Complexes *trans*-Pt(BODIPY)X(PEt_3)$_2$: Excitation Energy-Dependent Modulation of Fluorescence and Phosphorescence Emissions and Application to Oxygen Sensing and Photocatalysis

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NMR Spectra

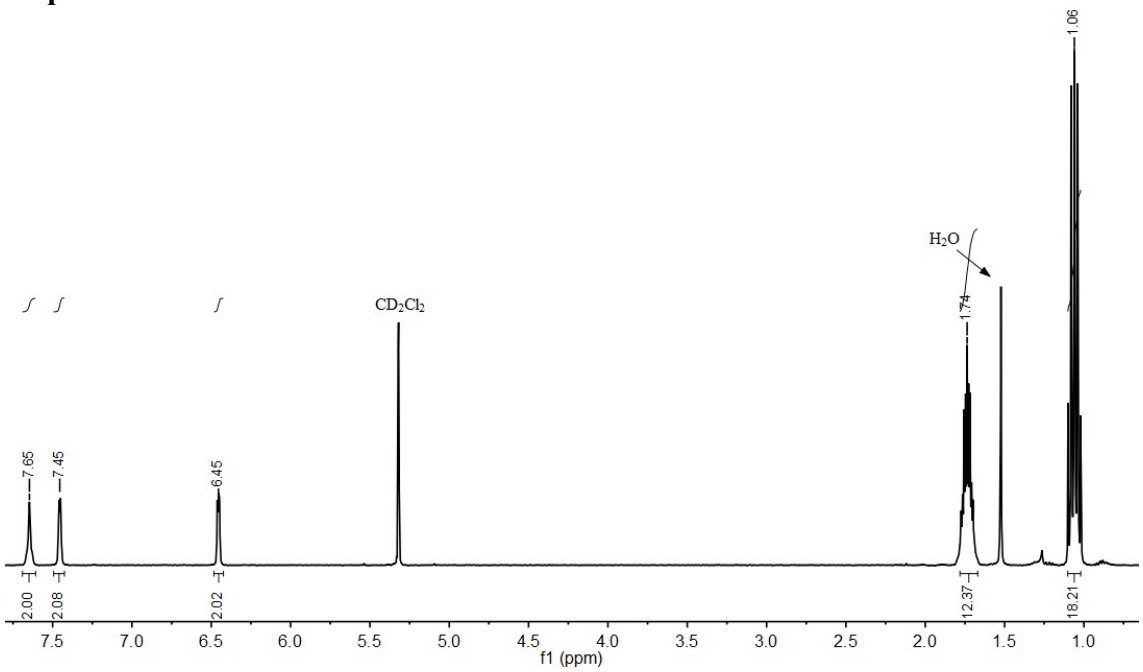

Figure S1: ^{1}H NMR spectrum of **Pt-Cl** in CD_2Cl_2.

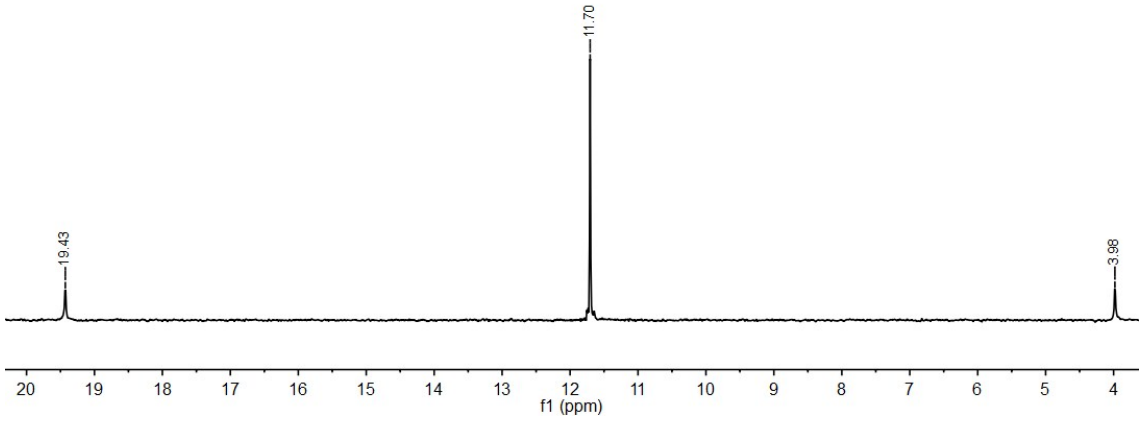

Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of **Pt-Cl** in CD_2Cl_2.

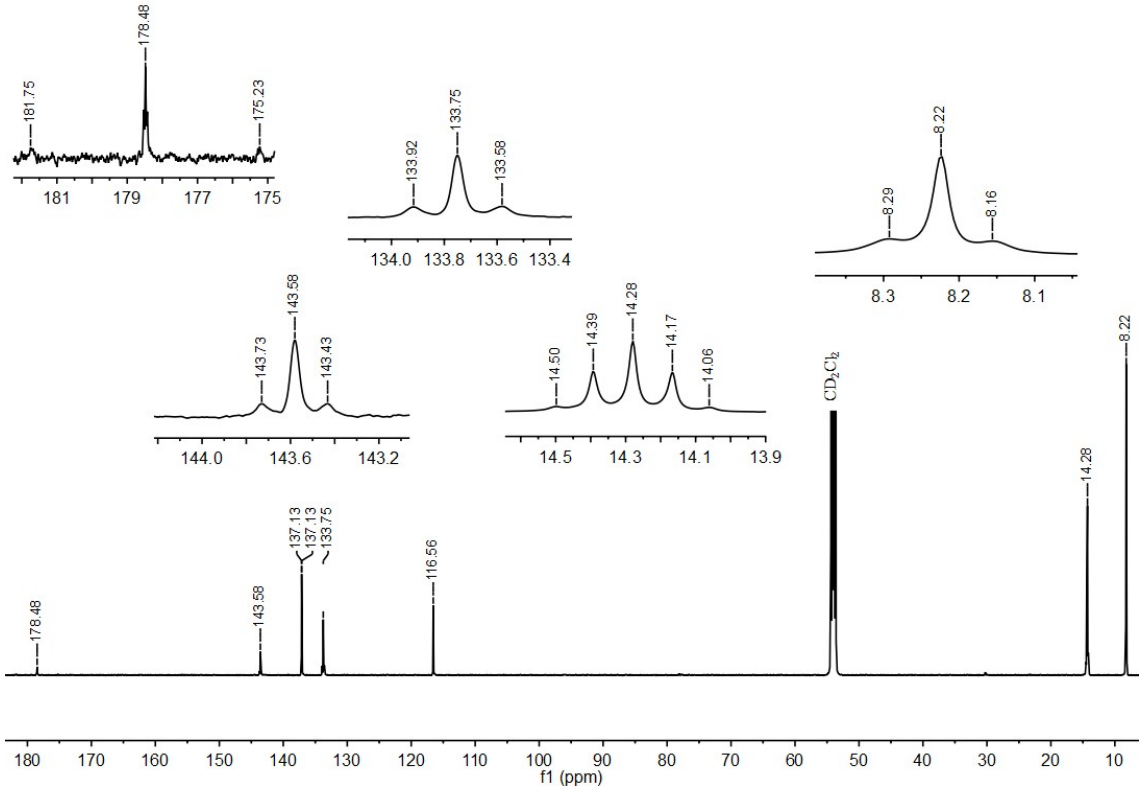

Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-Cl** in CD_2Cl_2.

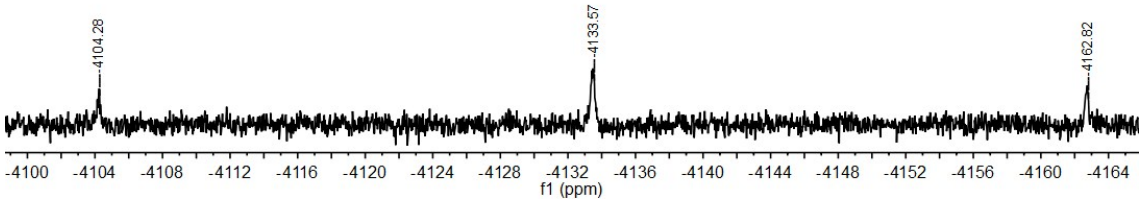

Figure S4: $^{195}Pt\{^{1}H\}$ NMR spectrum of **Pt-Cl** in CD_2Cl_2.

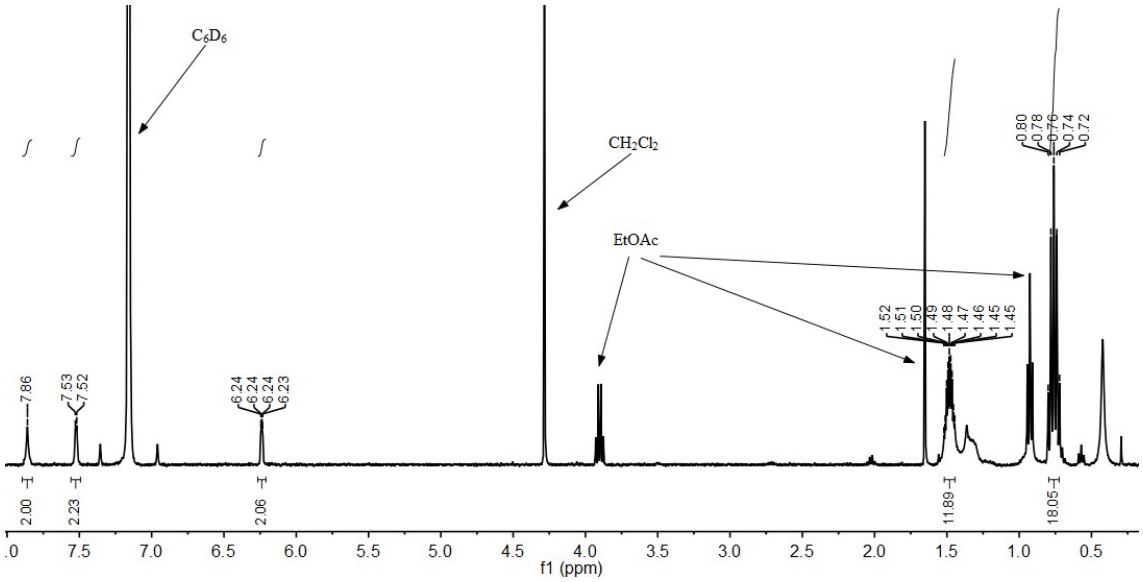

Figure S5: ^{1}H NMR spectrum of **Pt-Cl** in C_6D_6.

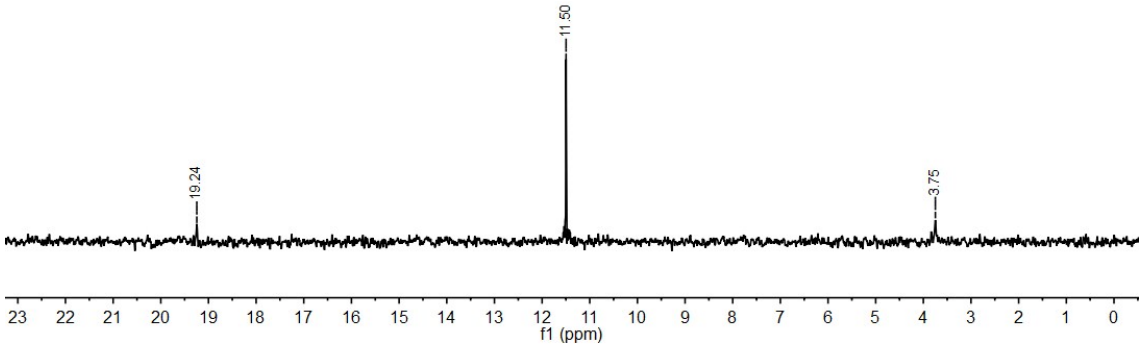

Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of **Pt-Cl** in C_6D_6.

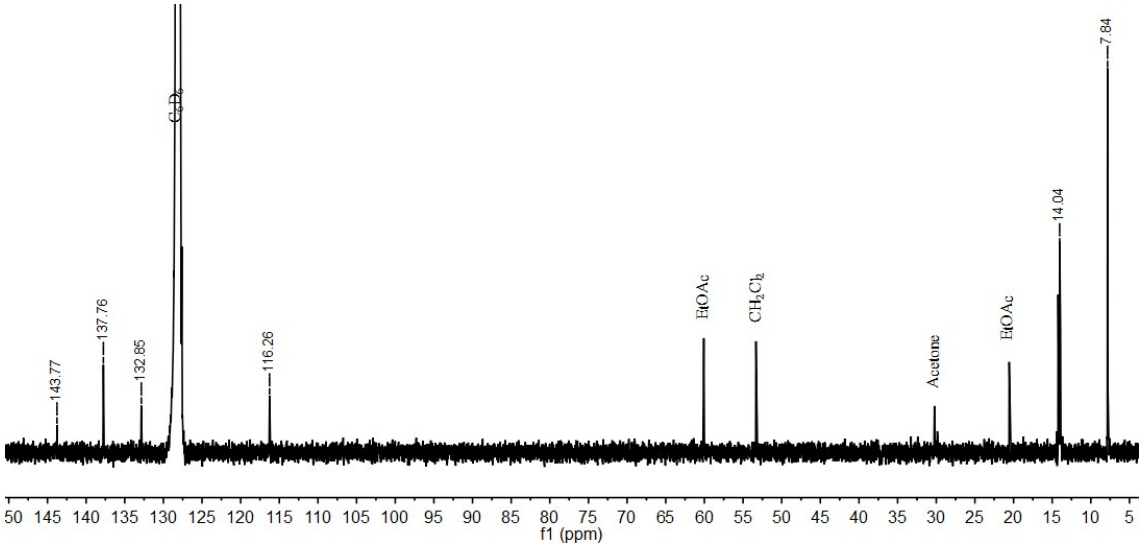

Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-Cl** in C_6D_6.

Pt-Cl: ^{1}H NMR (600 MHz, C_6D_6): δ 7.86 (br s, 2H, H5, H9), 7.52 (d, 2H, $^{3}J_{HH}$ = 3.56 Hz, H3, H7), 6.24 (dd, 2H, $^{3}J_{HH}$ = 3.56 Hz, $^{3}J_{HH}$ = 1.56 Hz, H3, H8), 1.48 (m, 12H, P-CH_2-), 0.76 (m, 18H, P-CH_2-CH_3). ^{31}P NMR (161.9 MHz, C_6D_6): δ 11.50 ppm (s, with satellites J_{PtP} = 2508 Hz). ^{13}C NMR (150.9 MHz, C_6D_6): δ 143.77 (s, C2, C6), 137.76 (s, C5, C9), 132.85 (s, C3, C7), 116.26 (s, C3, C7), 14.04 (t, J_{PC} = 17.1 Hz, P-CH_2-), 7.84 (br s, P-CH_2-CH_3), C1 was not detected due to a low signal to noise ratio.

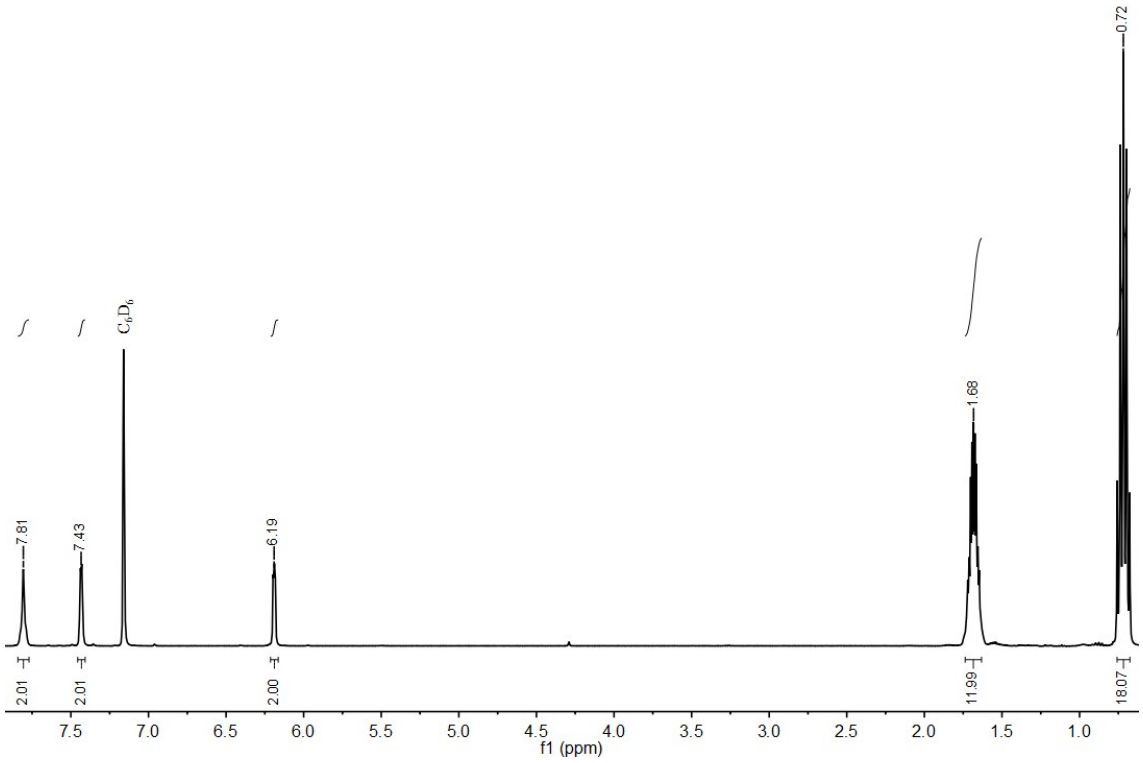

Figure S8: ^{1}H NMR spectrum of **Pt-I** in C_6D_6.

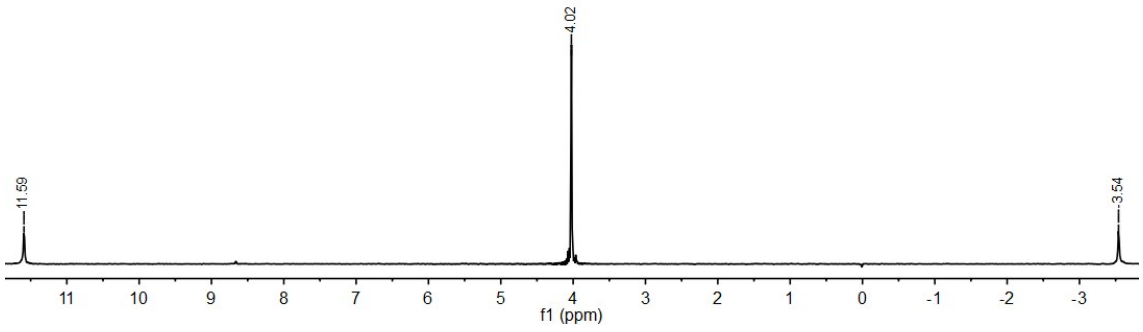

Figure S9: ^{31}P{^{1}H} NMR spectrum of **Pt-I** in C_6D_6.

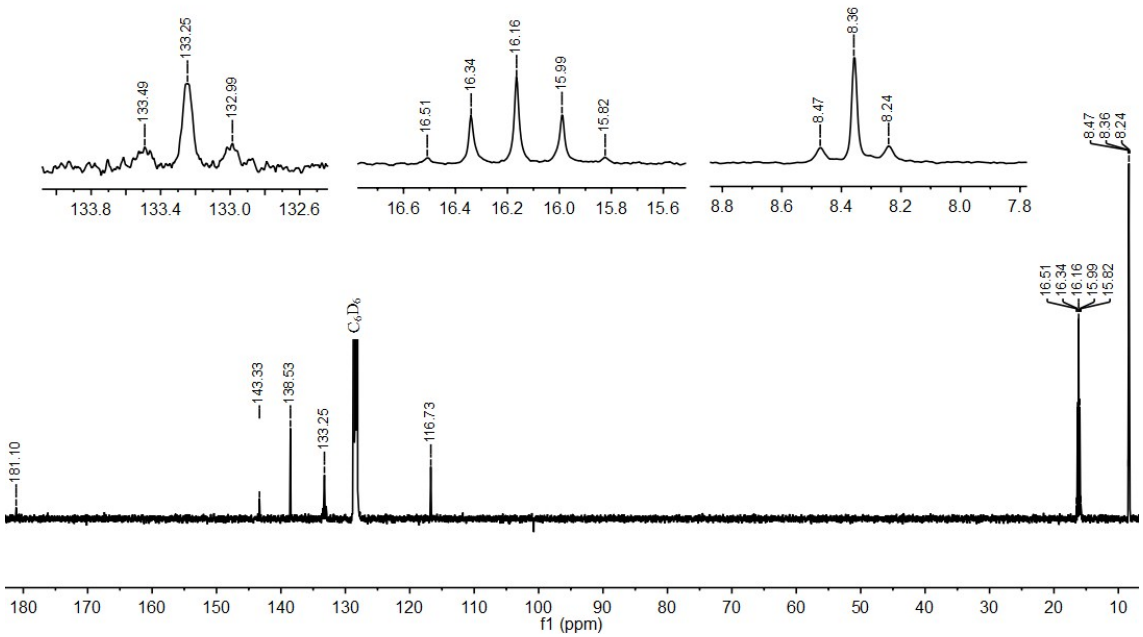

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-I** in C_6D_6.

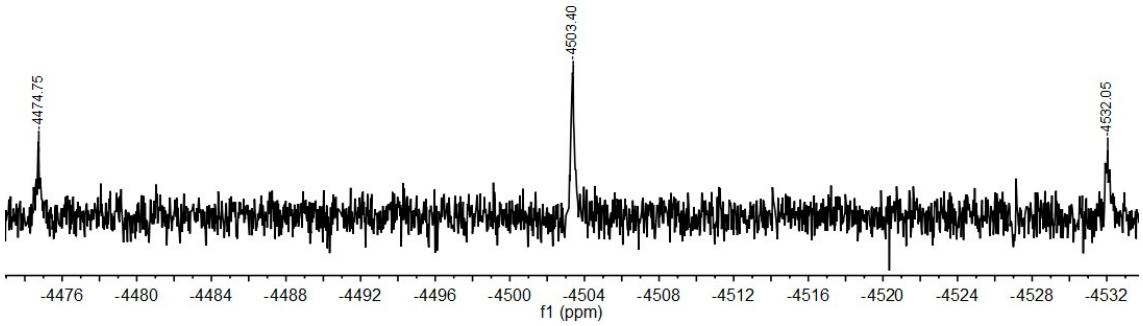

Figure S11: $^{195}Pt\{^{1}H\}$ NMR spectrum of **Pt-I** in C_6D_6.

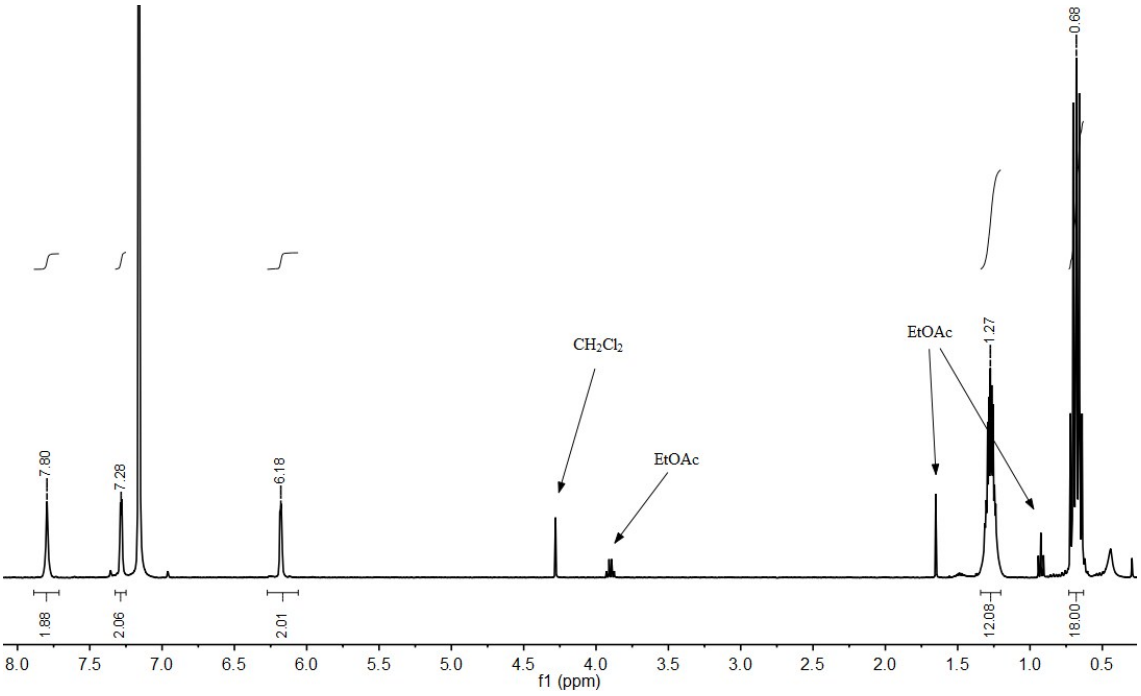

Figure S12: ^{1}H NMR spectrum of **Pt-NCS** in C_6D_6.

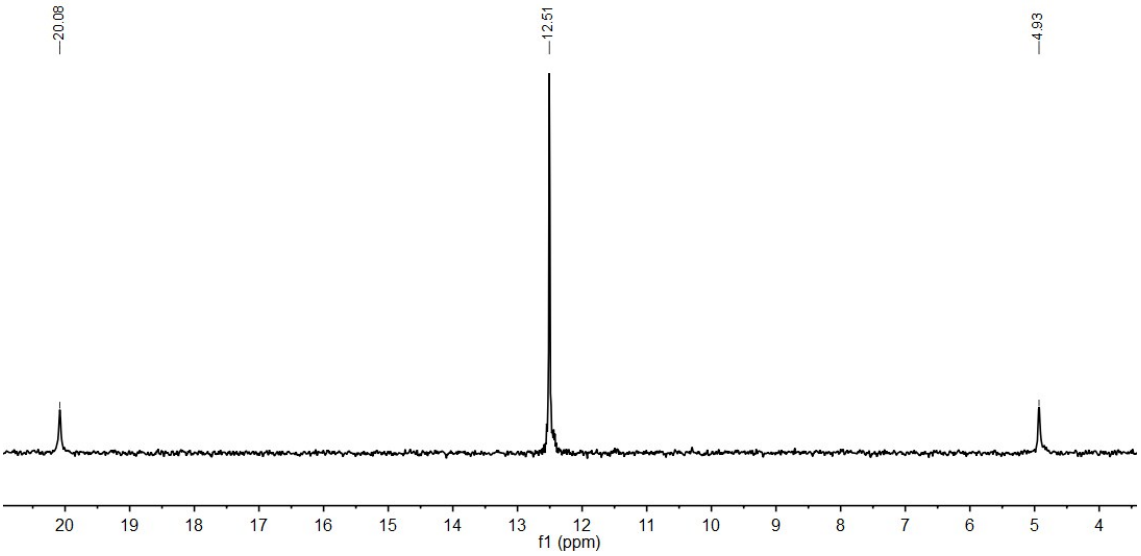

Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of **Pt-NCS** in C_6D_6.

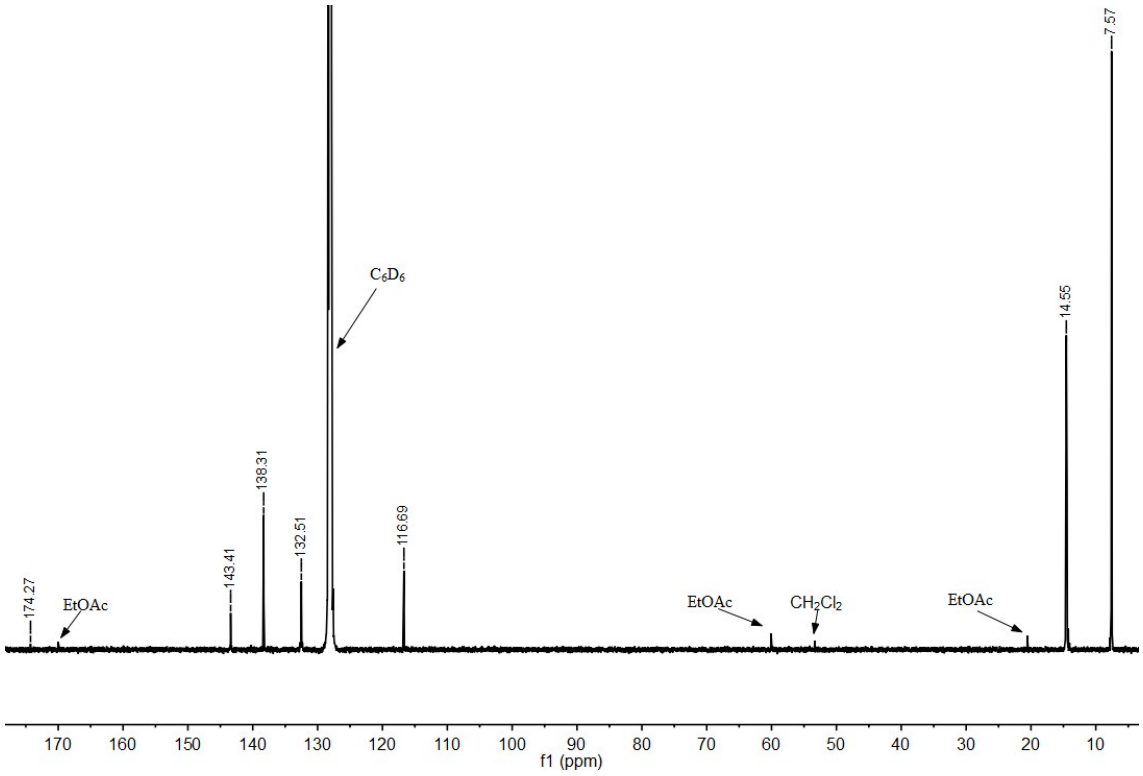

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-NCS** in C_6D_6.

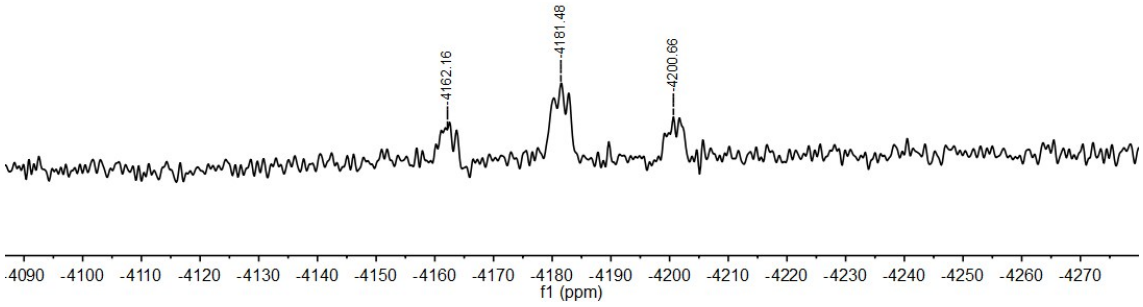

Figure S15: $^{195}Pt\{^{1}H\}$ NMR spectrum of **Pt-NCS** in C_6D_6.

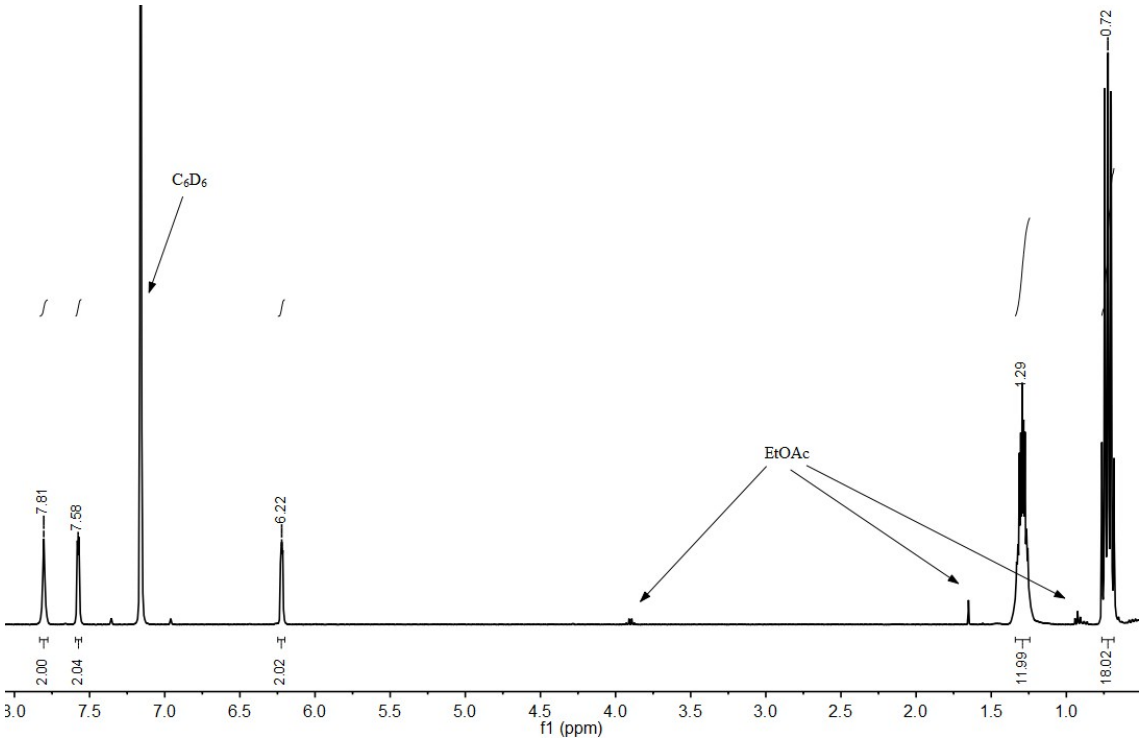

Figure S16: ^{1}H NMR spectrum of **Pt-NO_2** in C_6D_6.

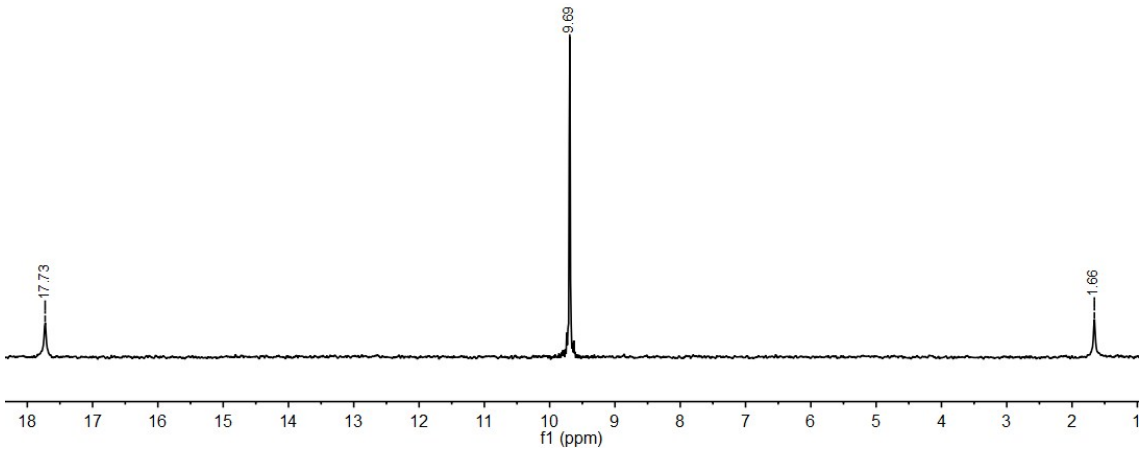

Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of **Pt-NO_2** in C_6D_6.

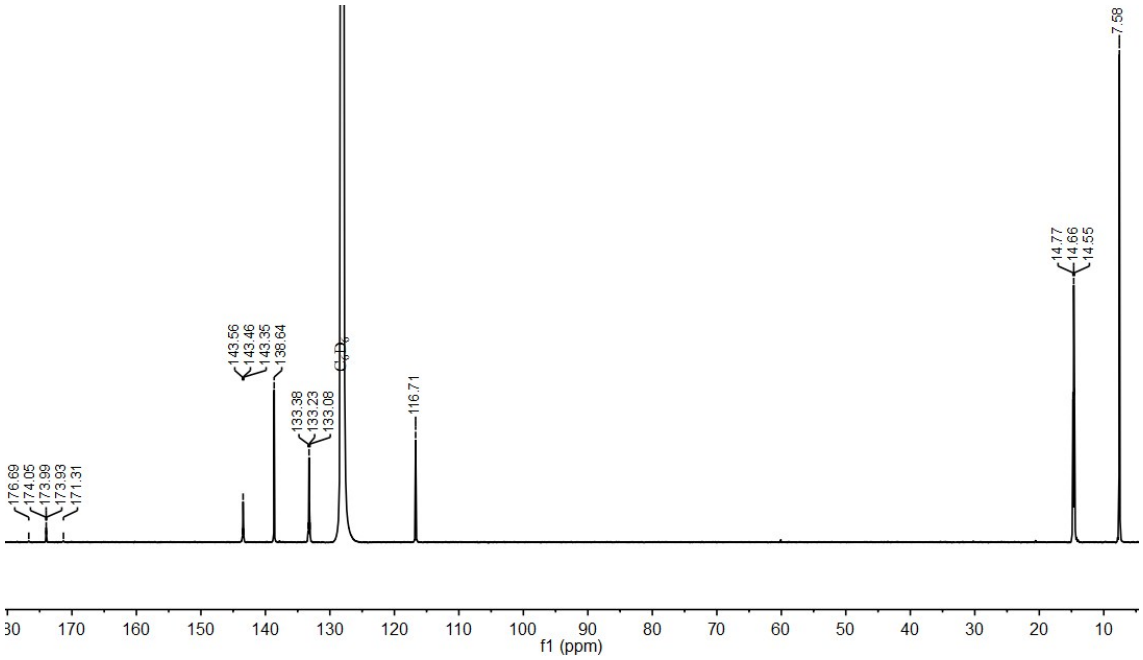

Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-NO$_2$** in C_6D_6.

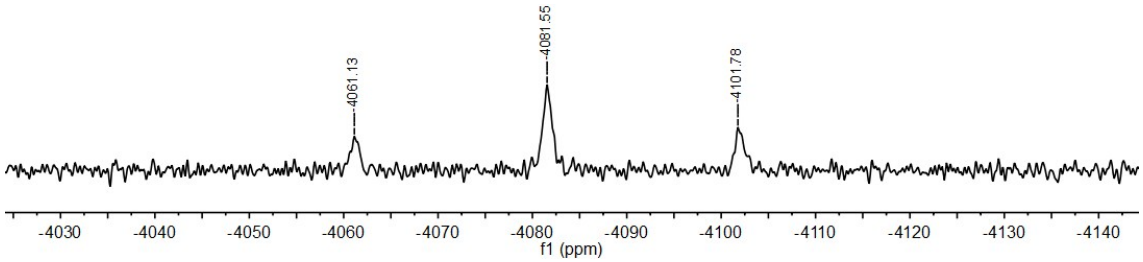

Figure S19: $^{195}Pt\{^{1}H\}$ NMR spectrum of **Pt-NO$_2$** in C_6D_6.

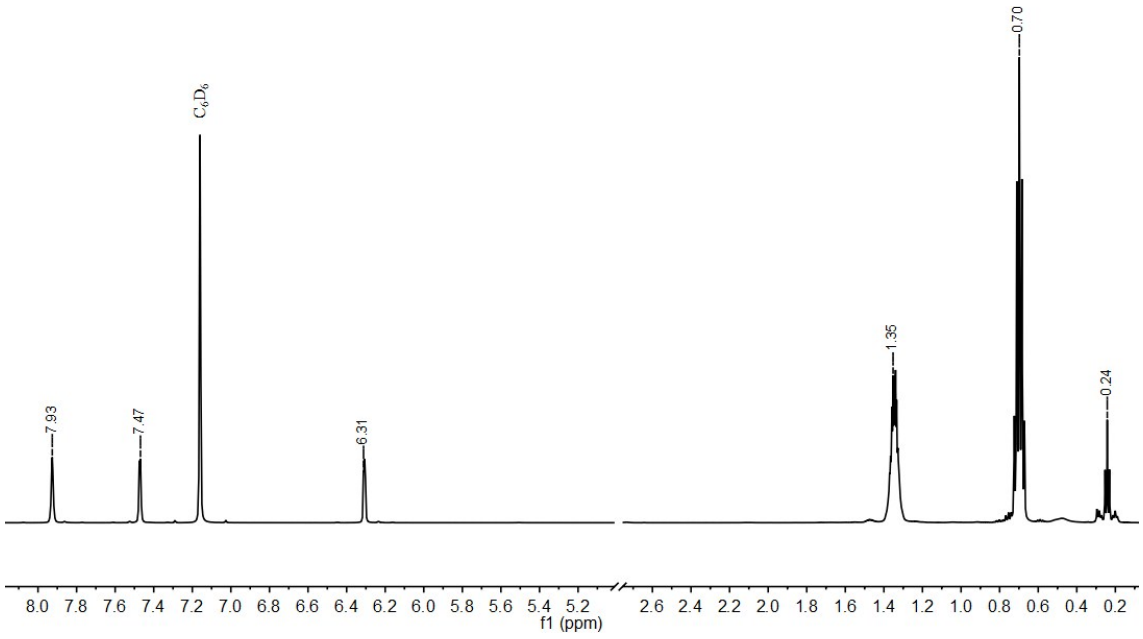

Figure S20: ^{1}H NMR spectrum of **Pt-CH$_3$** in C_6D_6.

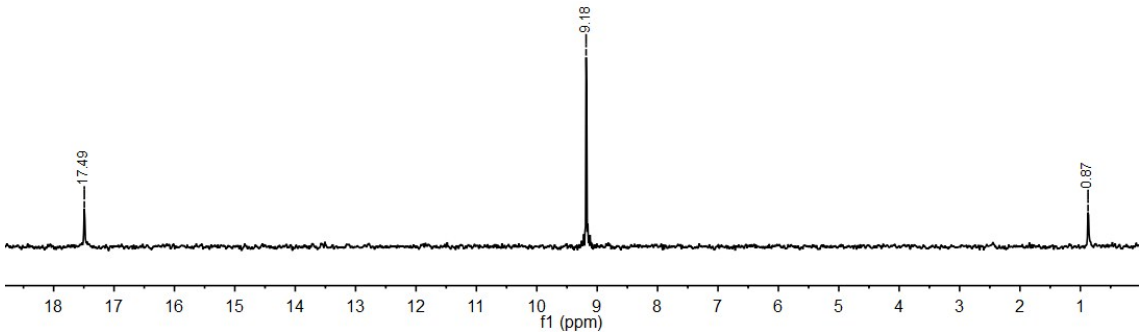

Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of **Pt-CH$_3$** in C_6D_6.

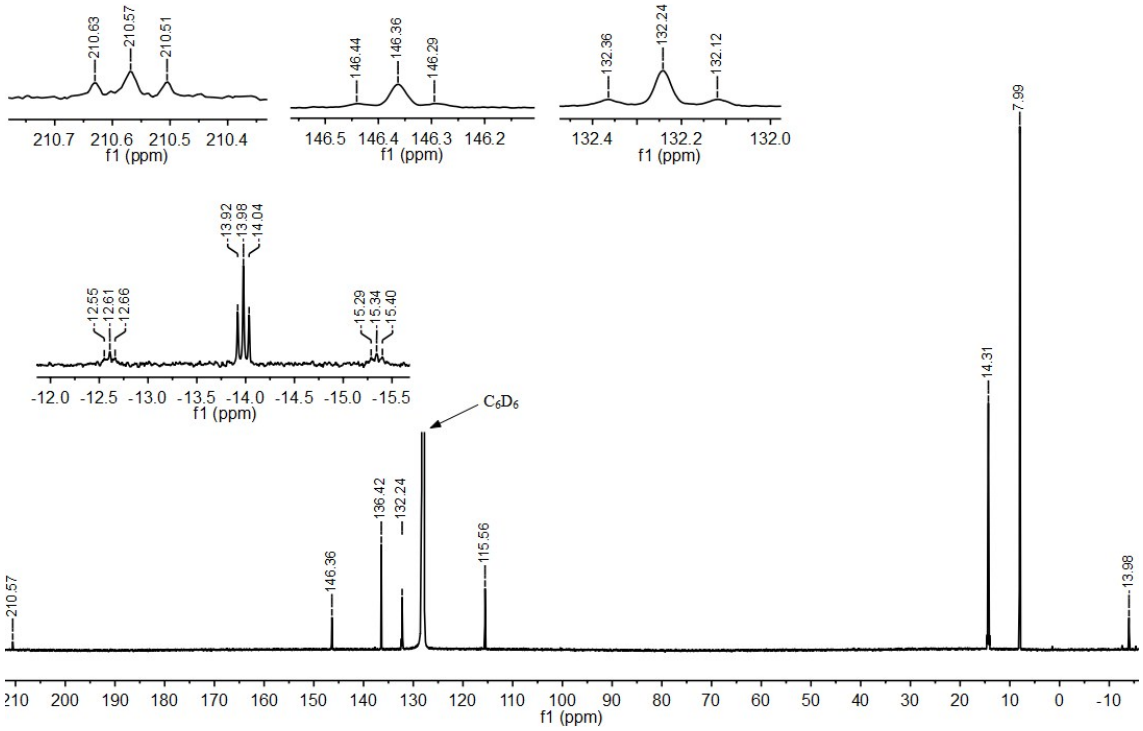

Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of **Pt-CH$_3$** in C_6D_6.

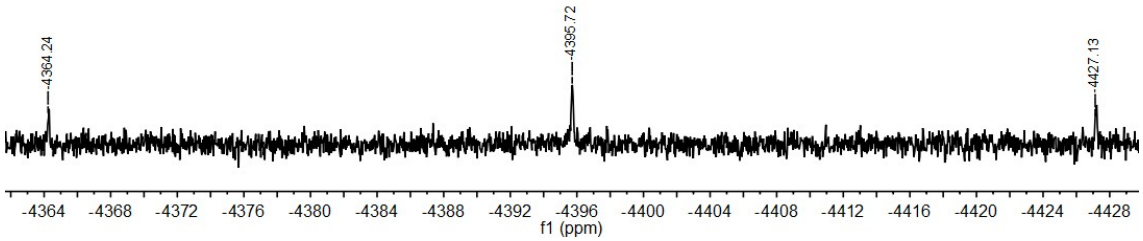

Figure S23: $^{195}Pt\{^{1}H\}$ NMR spectrum of **Pt-CH$_3$** in C_6D_6.

Single Crystal X-ray Diffraction

Table S1: Crystal and refinement data for **Pt-Cl**, **Pt-I**, **Pt-NCS**, **Pt-NO_2** and **Pt-CH_3**.

	Pt-Cl	**Pt-I**	**Pt-NCS**
Emp. formula / f. wt. / g mol^{-1}	$C_{21}H_{36}BClF_2N_2P_2Pt$ / 657.81	$C_{21}H_{36}F_2IN_2P_2Pt$ / 749.26	$C_{22}H_{36}BF_2N_3P_2PtS$ / 680.44
Temperature / K	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	P $2_1/c$	C m c 2_1	P $2_1/n$
a, b, c / Å	17.4058(6), 17.0196(5), 17.2625(6)	13.4838(7), 14.5951(10), 13.7759(7)	9.3599(4), 18.0669(7), 16.1360(7)
α, β, γ / deg	90, 94.973(3), 90	90, 90, 90	90, 104.104(3), 90
V / Å^3	5094.6(3)	2711.1(3)	2646.41(19)
Z	8	4	4
D_{calcd} / g cm^{-3}	1.715	1.836	1.708
Absorption coefficient / mm^{-1}	5.765	6.457	5.531
θ range for data collection / deg	1.677 to 28.061	2.056 to 26.795	1.722 to 27.343
Limiting Indices	-22≤h≤22, -22≤k≤22, -22≤l≤22	-17≤h≤17, -18≤k≤18, -17≤l≤17	-12≤h≤12, -23≤k≤23, -20≤l≤20
Reflections collected / unique (> 2σ(I))	83167 / 12219 [R(int) = 0.0818]	18705 / 2982 [R(int) = 0.0936]	41294 / 5964 [R(int) = 0.0666]
Data / Restraints / Parameter	12219 / 0 / 553	2982 / 1 / 160	5964 / 0 / 319
R (I> 2σ(I))	R_1 = 0.0484, wR_2 = 0.0747	R_1 = 0.0255, wR_2 = 0.0632	R_1 = 0.0311, wR_2 = 0.0757
R_w (all data)	R_1 = 0.0620, wR_2 = 0.0755	R_1 = 0.0282, wR_2 = 0.0640	R_1 = 0.0346, wR_2 = 0.0773
GooF (all Data)	2.128	1.120	1.040
Max. and min. res. dens. / eÅ^{-3}	2.559 and -2.016	1.607 and -1.633	2.892 and -1.740
	Pt-NO_2	**Pt-CH_3**	
Emp. formula / f. wt. / g mol^{-1}	$C_{21}H_{36}BF_2N_3O_2P_2Pt$ / 668.37	$C_{22}H_{39}BF_2N_2P_2Pt$ / 637.39	
Temperature / K	100(2)	100(2)	
Crystal system	monoclinic	monoclinic	
Space group	P $2_1/c$	P 2_1	
a, b, c / Å	9.6174(6), 16.8233(8), 16.3882(10)	11.0980(4), 13.1409(6), 18.4244(6)	
α, β, γ / deg	90, 103.184(5), 90	90, 106.287(3), 90	
V / Å^3	2581.7(3)	2579.14(18)	
Z	4	4	
D_{calcd} / g cm^{-3}	1.720	1.641	
Absorption coefficient / mm^{-1}	5.596	5.590	
θ range for data collection / deg	1.759 to 26.067	1.912 to 25.981	
Limiting Indices	-11≤h≤11, -20≤k≤20, -20≤l≤19	-13≤h≤13, -16≤k≤16, -22≤l≤22	
Reflections collected / unique (> 2σ(I))	33380 / 5044 [R(int) = 0.1517]	33984 / 10000 [R(int) = 0.0379]	
Data / Restraints / Parameter	5044 / 0 / 295	10000 / 1 / 555	
R (I> 2σ(I))	R_1 = 0.0544, wR_2 = 0.0560	R_1 = 0.0344, wR_2 = 0.0747	
R_w (all data)	R_1 = 0.0985, wR_2 = 0.0620	R_1 = 0.0370, wR_2 = 0.0756	
GooF (all Data)	0.995	1.049	
Max. and min. res. dens. / eA^{-3}	1.887 and -3.164	1.338 and -1.047	

Table S2: Bond lengths [Å] and angles [°] for **Pt-Cl**.

C(1)-C(2)	1.411(9)	B(2)-N(4)	1.549(9)	F(4)-B(2)-N(3)	110.4(6)
C(1)-C(6)	1.427(8)	Cl(1)-Pt(1)	2.3742(16)	F(3)-B(2)-N(4)	109.7(6)
C(1)-Pt(1)	1.980(6)	Cl(2)-Pt(2)	2.3842(16)	F(4)-B(2)-N(4)	109.6(6)
C(2)-C(3)	1.386(8)	P(1)-Pt(1)	2.3173(17)	N(3)-B(2)-N(4)	106.6(5)
C(2)-N(1)	1.393(8)	P(2)-Pt(1)	2.3097(16)	C(5)-N(1)-C(2)	108.4(5)
C(3)-C(4)	1.388(9)	P(3)-Pt(2)	2.3158(18)	C(5)-N(1)-B(1)	126.0(6)
C(4)-C(5)	1.403(9)	P(4)-Pt(2)	2.3120(18)	C(2)-N(1)-B(1)	125.3(6)
C(5)-N(1)	1.339(8)	C(2)-C(1)-C(6)	117.5(6)	C(9)-N(2)-C(6)	107.3(6)
C(6)-N(2)	1.394(8)	C(2)-C(1)-Pt(1)	120.6(4)	C(9)-N(2)-B(1)	125.2(5)
C(6)-C(7)	1.402(9)	C(6)-C(1)-Pt(1)	121.8(5)	C(6)-N(2)-B(1)	127.2(5)
C(7)-C(8)	1.378(9)	C(3)-C(2)-N(1)	107.3(6)	C(26)-N(3)-C(23)	107.4(5)
C(8)-C(9)	1.383(10)	C(3)-C(2)-C(1)	129.6(6)	C(26)-N(3)-B(2)	127.0(6)
C(9)-N(2)	1.360(8)	N(1)-C(2)-C(1)	122.7(6)	C(23)-N(3)-B(2)	125.5(5)
C(10)-C(11)	1.535(9)	C(4)-C(3)-C(2)	108.5(6)	C(30)-N(4)-C(27)	108.4(6)
C(10)-P(1)	1.820(7)	C(3)-C(4)-C(5)	106.1(6)	C(30)-N(4)-B(2)	126.8(6)
C(12)-C(13)	1.526(10)	N(1)-C(5)-C(4)	109.7(6)	C(27)-N(4)-B(2)	124.5(5)
C(12)-P(1)	1.799(8)	N(2)-C(6)-C(7)	107.8(5)	C(12)-P(1)-C(10)	107.4(3)
C(14)-C(15)	1.526(11)	N(2)-C(6)-C(1)	121.2(6)	C(12)-P(1)-C(14)	101.5(4)
C(14)-P(1)	1.838(7)	C(7)-C(6)-C(1)	131.0(6)	C(10)-P(1)-C(14)	106.9(3)
C(16)-C(17)	1.544(9)	C(8)-C(7)-C(6)	107.5(6)	C(12)-P(1)-Pt(1)	111.9(2)
C(16)-P(2)	1.823(7)	C(7)-C(8)-C(9)	107.6(6)	C(10)-P(1)-Pt(1)	114.6(2)
C(18)-C(19)	1.514(9)	N(2)-C(9)-C(8)	109.8(6)	C(14)-P(1)-Pt(1)	113.6(2)
C(18)-P(2)	1.823(7)	C(11)-C(10)-P(1)	116.3(6)	C(20)-P(2)-C(18)	102.3(3)
C(20)-C(21)	1.533(10)	C(13)-C(12)-P(1)	112.8(6)	C(20)-P(2)-C(16)	106.3(3)
C(20)-P(2)	1.817(6)	C(15)-C(14)-P(1)	114.0(5)	C(18)-P(2)-C(16)	107.3(3)
C(22)-C(23)	1.406(8)	C(17)-C(16)-P(2)	117.3(5)	C(20)-P(2)-Pt(1)	112.8(2)
C(22)-C(27)	1.414(8)	C(19)-C(18)-P(2)	114.8(4)	C(18)-P(2)-Pt(1)	112.5(2)
C(22)-Pt(2)	1.969(6)	C(21)-C(20)-P(2)	114.3(5)	C(16)-P(2)-Pt(1)	114.7(2)
C(23)-N(3)	1.391(8)	C(23)-C(22)-C(27)	117.1(6)	C(37)-P(3)-C(39)	106.4(4)
C(23)-C(24)	1.413(8)	C(23)-C(22)-Pt(2)	121.7(5)	C(37)-P(3)-C(41)	106.5(4)
C(24)-C(25)	1.409(9)	C(27)-C(22)-Pt(2)	121.2(5)	C(39)-P(3)-C(41)	102.7(3)
C(25)-C(26)	1.363(10)	C(22)-C(23)-N(3)	122.8(6)	C(37)-P(3)-Pt(2)	115.0(2)
C(26)-N(3)	1.370(9)	C(22)-C(23)-C(24)	129.3(6)	C(39)-P(3)-Pt(2)	111.8(2)
C(27)-C(28)	1.396(9)	N(3)-C(23)-C(24)	107.9(5)	C(41)-P(3)-Pt(2)	113.4(3)
C(27)-N(4)	1.397(8)	C(25)-C(24)-C(23)	106.7(6)	C(33)-P(4)-C(35)	105.5(3)
C(28)-C(29)	1.385(9)	C(26)-C(25)-C(24)	107.5(6)	C(33)-P(4)-C(31)	106.2(3)
C(29)-C(30)	1.397(10)	N(3)-C(26)-C(25)	110.5(6)	C(35)-P(4)-C(31)	103.4(3)
C(30)-N(4)	1.336(8)	C(28)-C(27)-N(4)	107.0(6)	C(33)-P(4)-Pt(2)	110.8(2)
C(31)-C(32)	1.526(9)	C(28)-C(27)-C(22)	130.4(6)	C(35)-P(4)-Pt(2)	109.7(2)
C(31)-P(4)	1.844(6)	N(4)-C(27)-C(22)	122.5(6)	C(31)-P(4)-Pt(2)	120.1(3)
C(33)-C(34)	1.537(9)	C(29)-C(28)-C(27)	108.3(6)	C(1)-Pt(1)-P(2)	93.91(17)
C(33)-P(4)	1.824(7)	C(28)-C(29)-C(30)	106.4(6)	C(1)-Pt(1)-P(1)	91.33(17)

C(35)-C(36)	1.556(10)	N(4)-C(30)-C(29)	109.9(6)	P(2)-Pt(1)-P(1)	174.76(6)
C(35)-P(4)	1.839(7)	C(32)-C(31)-P(4)	114.6(5)	C(1)-Pt(1)-Cl(1)	178.39(18)
C(37)-C(38)	1.533(10)	C(34)-C(33)-P(4)	114.5(5)	P(2)-Pt(1)-Cl(1)	87.59(6)
C(37)-P(3)	1.822(8)	C(36)-C(35)-P(4)	115.9(5)	P(1)-Pt(1)-Cl(1)	87.17(6)
C(39)-C(40)	1.525(9)	C(38)-C(37)-P(3)	116.7(5)	C(22)-Pt(2)-P(4)	92.85(18)
C(39)-P(3)	1.825(7)	C(40)-C(39)-P(3)	114.1(4)	C(22)-Pt(2)-P(3)	91.69(18)
C(41)-C(42)	1.508(9)	C(42)-C(41)-P(3)	114.3(5)	P(4)-Pt(2)-P(3)	175.07(6)
C(41)-P(3)	1.825(7)	F(1)-B(1)-F(2)	109.0(6)	C(22)-Pt(2)-Cl(2)	179.19(19)
B(1)-F(1)	1.388(8)	F(1)-B(1)-N(2)	110.1(6)	P(4)-Pt(2)-Cl(2)	87.82(6)
B(1)-F(2)	1.379(9)	F(2)-B(1)-N(2)	112.5(6)	P(3)-Pt(2)-Cl(2)	87.66(6)
B(1)-N(2)	1.528(10)	F(1)-B(1)-N(1)	108.9(5)		
B(1)-N(1)	1.561(9)	F(2)-B(1)-N(1)	110.5(6)		
B(2)-F(3)	1.389(9)	N(2)-B(1)-N(1)	105.6(5)		
B(2)-F(4)	1.404(8)	F(3)-B(2)-F(4)	108.9(6)		
B(2)-N(3)	1.527(10)	F(3)-B(2)-N(3)	111.6(6)		

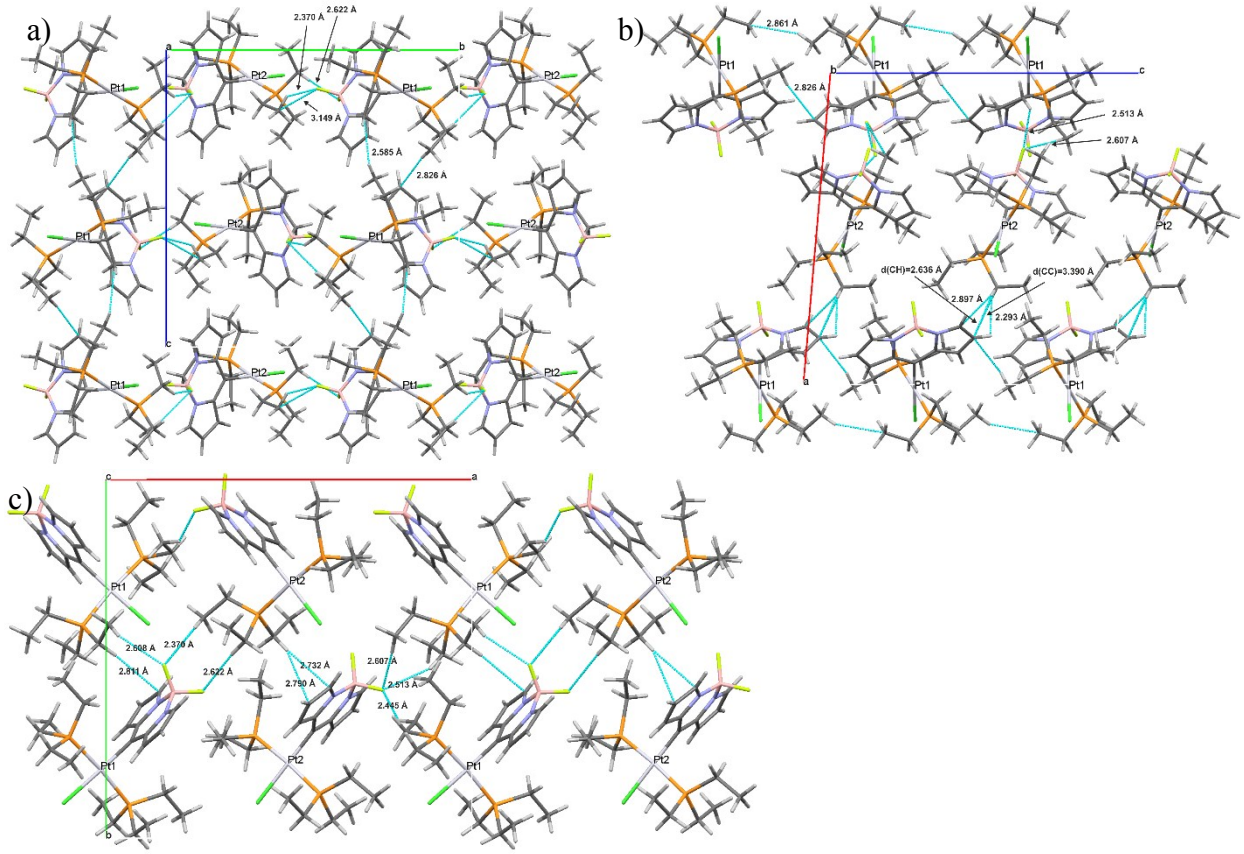

Figure S24: Packing of molecules of Pt-Cl along the crystallographic *a* (a), *b* (b), and *c* axis (c).

Table S3: Bond lengths [Å] and angles [°] for Pt-I.

Pt(1)-C(1)	1.994(10)	C(1)-Pt(1)-P(1)	91.37(7)	N(1)-C(5)-C(4)	108.9(9)
Pt(1)-P(1)	2.3206(15)	C(1)-Pt(1)-P(1)#1	91.37(7)	C(1)-C(6)-N(2)	121.1(9)
Pt(1)-P(1)#1	2.3207(15)	P(1)-Pt(1)-P(1)#1	176.03(8)	C(1)-C(6)-C(7)	132.0(9)
Pt(1)-I(1)	2.6689(8)	C(1)-Pt(1)-I(1)	176.8(3)	N(2)-C(6)-C(7)	106.9(8)
N(1)-C(5)	1.361(12)	P(1)-Pt(1)-I(1)	88.71(7)	C(8)-C(7)-C(6)	109.0(10)
N(1)-C(2)	1.402(13)	P(1)#1-Pt(1)-I(1)	88.71(7)	C(7)-C(8)-C(9)	106.3(10)
N(1)-B(1)	1.538(15)	C(5)-N(1)-C(2)	108.6(9)	N(2)-C(9)-C(8)	110.0(10)
N(2)-C(9)	1.351(14)	C(5)-N(1)-B(1)	124.1(10)	C(12)-P(1)-C(14)	102.3(4)
N(2)-C(6)	1.408(13)	C(2)-N(1)-B(1)	127.3(9)	C(12)-P(1)-C(10)	105.5(4)
N(2)-B(1)	1.556(13)	C(9)-N(2)-C(6)	107.8(9)	C(14)-P(1)-C(10)	105.7(4)
B(1)-F(1)	1.382(8)	C(9)-N(2)-B(1)	125.1(10)	C(12)-P(1)-Pt(1)	115.0(3)
B(1)-F(1)#1	1.382(8)	C(6)-N(2)-B(1)	127.0(9)	C(14)-P(1)-Pt(1)	113.1(2)
C(1)-C(6)	1.403(13)	F(1)-B(1)-F(1)#1	109.7(9)	C(10)-P(1)-Pt(1)	114.1(3)
C(1)-C(2)	1.412(13)	F(1)-B(1)-N(1)	111.6(6)	C(11)-C(10)-P(1)	116.2(6)
C(2)-C(3)	1.407(14)	F(1)#1-B(1)-N(1)	111.6(6)	C(13)-C(12)-P(1)	113.8(6)
C(3)-C(4)	1.393(14)	F(1)-B(1)-N(2)	109.7(6)	C(15)-C(14)-P(1)	113.9(6)
C(4)-C(5)	1.392(17)	F(1)#1-B(1)-N(2)	109.7(6)		
C(6)-C(7)	1.410(15)	N(1)-B(1)-N(2)	104.6(9)		
C(7)-C(8)	1.374(17)	C(6)-C(1)-C(2)	118.6(9)		
C(8)-C(9)	1.416(18)	C(6)-C(1)-Pt(1)	122.3(7)		
P(1)-C(12)	1.818(10)	C(2)-C(1)-Pt(1)	119.1(7)		
P(1)-C(14)	1.827(6)	N(1)-C(2)-C(3)	107.0(9)		
P(1)-C(10)	1.832(9)	N(1)-C(2)-C(1)	121.4(9)		
C(10)-C(11)	1.539(11)	C(3)-C(2)-C(1)	131.5(10)		
C(12)-C(13)	1.540(13)	C(4)-C(3)-C(2)	107.6(10)		
C(15)-C(14)	1.536(14)	C(5)-C(4)-C(3)	107.8(9)		

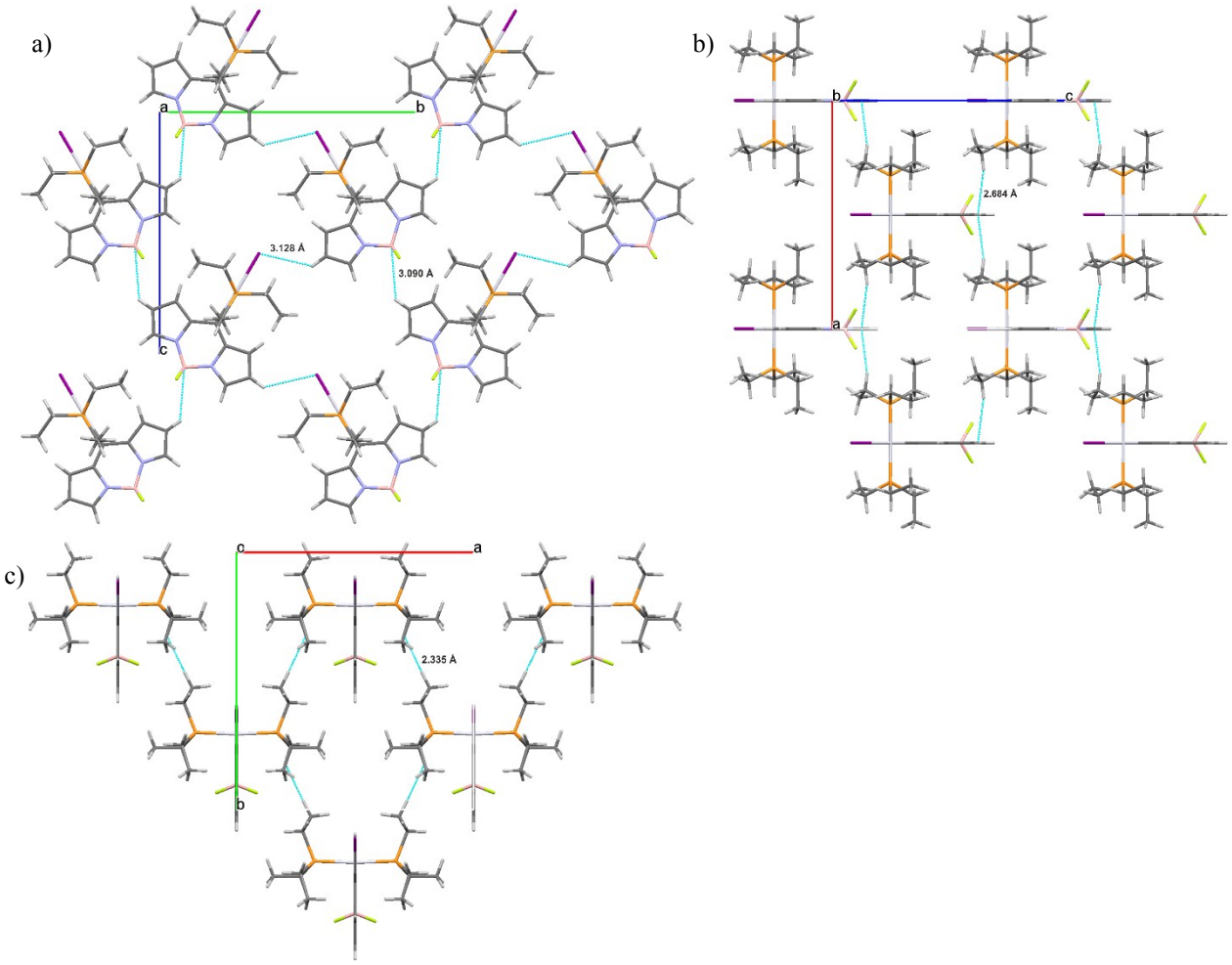

Figure S25: Packing of molecules of **Pt-I** along the crystallographic *a* (a), *b* (b), and *c* axis (c).

Table S4: Bond lengths [Å] and angles [°] for **Pt-NCS**.

C(1)-C(2)	1.404(6)	B(1)-N(1)	1.546(6)	F(2)-B(1)-N(1)	110.6(4)
C(1)-C(6)	1.413(6)	N(3)-Pt(1)	2.048(4)	N(2)-B(1)-N(1)	106.4(3)
C(1)-Pt(1)	1.984(4)	P(1)-Pt(1)	2.3135(13)	C(5)-N(1)-C(2)	108.4(4)
C(2)-N(1)	1.395(5)	P(2)-Pt(1)	2.3249(11)	C(5)-N(1)-B(1)	125.9(4)
C(2)-C(3)	1.412(6)	C(2)-C(1)-C(6)	117.9(4)	C(2)-N(1)-B(1)	125.6(3)
C(3)-C(4)	1.374(6)	C(2)-C(1)-Pt(1)	122.1(3)	C(9)-N(2)-C(6)	108.0(4)
C(4)-C(5)	1.395(6)	C(6)-C(1)-Pt(1)	119.9(3)	C(9)-N(2)-B(1)	126.3(4)
C(5)-N(1)	1.340(6)	N(1)-C(2)-C(1)	122.2(4)	C(6)-N(2)-B(1)	125.6(4)
C(6)-N(2)	1.396(5)	N(1)-C(2)-C(3)	106.8(3)	C(22)-N(3)-Pt(1)	162.2(4)
C(6)-C(7)	1.410(6)	C(1)-C(2)-C(3)	131.1(4)	C(14)-P(1)-C(10)	113.4(3)
C(7)-C(8)	1.391(6)	C(4)-C(3)-C(2)	108.0(4)	C(14)-P(1)-C(12)	103.2(3)
C(8)-C(9)	1.392(6)	C(3)-C(4)-C(5)	107.0(4)	C(10)-P(1)-C(12)	100.0(2)
C(9)-N(2)	1.348(6)	N(1)-C(5)-C(4)	109.8(4)	C(14)-P(1)-Pt(1)	113.0(2)
C(10)-C(11)	1.504(8)	N(2)-C(6)-C(7)	107.4(4)	C(10)-P(1)-Pt(1)	120.87(16)
C(10)-P(1)	1.815(5)	N(2)-C(6)-C(1)	122.2(4)	C(12)-P(1)-Pt(1)	103.07(19)
C(12)-C(13)	1.435(9)	C(7)-C(6)-C(1)	130.4(4)	C(18)-P(2)-C(16)	103.2(2)
C(12)-P(1)	2.038(8)	C(8)-C(7)-C(6)	107.6(4)	C(18)-P(2)-C(20)	105.5(2)
C(14)-C(15)	1.477(9)	C(7)-C(8)-C(9)	106.8(4)	C(16)-P(2)-C(20)	105.5(2)
C(14)-P(1)	1.765(6)	N(2)-C(9)-C(8)	110.3(4)	C(18)-P(2)-Pt(1)	111.63(16)
C(16)-C(17)	1.525(7)	C(11)-C(10)-P(1)	114.7(5)	C(16)-P(2)-Pt(1)	115.92(16)
C(16)-P(2)	1.823(4)	C(13)-C(12)-P(1)	112.4(5)	C(20)-P(2)-Pt(1)	113.93(16)
C(18)-C(19)	1.520(7)	C(15)-C(14)-P(1)	117.4(6)	C(1)-Pt(1)-N(3)	175.77(17)
C(18)-P(2)	1.822(4)	C(17)-C(16)-P(2)	113.9(3)	C(1)-Pt(1)-P(1)	91.44(12)
C(20)-C(21)	1.528(7)	C(19)-C(18)-P(2)	113.2(3)	N(3)-Pt(1)-P(1)	87.28(12)
C(20)-P(2)	1.826(4)	C(21)-C(20)-P(2)	115.1(3)	C(1)-Pt(1)-P(2)	90.79(12)
C(22)-N(3)	1.162(6)	N(3)-C(22)-S(1)	179.7(4)	N(3)-Pt(1)-P(2)	90.62(11)
C(22)-S(1)	1.625(4)	F(1)-B(1)-F(2)	108.7(3)	P(1)-Pt(1)-P(2)	177.17(5)
B(1)-F(1)	1.389(5)	F(1)-B(1)-N(2)	110.8(4)		
B(1)-F(2)	1.394(5)	F(2)-B(1)-N(2)	110.1(4)		
B(1)-N(2)	1.540(6)	F(1)-B(1)-N(1)	110.3(4)		

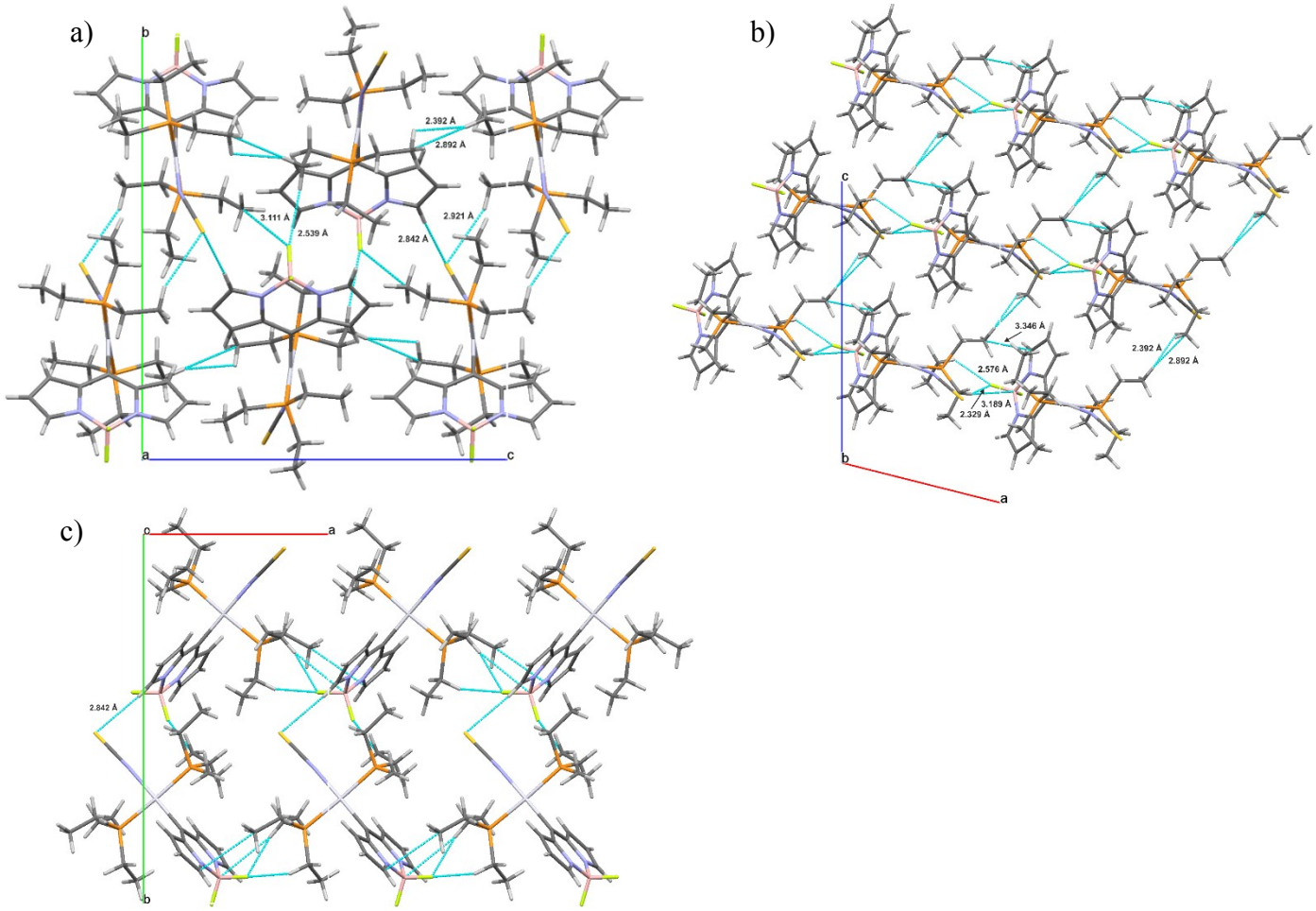

Figure S26: Packing of molecules of **Pt-NCS** along the crystallographic *a* (a), *b* (b), and *c* axis (c).

Table S5: Bond lengths [Å] and angles [°] for **Pt-NO$_2$**.

Pt(1)-C(1)	1.956(9)	C(14)-C(15)	1.515(12)	C(10)-P(1)-Pt(1)	115.0(3)
Pt(1)-N(3)	2.019(8)	C(16)-C(17)	1.546(11)	C(18)-P(2)-C(16)	105.9(4)
Pt(1)-P(1)	2.329(2)	C(18)-C(19)	1.527(11)	C(18)-P(2)-C(20)	104.2(4)
Pt(1)-P(2)	2.334(2)	C(20)-C(21)	1.521(11)	C(16)-P(2)-C(20)	105.4(4)
B(1)-F(2)	1.389(9)	C(1)-Pt(1)-N(3)	178.2(4)	C(18)-P(2)-Pt(1)	114.7(3)
B(1)-F(1)	1.398(10)	C(1)-Pt(1)-P(1)	92.3(3)	C(16)-P(2)-Pt(1)	113.1(3)
B(1)-N(1)	1.534(10)	N(3)-Pt(1)-P(1)	88.6(2)	C(20)-P(2)-Pt(1)	112.8(3)
B(1)-N(2)	1.548(11)	C(1)-Pt(1)-P(2)	89.3(3)	C(6)-C(1)-C(2)	115.5(8)
N(1)-C(5)	1.342(10)	N(3)-Pt(1)-P(2)	90.0(2)	C(6)-C(1)-Pt(1)	122.1(6)
N(1)-C(2)	1.419(9)	P(1)-Pt(1)-P(2)	173.83(8)	C(2)-C(1)-Pt(1)	122.4(6)
N(2)-C(9)	1.352(10)	F(2)-B(1)-F(1)	108.4(6)	C(3)-C(2)-N(1)	106.6(7)
N(2)-C(6)	1.409(9)	F(2)-B(1)-N(1)	111.1(6)	C(3)-C(2)-C(1)	130.9(7)
N(3)-O(1)	1.232(10)	F(1)-B(1)-N(1)	110.3(7)	N(1)-C(2)-C(1)	122.5(7)
N(3)-O(2)	1.293(10)	F(2)-B(1)-N(2)	110.0(7)	C(4)-C(3)-C(2)	108.4(7)
P(1)-C(14)	1.823(8)	F(1)-B(1)-N(2)	110.1(6)	C(3)-C(4)-C(5)	107.3(7)
P(1)-C(12)	1.826(8)	N(1)-B(1)-N(2)	107.0(6)	N(1)-C(5)-C(4)	110.5(7)
P(1)-C(10)	1.830(9)	C(5)-N(1)-C(2)	107.2(6)	C(1)-C(6)-N(2)	124.9(7)
P(2)-C(18)	1.814(9)	C(5)-N(1)-B(1)	127.1(7)	C(1)-C(6)-C(7)	128.9(7)
P(2)-C(16)	1.816(8)	C(2)-N(1)-B(1)	125.7(7)	N(2)-C(6)-C(7)	106.2(7)
P(2)-C(20)	1.830(8)	C(9)-N(2)-C(6)	108.2(7)	C(8)-C(7)-C(6)	108.3(8)
C(1)-C(6)	1.406(11)	C(9)-N(2)-B(1)	127.4(6)	C(9)-C(8)-C(7)	106.6(7)
C(1)-C(2)	1.440(11)	C(6)-N(2)-B(1)	124.2(6)	N(2)-C(9)-C(8)	110.7(7)
C(2)-C(3)	1.401(11)	O(1)-N(3)-O(2)	115.7(8)	C(11)-C(10)-P(1)	114.1(6)
C(3)-C(4)	1.368(11)	O(1)-N(3)-Pt(1)	124.0(6)	C(13)-C(12)-P(1)	113.0(5)
C(4)-C(5)	1.384(11)	O(2)-N(3)-Pt(1)	120.2(6)	C(15)-C(14)-P(1)	115.6(6)
C(6)-C(7)	1.423(11)	C(14)-P(1)-C(12)	104.3(4)	C(17)-C(16)-P(2)	115.6(5)
C(7)-C(8)	1.392(11)	C(14)-P(1)-C(10)	105.6(4)	C(19)-C(18)-P(2)	113.8(6)
C(8)-C(9)	1.389(12)	C(12)-P(1)-C(10)	105.9(4)	C(21)-C(20)-P(2)	114.9(6)
C(10)-C(11)	1.554(11)	C(14)-P(1)-Pt(1)	115.6(3)		
C(12)-C(13)	1.511(11)	C(12)-P(1)-Pt(1)	109.6(3)		

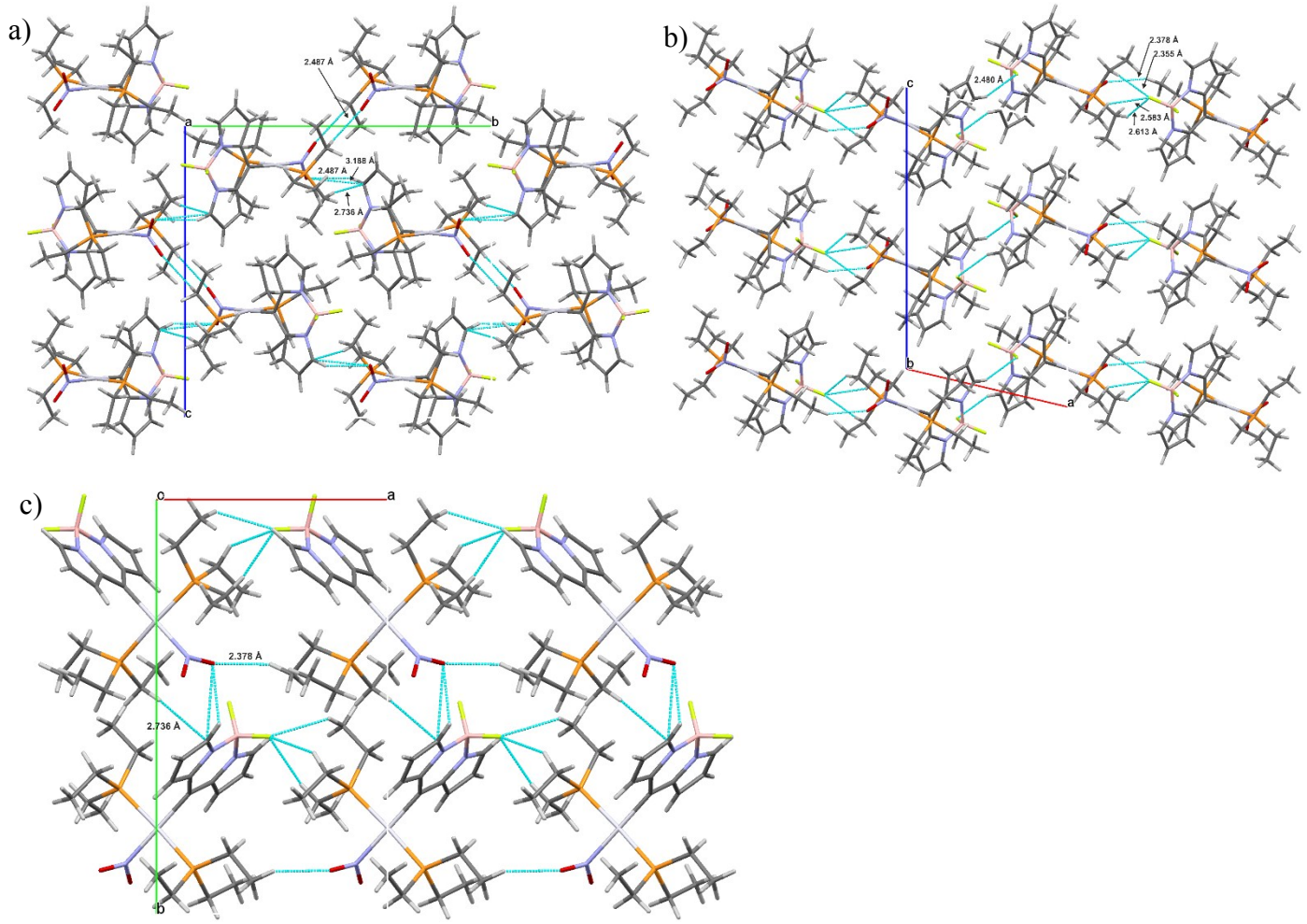

Figure S27: Packing of molecules of **Pt-NO_2** along the crystallographic *a* (a), *b* (b), and *c* axis (c).

Table S6: Bond lengths [Å] and angles [°] for Pt-CH_3.

Pt(1)-C(1)	2.039(11)	C(28)-C(29)	1.39(2)	C(16)-P(2)-Pt(1)	114.4(4)
Pt(1)-C(22)	2.127(12)	C(29)-C(30)	1.40(2)	C(20)-P(2)-Pt(1)	116.2(5)
Pt(1)-P(2)	2.290(3)	C(30)-C(31)	1.38(2)	C(36)-P(3)-C(34)	102.8(6)
Pt(1)-P(1)	2.299(3)	C(32)-C(33)	1.529(16)	C(36)-P(3)-C(32)	105.2(6)
Pt(2)-C(23)	2.053(12)	C(34)-C(35)	1.510(17)	C(34)-P(3)-C(32)	104.4(7)
Pt(2)-C(44)	2.137(11)	C(36)-C(37)	1.52(2)	C(36)-P(3)-Pt(2)	114.4(4)
Pt(2)-P(4)	2.285(3)	C(38)-C(39)	1.56(2)	C(34)-P(3)-Pt(2)	113.9(4)
Pt(2)-P(3)	2.304(3)	C(40)-C(41)	1.40(3)	C(32)-P(3)-Pt(2)	114.8(4)
B(1)-F(1)	1.382(15)	C(42)-C(43)	1.55(3)	C(38)-P(4)-C(42)	108.8(10)
B(1)-F(2)	1.411(17)	C(1)-Pt(1)-C(22)	177.6(4)	C(38)-P(4)-C(40)	100.0(13)
B(1)-N(2)	1.53(2)	C(1)-Pt(1)-P(2)	91.9(3)	C(42)-P(4)-C(40)	104.0(11)
B(1)-N(1)	1.55(2)	C(22)-Pt(1)-P(2)	90.5(3)	C(38)-P(4)-Pt(2)	115.2(5)
B(2)-F(3)	1.395(16)	C(1)-Pt(1)-P(1)	91.3(3)	C(42)-P(4)-Pt(2)	116.9(6)
B(2)-F(4)	1.403(15)	C(22)-Pt(1)-P(1)	86.3(3)	C(40)-P(4)-Pt(2)	110.1(7)
B(2)-N(3)	1.525(19)	P(2)-Pt(1)-P(1)	176.05(12)	C(6)-C(1)-C(2)	117.5(11)
B(2)-N(4)	1.54(2)	C(23)-Pt(2)-C(44)	177.2(5)	C(6)-C(1)-Pt(1)	121.8(8)
N(1)-C(5)	1.329(19)	C(23)-Pt(2)-P(4)	92.7(3)	C(2)-C(1)-Pt(1)	120.2(9)
N(1)-C(2)	1.398(15)	C(44)-Pt(2)-P(4)	89.9(3)	C(3)-C(2)-N(1)	107.5(12)
N(2)-C(9)	1.33(2)	C(23)-Pt(2)-P(3)	90.7(3)	C(3)-C(2)-C(1)	129.9(12)
N(2)-C(6)	1.419(16)	C(44)-Pt(2)-P(3)	86.7(3)	N(1)-C(2)-C(1)	122.2(12)
N(3)-C(27)	1.347(18)	P(4)-Pt(2)-P(3)	176.57(12)	C(2)-C(3)-C(4)	107.9(15)
N(3)-C(24)	1.402(14)	F(1)-B(1)-F(2)	108.3(11)	C(5)-C(4)-C(3)	105.8(15)
N(4)-C(31)	1.342(18)	F(1)-B(1)-N(2)	111.4(13)	N(1)-C(5)-C(4)	110.8(13)
N(4)-C(28)	1.405(16)	F(2)-B(1)-N(2)	109.5(12)	C(7)-C(6)-C(1)	130.8(11)
P(1)-C(10)	1.830(12)	F(1)-B(1)-N(1)	111.6(13)	C(7)-C(6)-N(2)	107.0(12)
P(1)-C(14)	1.832(13)	F(2)-B(1)-N(1)	108.9(12)	C(1)-C(6)-N(2)	122.0(12)
P(1)-C(12)	1.842(13)	N(2)-B(1)-N(1)	107.1(11)	C(8)-C(7)-C(6)	108.1(13)
P(2)-C(18)	1.830(14)	F(3)-B(2)-F(4)	108.5(10)	C(9)-C(8)-C(7)	106.3(14)
P(2)-C(16)	1.831(13)	F(3)-B(2)-N(3)	109.6(13)	N(2)-C(9)-C(8)	111.5(13)
P(2)-C(20)	1.831(15)	F(4)-B(2)-N(3)	109.9(10)	C(11)-C(10)-P(1)	116.4(9)
P(3)-C(36)	1.816(14)	F(3)-B(2)-N(4)	111.2(10)	C(13)-C(12)-P(1)	115.2(9)
P(3)-C(34)	1.818(12)	F(4)-B(2)-N(4)	110.9(13)	C(15)-C(14)-P(1)	112.5(10)
P(3)-C(32)	1.833(11)	N(3)-B(2)-N(4)	106.6(10)	C(17)-C(16)-P(2)	116.8(9)
P(4)-C(38)	1.744(17)	C(5)-N(1)-C(2)	108.0(13)	C(19)-C(18)-P(2)	114.6(9)
P(4)-C(42)	1.824(16)	C(5)-N(1)-B(1)	127.5(12)	C(21)-C(20)-P(2)	113.6(9)
P(4)-C(40)	1.88(2)	C(2)-N(1)-B(1)	124.3(11)	C(24)-C(23)-C(28)	116.8(11)
C(1)-C(6)	1.412(18)	C(9)-N(2)-C(6)	107.1(13)	C(24)-C(23)-Pt(2)	122.4(9)
C(1)-C(2)	1.425(16)	C(9)-N(2)-B(1)	128.0(13)	C(28)-C(23)-Pt(2)	120.5(9)
C(2)-C(3)	1.385(19)	C(6)-N(2)-B(1)	124.9(12)	N(3)-C(24)-C(23)	123.3(12)
C(3)-C(4)	1.40(2)	C(27)-N(3)-C(24)	107.9(11)	N(3)-C(24)-C(25)	106.8(11)
C(4)-C(5)	1.39(3)	C(27)-N(3)-B(2)	127.5(10)	C(23)-C(24)-C(25)	129.9(11)

C(6)-C(7)	1.398(19)	C(24)-N(3)-B(2)	124.0(11)	C(26)-C(25)-C(24)	108.4(11)
C(7)-C(8)	1.391(18)	C(31)-N(4)-C(28)	107.9(12)	C(25)-C(26)-C(27)	106.5(12)
C(8)-C(9)	1.38(2)	C(31)-N(4)-B(2)	127.0(11)	N(3)-C(27)-C(26)	110.4(11)
C(10)-C(11)	1.536(15)	C(28)-N(4)-B(2)	124.3(11)	C(29)-C(28)-N(4)	107.0(12)
C(12)-C(13)	1.508(19)	C(10)-P(1)-C(14)	105.7(6)	C(29)-C(28)-C(23)	130.5(12)
C(14)-C(15)	1.53(2)	C(10)-P(1)-C(12)	105.9(7)	N(4)-C(28)-C(23)	122.4(12)
C(16)-C(17)	1.520(16)	C(14)-P(1)-C(12)	102.4(7)	C(28)-C(29)-C(30)	108.1(14)
C(18)-C(19)	1.517(17)	C(10)-P(1)-Pt(1)	114.3(4)	C(31)-C(30)-C(29)	106.4(15)
C(20)-C(21)	1.51(2)	C(14)-P(1)-Pt(1)	112.3(4)	N(4)-C(31)-C(30)	110.6(13)
C(23)-C(24)	1.404(17)	C(12)-P(1)-Pt(1)	115.1(4)	C(33)-C(32)-P(3)	116.7(9)
C(23)-C(28)	1.409(17)	C(18)-P(2)-C(16)	103.4(7)	C(35)-C(34)-P(3)	114.8(9)
C(24)-C(25)	1.405(17)	C(18)-P(2)-C(20)	104.2(6)	C(37)-C(36)-P(3)	114.1(12)
C(25)-C(26)	1.384(17)	C(16)-P(2)-C(20)	104.2(7)	C(39)-C(38)-P(4)	117.6(12)
C(26)-C(27)	1.39(2)	C(18)-P(2)-Pt(1)	113.0(4)	C(41)-C(40)-P(4)	115.3(17)
				C(43)-C(42)-P(4)	110.9(13)

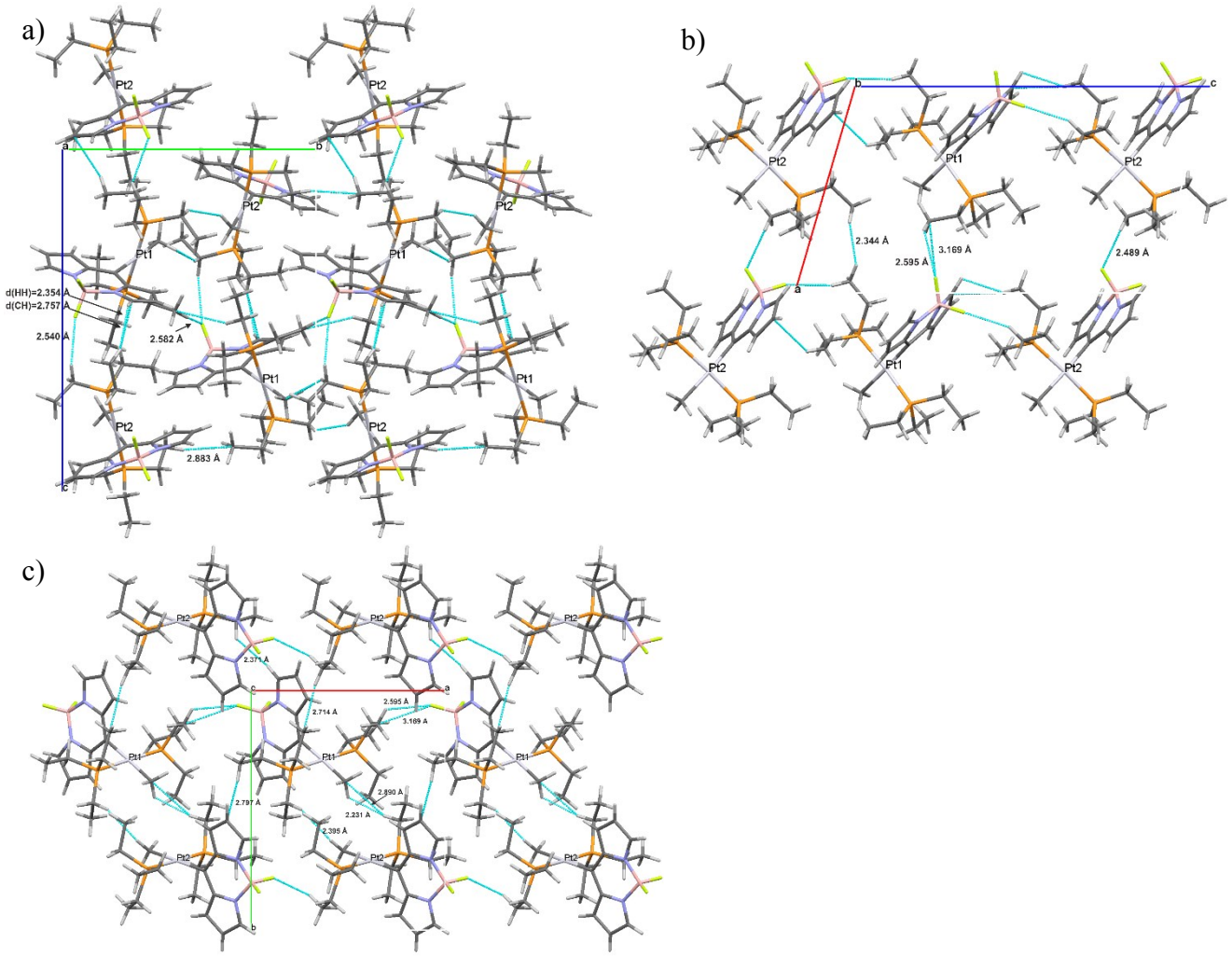

Figure S28: Packing of molecules of **Pt-CH$_3$** along the crystallographic *a* (a), *b* (b), and *c* axis (c).

DFT and TD-DFT calculations

Table S7: Atomic coordinates of **Pt-Cl** in the optimized ground state geometry.

Atom	X	Y	Z
Pt	5.92902	9.33451	3.12565
B	10.63911	10.54426	1.72252
F	11.5403	10.26961	2.75179
F	11.35508	11.04624	0.62428
N	9.91030	9.26302	1.32638
N	9.55581	11.54428	2.17879
P	6.92251	8.88588	5.15589
P	4.82302	9.77157	1.17428
C	7.74125	9.88064	2.33088
C	8.59559	8.95947	1.70483
C	8.35976	7.62961	1.3193
H	7.55369	7.14602	1.45724
C	9.49963	7.14208	0.7074
H	9.61975	6.27609	0.33425
C	10.43536	8.16838	0.741
H	11.3203	8.10793	0.40145
C	8.23908	11.18685	2.51481
C	7.63372	12.31828	3.05597
H	6.73691	12.38004	3.36015
C	8.58068	13.35115	3.07012
H	8.44994	14.23685	3.38845
C	9.73828	12.82552	2.53426
H	10.55229	13.30385	2.42992
C	8.69677	9.33661	5.25952
H	9.17897	8.85697	4.53974
H	8.77988	10.30509	5.07383
C	9.40342	9.04357	6.58236
H	10.3453	9.30901	6.51516
H	9.34769	8.08428	6.7769
H	8.97116	9.54818	7.30214
C	6.87140	7.13157	5.63091
H	7.33958	7.02644	6.49747
H	5.92661	6.87006	5.76885
C	7.49184	6.18542	4.6317
H	7.47855	5.27476	4.99248
H	8.41752	6.45481	4.45662
H	6.98047	6.21302	3.7952
C	6.13927	9.70981	6.57175
H	5.24628	9.30770	6.71853
H	6.68332	9.53635	7.37995
C	5.97698	11.2105	6.40551
H	5.61360	11.59422	7.2314
H	5.36276	11.39185	5.66274
H	6.84900	11.61393	6.21274
C	5.82206	9.80311	-0.25466
H	6.53146	10.47855	-0.11495
H	6.26874	8.92136	-0.33248
C	5.12685	10.10535	-1.61287
H	5.73467	9.88327	-2.34857
H	4.90005	11.0607	-1.65709
H	4.30895	9.57446	-1.68892
C	4.19702	11.54691	1.17075
H	4.97333	12.15533	1.11946
H	3.65170	11.6862	0.35547
C	3.42306	11.9096	2.28137
H	3.04933	12.80449	2.13989

H	3.98693	11.91354	3.0825
H	2.69422	11.26569	2.39809
C	3.33292	8.77681	0.8312
H	2.68522	8.88588	1.57043
H	2.90597	9.10139	-0.00177
C	3.69357	7.27612	0.67557
H	4.04707	6.93708	1.52445
H	4.36986	7.17362	-0.02476
H	2.89036	6.77151	0.43151
Cl	4.07992	8.78863	4.0481

Table S8: Atomic coordinates of **Pt-Cl** in the optimized geometry of the first excited triplet state.

Atom	X	Y	Z
Pt	0.95950	0.24470	0.02348
B	-3.93644	-0.82976	0.01013
F	-4.69757	0.33577	0.07523
F	-4.76201	-1.94281	-0.03828
N	-3.0084	-0.78449	-1.22772
N	-2.98719	-0.90666	1.23087
P	0.39809	2.52047	-0.02308
P	1.62197	-2.00746	0.06879
C	-0.94813	-0.30095	0.01021
C	-1.66007	-0.44774	-1.20037
C	-1.21264	-0.37971	-2.53764
H	-0.19617	-0.15600	-2.83458
C	-2.2959	-0.67873	-3.35823
H	-2.3119	-0.73154	-4.43854
C	-3.38391	-0.91743	-2.50724
H	-4.40556	-1.17288	-2.758
C	-1.6387	-0.56881	1.21424
C	-1.17168	-0.62553	2.54555
H	-0.15238	-0.42481	2.84987
C	-2.24329	-0.99895	3.35125
H	-2.24357	-1.14963	4.42238
C	-3.34372	-1.15752	2.49833
H	-4.36197	-1.43483	2.73957
C	-1.39745	2.90296	-0.15218
H	-1.75164	2.42733	-1.07383
H	-1.89056	2.36456	0.66604
C	-1.77069	4.38169	-0.12808
H	-2.85745	4.48890	-0.21065
H	-1.32277	4.93169	-0.96203
H	-1.46238	4.86750	0.80352
C	1.20545	3.42729	-1.40459
H	0.92789	4.48522	-1.31988
H	2.28133	3.35528	-1.21078
C	0.88000	2.88413	-2.79073
H	1.37285	3.49083	-3.55781
H	-0.1956	2.89626	-2.9976
H	1.23478	1.85395	-2.89714
C	0.99674	3.42985	1.45931
H	2.07727	3.25088	1.49353
H	0.84931	4.50255	1.28162
C	0.33956	2.99753	2.76486
H	0.76592	3.55640	3.6045
H	0.49991	1.93121	2.95233
H	-0.74064	3.17876	2.75982
C	0.38250	-3.1894	-0.61114
H	-0.51488	-3.08011	0.00988
H	0.10341	-2.81818	-1.60377

C	0.81391	-4.65102	-0.68303
H	-0.00557	-5.25657	-1.08458
H	1.06757	-5.05539	0.30205
H	1.67786	-4.79108	-1.3409
C	1.95312	-2.63971	1.76614
H	0.98502	-2.65366	2.28197
H	2.28378	-3.6818	1.67764
C	2.96868	-1.82083	2.5559
H	3.07115	-2.2275	3.56764
H	2.66102	-0.77325	2.63194
H	3.95708	-1.83993	2.08605
C	3.16557	-2.33512	-0.87171
H	3.93885	-1.70298	-0.42469
H	3.45187	-3.38056	-0.70335
C	3.03345	-2.02831	-2.35975
H	2.74042	-0.98438	-2.51505
H	2.28954	-2.6687	-2.84636
H	3.99123	-2.18934	-2.86556
Cl	3.28199	0.97402	0.07211

Table S9: Atomic coordinates of **Pt-I** in the optimized ground state geometry.

Atom	X	Y	Z
Pt	1.06754	0.27428	0.0463
B	-3.92647	-0.84735	-0.02201
F	-4.76401	0.26602	0.0524
F	-4.68793	-2.00788	-0.09856
N	-2.99214	-0.72936	-1.2476
N	-2.99147	-0.89104	1.20866
P	0.59145	2.54162	0.01073
P	1.70935	-1.96283	0.05867
C	-0.9255	-0.26361	0.01567
C	-1.64331	-0.3908	-1.19661
C	-1.18745	-0.2869	-2.52817
H	-0.16839	-0.05073	-2.80748
C	-2.26311	-0.56543	-3.36853
H	-2.27058	-0.58717	-4.45025
C	-3.35677	-0.82975	-2.53441
H	-4.37493	-1.08318	-2.80172
C	-1.6423	-0.54857	1.20228
C	-1.18911	-0.61125	2.53767
H	-0.17241	-0.40585	2.84849
C	-2.26633	-0.99175	3.33502
H	-2.27623	-1.14601	4.40585
C	-3.35814	-1.15029	2.47252
H	-4.37678	-1.43469	2.70461
C	-1.18965	2.98266	-0.16228
H	-1.54618	2.47591	-1.06629
H	-1.70511	2.48756	0.66942
C	-1.52821	4.46878	-0.20315
H	-2.61138	4.60018	-0.30006
H	-1.06001	4.97218	-1.05553
H	-1.21581	4.98747	0.70939
C	1.44011	3.45200	-1.34833
H	1.21693	4.52014	-1.23735
H	2.51546	3.33133	-1.17588
C	1.07489	2.96128	-2.74472
H	1.61665	3.53646	-3.50328
H	0.00403	3.06751	-2.94938
H	1.33834	1.90565	-2.86713
C	1.15217	3.46067	1.508
H	2.23285	3.29650	1.58595

H	1.00651	4.53292	1.32696
C	0.45921	3.02758	2.79513
H	0.86535	3.57987	3.6493
H	0.60647	1.95874	2.98049
H	-0.61923	3.21591	2.76154
C	0.47902	-3.12528	-0.67555
H	-0.43274	-3.0113	-0.07666
H	0.22894	-2.73184	-1.66751
C	0.88845	-4.59206	-0.7627
H	0.07304	-5.17843	-1.2001
H	1.10596	-5.01859	0.22183
H	1.77038	-4.73514	-1.39593
C	1.98051	-2.65265	1.74831
H	0.99041	-2.69248	2.21945
H	2.32776	-3.68783	1.64403
C	2.94331	-1.85051	2.61661
H	3.01349	-2.29799	3.61396
H	2.60357	-0.81552	2.72584
H	3.95291	-1.82889	2.19242
C	3.27063	-2.32873	-0.84685
H	4.05350	-1.70797	-0.3999
H	3.54396	-3.37462	-0.66177
C	3.16613	-2.04679	-2.34258
H	2.84413	-1.01559	-2.52395
H	2.44932	-2.71453	-2.83272
H	4.13751	-2.18981	-2.82785
I	3.12137	0.82342	0.06675

Table S10: Atomic coordinates of **Pt-I** in the optimized geometry of the first excited triplet state.

Atom	X	Y	Z
Pt	0.63375	0.02754	-0.00791
B	-4.39671	-0.09788	0.01699
F	-4.99919	1.15626	0.07064
F	-5.36201	-1.09322	-0.01834
N	-3.47515	-0.18918	-1.22405
N	-3.46381	-0.28785	1.23867
P	0.51701	2.37608	-0.04291
P	0.73844	-2.32765	0.08287
C	-1.35595	-0.10193	0.00213
C	-2.08733	-0.10831	-1.20348
C	-1.64162	-0.10742	-2.54321
H	-0.60269	-0.06273	-2.84322
C	-2.76511	-0.19103	-3.35891
H	-2.79687	-0.22311	-4.43962
C	-3.87422	-0.23704	-2.50218
H	-4.9264	-0.29912	-2.74922
C	-2.07547	-0.20878	1.21214
C	-1.61994	-0.30847	2.54493
H	-0.5799	-0.28378	2.84266
C	-2.73721	-0.45017	3.3616
H	-2.75978	-0.5612	4.43729
C	-3.8527	-0.42996	2.51321
H	-4.90301	-0.5083	2.76344
C	-1.19062	3.06892	-0.10576
H	-1.63098	2.71537	-1.04548
H	-1.76274	2.57917	0.69058
C	-1.31016	4.58561	0.00571
H	-2.36263	4.87608	-0.08037
H	-0.76249	5.10454	-0.78763
H	-0.94634	4.95626	0.96932
C	1.39815	3.15596	-1.45949

H	1.25759	4.24089	-1.3794
H	2.46244	2.95428	-1.2958
C	0.97142	2.64736	-2.83087
H	1.51199	3.18688	-3.6158
H	-0.10014	2.78668	-3.00976
H	1.19904	1.58163	-2.93743
C	1.31357	3.17907	1.40883
H	2.37367	2.90699	1.35673
H	1.25018	4.26452	1.26334
C	0.72577	2.76902	2.7534
H	1.23340	3.30175	3.56444
H	0.85484	1.69528	2.92279
H	-0.3436	2.99611	2.82369
C	-0.73881	-3.17736	-0.62474
H	-1.59662	-2.84192	-0.03047
H	-0.89303	-2.76639	-1.62862
C	-0.68673	-4.70172	-0.67007
H	-1.63327	-5.08702	-1.06408
H	-0.54306	-5.14123	0.3221
H	0.11203	-5.06704	-1.32331
C	0.80964	-2.96544	1.81069
H	-0.1631	-2.73314	2.26127
H	0.88511	-4.05836	1.75743
C	1.93994	-2.39532	2.66045
H	1.90293	-2.82691	3.66646
H	1.86199	-1.30707	2.74947
H	2.92354	-2.61979	2.23541
C	2.16174	-3.12295	-0.76771
H	3.07148	-2.73963	-0.29612
H	2.11075	-4.19799	-0.55591
C	2.19338	-2.85732	-2.26863
H	2.25547	-1.78291	-2.47132
H	1.30475	-3.25168	-2.77367
H	3.06996	-3.33592	-2.71776
I	3.39136	0.25810	0.00283

Table S11: Atomic coordinates of **Pt-NCS** in the optimized ground state geometry.

Atom	X	Y	Z
C	4.26823	12.6649	9.25673
C	4.70155	12.0705	8.0611
C	4.37516	12.34873	6.71523
H	3.77940	13.02262	6.41163
C	5.07285	11.47067	5.92024
H	5.05374	11.43093	4.97187
C	5.81218	10.64863	6.77001
H	6.38504	9.94402	6.48675
C	4.76673	12.14638	10.4727
C	4.48827	12.51494	11.80448
H	3.90028	13.2051	12.08461
C	5.23138	11.68025	12.63547
H	5.24542	11.6929	13.5854
C	5.94935	10.82388	11.80448
H	6.54737	10.14998	12.10651
C	1.47628	10.93047	8.74968
H	0.63337	10.49687	8.35688
H	2.21596	10.93047	7.98129
C	1.81045	10.1554	9.99382
H	2.12717	9.26109	9.74656
H	1.01020	10.07591	10.55251
H	2.51189	10.62334	10.49148
C	0.43959	13.21594	7.19098

H	0.27302	14.19155	7.1722
H	1.11104	13.00997	6.49301
C	-0.78086	12.52578	6.88895
H	-0.59546	11.57004	6.77314
H	-1.16519	12.88712	6.06421
H	-1.41628	12.64683	7.62604
C	-0.14703	13.04069	10.11432
H	-0.6026	13.86092	9.79664
H	-0.79591	12.29633	10.04077
C	0.17818	13.22316	11.54313
H	0.69099	12.45171	11.86395
H	-0.6517	13.30085	12.05957
H	0.70866	14.03979	11.65581
C	6.24660	15.27737	8.61353
H	6.40971	14.25478	8.87331
H	6.82847	15.8266	8.92026
C	6.17366	15.42552	7.09708
H	7.00868	15.10573	6.69802
H	6.04333	16.36861	6.86704
H	5.42339	14.89797	6.75279
C	5.22253	15.90791	11.20666
H	5.51363	15.04973	11.47114
H	6.02432	16.51315	11.18945
C	4.10917	16.39752	12.11747
H	4.43823	16.4463	13.03923
H	3.35307	15.77602	12.07209
H	3.81782	17.28822	11.82795
C	4.26266	17.38216	8.89522
H	4.06239	17.3370	7.92651
H	3.43625	17.66943	9.35688
C	5.33804	18.4445	9.11901
H	5.47382	18.57458	10.0799
H	5.05317	19.28822	8.71056
H	6.17808	18.15001	8.70743
C	0.76172	16.37222	9.85767
B	6.18960	10.30355	9.29116
F	5.77480	8.97907	9.34765
F	7.58340	10.33607	9.25344
S	-0.38317	17.36789	10.43577
N	5.59468	10.99895	8.04545
N	5.67604	11.08874	10.51182
N	1.58219	15.6640	9.43826
P	1.19226	12.70302	9.01431

Table S12: Atomic coordinates of **Pt-NCS** in the optimized geometry of the first excited triplet state.

Atom	X	Y	Z
C	1.27376	-0.17925	-0.00132
C	2.01624	-0.43795	-1.17591
C	1.58514	-0.75642	-2.48293
H	0.55022	-0.80128	-2.79793
C	2.7189	-1.00632	-3.24985
H	2.76111	-1.293	-4.29194
C	3.81994	-0.82241	-2.40162
H	4.8763	-0.90709	-2.62222
C	1.989	-0.06788	1.21229
C	1.52718	0.00243	2.54583
H	0.48455	0.01753	2.83781
C	2.64327	-0.00575	3.37679
H	2.66163	0.01817	4.45799
C	3.76399	-0.06936	2.53621
H	4.81486	-0.08061	2.79566

C	0.29372	-3.45231	0.0926
H	-0.04377	-4.42133	-0.29415
H	1.0766	-3.09363	-0.58542
C	0.84153	-3.6208	1.50623
H	1.71313	-4.28334	1.48449
H	0.10162	-4.07445	2.17345
H	1.15757	-2.66694	1.93802
C	-1.86831	-2.73684	-1.70859
H	-2.63117	-1.9763	-1.91004
H	-1.08371	-2.59842	-2.46233
C	-2.46793	-4.13697	-1.80918
H	-1.72528	-4.9215	-1.63269
H	-2.87178	-4.28998	-2.81555
H	-3.28943	-4.27885	-1.10021
C	-2.37449	-2.77487	1.16575
H	-3.34904	-2.51817	0.73395
H	-2.34412	-3.86747	1.26133
C	-2.22202	-2.09766	2.52512
H	-1.25627	-2.31536	2.99057
H	-3.00804	-2.44483	3.20437
H	-2.31373	-1.01141	2.42565
C	1.0394	3.02079	-0.97483
H	1.92294	2.48569	-0.60704
H	1.16554	4.07204	-0.68742
C	0.9243	2.88527	-2.48958
H	1.83913	3.25182	-2.96644
H	0.08666	3.46722	-2.88802
H	0.78958	1.84072	-2.78674
C	-0.16095	3.02653	1.64635
H	0.75583	2.5554	2.01971
H	0.04269	4.10165	1.56664
C	-1.32559	2.76092	2.59448
H	-1.08464	3.12824	3.59736
H	-1.54441	1.69022	2.66937
H	-2.24013	3.26661	2.26737
C	-1.86911	3.26805	-0.72824
H	-2.02462	2.89037	-1.74561
H	-2.73686	2.93001	-0.15241
C	-1.76574	4.78992	-0.71817
H	-1.6543	5.18477	0.29684
H	-2.67856	5.22351	-1.1401
H	-0.92291	5.1508	-1.31662
C	-3.92425	0.31156	-0.17255
B	4.27787	0.01136	0.00266
F	5.42218	-0.75445	0.13538
F	4.59866	1.35444	-0.20356
S	-5.54863	0.40471	-0.21345
N	3.40476	-0.49207	-1.17154
N	3.37724	-0.11295	1.25479
N	-2.74828	0.24965	-0.14301
P	-1.11607	-2.28152	-0.08741

Table S13: Atomic coordinates of **Pt-NO_2** in the optimized ground state geometry.

Atom	X	Y	Z
Pt	-2.41755	3.46964	10.11004
B	-5.7657	7.23402	10.30933
F	-7.1456	7.19532	10.53432
F	-5.39204	8.55633	10.1019
N	-5.01526	6.63006	11.50286
N	-5.40506	6.37939	9.06953
N	-1.02448	2.01711	9.94872

O	-0.19774	1.75467	10.82472
O	-0.97804	1.27352	8.89242
P	-4.00439	1.81978	10.54182
P	-0.74985	5.08938	9.91362
C	-3.75578	4.8939	10.20721
C	-4.06897	5.57524	11.43744
C	-3.60533	5.37168	12.74266
H	-2.96894	4.71893	13.01073
C	-4.22463	6.27004	13.5676
H	-4.0836	6.36762	14.50104
C	-5.09458	7.01027	12.78574
H	-5.6688	7.69329	13.11444
C	-4.43851	5.35486	9.06953
C	-4.34366	4.89894	7.72442
H	-3.77798	4.20414	7.41168
C	-5.22301	5.64758	6.94576
H	-5.36522	5.56346	6.00912
C	-5.85304	6.53922	7.8042
H	-6.50845	7.17345	7.53933
C	-5.65029	2.44274	11.04013
H	-5.53888	3.06184	11.80443
H	-6.03493	2.95922	10.28859
C	-6.65466	1.32736	11.44382
H	-7.54992	1.71429	11.54594
H	-6.3736	0.92696	12.2927
H	-6.67539	0.6376	10.74813
C	-3.43132	0.76546	11.91772
H	-4.13331	0.09926	12.12675
H	-2.62254	0.27254	11.63051
C	-3.10981	1.54942	13.16869
H	-2.79939	0.93706	13.86758
H	-3.91421	2.01711	13.47824
H	-2.40793	2.20553	12.97243
C	-4.31331	0.64938	9.17963
H	-3.43903	0.34824	8.82221
H	-4.77377	-0.14468	9.54822
C	-5.1379	1.18772	8.02759
H	-5.27708	0.47946	7.36541
H	-4.66489	1.93804	7.60954
H	-6.00502	1.49559	8.36267
C	-1.29443	6.56613	9.0073
H	-1.65703	6.27845	8.1329
H	-2.03613	6.98503	9.51312
C	-0.20802	7.6361	8.75839
H	-0.607	8.4066	8.30204
H	0.50214	7.25757	8.19832
H	0.17022	7.92377	9.61524
C	0.75996	4.52547	9.0807
H	1.44243	5.24046	9.13974
H	1.11176	3.73309	9.55779
C	0.55313	4.16377	7.61113
H	1.41346	3.91646	7.21063
H	0.18018	4.93427	7.13404
H	-0.06629	3.40672	7.54571
C	-0.16403	5.7031	11.53477
H	0.3843	6.51398	11.38638
H	-0.95071	5.96891	12.0725
C	0.65587	4.70548	12.33737
H	0.85272	5.08064	13.22135

Table S14: Atomic coordinates of **Pt-NO_2** in the optimized geometry of the first excited triplet state.

Atom	X	Y	Z
Pt	-0.93063	0.04278	-0.01087
B	4.12903	-0.24379	-0.00969
F	5.07467	0.77316	0.00665
F	4.76069	-1.48359	-0.03238
N	3.20431	-0.14217	1.22899
N	3.19833	-0.10007	-1.23896
N	-3.02118	0.13693	-0.05396
O	-3.66739	0.09495	0.99615
O	-3.6016	0.24417	-1.13809
P	-0.9472	2.39103	-0.03878
P	-1.00741	-2.30186	0.11043
C	1.08094	-0.03997	0.002
C	1.81471	-0.08919	1.20579
C	1.36986	-0.0686	2.54629
H	0.33156	-0.02283	2.84755
C	2.49423	-0.10672	3.36401
H	2.52694	-0.09993	4.44513
C	3.60352	-0.15203	2.50819
H	4.65624	-0.19159	2.75769
C	1.80928	-0.04398	-1.20569
C	1.35514	0.00906	-2.54179
H	0.31422	0.05828	-2.83345
C	2.47388	-0.01168	-3.36774
H	2.49936	0.02017	-4.44864
C	3.58899	-0.07992	-2.52086
H	4.63992	-0.11547	-2.77849
C	0.70285	3.20299	-0.03392
H	1.24013	2.80919	0.83679
H	1.24063	2.82239	-0.91004
C	0.69052	4.72787	-0.02211
H	1.71899	5.10371	-0.01606
H	0.18984	5.1271	0.86586
H	0.19553	5.14086	-0.90684
C	-1.86765	3.08996	1.39401
H	-1.9505	4.17339	1.24286
H	-2.88117	2.67746	1.32873
C	-1.26043	2.7731	2.75522
H	-1.86262	3.22813	3.54842
H	-0.23927	3.15716	2.85162
H	-1.23571	1.69335	2.93051
C	-1.86573	3.09956	-1.46721
H	-2.88994	2.71946	-1.38179
H	-1.91037	4.18653	-1.32604
C	-1.29191	2.74724	-2.83396
H	-1.87518	3.23656	-3.62094
H	-1.33597	1.66804	-3.00689
H	-0.25073	3.06919	-2.94312
C	0.37015	-3.15755	-0.76194
H	0.40671	-2.74984	-1.77858
H	1.29212	-2.821	-0.27353
C	0.30142	-4.68156	-0.78803
H	1.18113	-5.07828	-1.3056
H	-0.584	-5.04425	-1.3199
H	0.29273	-5.11053	0.21891
C	-2.54717	-3.05321	-0.56078
H	-2.54329	-4.11559	-0.28612
H	-3.38827	-2.59151	-0.03222
C	-2.70389	-2.87676	-2.06856
H	-3.64438	-3.32881	-2.4004
H	-1.89143	-3.3598	-2.62184

H	-2.72732	-1.81676	-2.33745
C	-0.89819	-2.9136	1.8421
H	-0.91024	-4.00999	1.81151
H	0.08986	-2.61253	2.21065
C	-1.99451	-2.38924	2.76372
H	-1.82816	-2.75285	3.78319

Table S15: Selected bond lengths and bond angles of the calculated structures of **Pt-Cl**, **Pt-I**, **Pt-NCS**, and **Pt-NO_2** in comparison with the structure data from X-ray crystal structure analysis.

		Pt-Cl		**Pt-I**	**Pt-NCS**	**Pt-NO_2**
		molecule 1	molecule 2			
		bond lengths / Å				
C1-Pt1	X-ray	1.976(7)	1.971(8)	1.994(10)	1.984(4)	1.956(9)[c]
	S_0	1.984	-	1.994	1.989	2.013
	T_1	2.013	-	2.021	2.017	2.038
X1-Pt1[a]	X-ray	2.3750(19)	2.385(2)	2.6689(8)	2.048(4)	2.019(8)
	S_0	2.435	-	2.767	2.058	2.093
	T_1	2.443	-	2.773	2.060	2.087
P1-Pt1	X-ray	2.319(2)	2.316(2)	2.3206(15)	2.3135(13)	2.329(2)
	S_0	2.348	-	2.352	2.349	2.348
	T_1	2.339	-	2.350	2.342	2.342
P2-Pt1	X-ray	2.309(2)	2.310(2)	-[b]	2.3249(11)	2.334(2)
	S_0	2.344	-	2.359	2.356	2.349
	T_1	2.336	-	2.345	2.347	2.345
		bond angles / deg				
C1-Pt1-P1	X-ray	91.2(2)	91.6(2)	91.37(7)	91.44(12)	92.3(3)[c]
	S_0	90.4	-	88.8	94.1	92.8
	T_1	89.7	-	88.2	93.8	91.9
C1-Pt1-P2	X-ray	94.0(2)	93.0(2)	-[b]	90.79(12)	89.3(3)[c]
	S_0	92.1	-	90.9	89.0	89.5
	T_1	91.4	-	90.1	88.1	88.1
P1-Pt1-X[a]	X-ray	87.13(7)	87.68(8)	88.71(7)	87.28(12)	88.6(2)
	S_0	91.0	-	92.2	86.0	87.0
	T_1	91.8	-	92.9	86.5	87.8
P2-Pt1-X[a]	X-ray	87.61(7)	87.76(8)	-[b]	90.62(11)	90.0(2)
	S_0	86.4	-	88.1	91.0	90.8
	T_1	87.1	-	88.7	91.7	92.4
P1-Pt1-P2	X-ray	174.74(8)	175.00(7)	176.8(3)	177.17(5)	173.83(8)
	S_0	177.5	-	178.6	176.9	176.8
	T_1	178.6	-	178.4	178.0	175.0
C1-Pt1-X[a]	X-ray	178.3(2)	179.0(2)	176.03(8)	175.77(17)	178.2(4)[c]
	S_0	178.3	-	178.8	179.7	179.2
	T_1	178.1	-	178.2	179.7	178.1

[a]X represents here the atom of the anionic ligand in *trans*-position to the dye bond to the Pt ion. [b]The molecule has a mirror plane which is defined by the plane of the dye's inner heterocycle. [c]C1 remained isotropic and could not further be refined.

Photophysical properties

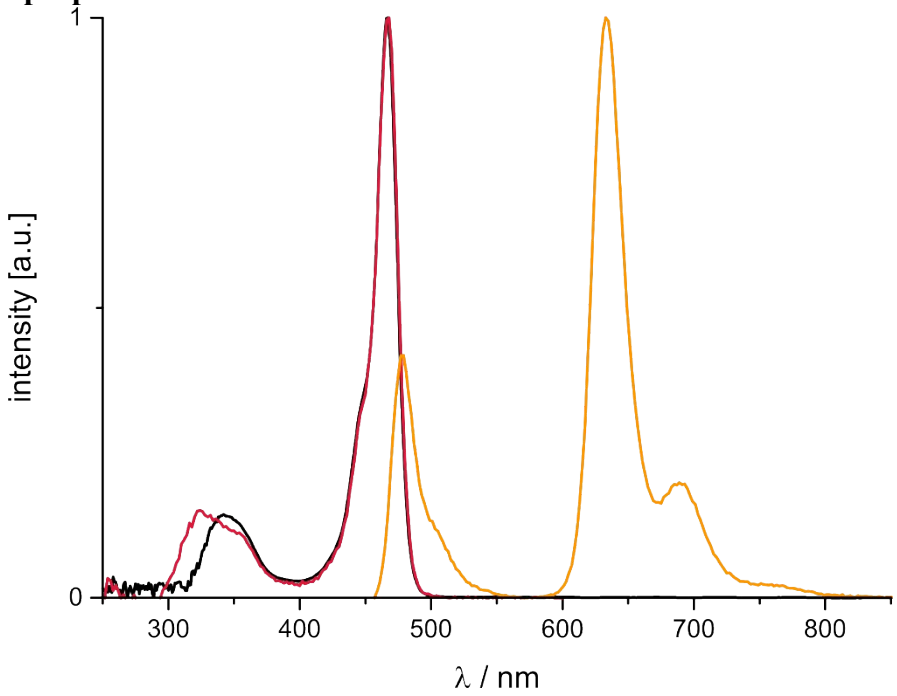

Figure S29: UV-Vis absorption (black), excitation (detection at 635 nm, red) and emission spectra (orange, excited at 450 nm) of **Pt-Cl** in a ca. 10^{-6} M CH_2Cl_2 solution at r.t.

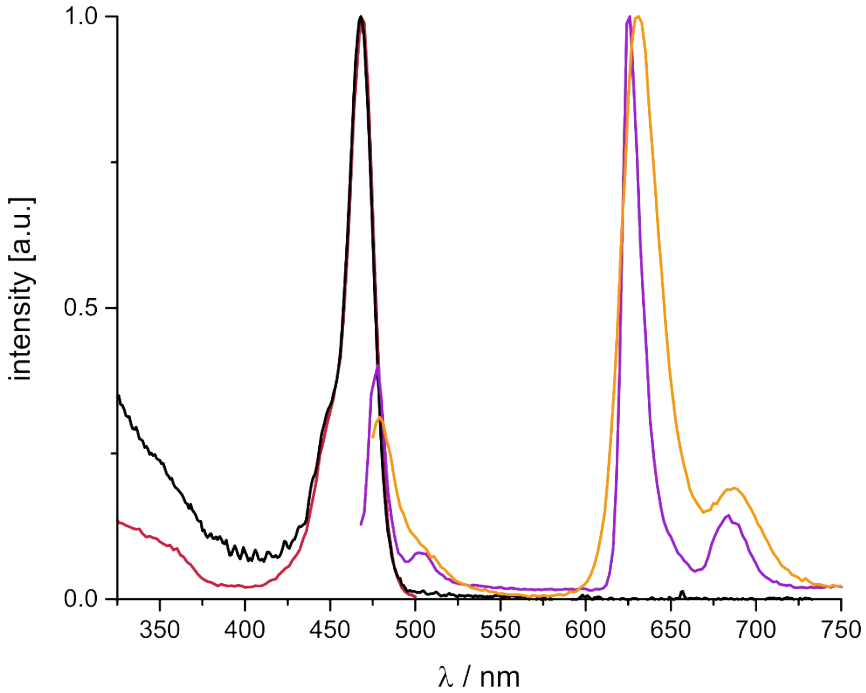

Figure S30: UV-Vis absorption (black), excitation (detection at 635 nm, r.t., red) and emission spectra (orange, r.t., excited at 468 nm; violet, 77 K, excited at 450 nm) of **Pt-Cl** in a ca. 10^{-6} M toluene solution.

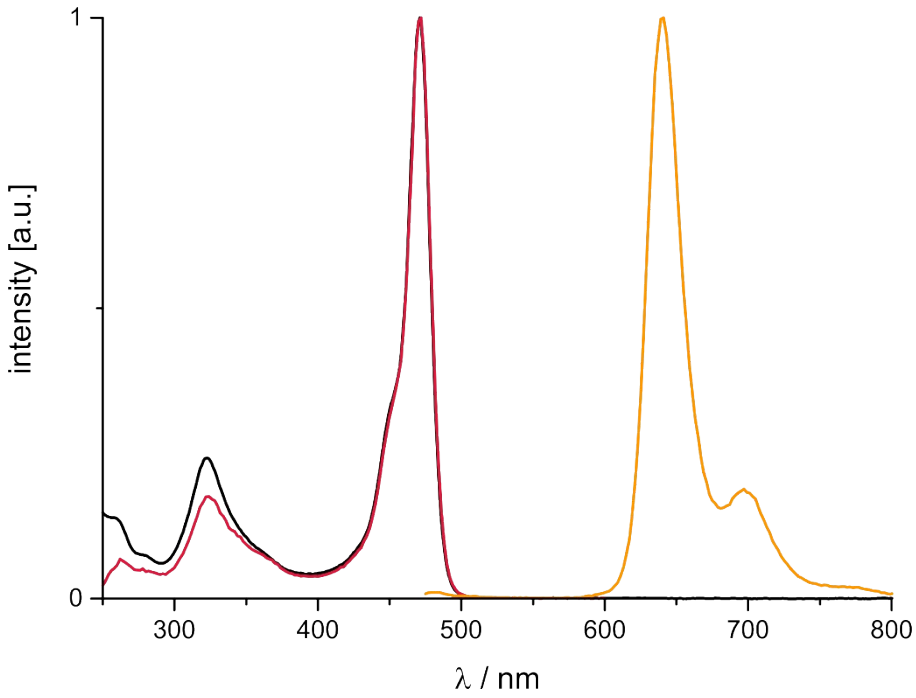

Figure S31: UV-Vis absorption (black), excitation (detection at 640 nm, red) and emission spectra (orange, excited at 471 nm) of **Pt-I** in a ca. 10^{-6} M CH_2Cl_2 solution at r.t.

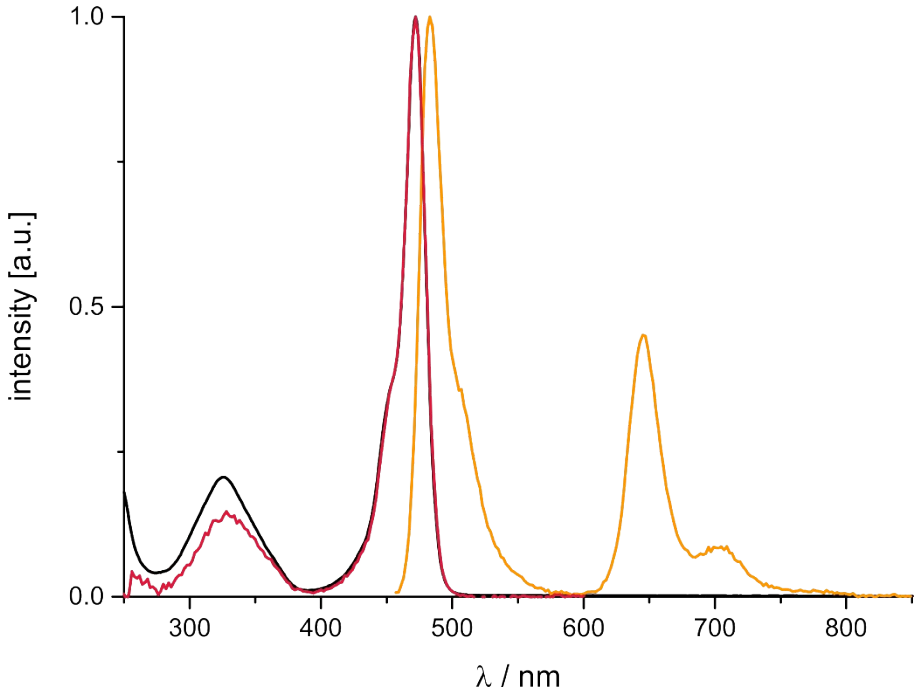

Figure S32: UV-Vis absorption (black), excitation (detection at 646 nm, red) and emission spectra (orange, excited at 450 nm) of **Pt-NO_2** in a ca. 10^{-6} M CH_2Cl_2 solution at r.t.

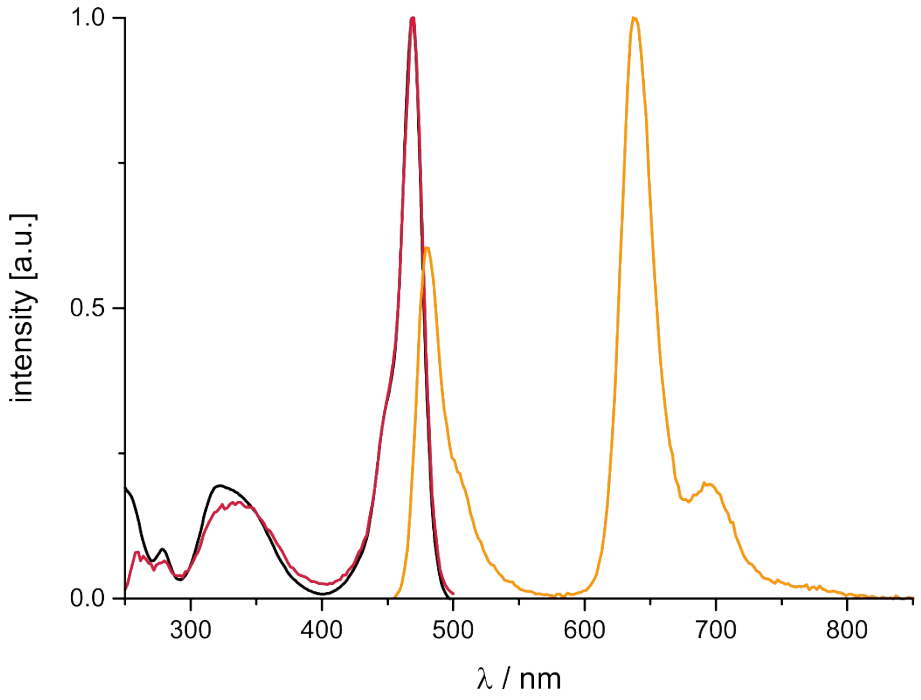

Figure S33: UV-Vis absorption (black), excitation (detection at 638 nm, red) and emission spectra (orange, excited at 450 nm) of **Pt-NCS** in a ca. 10^{-6} M CH_2Cl_2 solution at r.t.

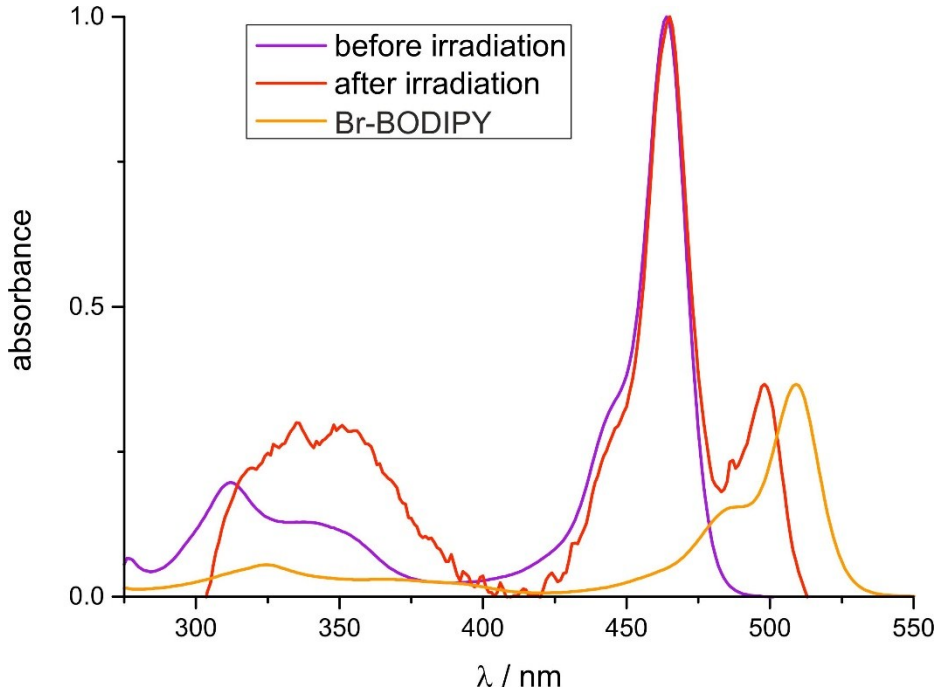

Figure S34: Electronical absorption spectra of **Pt-CH_3** in a ca. 10^{-6} M benzene solution before and after irradiating the sample into its lowest energy absorption band, and of **Br-BODIPY** in benzene solution, respectively.

Stern-Volmer quenching experiments

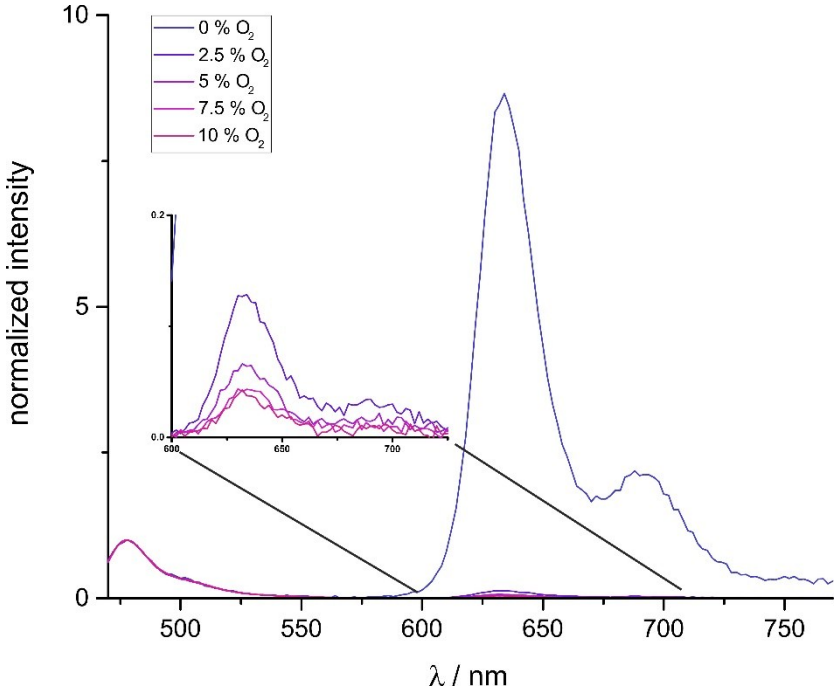

Figure S35: Stacked luminescence spectra of **Pt-Cl** at different oxygen concentrations.

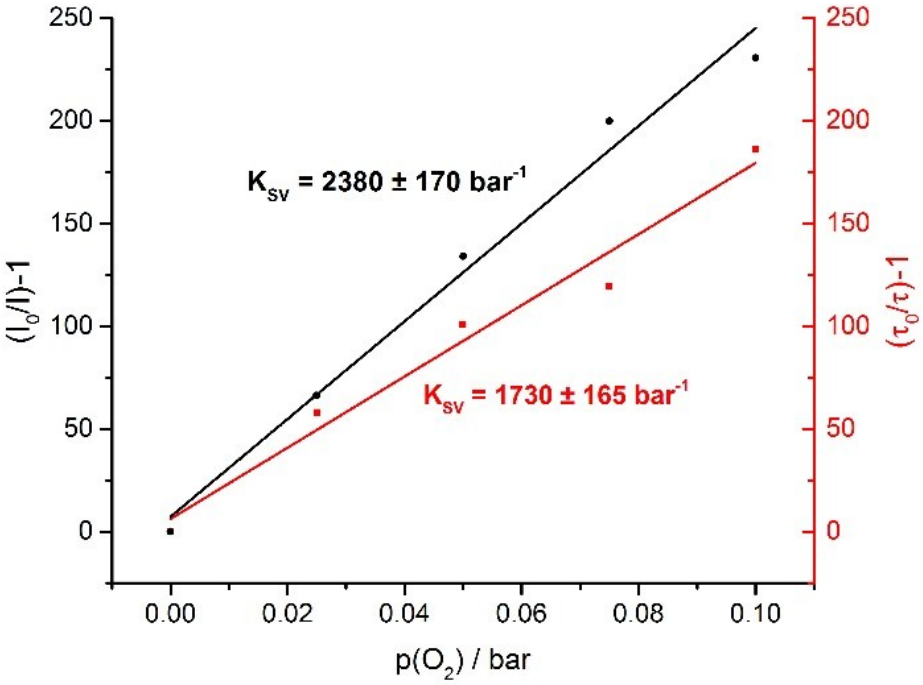

Figure S36: Stern-Volmer plot of **Pt-Cl**.

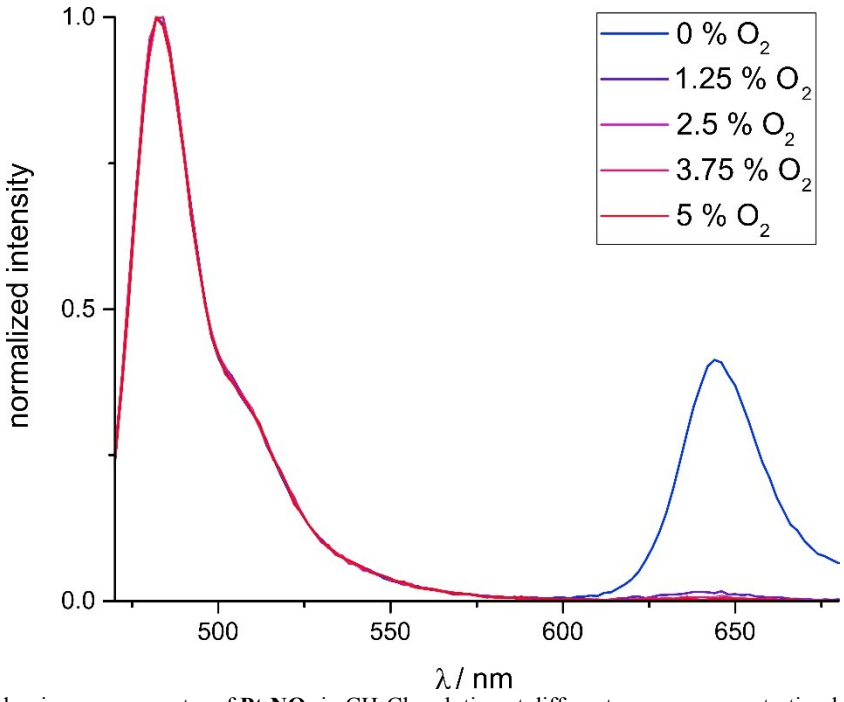

Figure S37: Stacked luminescence spectra of **Pt-NO$_2$** in CH_2Cl_2 solution at different oxygen concentration levels.

Photoreaction

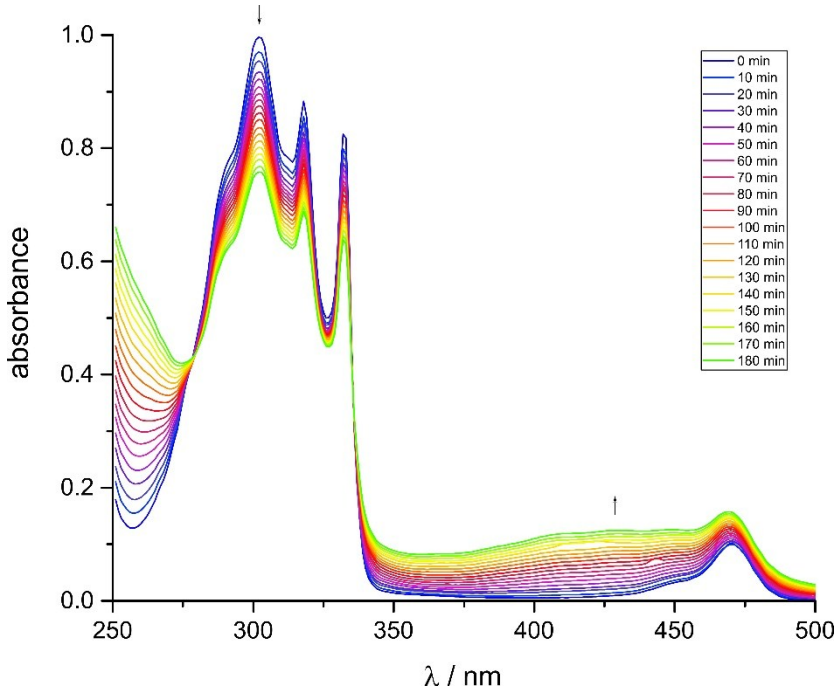

Figure S38: Spectral change in the absorption spectra of the reaction mixture containing **DHN** and **Pt-I**.

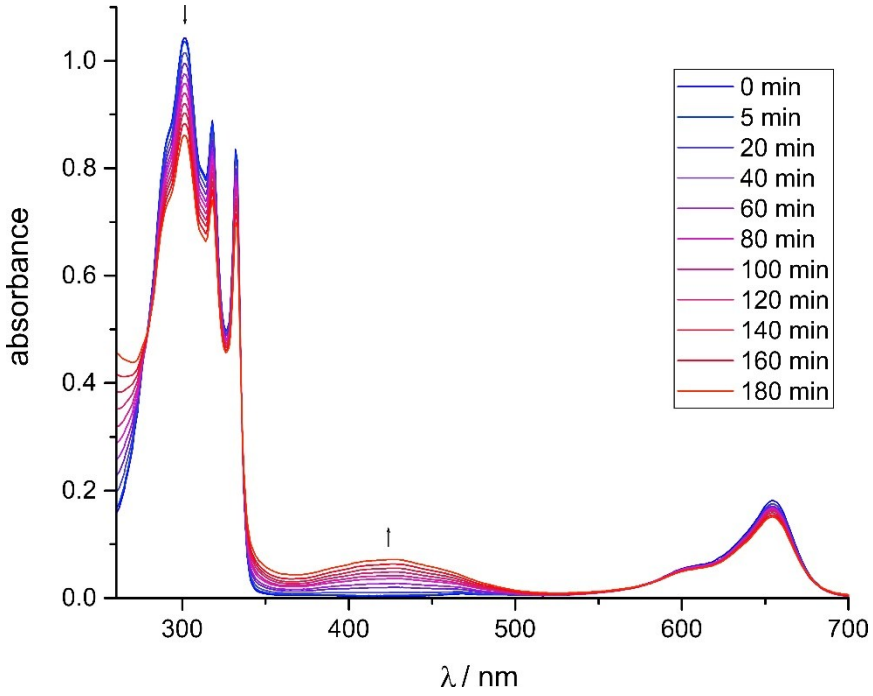

Figure S39: Spectral change in the absorption spectra of the reaction mixture containing **DHN** and the reference sensitizer **MB**.

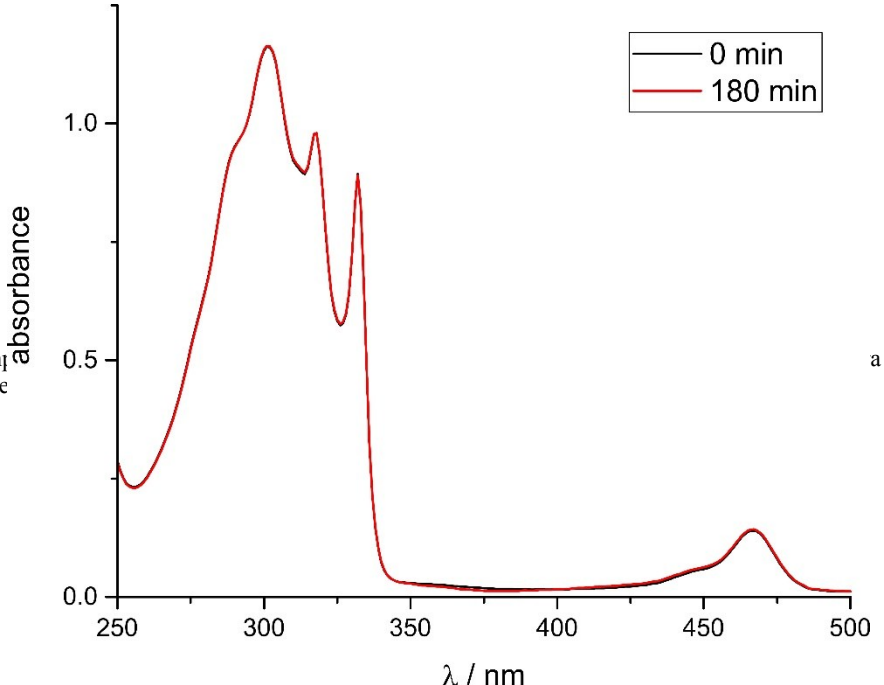

Figure S40: Samp a were taken before and after that time

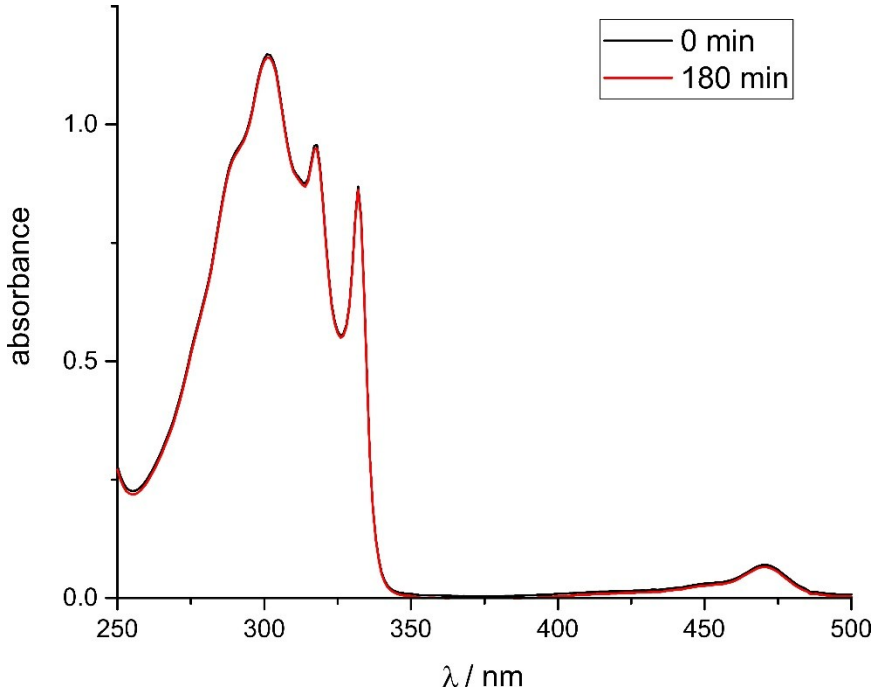

Figure S41: Sample of the reaction mixture of **DHN** and **Pt-I** kept in the dark for 180 min; UV-Vis spectra were taken before and after that time period.