

Supporting Information for

Dibenzothiophene-platinated complexes: probing the effect of ancillary ligands on the photophysical performance

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Synthesis of HPyDBTO₂ ligand.

Table S1. Crystal data and structure refinement for **1–6**, **8–11**.

Table S2. Selected bond lengths (Å) and angles (deg.) for complexes **1–6** and **11**.

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Figure S2. Molecular views of complexes **10**.

Figure S3. 162 MHz ³¹P{¹H} NMR spectrum of **8**.

Figure S4. ESI-MS of complexes **8–10**.

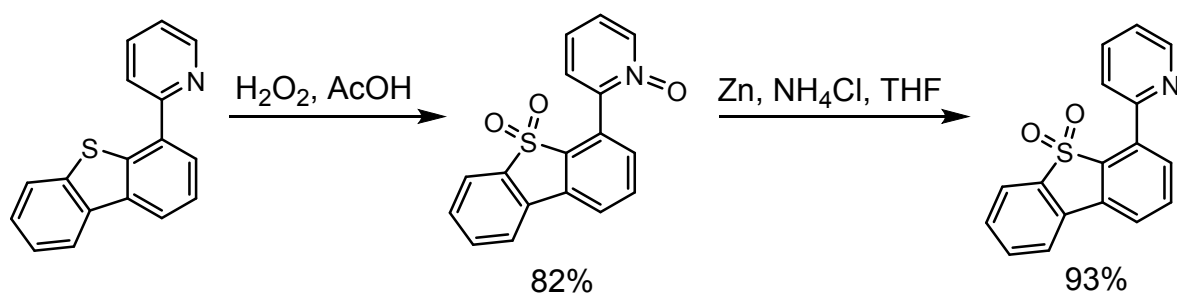
Figure S5. Absorption spectra of complexes **1–7**, **10** and **11**.

Figure S6. Solid state excitation spectra of complexes **1**, **3–10**.

Figure S7. Solid state excitation and emission spectra of complexes **2** and **11**.

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Synthesis of HPyDBTO₂.



HPyDBT (0.4 g, 1.53 mmol) was dissolved in acetic acid (15 mL) and 30% water solution of H₂O₂ (2.5 mL) was added. The reaction mixture was heated at 100 °C for 7 h under a nitrogen atmosphere. After cooling to room temperature the resulting dibenzothiophene-S,S-dioxide-pyridyl-N-oxide was precipitated with water (40 mL) as a white amorphous solid, which was washed with water (2 × 20 mL), dried on air (0.388 g, 82%) and used in the next step without additional purification. ¹H NMR (400 MHz, CDCl₃, 298 K δ): 8.48 (d, ³J_{HH} 6.3 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.86 (d, ³J_{HH} 7.6 Hz, 2H), 7.79 – 7.74 (m, 2H), 7.68 (t, ³J_{HH} 7.6 Hz, 1H), 7.55 (t, ³J_{HH} 7.6 Hz, 1H), 7.50 (t, ³J_{HH} 7.8 Hz, 1H), 7.44 (t, ³J_{HH} 6.4 Hz, 1H).

The sulfone N-oxide (0.37 g, 1.26 mmol) was dissolved in freshly distilled tetrahydrofuran (60 mL) and 30% water solution of NH₄Cl (30 mL) was added, followed by Zn dust (0.255 g, 4.25 mmol). The reaction mixture was vigorously stirred under a nitrogen atmosphere for 1 h, the completion was checked by the TLC test (eluent CH₂Cl₂/methanol 100:1 v/v mixture). The organic layer was separated, the aqueous one was washed with CH₂Cl₂ (2 × 15 mL). The organic fractions were combined, dried over anhydrous Na₂SO₄, filtered and evaporated. Pale oily residue was treated with diethyl ether (10 mL) to afford colourless HPyDBTO₂ (0.33 g, 93%). ¹H NMR (400 MHz, CDCl₃, 298 K, δ): 8.91 (d, ³J_{HH} 4.6 Hz, 1H), 8.20 (d, ³J_{HH} 7.9 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.89 – 7.81 (m, 3H), 7.76 (t, ³J_{HH} 7.7 Hz, 1H), 7.66 (td, ³J_{HH} 7.6, ⁴J_{HH} 1.1 Hz, 1H), 7.55 (td, ³J_{HH} 7.5, ⁴J_{HH} 0.8 Hz, 1H), 7.45 (dd, ³J_{HH} 7.2, 5.3 Hz, 1H). Anal. calc. for C₁₇H₁₁NO₂S (%): C 69.61; H 3.78; N 4.78; S 10.93. Found: C 69.94; H 3.61; N 4.56; S 11.12.

Table S1. Crystal data and structure refinement for **1–6, 8–11.**

Identification code	1	2	3	4	5
Empirical formula	C ₁₉ H ₁₆ ClNOPtS ₂	C ₃₆ H ₂₇ Cl ₃ NPtS	C ₃₈ H ₂₂ ClF ₉ NPtS	C ₃₈ H ₃₁ ClNO ₃ PPtS	C ₁₄₅ H ₁₁₂ C ₁₆ N ₈ OP ₂ Pt ₂ S ₂
Formula weight	568.99	838.05	957.13	843.21	2711.36
Temperature (K)			150(2)		120(2)
Wavelength (Å)			0.71073		
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>Pbca</i>	<i>Pbca</i>	<i>P 1</i>
Unit cell dimensions					
a (Å)	14.1551(3)	19.685(3)	15.7792(3)	14.9248(19)	14.3412(5)
b (Å)	12.8383(3)	9.0677(13)	24.0043(5)	19.983(3)	14.7639(5)
c (Å)	10.3284(2)	18.272(3)	39.2309(9)	21.437(3)	16.5461(6)
a (°)	90	90	90	90	65.2770(10)
β (°)	110.2640(10) ^o	111.318(4)	90	90	69.1760(10)
γ (°)	90	90	90	90	82.2040(10)
Volume (Å ³)	1760.78(7)	3038.4(8)	14859.4(5)	6393.3(14)	2974.00(18)
Z	4	4	16	8	1
ρ _{calc} (Mg/m ³)	2.146	1.832	1.711	1.752	1.514
μ (mm ⁻¹)	8.365	5.032	4.022	4.629	2.605
F(000)	1088	1640	7424	3328	1366
Crystal size (mm ³)	0.110 × 0.081 × 0.071	0.180 × 0.089 × 0.014	0.618 × 0.219 × 0.196	0.444 × 0.419 × 0.390	0.765 x 0.263 x 0.238
θ range for data collection (°)	2.207 to 31.998	1.110 to 26.999	1.629 to 30.014	1.900 to 30.030	1.436 to 25.999
Index ranges	-21 ≤ h ≤ 21, - 19 ≤ k ≤ 19, -	-25 ≤ h ≤ 25, - 11 ≤ k ≤ 11, -	-21 ≤ h ≤ 21, - 33 ≤ k ≤ 30, -	-20 ≤ h ≤ 20, - 28 ≤ k ≤ 28, -	-17 ≤ h ≤ 17, - 18 ≤ k ≤ 18, -20 ≤ l ≤ 20

	15<=l<=15	23<=l<=23	55<=l<=25	30<=l<=30	
Reflections collected	64015	40002	97349	141752	79921
Independent reflections	6099 [R(int) = 0.0258]	6571 [R(int) = 0.0761]	21577 [R(int) = 0.0511]	9328 [R(int) = 0.0244]	11686 [R(int) = 0.0323]
Completeness to $\theta=25.24^\circ$	99.8 %	99.0	99.9	99.9	99.9
Absorption correction	Numerical	Numerical	Multi-scan	Numerical	Numerical
Max. and min. transmission	0.552 and 0.448	0.932 and 0.590	0.455 and 0.361	0.164 and 0.147	0.538 and 0.444
Data/restraints/parameters	6099 / 0 / 226	6571 / 0 / 388	21577 / 60 / 965	9328 / 0 / 418	11686 / 12 / 753
GOOF on F ²	1.099	1.058	1.015	1.086	1.068
Final R indices [I>2 σ (I)] ^a	R1 = 0.0157, wR2 = 0.0296	R1 = 0.0388, wR2 = 0.0769	R1 = 0.0318, wR2 = 0.0581	R1 = 0.0184, wR2 = 0.0430	R1 = 0.0322, wR2 = 0.0853
R indices (all data)	R1 = 0.0182, wR2 = 0.0301	R1 = 0.0530, wR2 = 0.0807	R1 = 0.0527, wR2 = 0.0630	R1 = 0.0234, wR2 = 0.0455	R1 = 0.0367, wR2 = 0.0884
Largest diff. peak and hole (e.Å ⁻³)	0.799 and -0.956	1.373 and -2.382	1.063 and -0.852	0.760 and -0.421	2.689 and -1.140

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}]^{1/2}$$

Table S1. Continued.

Identification code	6	8	9	10	11
Empirical formula	C ₂₄ H ₂₄ Cl ₃ N ₄ PtS	C ₇₉ H ₄₆ BF ₂₄ NP ₂ PtS	C ₅₉ H ₃₀ BF ₂₄ N ₃ PtS	C ₆₁ H ₃₀ BF ₂₄ N ₃ Pt S	C ₃₆ H ₂₇ Cl ₃ NO ₂ PtS
Formula weight	732.94	1765.07	1474.82	1498.84	870.05
Temperature (K)	120(2)	150(2)	120(2)	120(2)	150(2)
Wavelength (Å)			0.71073		
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic

Space group	<i>Fdd2</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P 1</i>	<i>P 1</i>
Unit cell dimensions					
a (Å)	22.8514(7)	10.4003(8)	18.0471(4)	9.7875(7)	9.0984(5)
b (Å)	72.360(2)	36.096(3)	9.7853(2)	16.9299(12)	12.7450(8)
c (Å)	5.8722(2)	19.1737(15)	31.2267(7)	18.1399(12)	14.8158(9)
α (°)	90	90	90	109.001(2)	73.077(2)
β (°)	90	90.873	104.7500(10)	91.579(2)	86.803(2)
γ (°)	90	90	90	106.545(2)	84.281(2)
Volume (Å ³)	9709.9(5)	7197.2(10)	5332.8(2)	2700.3(3)	1634.80(17)
Z	16	4	4	2	2
ρ _{calc} (Mg/m ³)	2.006	1.629	1.837	1.843	1.768
μ (mm ⁻¹)	6.286	2.131	2.800	2.767	4.685
F(000)	5696	3488	2880	1464	852
Crystal size (mm ³)	0.146 × 0.063 × 0.034	0.703 × 0.352 × 0.110	0.646 × 0.551 × 0.152	0.142 × 0.052 × 0.047	0.971 × 0.182 × 0.126
θ range for data collection (°)	1.869 to 26.995	1.203 to 30.000	1.349 to 28.999	2.084 to 26.000	2.503 to 38.267
Index ranges	-28 ≤ h ≤ 28, - 92 ≤ k ≤ 88, -7 ≤ l ≤ 7	-14 ≤ h ≤ 14, - 50 ≤ k ≤ 50, -26 ≤ l ≤ 26	-24 ≤ h ≤ 24, - 13 ≤ k ≤ 13, -42 ≤ l ≤ 42	-12 ≤ h ≤ 12, - 20 ≤ k ≤ 20, -22 ≤ l ≤ 22	-15 ≤ h ≤ 15, - 22 ≤ k ≤ 21, -24 ≤ l ≤ 25
Reflections collected	36977	195720	194827	84786	47425
Independent reflections	5312 [R(int) = 0.0600]	20988 [R(int) = 0.0430]	14180 [R(int) = 0.0389]	10116 [R(int) = 0.0669]	16973 [R(int) = 0.0208]
Completeness to θ = 25.24°	100.0	99.9	99.9	96.9	98.7
Absorption correction	Numerical	Multi-scan	Numerical	Multi-scan	Numerical
Max. and min. transmission	0.808 and 0.628	0.791 and 0.423	0.653 and 0.179	0.878 and 0.841	0.554 and 0.374

Data/ parameters	restrains/	5312 / 1 / 308	20988 / 117 / 1066	14180 / 278 / 948	10116 / 42 / 848	16973 / 0 / 406
GOOF on F ²		1.055	1.087	1.080	1.067	1.035
Final R [I>2σ(I)] ^a	indices	R1 = 0.0256, wR2 = 0.0442	R1 = 0.0337, wR2 = 0.0645	R1 = 0.0267, wR2 = 0.0552	R1 = 0.0489, wR2 = 0.0731	R1 = 0.0196, wR2 = 0.0444
R indices (all data)		R1 = 0.0321, wR2 = 0.0453	R1 = 0.0422, wR2 = 0.0671	R1 = 0.0322, wR2 = 0.0573	R1 = 0.0613, wR2 = 0.0761	R1 = 0.0242, wR2 = 0.0462
Largest diff. peak and hole (e.Å ⁻³)		0.935 and -1.237	0.957 and -1.414	1.051 and -0.750	2.501 and -1.045	1.693 and -1.915
^a R ₁ = Σ F _o - F _c /Σ F _o ; wR ₂ = [Σ [w(F _o ² - F _c ²)]/ Σ[w(F _o ²)]] ^{1/2}						

Table S2. Selected bond lengths (Å) and angles (deg.) for complexes **1–6** and **11**.

	1	2	3	4	5	6	11
Bond lengths, Å							
C(1)-Pt(1)	2.006(2)	1.994(5)	2.011(3)/ 2.018(3)	2.008(2)	1.994(5)	2.001(6)	1.996(1)
N(1)-Pt(1)	2.051(1)	2.083(5)	2.075(2)/ 2.077(2)	2.084(2)	2.078(3)	2.096(5)	2.080(1)
P(1)-Pt(1)	2.2202(4)	2.232(2)	2.222(1)/ 2.230(1)	2.2429(6)	2.238(1)	2.219(2)	2.2432(5)
Cl(1)-Pt(1)	2.4090(5)	2.365(1)	2.3852(9)/ 2.384(1)	2.3734(7)	2.393(1)	2.404(2)	2.3763(3)
Bond angles, °							
N(1)-Pt(1)-Cl(1)	92.97(4)	93.1(1)	93.00(7)/ 91.97(7)	92.43(5)	92.99(9)	92.9(1)	92.27(3)
C(1)-Pt(1)-P(1)	99.63(5)	96.6(2)	95.67(9)/ 97.33(9)	96.26(6)	99.0(1)	98.0(2)	96.80(4)
C(1)-Pt(1)-Cl(1)	171.79(5)	172.5(2)	171.06(9)/ 170.89(9)	169.32(6)	170.0(1)	167.3(2)	172.00(4)
N(1)-Pt(1)-P(1)	174.02(5)	172.5(1)	175.26(8)/ 172.43(7)	170.58(5)	171.99(9)	164.4(1)	175.55(3)

Table S3. Selected bond lengths (Å) and angles (deg.) for complexes **8–10**.

	8	9	10
Bond lengths, Å			
C(1)-Pt(1)	2.064(2)	2.002(2)	1.998(5)
N(1)-Pt(1)	2.096(2)	2.016(2)	2.013(4)
N(2)-Pt(1)	-	2.032(2)	2.044(4)
N(3)-Pt(1)	-	2.115(2)	2.130(4)
P(1)-Pt(1)	2.3288(8)	-	-
P(2)-Pt(1)	2.2531(8)	-	-
Bond angles, °			
C(1)-Pt(1)-N(1)	79.46(8)	79.80(9)	79.97(17)
P(1)-Pt(1)-P(2)	81.26(2)	-	-
N(2)-Pt(1)-N(3)	-	77.40(8)	78.40(15)
N(1)-Pt(1)-N(3)/P(1)	99.22(6)	101.08(8)	100.4(1)
C(1)-Pt(1)-N(3)/P(1)	177.51(7)	178.46(8)	178.3(2)
N(1)-Pt(1)-N(2)/P(2)	178.87(6)	177.85(8)	178.8(1)

Table S4. UV-vis absorption spectra for complexes **1–11**^a.

	λ_{abs} , nm, ($\epsilon \times 10^{-3}$, M ⁻¹ cm ⁻¹)
1	285sh (29), 293sh (25), 305 (24), 354sh (5.9), 367 (8.6), 390sh (4.6), 405sh (3.2)
2	295 (23), 305 (24), 349sh (3.8), 365 (5.5), 396 (3.2), 410sh (2.9)
3	278sh (28), 287sh (25), 294 (25), 305 (26), 353sh (4.6), 367 (6.6), 395sh (4.0), 410sh (3.4)
4	285sh (29), 295 (28), 305 (30), 351sh (5.1), 365 (6.9), 398 (4.0), 410sh (3.6)
5	297sh (71), 305 (76), 326sh (64), 399 (4.8), 414sh (4.3)
6	270sh (27), 294 (24), 305 (27), 352sh (6.3), 363.5 (7.1), 395 (3.4), 410sh (3.0)
7	265 (54), 285sh (34), 295sh (29), 307 (33), 370 (9.8), 395sh (5.1), 414sh (3.9)
8	270 (58), 298 (25), 307 (29), 385 (11)
9	239sh (58), 269 (51), 301 (31), 375 (9.7), 390sh (9.1), 440sh (4.1)
10	272 (65), 298sh (29), 332sh (8.4), 372 (9.7), 395sh (8.0), 440sh (3.3)
11	269sh (20), 290sh (20), 297 (23), 307 (24), 349sh (6.9), 362 (9.6), 405 (2.1), 415sh (2.0)

^a Complexes **1–6** and **11** were measured in DMSO, **7–10** in CH₂Cl₂

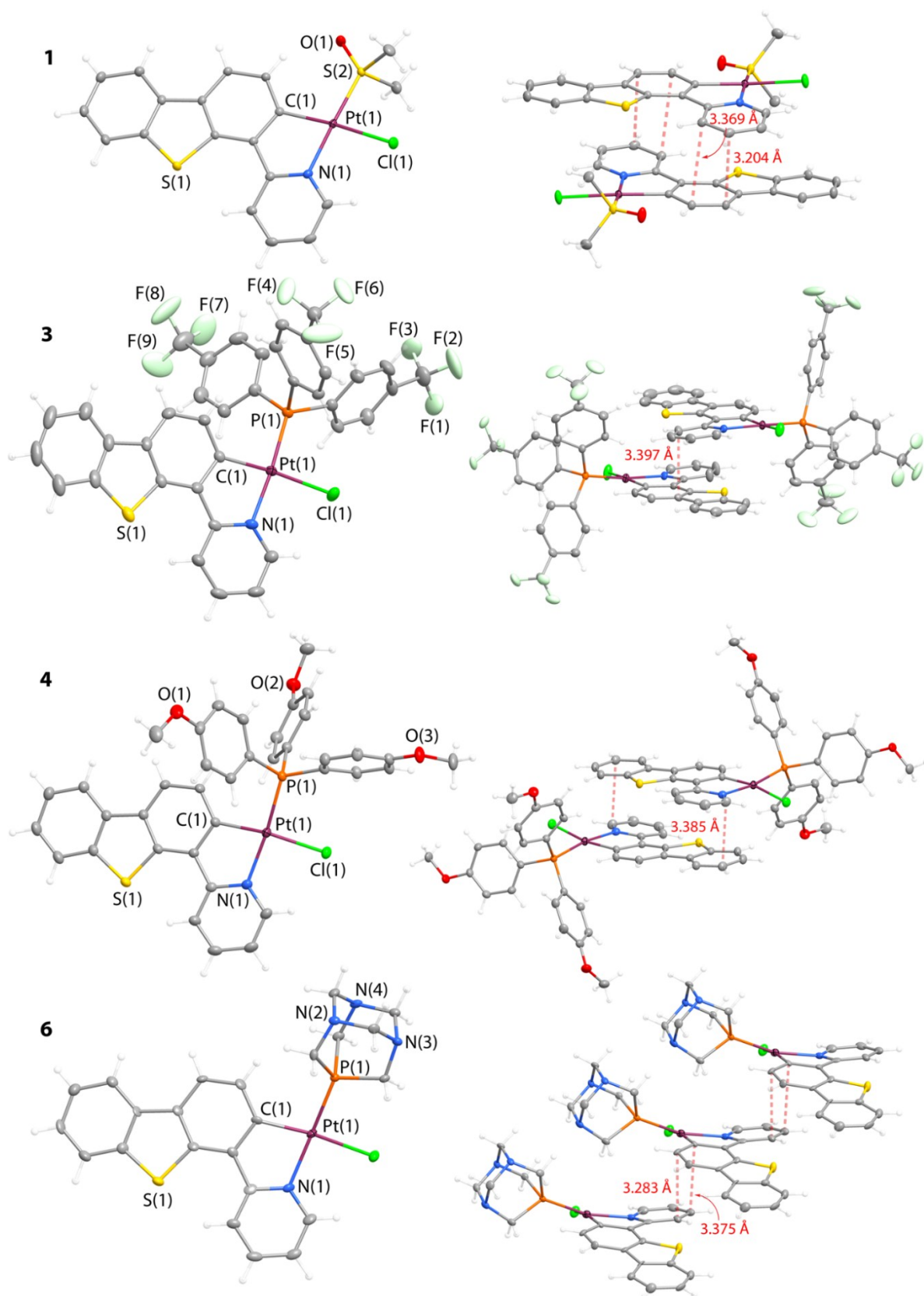


Figure S1. Molecular views of complexes **1**, **3**, **4** and **6**. One of two independent molecules found in the unit cell of **3** is presented. Thermal ellipsoids are shown at the 50% probability level.

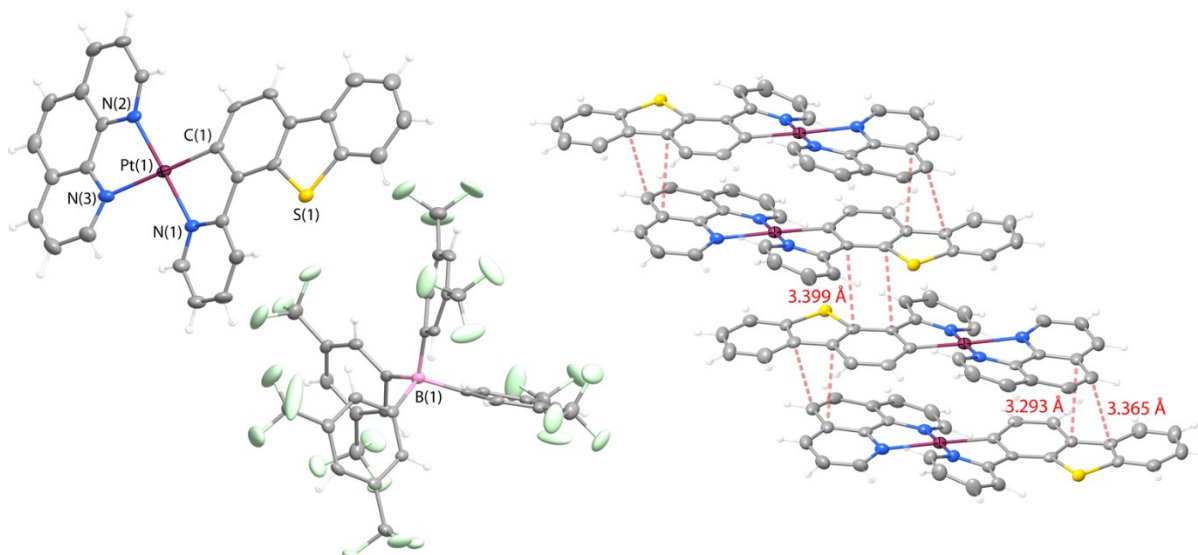


Figure S2. Molecular view of complex **10**. Thermal ellipsoids are shown at the 50% probability level.

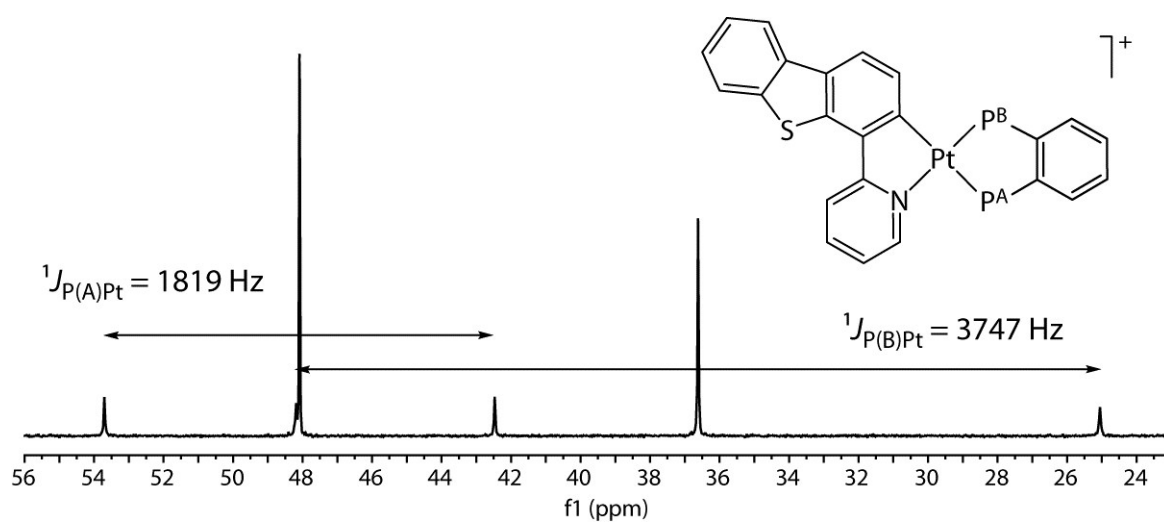


Figure S3. 162 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** (CD_2Cl_2 , 298 K).

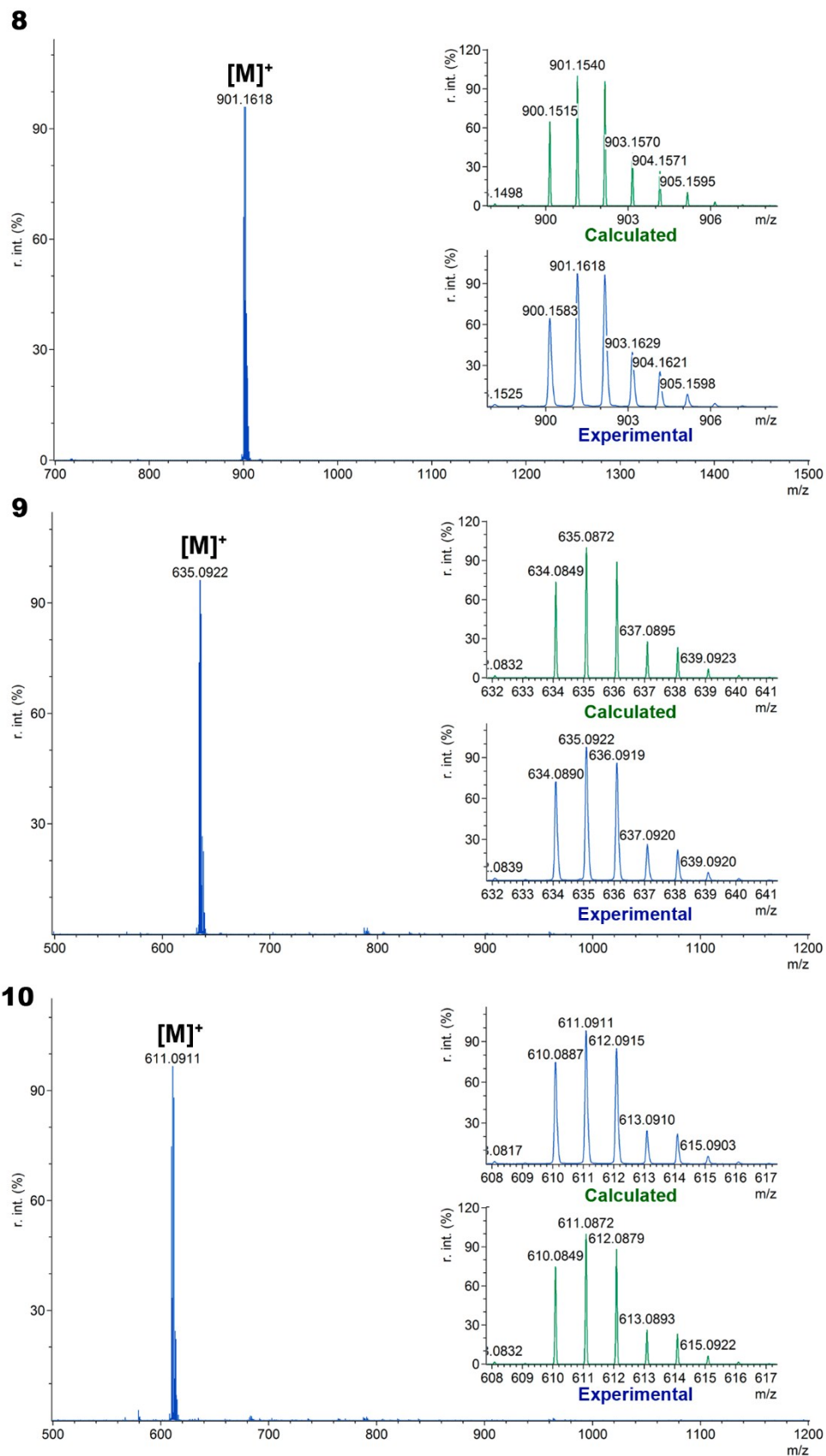


Figure S4. ESI-MS of complexes 8–10.

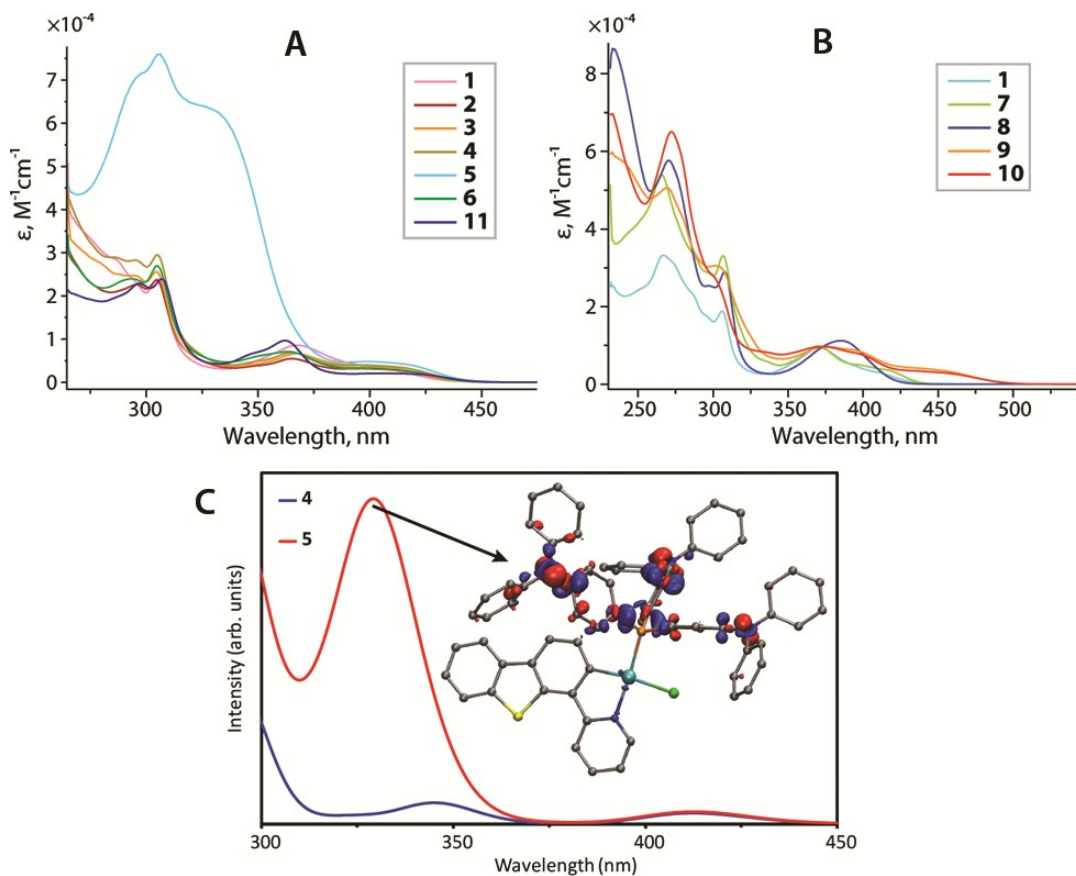


Figure S5. Absorption spectra of complexes 1–6 and 11 in DMSO (A); of 1, 7–10 in CH_2Cl_2 (B); TDDFT-PBE0 vertical excitation spectra for the complexes 4 and 5 (C), the inset shows electron density difference plot for the $S_0 \rightarrow S_{10}$ singlet excitation of complex 5 (328 nm; oscillator strength 0.53 a.u.; plot isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. The raw vertical excitations have been convoluted with Gaussian peak profile (width 0.05 eV).

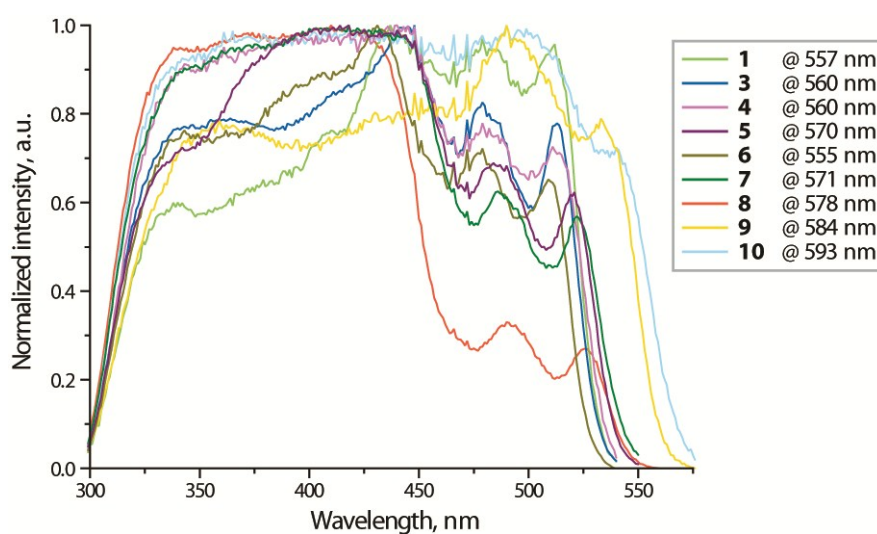


Figure S6. Normalized solid state excitation spectra of complexes 1, 3–10, 298 K.

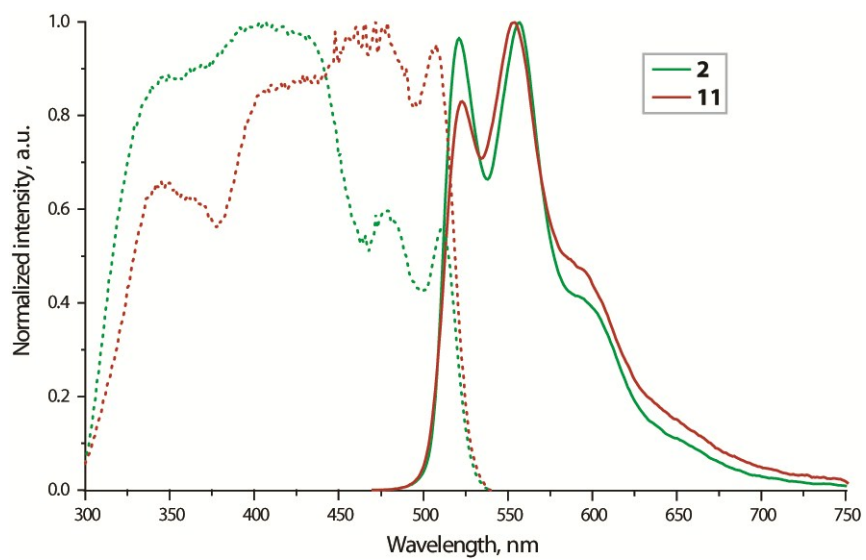


Figure S7. Normalized solid state excitation (dotted lines) and emission (solid lines) spectra of complexes **2** and **11**, 298 K.

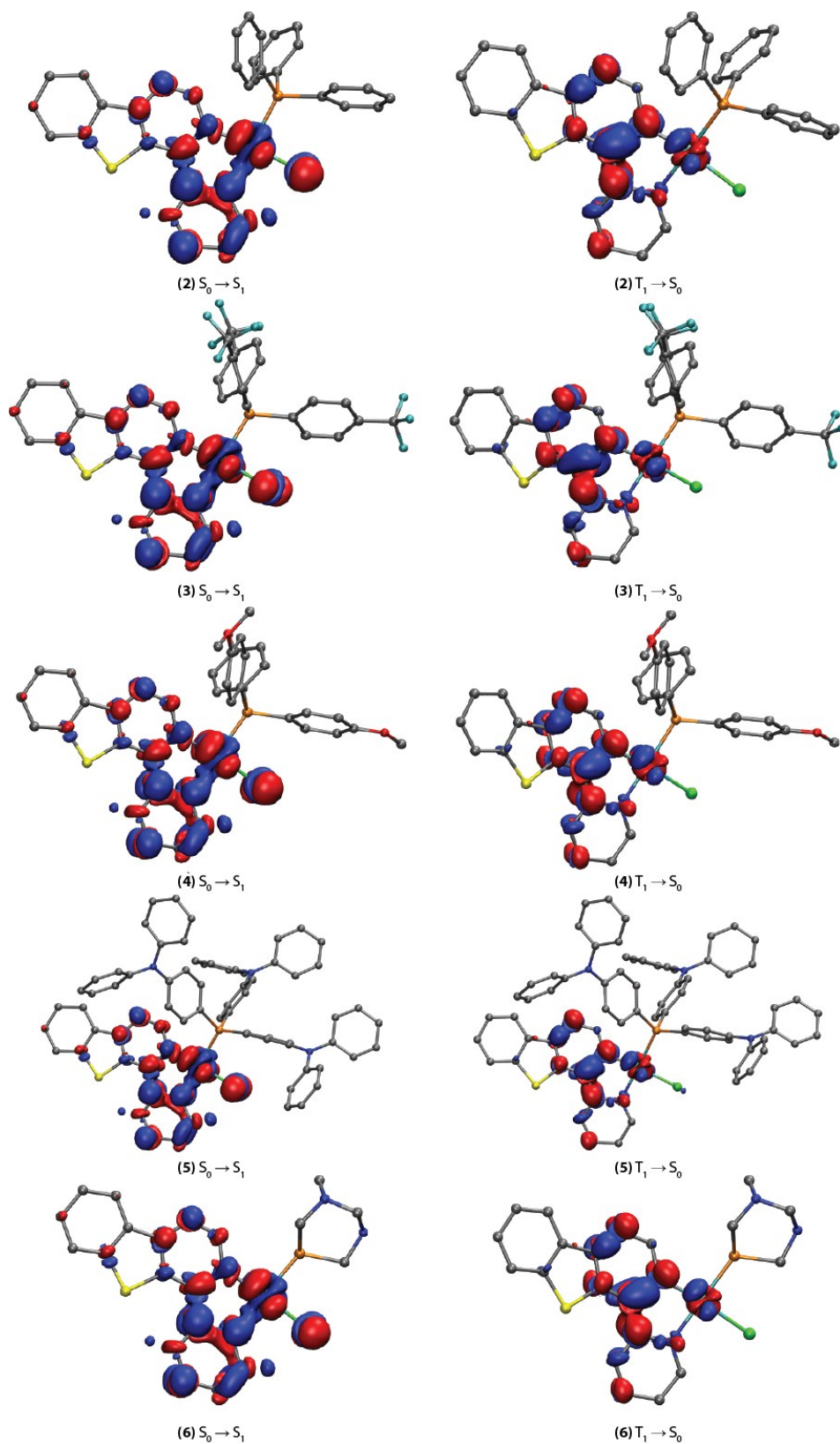


Figure S8. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the complexes **2–6** (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms are omitted for clarity.

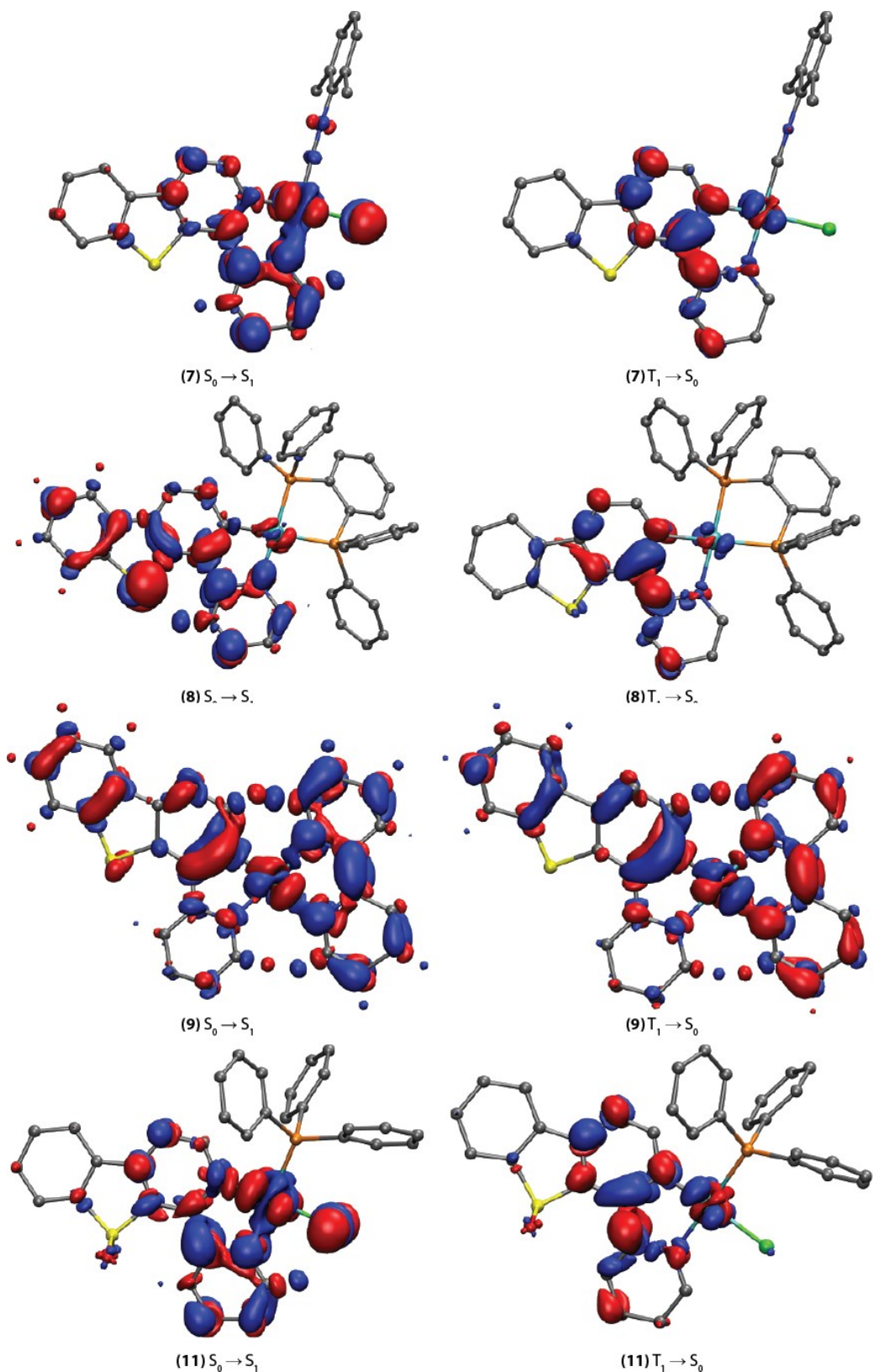


Figure S9. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the complexes 7–9 and 11 (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms are omitted for clarity.