Phosphorescent, cyclometalated cinchophen-derived platinum complexes: syntheses, structures and electronic properties

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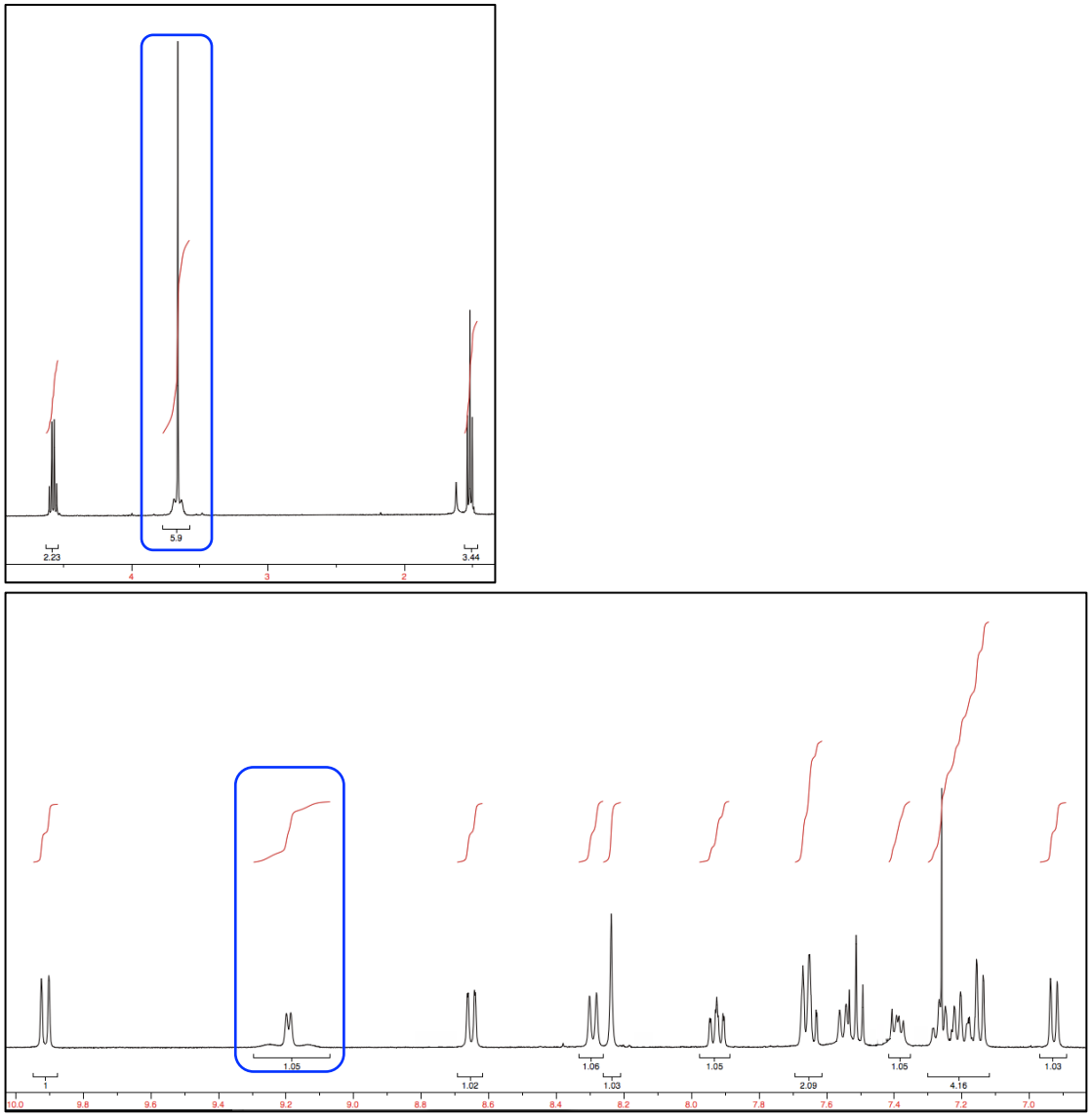


Figure S1 Top: ^{1}H NMR spectrum (aliphatic region) for [Pt(**L1**)(DMSO)Cl]. Highlighted: SO(CH_3)$_2$ with $^{3}J_{HPt}$ coupling. Bottom: ^{1}H NMR spectrum for [Pt(**L1**)(8-Q)]. Highlighted: NC^{2}H of 8-quinolinato with $^{3}J_{HPt}$ coupling.

	[Pt(**L1**)(DMSO)Cl]	[Pt(L1)(acac)]	[Pt(**L1**)(bpy)](PF$_6$)
Empirical formula	$C_{20}H_{20}ClNO_3PtS$	$C_{23}H_{21}NO_4Pt$	$C_{28}H_{22}F_6N_3O_2PPt$
Formula weight	584.97	570.50	772.54
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71075 Å	0.71075 Å	0.71075 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*I*2/*a*
Unit cell dimensions	a = 9.8021(7) Å a = 115.732(5)°	a = 10.1757(4) Å α = 75.248(2)°	a = 24.9815(10) Å α = 90°
	b = 10.3147(7) Å b = 107.041(5)°	b = 10.2522(3) Å β = 73.403(3)°	b = 7.2648(3) Å β = 102.905(4)°
	c = 11.2998(7) Å g = 96.348(4)°	c = 10.5639(2) Å γ = 69.265(3)°	c = 28.8575(11) Å γ = 90°
Volume	945.74(12) Å^3	973.14(6) Å^3	5104.9(4) Å^3
Z	2	2	8
Density (calculated)	2.054 Mg / m^{-3}	1.947 Mg / m^3	2.010 Mg / m^3
Absorption coefficient	7.691 mm^{-1}	7.240 mm-**1**	5.638 mm-**1**
F(000)	564	552	2992
Crystal	Cut Block; Red	Cut Block; Dark Red	Needle; Orange
Crystal size	0.110 ´ 0.070 ´ 0.030 mm^3	0.100 × 0.060 × 0.010 mm^3	0.060 × 0.010 × 0.010 mm^3
q range for data collection	3.045 - 27.483°	3.214 – 27.485°	2.445 – 29.948°
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	–13 ≤ h ≤ 13, –13 ≤ k ≤ 13, –13 ≤ l ≤ 12	–34 ≤ h ≤ 33, –9 ≤ k ≤ 10, –38 ≤ l ≤ 39
Reflections collected	16283	15013	31626
Independent reflections	4325 [R_{int} = 0.0277]	4458 [R_{int} = 0.0379]	6799 [R_{int} = 0.1164]
Completeness to q = 25.242°	99.70%	99.8 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi–empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.820	1.00000 and 0.76530	1.000 and 0.80453
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4325 / 0 / 247	4458 / 0 / 265	6799 / 339 / 435
Goodness-of-fit on F2	1.044	1.009	0.984
Final R indices [F2 > 2s(F2)]	*R1* = 0.0167, *wR2* = 0.0442	*R1* = 0.0312, *wR2* = 0.0797	*R1* = 0.0531, *wR2* = 0.0900
R indices (all data)	*R1* = 0.0168, *wR2* = 0.0443	*R1* = 0.0317, *wR2* = 0.0802	*R1* = 0.0988, *wR2* = 0.1034
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	0.783 and -1.207 e Å^{-3}	3.873 and –2.815 e Å-**3**	1.491 and –1.362 e Å-**3**

Table S1 Crystal structure data for [Pt(**L1**)(DMSO)Cl], [Pt(**L1**)(acac)] and [Pt(L1)(bpy)](PF$_6$).

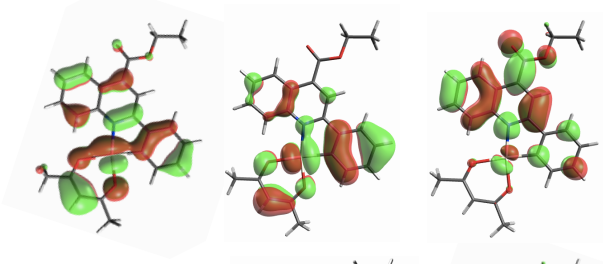
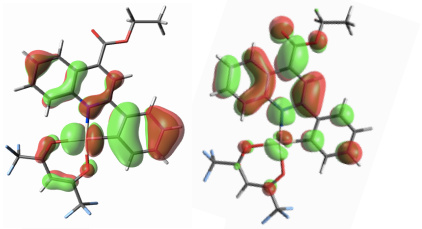
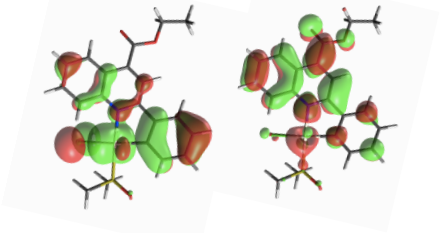
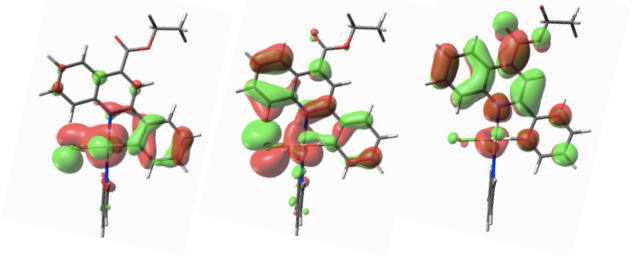
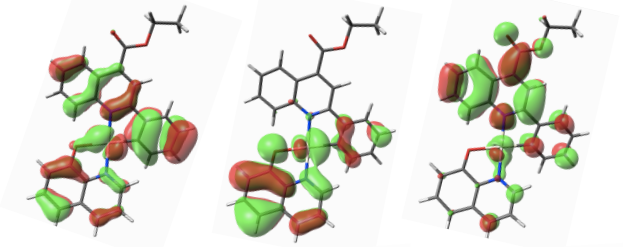
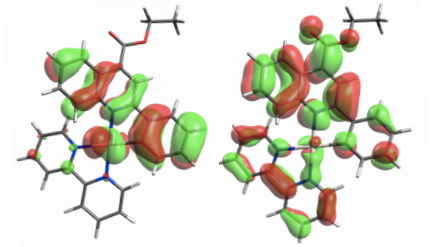
Compound	HOMO -1	HOMO	LUMO	Band Gap
[Pt(**L1**)(acac)]				249 eV 498 nm
[Pt(**L1**)(hfacac)]				2.61 eV 474 nm
[Pt(**L1**)(DMSO)Cl]				2.55 eV 487 nm
	HOMO-2	HOMO-1	LUMO	
[Pt(**L1**)(py)Cl]				2.66 eV 466 nm
	HOMO-1	HOMO	LUMO	
[Pt(**L1**)(8-Q)]				2.63 eV 472 nm
[Pt(**L1**)(bpy)](PF$_6$)				2.53 eV 490 nm

Figure S2 Frontier orbitals for selected complexes.

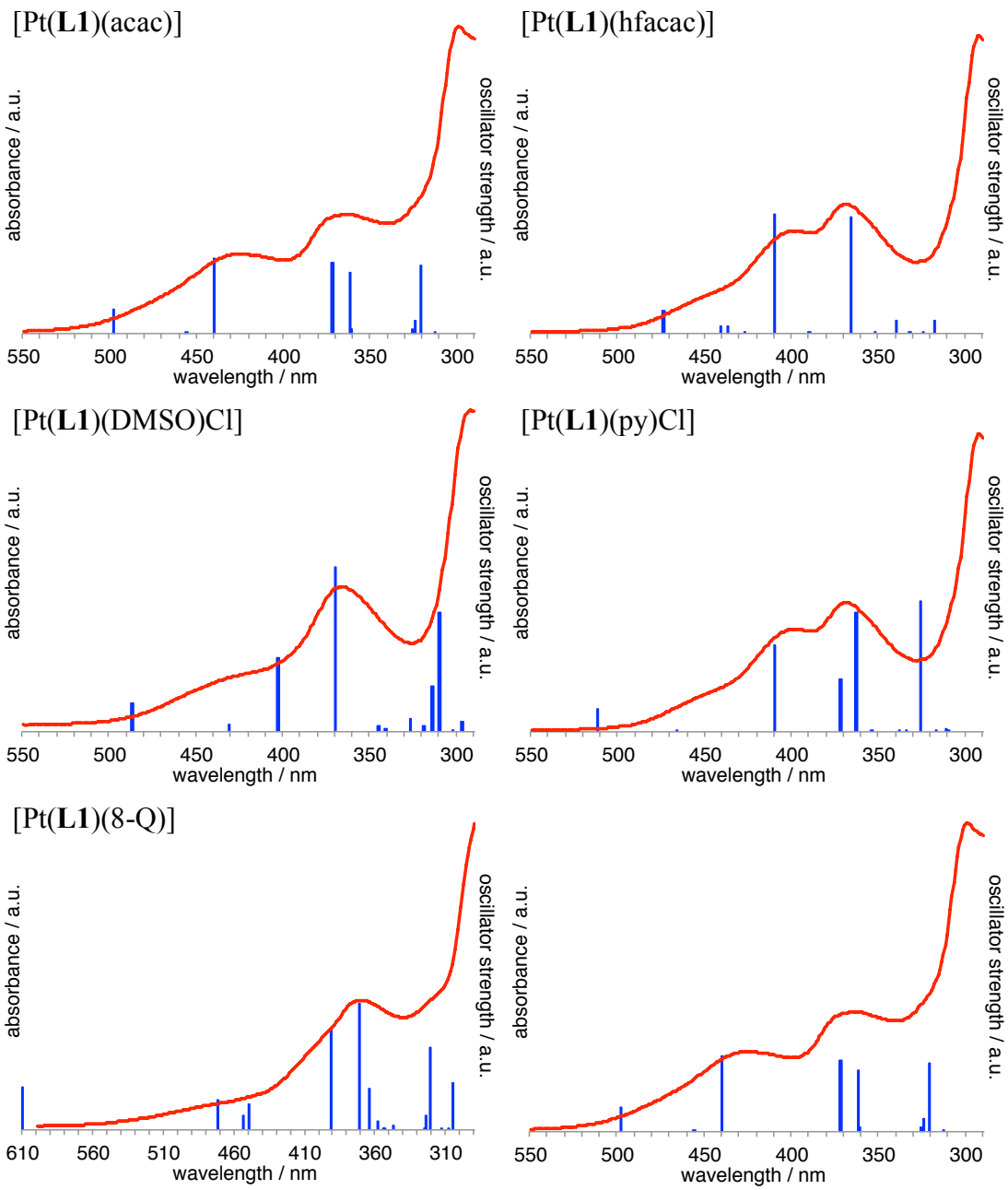


Figure S3 TD-DFT predicted absorption spectra.

Complex	λ /nm	f / au	Transition(s)
[Pt(**L1**)(acac)]	498	0.044	HOMO → LUMO
[Pt(**L1**)(hfacac)]	474	0.042	HOMO → LUMO
[Pt(**L1**)(DMSO)Cl]	489	0.035	HOMO → LUMO
[Pt(**L1**)(py)Cl]	512	0.031	HOMO → LUMO
[Pt(**L1**)(8-Q)]	610	0.063	HOMO → LUMO

Table S2. Summary of lowest energy absorptions predicted from TD-DFT.