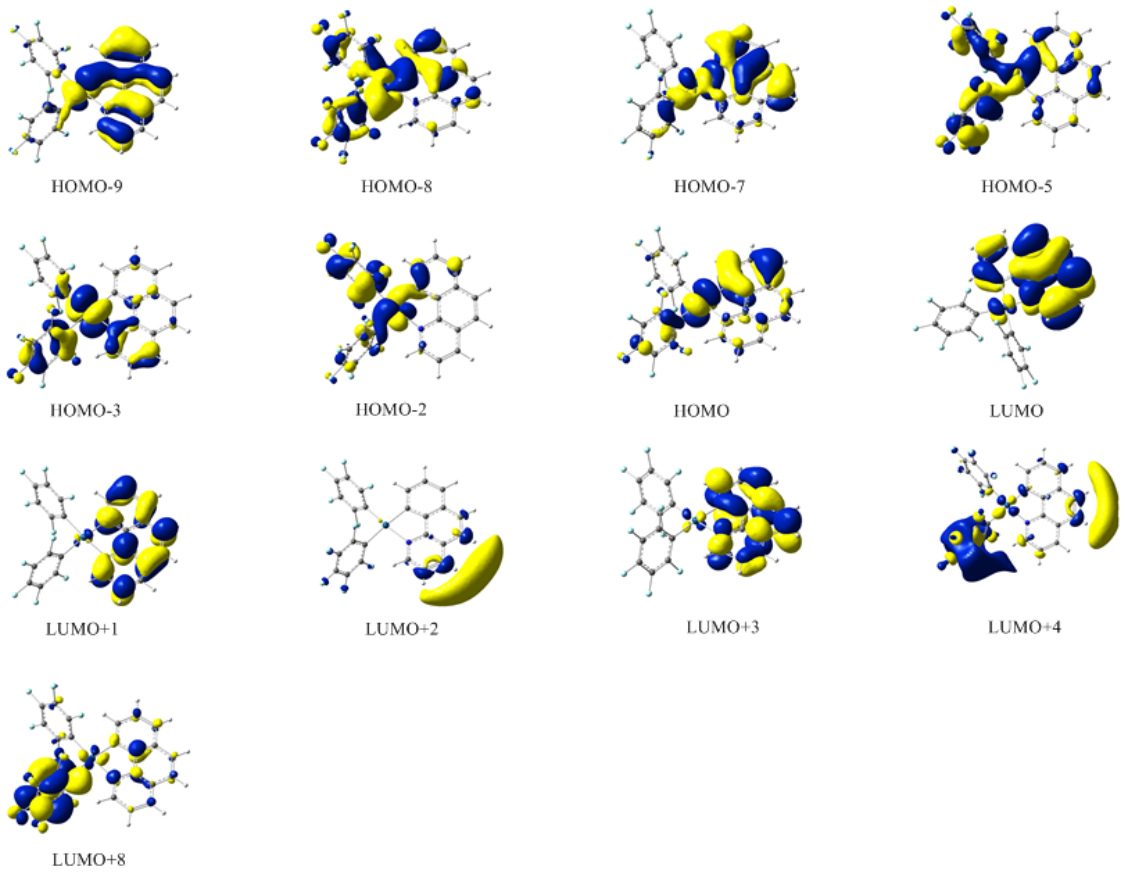

Figure S5. Molecular orbitals involved in the electronic transitions observed in the absorption spectrum of **1** calculated at the PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level of theory.

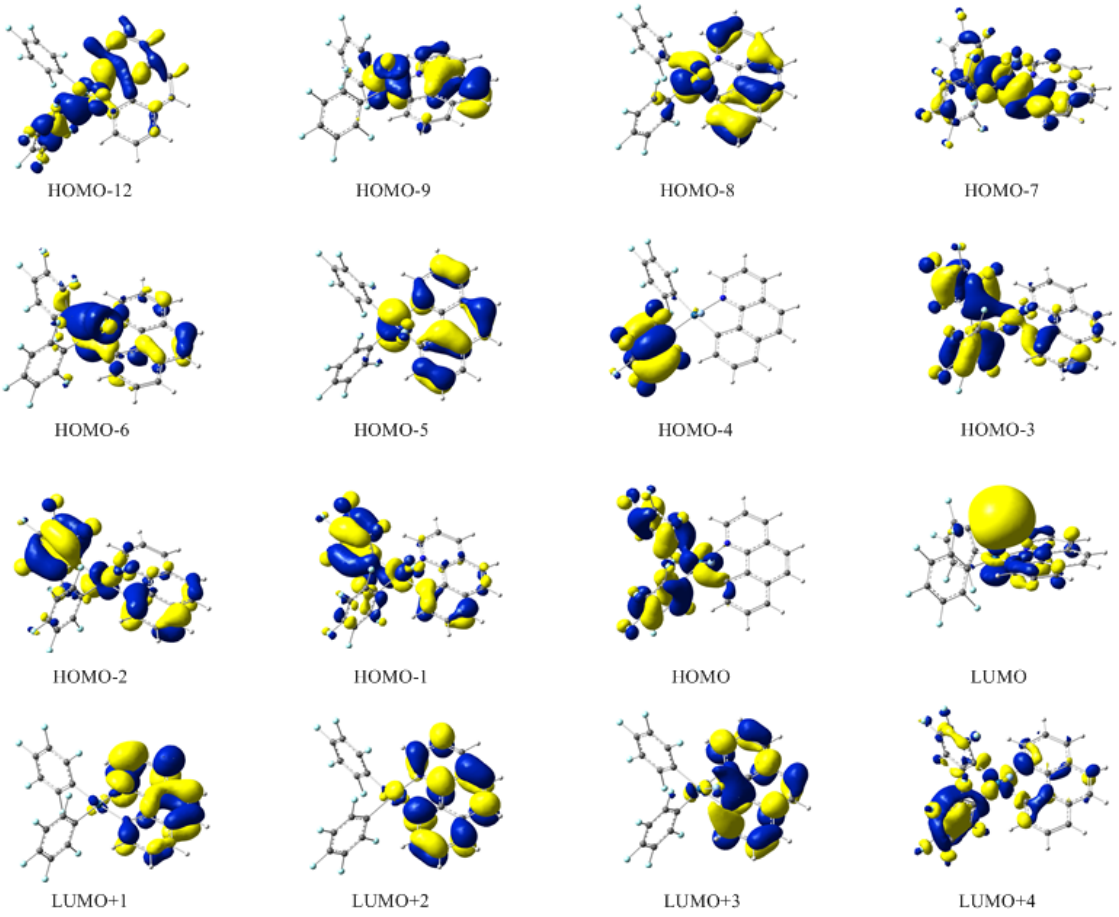

Figure S6. Molecular orbitals involved in the electronic transitions observed in the absorption spectrum of **2** calculated at the PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level of theory.

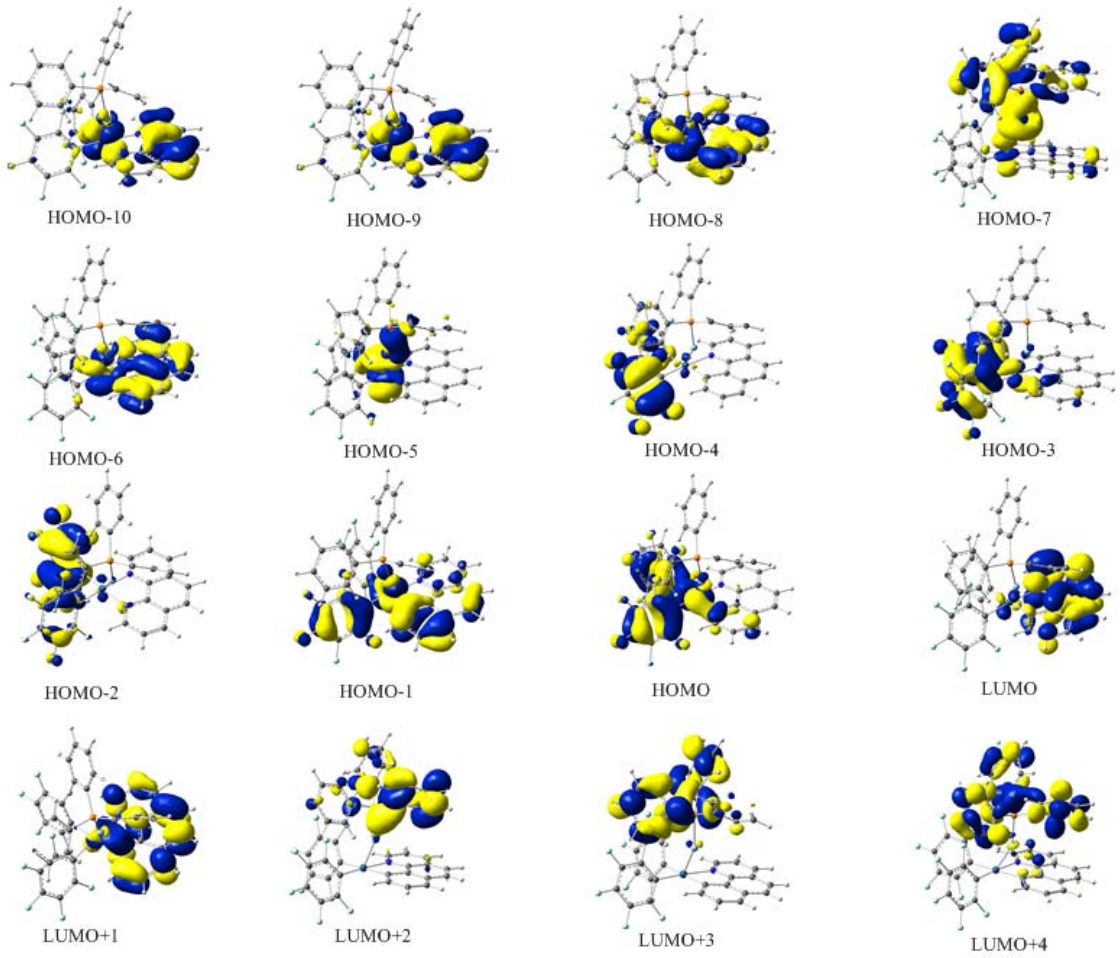

Figure S7. Molecular orbitals involved in the electronic transitions observed in the absorption spectrum of **3** calculated at the PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level of theory.

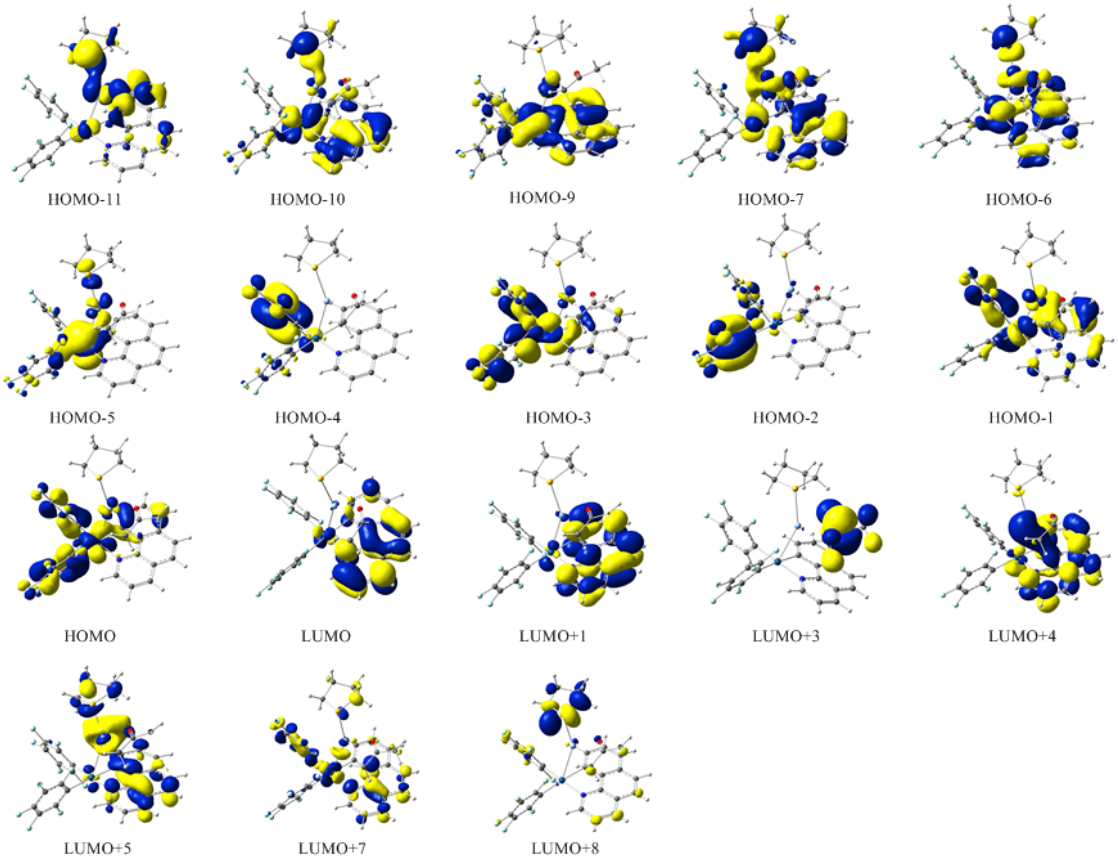

Figure S8. Molecular orbitals involved in the electronic transitions observed in the absorption spectrum of **4'** calculated at the PBE1PBE/Def2-TZVP(M)U6-31+G(d,p)(X) level of theory.

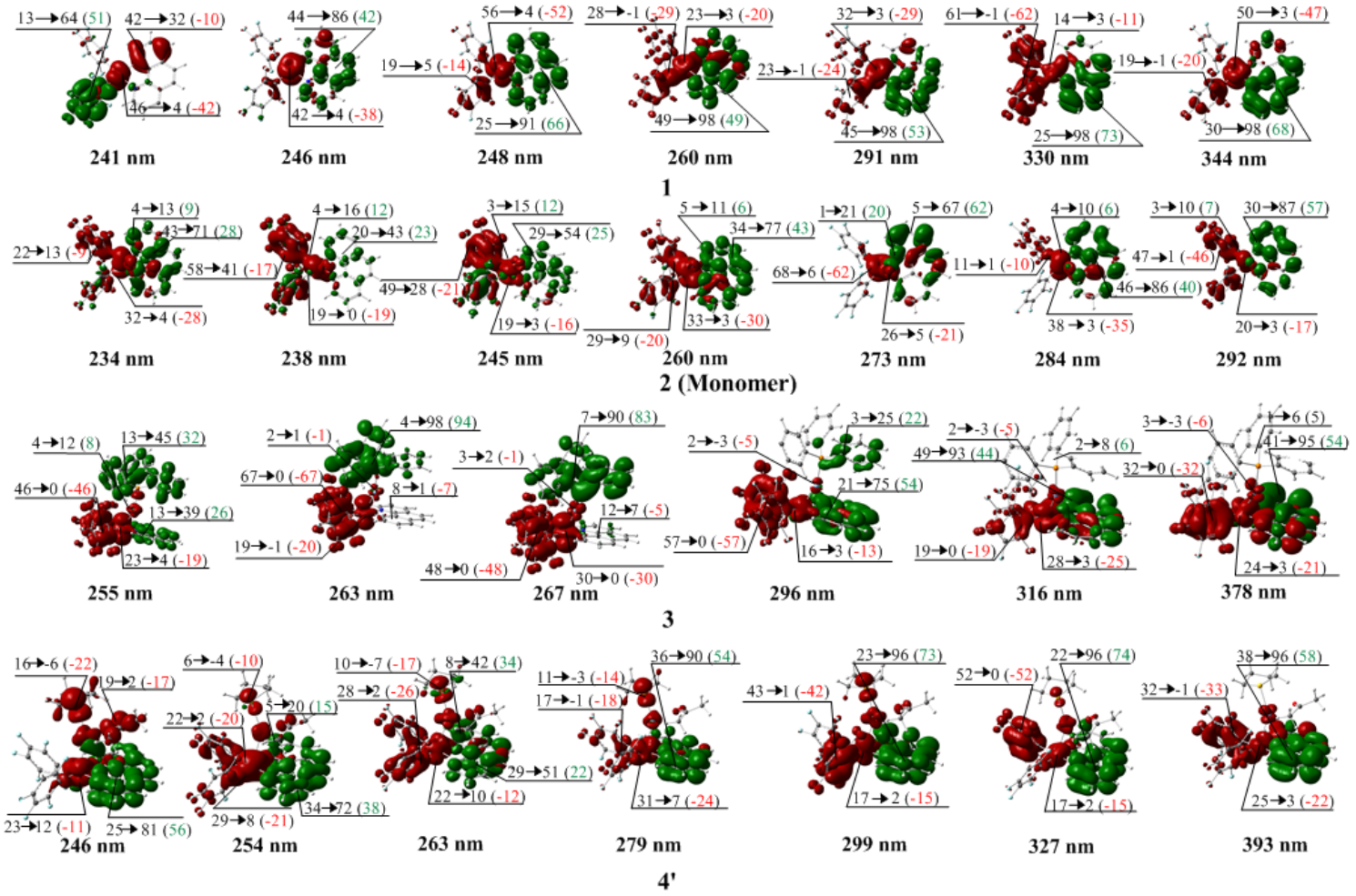

Figure S9. Electron density difference maps corresponding to electronic transitions in the absorption spectra of DCSs **1-3** and **4'** along with the respective % percentage changes in the group charge density (negative sign means % charge depletion). Green and red colors show the regions of increased and decreased electron density, respectively.

X-ray structure determination of 3 and 5

Crystal data and other details of the structure analyses are presented in Table S1. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes in 3 mL ofCH_2Cl_2. Crystals were mounted at the end of a quartz fibre. The radiation used in all cases was graphite monochromated $Mo_{K\alpha}$ (λ = 0.71073 Å). For **3**·3CH_2Cl_2, X-ray intensity data were collected on a Bruker Smart Apex diffractometer. The diffraction frames were integrated using the SAINT program[S1] and the reflections corrected from absorption with SADABS.[S2] For **5**, X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.[S3] The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with SHELXL-97.[S4] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of **3**·3CH_2Cl_2, One of the dichloromethane solvent molecules was found to have a chlorine atom (Cl(6) and Cl(6'))disordered over two positions, which were refined with partial occupancy 0.7/0.3. The C–Cl distances for these atoms were constrained to sensible values and a common set of thermal anisotropic displacement parameters was used for the two disordered Cl atoms. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 6.

References

S1 *SAINT Program for X-tay data integration version 5.0*, Briker Analytical X-ray Systems, Madison, WI, 2000.

S2 G. M. Sheldrick, *SADABS Empirical absortion correction program*, University of Göttingen, Göttingen, Germany, 1996.

S3 *CrysAlis RED Program for X-ray CCD camera data reduction*, Oxford Difraction Ltd, Oxford, UK, 2008.

S4 G. M. Sheldrick, *SHELXL-97 Program for crystal structure refinement from diffraction data*, University of Göttingen, Göttingen, Germany, 1997.

Table S1. Crystal data and structure refinement for complexes [{Pt(bzq)(C_6F_5)$_2$}Ag(PPh_3)]·3CH_2Cl_2 (**3**·3CH_2Cl_2) and [Pt(bzq)(C_6F_5)py] (**5**).

	3·3CH_2Cl_2	**5**
Formula	$C_{43}H_{23}AgF_{10}NPPt$·3CH_2Cl_2	$C_{24}H_{13}F_5N_2Pt$
M_t	1332.33	619.45
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a/Å	11.0608(2)	9.4647(2)
b/Å	12.3316(2)	10.2895(3)
c/Å	17.3806(3)	10.5812(2)
α/º	88.838(1)	106.468(2)
β/º	75.595(1)	96.835(2)
γ/º	89.594(1)	92.411(2)
V/Å^3	2295.66(7)	978.06(4)
Z	2	2
D_c/g cm^{-3}	1.927	2.103
T/K	123(1)	100(1)
μ/mm^{-1}	3.931	7.235
F(000)	1288	588
2θ range/º	7.6-50.2	8.0-57.9
Collected reflections	14528	15035
Unique reflections	7951	4516
R_{int}	0.0170	0.0177
R_1, wR_2[a] ($I > 2\sigma(I)$)	0.0245, 0.0706	0.0145, 0.0344
R_1, wR_2[a] (all data)	0.0265, 0.0713	0.0159, 0.0346
GOF (F^2)[b]	1.039	1.049

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. [b] Goodness-of-fit = $[\sum w (F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) for [Pt(bzq)(C_6F_5)py] (**5**)

Pt-C(17)	1.990(2)	Pt-C(1)	2.006(2)
Pt-N(1)	2.0868(19)	Pt-N(2)	2.1167(18)
C(17)-Pt-C(1)	93.37(9)	C(17)-Pt-N(1)	81.96(8)
C(1)-Pt-N(1)	174.84(8)	C(17)-Pt-N(2)	175.18(8)
C(1)-Pt-N(2)	91.24(8)	N(1)-Pt-N(2)	93.49(7)

Table S3. Selected bond lengths (Å) and angles (°) for [{Pt(bzq)(C_6F_5)$_2$}Ag(PPh_3)]·3CH_2Cl_2 (**3**·3CH_2Cl_2)

Pt–C(7)	2.014(3)	Pt–C(23)	2.069(3)
Pt–C(1)	2.070(3)	Pt–N	2.087(3)
Pt–Ag	2.727(1)	Ag–P	2.370(1)
Ag–C(23)	2.387(3)		
C(7)–Pt–C(23)	97.76(13)	C(7)–Pt–C(1)	87.63(13)
C(23)–Pt–C(1)	173.51(12)	C(7)–Pt–N	176.17(12)
C(23)–Pt–N	80.88(12)	C(1)–Pt–N	93.97(12)
C(7)–Pt–Ag	85.14(10)	C(23)–Pt–Ag	57.76(9)
C(1)–Pt–Ag	119.49(9)	N–Pt–Ag	97.07(7)
P–Ag–C(23)	166.21(8)	P–Ag–Pt	146.65(2)
C(23)–Ag–Pt	47.14(8)		

Table S4. Selected principal singlet-singlet optical transitions in the absorption spectra of complexes **1** and **2** in the gas phase calculated at the TD-DFT-PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level**.**

Excitation (% composition)	*E* (eV)	*λ* (nm)	*f*	%CT	Assignment
		$[Pt(bzq)(C_6F_5)_2]^-$ (**1**)			
HOMO→LUMO (84%)	2.847	435.5	0.013	40.0	MLCT/LC
H-2→L (92%)[a]	3.054	406.0	0.013	35.0	MLCT/LL'CT
H[b] →L+1 (48%), H-3→L (39%)	3.414	363.2	0.018	21.6	MLCT/LL'CT
H-3→L (41%), H→L+1 (39%)	3.605	344.0	0.117	20.3	MLCT/L'LCT
H-5→L (59%)	3.756	330.1	0.052	9.0	MLCT/L'LCT
H-7→L (59%)	4.045	306.5	0.022	20.0	MLCT/LC/L'LCT
H-9→L (42%), H-3→L+1 (17%)	4.264	290.7	0.044	10.7	MLCT/LC/LL'CT
H-7→L+1 (38%), H-8→L+1 (19%)	4.763	260.3	0.053	5.3	MLCT/LC/L'LCT
H-3→L+3 (59%)	4.996	248.2	0.085	59.1	MLCT/L'LCT
H-9→L+1 (32%)	5.032	246.4	0.100	26.7	MLCT/LC/L'LCT
H-9→L+1 (16%), H-3→L+2 (16%)	5.052	245.4	0.048	8.9	MLCT/LC
H→L+8 (65%)	5.143	241.1	0.074	37.0	LC/ML'CT
		$[\{Pt(bzq)(C_6F_5)_2\}Ag]$ (**2**)			
HOMO→LUMO (95%)	2.502	495.6	0.0007	12.0 (-71.0)	L'M'CT
H-2→L (44%), H-1→L (38%)	2.682	462.2	0.031	0.9 (-28.0)	L'M'CT
H-5→L (84%)	3.263	380.0	0.016	30.0 (-8.0)	L'MM'CT

H-6→L (81%)	3.302	375.4	0.028	34 (-60.0)	LMM'CT
H-2→L+1 (39%), H-1→L+1 (35%)	3.454	359.0	0.024	3.7 (-2.7)	MLCT/LL'CT
H-4→L+1 (70%)	3.986	311.0	0.014	1.0 (-10.0)	LL'CT/L'M'CT
H-6→L+1 (46%), H-5→L+1 (25%)	4.024	308.1	0.018	14.8 (-1.4)	MLCT/LC
H-3→L+2 (37%), H-1→L+2 (36%)	4.187	296.1	0.026	4.3 (-2.5)	L'LCT/LC/L'M'CT
H-2→L+2 (56%), H-1→L+2 (21%)	4.223	293.6	0.025	3.9 (-2.5)	L'LCT/MLCT/L'M'CT
H-3→L+2 (47%), H-6→L+1 (16%)	4.244	292.2	0.060	6.5 (-2.7)	MLCT/LL'CT/LC
H-8→L+1 (20%), H-5→L+2 (37%)	4.361	284.3	0.035	12.1 (-0.5)	MLCT/LC
H-9→L+1 (61%), H-8→L+1 (23%)	4.545	272.8	0.035	19.2 (-1.5)	MLCT/LC
H-8→L+1 (11%), H-7→L+2 (26%)	4.764	260.3	0.076	12.1 (-54.7)	MLCT/LC/LL'CT
H-5→L+3 (24%)	5.304	233.8	0.265	36.0 (-9.0)	LMMLCT

[a] L = LUMO. [b] H = HOMO

Table S5. Selected principal singlet-singlet optical transitions in the absorption spectra of complexes **3** and **4'** in the gas phase calculated at the TD-DFT-PBE1PBE/Def2-TZVP(M)∪6-31+G(d,p)(X) level.

Excitation (% composition)	*E* (eV)	*λ* (nm)	*f*	%CT	Assignment*
[{Pt(bzq)(C_6F_5)$_2$}Ag(PPh_3)] (**3**)					
HOMO→LUMO (89%)	3.085	402.0	0.006	25.0 (2.0)	MLCT/L'LCT
H-1→L (78%)[a]	3.280	378.1	0.049	21.2 (1.2)	MLCT/L'LCT
H-5→L (51%), H-3→L (31%)	3.549	349.3	0.012	16.5 (0.8)	LC/MLCT
H[b] →L+1 (54%), H-2→L (29%)	3.632	341.4	0.015	10.7 (0.4)	MLCT/L'LCT
H-1→L+1 (56%), H-6→L (25%)	3.760	329.7	0.015	9.5 (0.2)	LC/MLCT/LL'CT
H-6→L (35%), H-1→L+1 (27%)	3.926	315.8	0.087	7.8 (0.2)	L'LCT/MLCT/LC
H-3→L+1 (46%), H-2→L+1 (27%)	4.098	302.5	0.026	1.3 (-0.1)	L'LCT
H-2→L+1 (34%), H→L+2 (17%)	4.182	296.5	0.026	3.6 (-0.6)	L'LCT/MLCT
H-7→L (40%), H-10→L (11%)	4.425	280.2	0.025	4.4 (1.9)	M'L''LCT/LC/MLCT
H-8→L+1 (24%), H-9→L (17%)	4.538	273.2	0.033	5.4 (0.7)	LC/MLCT/LL'CT
H-5→L+2 (34%), H-4→L+2 (16%)	4.637	267.4	0.057	10.6 (-0.3)	LC/L'LCT/ML''CT
H-4→L+4 (27%), H-5→L+4 (15%)	4.868	254.7	0.059	4.2 (-3.3)	L"L'/MM'L'CT
[{Pt(bzq)(C_6F_5)$_2$}Ag(tht)(Me_2CO)] (**4'**)					
HOMO→LUMO (88%)	2.993	414.0	0.008	27.0 (0.0)	MLCT/L'LCT
H-1→L (80%)	3.152	393.3	0.039	22.3 (0.1)	MLCT/L'LCT
H-4→L (34%), H-1→L+1 (30%)	3.792	327.0	0.066	5.6 (0.8)	LC/L'LCT

H-4→L (60%), H-1→L+1 (17%)	3.802	326.1	0.047	8.0 (0.1)	L'LCT/LC
H-2→L+1 (34%), H-7→L (23%)	4.154	298.5	0.022	4.5 (1.9)	L'LCT/LC/L''LCT
H-9→L (28%), H-6→L+1 (14%)	4.331	286.3	0.027	7.0 (1.3)	L'LMLCT
H-10→L (42%), H-1→L+3 (15%)	4.443	279.0	0.029	9.0 (0.5)	LC/MLCT
H-7→L+1 (31%), H→L+4 (24%)	4.721	262.6	0.048	3.5 (-5.5)	LC/L''LCT/ML'M'CT
H-9,-10→L+1 (21%)	4.882	254.0	0.152	4.7 (-2.7)	L"LMLCT
H-6→L+3 (33%), H-11→L (23%)	5.048	245.6	0.047	2.9 (1.8)	L''LMM'LCT/L'''L''M'LCT

* L = bzq; L' = C_6F_5; L'' = PPh_3 or tht; L''' = Acet

[a] L = LUMO. [b] H = HOMO

Table S6. Partial molecular orbital compositions of **1** calculated by TD-DFT

MO	Energy (eV)	Composition(%)			Orbital Assignment
		%Pt	%bzq	%Arfs	
L+8	2.73	6.0	18.0	76.0	$d_{x^2-y^2}$(Pt) – π*(bzq) – π*(Arfs)
L+4	2.16	26.0	51.0	23.0	d_{xy}(Pt) – π*(bzq) – π*(Arfs)
L+3	2.01	5.0	94.1	1.0	π*(bzq)
L+2	1.95	14.2	77.3	8.5	π*(bzq)
L+1	1.11	3.0	97.0	0.0	d_{xz}(Pt) – π*(bzq)
LUMO	0.47	3.0	97.0	0.0	d_{xz}(Pt) – π*(bzq)
HOMO	-3.27	43.0	46.0	11.0	d_{yz}(Pt) – π*(bzq)
H-2	-3.39	38.0	14.0	48.0	$d_{x^2-y^2}$(Pt) – π*(bzq) – π*(Arfs)
H-3	-3.87	64.0	16.0	20.0	d_{yz}(Pt) – π*(bzq) – π*(Arfs)
H-5	-4.09	12.0	23.0	65.0	d_{yz}(Pt) – π*(bzq) – π*(Arfs)
H-7	-4.46	23.0	66.0	11.0	d_{xz}(Pt) – π*(bzq) – π*(Arfs)
H-8	-4.57	19.0	37.0	44.0	d_{xz}(Pt) – π*(bzq) – π*(Arfs)
H-9	-4.65	29.7	62.4	7.9	d_{yz}(Pt) – π*(bzq) – π*(Arfs)

Table S7. Partial molecular orbital compositions of **2** calculated by TD-DFT

MO	Energy (eV)	% Composition				Orbital Assignment
		%Pt	%Ag	%bzq	%Arfs	
L+4	-0.66	1.0	20.2	29.3	49.5	d_{yz}(Ag) – π*(bzq) – π*(Arfs)
L+3	-1.25	5.0	11.0	81.0	3.0	π*(bzq)
L+2	-2.03	3.0	9.1	87.9	0.0	π*(bzq)
L+1	-2.51	2.0	10.0	87.0	1.0	π*(bzq)
LUMO	-3.22	11.0	71.0	17.0	1.0	d_{z^2}(Ag)
HOMO	-6.61	23.0	0.0	4.0	73.0	$d_{x^2-y^2}$(Pt) – π*(Arfs)
H-1	-6.8	10.0	2.0	20.0	68.0	π*(bzq) – π*(Arfs)
H-2	-6.84	14.1	3.0	30.3	52.5	d_{xz}(Pt) – π*(bzq) – π*(Arfs)
H-3	-6.94	6.9	2.0	17.8	73.3	π*(bzq) – π*(Arfs)
H-4	-7.06	1.0	0.0	1.0	98.0	π*(Arfs)
H-5	-7.47	41.0	2.0	56.0	1.0	d_{yz}(Pt) – π*(bzq)
H-6	-7.52	45.0	11.0	43.0	1.0	d_{z^2}(Pt) – π*(bzq)
H-7	-7.87	21.0	7.0	37.0	35.0	d_{yz}(Pt) – π*(bzq) – π*(Arfs)
H-8	-7.97	46.0	5.0	44.0	5.0	d_{yz}(Pt) – π*(bzq)
H-9	-8.04	48.0	7.0	40.0	5.0	d_{xz}(Pt) – π*(bzq)
H-12	-8.04	48.0	7.0	40.0	5.0	$d_{x^2-y^2}$(Pt) – π*(bzq) – π*(Arfs)

Table S8. Partial molecular orbital compositions of **3** calculated by TD-DFT

MO	Energy (eV)	% Composition					Orbital Assignment
		Pt	Ag	Phos	Arfs	bzq	
L+4	-1.24	4.0	20.0	53.0	0.0	23.0	$d_{x^2-y^2}$(Pt) – π*(Phos) – π*(bzq)
L+3	-1.42	0.0	1.0	98.0	0.0	1.0	π*(Phos)
L+2	-1.52	1.0	2.0	93.0	0.0	4.0	π*(Phos)
L+1	-1.82	2.8	2.8	9.3	0.9	84.1	π*(bzq)
LUMO	-2.28	2.8	1.9	5.7	0.0	89.6	π*(bzq)
HOMO	-6.24	27.7	4.0	0.0	56.4	11.9	d_{xy}(Pt) – π*(Arfs) – π*(bzq)
H-1	-6.39	24.0	3.0	1.0	28.0	44.0	$d_{x^2-y^2}$(Pt) – π*(Arfs) – π*(bzq)
H-2	-6.58	2.0	1.0	0.0	94.0	3.0	π*(Arfs)
H-3	-6.65	9.0	2.0	0.0	81.0	8.0	π*(Arfs)
H-4	-6.7	1.0	0.0	0.0	96.0	3.0	π*(Arfs)
H-5	-6.89	63.4	5.0	12.9	0.0	18.8	d_{xz}(Pt) – π*(Phos) – π*(bzq)
H-6	-7.07	31.0	1.0	3.0	5.0	60.0	d_{z^2}(Pt) – π*(bzq)
H-7	-7.31	6.0	11.0	60.0	2.0	21.0	$d_{x^2-y^2}$(Ag) – π*(Phos) – π*(bzq)
H-8	-7.47	27.0	5.0	0.0	16.0	52.0	d_{z^2}(Pt) – π*(Arfs) – π*(bzq)
H-9	-7.61	31.0	7.0	3.0	21.0	38.0	d_{z^2}(Pt) – π*(Arfs) – π*(bzq)
H-10	-7.65	45.0	2.0	5.0	8.0	40.0	$d_{x^2-y^2}$(Pt) – π*(bzq)

Table S9. Partial molecular orbital compositions of **4'** calculated by TD-DFT

MO	Energy (eV)	% Composition						Orbital Assignment
		Pt	Ag	Acet	S-ligand	Arfs	bzq	
L+8	-0.04	10.9	4.0	10.9	17.8	48.5	7.9	d_{xy}(Pt) – π*(Acet) – π*(Arfs) – π*(S-ligand)
L+7	-0.23	3.7	19.3	5.5	27.5	11.9	32.1	d_{xz}(Ag) – π*(S-ligand) – π*(bzq)
L+5	-0.44	6.1	8.7	12.2	19.1	15.7	38.3	π*(Acet) – π*(S-ligand) – π*(Arfs) – π*(S-ligand)
L+4	-0.64	14.9	63.7	2.4	14.9	0.6	3.6	d_{xz}(Pt) – d_{z2}(Ag) – π*(S-ligand)
L+3	-0.97	15.0	10.8	2.5	6.7	0.8	64.2	d_{xy}(Pt) – d_{xz}(Ag) – π*(bzq)
L+1	-1.81	1.0	2.0	0.0	0.0	2.0	95.0	π*(bzq)
LUMO	-2.34	3.0	2.0	0.0	0.0	0.0	95.0	π*(bzq)
HOMO	-6.21	30.0	2.0	0.0	0.0	55.0	13.0	d_{xy}(Pt) – π*(Arfs)
H-1	-6.32	25.3	4.0	0.0	1.0	28.3	41.4	d_{xz}(Pt) – π*(Arfs) – π*(bzq)
H-2	-6.55	2.0	1.0	0.0	0.0	95.0	2.0	π*(Arfs)
H-3	-6.61	16.2	3.0	0.0	0.0	73.7	7.1	d_{yz}(Pt) – π*(Arfs)
H-4	-6.72	1.0	0.0	0.0	1.0	97.0	1.0	π*(Arfs)
H-5	-6.85	54.0	7.0	0.0	5.0	7.0	27.0	d_{z2}(Pt) – π*(bzq)
H-6	-6.90	31.7	11.9	5.0	16.8	5.0	29.7	d_{yz}(Pt) – π*(S-ligand) – π*(bzq)
H-7	-7.25	12.0	15.0	6.0	23.0	3.0	41.0	π*(S-ligand) – π*(bzq)
H-9	-7.52	37.0	6.0	0.0	1.0	15.0	41.0	d_{yz}(Pt) – π*(bzq)
H-10	-7.67	40.6	2.0	1.0	13.9	6.9	35.6	d_{yz}(Pt) – π*(bzq)
H-11	-8.13	4.0	16.0	49.0	17.0	2.0	12.0	π*(Acet) – π*(S-ligand)

Table S10. Cartesian Coordinates of the Stationary Points on the PES of **1-3** and **4'** in their S_0 and T_1 states.

1, S_0

Pt 0.4261111942 -0.0239988367 -0.0142054196
F -1.456852065 -0.9409307559 2.4077391287
F -3.309305245 -2.8619928121 2.5984570043
F -3.8919044418 -4.4443194527 0.4529222979
F -2.5640512564 -4.0648791685 -1.8995724418
F -0.6959048101 -2.1656315734 -2.1166361431
F -0.5186701716 2.2802391259 2.0849524729
F -2.4539412002 4.1312923756 2.0280595762
F -4.0702865987 4.3741285636 -0.1542083949
F -3.720582689 2.7148210642 -2.287512093
F -1.8080145423 0.8398858296 -2.2508135349
N 2.023280803 1.3192802054 -0.1826940025
C -0.9762268853 -1.4449664054 0.1340502435
C -1.6899123846 -1.6845933592 1.3090708069
C -2.6588159772 -2.6739632777 1.4371973515
C -2.9597535986 -3.4825856979 0.3504415748
C -2.2800297589 -3.2842061028 -0.8428209865
C -1.3150967036 -2.2856976689 -0.9278341955
C -1.065168324 1.4466123514 -0.0757478149
C -1.2934074678 2.32850909 0.9778194574
C -2.283699144 3.3063441143 0.9793790546
C -3.1101709211 3.4357697412 -0.1277567084
C -2.9262064543 2.586337429 -1.2102871898
C -1.9225176763 1.6242713089 -1.158866816
C 1.9640907516 2.6388275631 -0.324482711
H 0.9685617679 3.0688694279 -0.3513572848
C 3.1090056289 3.4397579801 -0.4336722875
H 2.9952705191 4.5131836672 -0.5449303672
C 4.3562551102 2.8463870134 -0.3945238182
H 5.261901586 3.4437277348 -0.4753738789
C 4.4511243976 1.4512363784 -0.2496579963
C 5.6873501371 0.7269749659 -0.200423787
H 6.6189922824 1.2831926497 -0.2760190002
C 5.6966263765 -0.6299774878 -0.0625890969
H 6.644218696 -1.1644938528 -0.0269643505
C 4.4825171276 -1.388449679 0.0369735105
C 4.4559030367 -2.7893293903 0.1765779131
H 5.3883170459 -3.3484589325 0.2144809175
C 3.2328883207 -3.4351185888 0.2627056065
H 3.2098669166 -4.5182930335 0.3698060219
C 2.017491502 -2.7270985069 0.2139766904
H 1.0893425624 -3.2891736184 0.2859502609
C 1.9720056159 -1.338710851 0.0750950319
C 3.2436671069 -0.7018463334 -0.0079638308
C 3.2471078307 0.7171228059 -0.1483747712

1, $\mathbf{T_1}$

Pt 0.4516904134 -0.0238557078 -0.045960708
F -1.4557486354 -0.9364979589 2.3626684649
F -3.3234388482 -2.8466524404 2.5413831878
F -3.8898104763 -4.4334162072 0.3961509939
F -2.5333273418 -4.0734198273 -1.9419203505
F -0.6499363803 -2.1851792015 -2.1442972488
F -0.4559625404 2.2685731348 2.0785666348
F -2.4074573493 4.1079891761 2.0745325331
F -4.0866620044 4.3318111528 -0.0594439652
F -3.7898406938 2.6685571715 -2.1973837538
F -1.8615670454 0.8044857684 -2.208331839
N 2.0434229842 1.3378795237 -0.219864021
C -0.9565915187 -1.4540584625 0.0980027807
C -1.6835922526 -1.6836542143 1.2661429414
C -2.659634257 -2.667017141 1.387776878
C -2.9523262978 -3.4780243679 0.3002632177
C -2.2581173132 -3.2897409563 -0.8864613251
C -1.2870882428 -2.2964817901 -0.9640907232
C -1.0602223618 1.4363257702 -0.0634761719
C -1.2596173859 2.3165679907 0.9959330775
C -2.2588328772 3.2843342 1.0233888492
C -3.1184837175 3.4030314805 -0.0599950378
C -2.9621564244 2.5519859922 -1.1454106832
C -1.9510404546 1.5969778688 -1.1199886245
C 1.9788474975 2.6905555024 -0.39262885
H 0.9850986049 3.1175225335 -0.4392680042
C 3.1261848486 3.4685454552 -0.5003298975
H 3.0162045927 4.5411360291 -0.6337335028
C 4.3869695924 2.8889982361 -0.437617142
H 5.28955026 3.488062628 -0.5195044463
C 4.4865588636 1.4680716318 -0.2647904264
C 5.6754201757 0.7433260016 -0.1903497207
H 6.6198058644 1.2777525195 -0.2643605837
C 5.6874697857 -0.6779183481 -0.0236514081
H 6.6355743398 -1.2075308776 0.0238256845
C 4.4889431048 -1.3789781581 0.0711710769
C 4.408009531 -2.8041300456 0.2328272169
H 5.329909834 -3.3790577117 0.2924776153
C 3.17649768 -3.4433522312 0.3144087785
H 3.143847472 -4.5238079702 0.4375623347
C 1.9837760364 -2.7198854399 0.2457359702
H 1.0359299533 -3.2439994716 0.3229679348
C 1.9826921645 -1.2918506809 0.0711114367
C 3.2509985471 -0.6724349364 0.0006045338
C 3.249430273 0.7465103796 -0.1642777077

2, S_0

Pt 0.2699999271 0.1370473863 -0.2182779012
Ag 1.1665317456 -0.9500080295 2.0287383591
F -1.0553199179 1.789712889 2.1968466335
F -3.1371234245 3.4765292859 2.3345589801
F -4.5563203264 4.10098786 0.0948001662
F -3.8600083546 3.0048959112 -2.2988191943
F -1.7855604183 1.3036988734 -2.4590087966
F -1.4586528798 -1.4100626786 2.1031482707
F -3.2278341437 -3.3998466005 1.9026292266
F -3.7785153301 -4.536768356 -0.5184091816
F -2.5001488494 -3.6316834874 -2.7471799912
F -0.7261855051 -1.6330381578 -2.5808734557
N 1.7348557421 1.6467290566 -0.298504814
C -1.3341925847 1.4563894729 -0.1399755262
C -1.7312084038 2.05077858 1.0528263867
C -2.8009014007 2.9328801515 1.1594976242
C -3.5275601939 3.2545890749 0.0198515408
C -3.1684043578 2.6921784188 -1.1989995067
C -2.0907938916 1.8139017845 -1.2506451808
C -1.032652874 -1.3964063694 -0.242505747
C -1.7061685724 -1.9101392184 0.8593708314
C -2.6247478643 -2.9511294695 0.7982671683
C -2.9037190397 -3.5344436384 -0.4300135496
C -2.2489955712 -3.0682961812 -1.5639876888
C -1.3348607404 -2.026542794 -1.4515433195
C 1.5377746148 2.9601269403 -0.2962174859
H 0.5089857957 3.2884071639 -0.1913484813
C 2.5904167579 3.8770467235 -0.4282113315
H 2.370785006 4.9390610331 -0.4158170766
C 3.8797221781 3.4101308308 -0.5816690718
H 4.7115870107 4.1005344032 -0.6960288727
C 4.1165968836 2.0218463895 -0.5954543037
C 5.4083853043 1.4274927314 -0.7708864081
H 6.2678939312 2.0805410448 -0.8960100757
C 5.5592787755 0.0725851856 -0.7933571938
H 6.5448720084 -0.3622129129 -0.9400788224
C 4.4389553098 -0.8081050386 -0.629351489
C 4.5550002078 -2.2163398926 -0.6504078369
H 5.5317341737 -2.6702244947 -0.7971324263
C 3.4328511411 -3.0043444026 -0.4883568452
H 3.5285539997 -4.0868186102 -0.5119712701
C 2.1573822548 -2.4287175546 -0.2961296089
H 1.2947780221 -3.0859764521 -0.2079383057
C 1.9746802917 -1.0404809824 -0.2748218914
C 3.155046143 -0.2519059171 -0.4371222198
C 3.0041654198 1.1681170476 -0.4397483179

2, $\mathbf{T_1}$

Pt 0.2332248083 0.126696245 -0.5243251492
Ag 1.0876045906 -0.4547739781 2.1887082785
F -0.2580270166 2.115925979 2.0626821892
F -2.2726689663 3.7657727737 2.6517969872
F -4.3934355995 4.0210663337 0.9653100013
F -4.4627078391 2.5858240654 -1.3472727902
F -2.461944678 0.9186324418 -1.9682500883
F -1.8477125524 -1.2482667504 1.5824307471
F -3.5429911811 -3.2910076265 1.2646073329
F -3.6917388336 -4.6048671337 -1.1132905528
F -2.1036201541 -3.8420310824 -3.1865024214
F -0.3927832571 -1.7965011598 -2.8985859725
N 1.6799706261 1.6686547881 -0.6228725076
C -1.2779646354 1.4273194695 0.0265673145
C -1.2812482653 2.187785917 1.1899458231
C -2.3150437999 3.0553881162 1.5236357226
C -3.3996890217 3.1882773666 0.66584844
C -3.431929247 2.4532201285 -0.5123690983
C -2.3825185755 1.5894180391 -0.8077692139
C -1.0438656994 -1.4224061717 -0.6492443215
C -1.8780138118 -1.8541886285 0.3821018951
C -2.7671491855 -2.9137093401 0.2469826608
C -2.8455563041 -3.5885169977 -0.965532061
C -2.0319748923 -3.1954003874 -2.0219654378
C -1.1553347883 -2.1325400956 -1.8466351538
C 1.488479239 2.9716199385 -0.8197987466
H 0.4568110088 3.3035583897 -0.8743568503
C 2.5498372852 3.871024642 -0.9543937865
H 2.3347172138 4.9223286352 -1.1108540051
C 3.8530735766 3.4032297313 -0.8984047319
H 4.6924232743 4.0839549955 -1.0134701314
C 4.0856991507 2.032191165 -0.7008811124
C 5.383214664 1.423125149 -0.6610446267
H 6.2580924682 2.0568858144 -0.7777656718
C 5.5219952228 0.0767370152 -0.4993075443
H 6.5125955904 -0.3708172126 -0.4923490927
C 4.3832186489 -0.7824237787 -0.3358299541
C 4.4773091558 -2.1788746893 -0.1845297463
H 5.4554691595 -2.6521671425 -0.179831334
C 3.3248738433 -2.9503966395 -0.0597693844
H 3.4099240553 -4.0303539665 0.0237193549
C 2.0558372493 -2.3655443761 -0.0135507659
H 1.18155837 -2.994959075 0.1185761374
C 1.9086266555 -0.972460312 -0.1419331533
C 3.0957382285 -0.1977883373 -0.3407994809
C 2.9585822191 1.1940747424 -0.5556959981

3, S_0

Pt -1.558396 0.74168 -0.378154
Ag 1.100678 0.290902 -0.312576
P 3.138504 -0.614357 0.520676
F -4.713412 -0.00471 -0.506431
F -6.398488 -1.087253 1.281334
F -5.522507 -1.750384 3.772916
F -2.920393 -1.303418 4.456716
F -1.224819 -0.205661 2.696037
F -2.743324 0.054924 -3.209519
F -2.938638 -2.229037 -4.588614
F -1.957201 -4.554942 -3.559924
F -0.776857 -4.54898 -1.103182
F -0.571421 -2.28188 0.301924
N -1.449113 2.629699 0.546486
C -2.887212 -0.063469 1.001742
C -4.224566 -0.313426 0.70986
C -5.121293 -0.873003 1.61409
C -4.679965 -1.213231 2.886956
C -3.354321 -0.982195 3.230457
C -2.500835 -0.417493 2.289376
C -1.639968 -0.994834 -1.388905
C -2.238244 -1.056283 -2.649123
C -2.356789 -2.230259 -3.385338
C -1.861397 -3.418581 -2.86446
C -1.261743 -3.410245 -1.612464
C -1.167161 -2.214998 -0.907771
C -2.05804 3.014872 1.662329
H -2.645406 2.258554 2.171411
C -1.963201 4.322319 2.158585
H -2.48069 4.578093 3.076844
C -1.223713 5.257734 1.463801
H -1.142952 6.281324 1.821089
C -0.574048 4.87978 0.273758
C 0.196682 5.773224 -0.539261
H 0.300647 6.806898 -0.220013
C 0.774508 5.343454 -1.696656
H 1.342835 6.03772 -2.311119
C 0.646757 3.984673 -2.13943
C 1.216511 3.510269 -3.340788
H 1.78522 4.190512 -3.969897
C 1.038523 2.191636 -3.711309
H 1.469376 1.83267 -4.642647
C 0.304373 1.297857 -2.902943
H 0.173335 0.274815 -3.248284
C -0.279443 1.701768 -1.697745
C -0.087185 3.072768 -1.346426
C -0.708071 3.539372 -0.148163
C 4.644612 0.128622 -0.203205
C 4.62847 1.495092 -0.509529
H 3.724276 2.0774 -0.344543
C 5.76128 2.110835 -1.034105
H 5.738804 3.171377 -1.267763
C 6.914101 1.363585 -1.273386
H 7.794891 1.841959 -1.692323
C 6.931007 0.000159 -0.985851
H 7.823831 -0.587462 -1.180157
C 5.801763 -0.617832 -0.451254
H 5.81884 -1.682734 -0.235886
C 3.303898 -2.411412 0.241736
C 2.822325 -2.945051 -0.959652
H 2.342239 -2.295679 -1.68868
C 2.939495 -4.306919 -1.219615
H 2.551251 -4.71429 -2.148386
C 3.529449 -5.147662 -0.276729

H 3.607216 -6.213063 -0.473453
C 4.001395 -4.623912 0.925169
H 4.450274 -5.278572 1.666811
C 3.889745 -3.259782 1.187428
H 4.246476 -2.858972 2.132367
C 3.308805 -0.39272 2.326157
C 4.52795 -0.071964 2.932811
H 5.416925 0.078284 2.326366
C 4.602042 0.063379 4.318257
H 5.550748 0.316098 4.783494
C 3.464897 -0.122838 5.102286
H 3.52568 -0.015641 6.181693
C 2.247018 -0.438066 4.500222
H 1.354045 -0.575462 5.102978
C 2.164665 -0.565645 3.116507
H 1.206494 -0.795199 2.655759

3, $\mathbf{T_1}$

Pt -1.3994 0.6274 -0.1257
Ag 1.3241 0.4674 -0.5443
P 3.3228 -0.5227 0.3576
F -4.6111 0.5737 -0.6355
F -6.6686 -0.0755 0.9600
F -6.2277 -0.8460 3.5312
F -3.6812 -0.9491 4.4987
F -1.6078 -0.2790 2.9292
F -2.8178 -0.5556 -2.7589
F -2.9533 -3.0309 -3.7509
F -1.7140 -5.1004 -2.4873
F -0.3354 -4.6396 -0.1797
F -0.1882 -2.1774 0.8425
N -1.3157 2.5858 0.6231
C -3.0207 0.1577 1.0700
C -4.3360 0.1983 0.6220
C -5.4198 -0.1321 1.4295
C -5.2000 -0.5253 2.7440
C -3.9011 -0.5763 3.2332
C -2.8478 -0.2313 2.3936
C -1.4838 -1.2341 -0.9135
C -2.1862 -1.5281 -2.0843
C -2.2738 -2.8080 -2.6225
C -1.6460 -3.8678 -1.9806
C -0.9444 -3.6286 -0.8069
C -0.8833 -2.3347 -0.3031
C -1.7931 3.0622 1.7729
H -2.2722 2.3426 2.4281
C -1.6959 4.4046 2.1430
H -2.1122 4.7176 3.0940
C -1.0634 5.3147 1.2923
H -0.9733 6.3629 1.5644
C -0.5499 4.8595 0.0765
C 0.1241 5.6816 -0.8815
H 0.2555 6.7372 -0.6571
C 0.5904 5.1642 -2.0568
H 1.0946 5.8087 -2.7729
C 0.4222 3.7759 -2.3825
C 0.8056 3.2144 -3.6092
H 1.2704 3.8469 -4.3614
C 0.5262 1.8476 -3.9105
H 0.7720 1.4595 -4.8944
C -0.0691 1.0301 -2.9780
H -0.2984 0.0010 -3.2397
C -0.3733 1.4985 -1.6466
C -0.2191 2.9436 -1.4309
C -0.7037 3.4791 -0.2437
C 4.8932 0.2587 -0.1558
H 5.7466 -0.2765 0.3174
H 4.9045 1.3217 0.1739
H 4.4111 -2.7007 0.3166
H 3.5246 -2.3607 -1.2270
H 4.2832 -0.9605 2.5516
H 2.4744 -1.0700 2.5731
H 4.9950 0.1961 -1.2624
H 3.2980 0.5605 2.5380
H 2.6054 -2.8483 0.2748
C 3.4773 -2.2789 -0.1180
C 3.3427 -0.4934 2.1828

4', S_0

Pt 3.1608212985 4.3041637359 9.1624459625
Ag 0.4927524451 3.8245920061 8.8497682806
S -1.5106942777 2.6440757033 9.7330328891
F 1.95861535 5.7212732763 11.800185751
F 2.9912304659 6.2661649615 14.2120239081
F 5.5839503786 5.639358578 14.7776545457
F 7.1300631192 4.4425648525 12.8829935578
F 6.1140523043 3.8681837338 10.4653214193
F 1.6533489046 2.4592425245 11.3868286058
F 1.9131100669 -0.1308993838 11.972885322
F 3.6661864526 -1.6999724385 10.5902898508
F 5.1549068353 -0.606922723 8.584896595
F 4.9055895718 1.9811174651 7.963184811
N 3.0860695632 6.3024078835 8.5079923711
O -1.1515316647 5.7081699846 8.1689422384
C 3.987004442 4.7556570569 11.0170753585
C 3.2493579905 5.3695757134 12.0235463246
C 3.7528028119 5.6726349733 13.2836912166
C 5.0725391612 5.3547984454 13.577129382
C 5.8567802653 4.7437453629 12.606341105
C 5.3020592048 4.4601624897 11.3625215599
C 3.267386795 2.3563311609 9.6397304451
C 2.5415040669 1.7455341713 10.6610795782
C 2.6568236608 0.3996751643 10.9927169088
C 3.5435090616 -0.4044101097 10.2901129975
C 4.2967070747 0.1573698302 9.2673333903
C 4.1456759071 1.5063512313 8.9634771134
C 3.4909593012 7.3804220092 9.1705759778
H 3.8620073336 7.2111187326 10.1756724442
C 3.4517695864 8.6660403757 8.6125259645
H 3.7973528607 9.5090756618 9.2012837118
C 2.9879983732 8.8293120184 7.3220225943
H 2.9582215006 9.8137665556 6.8612105456
C 2.5632273606 7.7031875496 6.5921072424
C 2.0921457841 7.7531897522 5.2395184137
H 2.0436503086 8.717848451 4.7409309171
C 1.7317004655 6.6139256123 4.5832364437
H 1.3910399883 6.6659644879 3.5518125048
C 1.7992774667 5.3285040512 5.2165356504
C 1.4560951361 4.128638341 4.5576919265
H 1.1193046278 4.1605005906 3.5245955056
C 1.5636241985 2.9252653489 5.2274054244
H 1.3149302745 2.000787179 4.7115091867
C 1.9985232692 2.8694411981 6.5690609131
H 2.0935651064 1.8952957474 7.0435772147
C 2.3468189116 4.022183513 7.2819723048
C 2.2371582194 5.2484264165 6.5582670903
C 2.6280426559 6.4449917137 7.2311763191
C -1.0549456057 0.8607982518 9.8458685689
H -0.0056278846 0.7497993283 9.5660680765
H -1.172767614 0.5417270774 10.883203858
C -1.9835794235 0.1312204966 8.8782068165
H -1.5512078017 -0.8320223261 8.5882614072
H -2.9453415428 -0.0711866121 9.3649685476
C -2.198767696 1.0556511693 7.6824573711
H -2.9775890827 0.6838291416 7.0078026085
H -1.2707528309 1.1492795314 7.1052035342
C -2.5844951425 2.410979646 8.2603147697
H -3.6244231115 2.4177045293 8.6008852994
H -2.4290134906 3.2500176004 7.5794860578
C -1.2209739992 6.8621099402 8.5671499779
C -0.3365881583 7.3842673128 9.6620188778
H 0.1961319296 6.5750354825 10.1642702101
H -0.9166070509 7.9607992561 10.3903431362

H 0.3980358416 8.073528451 9.2263949726
C -2.2116525048 7.8218503642 7.9648476412
H -2.6673992363 7.3891136228 7.073355728
H -1.7305390191 8.7747647518 7.7206239507
H -2.993930561 8.0419020285 8.701378807

4', T_1

Pt 0.6814545923 -0.2802239264 -0.0357341914
Ag -2.075243675 0.2721639169 -0.2303596499
S -3.471518999 1.8315666511 -1.5881123633
F 2.6020122957 0.940190042 -2.3120709101
F 5.2517410577 0.7230755983 -2.7225573208
F 6.7870183004 -0.7487911213 -1.0221189171
F 5.6389899247 -2.0093089809 1.096381535
F 2.9947459054 -1.8115322933 1.5243466797
F -0.145882678 2.3756654676 -1.6736198659
F 0.1789215928 4.9710403794 -1.1314551986
F 1.4001632562 5.761365391 1.1728364888
F 2.292544964 3.8899056785 2.9391784063
F 1.973730862 1.2823901204 2.4271139634
N 0.4197639212 -2.3069187887 -0.4238880114
O -3.8275579904 -1.5104432028 -0.8959951355
C 2.6951092776 -0.4274053862 -0.3769210021
C 3.3213371439 0.2069675747 -1.4434456813
C 4.6885606824 0.1083238039 -1.6788194128
C 5.4744407848 -0.6429111877 -0.8144794904
C 4.8836232471 -1.2865816774 0.2663067758
C 3.5124725992 -1.1707779637 0.4678595607
C 0.8921500296 1.6958159861 0.356657317
C 0.4674948849 2.6968915083 -0.5162263088
C 0.6253168984 4.054638994 -0.2636253711
C 1.2442873788 4.463586269 0.9102417194
C 1.6951721769 3.5045592262 1.8090668501
C 1.5152117663 2.1565735604 1.5185089471
C 1.0647725452 -3.0838632707 -1.3252057188
H 1.7460725152 -2.5693508138 -1.9954318284
C 0.869414845 -4.4495046818 -1.4104346499
H 1.4177614929 -5.0101811762 -2.1601327773
C -0.030766084 -5.0961133518 -0.5380076086
H -0.1871850682 -6.1695423916 -0.5884952924
C -0.6978363384 -4.3240875716 0.424306286
C -1.6260258725 -4.8403795999 1.3926797748
H -1.8272807236 -5.9093394244 1.3891769035
C -2.2352954721 -4.0341796899 2.3139037117
H -2.9201988477 -4.4608427724 3.0430875726
C -1.9676015457 -2.6288495222 2.3584514248
C -2.4929491023 -1.7583066877 3.3256076599
H -3.1600201234 -2.155858772 4.0873410061
C -2.1461598812 -0.4024121231 3.3471974627
H -2.5358138394 0.2426183963 4.1291122974
C -1.2760043673 0.1270437655 2.3859197624
H -0.9879805702 1.173525122 2.4445830917
C -0.7420162328 -0.6875363314 1.3593509232
C -1.0613343898 -2.1011820125 1.3986973471
C -0.4414343193 -2.9312905226 0.4619642422
C -3.2825183785 3.5183780937 -0.8693814857
H -2.600777775 3.4652118285 -0.0180666006
H -2.8406966352 4.1660446955 -1.6288950122
C -4.6855191387 3.9447775017 -0.4463881645
H -4.633079212 4.7434382286 0.3008390956
H -5.2327040397 4.3372487356 -1.3120166466
C -5.3879442778 2.6975151248 0.0843984255
H -6.454321033 2.8696398453 0.2657509491
H -4.9344583791 2.3849076012 1.0330581583
C -5.1876863998 1.6138976295 -0.9677435339
H -5.8642896577 1.7512745793 -1.816387673
H -5.2941436263 0.5950142532 -0.5908626839
C -3.6082036756 -2.5688465371 -1.4727422639
C -2.484414735 -2.7244730049 -2.4542982943
H -1.8252735166 -1.8542982876 -2.4367201679
H -2.905161545 -2.8393516077 -3.4611891962

H -1.9057747504 -3.6305609685 -2.2424361396
C -4.4667001429 -3.7746562876 -1.2120932353
H -5.388464882 -3.4852443235 -0.7054377072
H -3.9035055015 -4.4549876612 -0.5609604609
H -4.6870475189 -4.3182716463 -2.1358483664

Table S11. Energetic Results[a]

Energetic Parameter (Hartree)	**1**, S_0	**1**, T_1	**2**, S_0	**2**, T_1	**3**, S_0	**4'**, S_0	**4'**, T_1
Zero-point correction	0.272937	0.268085	0.274813	0.273562	0.551817	0.475809	0.473080
Thermal correction to Energy	0.303661	0.299449	0.307737	0.306912	0.602637	0.523066	0.520496
Thermal correction to Enthalpy	0.304605	0.300394	0.308681	0.307857	0.603582	0.524011	0.521440
Thermal correction to Gibbs Free Energy	0.208318	0.201658	0.205785	0.20326	0.457053	0.385456	0.382121
Sum of electronic and zero-point Energies	-2127.802901	-2127.718810	-2274.700953	-2274.626621	-3309.845605	-3022.595063	-3022.509020
Sum of electronic and thermal Energies	-2127.772178	-2127.687446	-2274.668029	-2274.593271	-3309.794785	-3022.547806	-3022.461604
Sum of electronic and thermal Enthalpies	-2127.771233	-2127.686502	-2274.667085	-2274.592327	-3309.793841	-3022.546862	-3022.460660
Sum of electronic and thermal Free Energies	-2127.867520	-2127.785237	-2274.769981	-2274.696924	-3309.940369	-3022.685416	-3022.599979

[a] Frequencies calculation for the T_1 state of **3** has not been completed due to its very large size.