Electronic Supplementary Material (ESI) for Dalton Transactions

The Synthesis and Photophysical Studies of Cyclometalated Pt(II) Complexes with *C,N,N*-Ligands Containing Imidazolyl Donors

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Supporting Information

Table S1 Crystal data and refinement details for **1**, **3**·ClO_4 and **4**·ClO_4

	1	**3**·ClO_4	**4**·ClO_4
Empirical formula	C_{14} H_{10} Cl N_3 Pt	C_{32} H_{25} Cl N_3 O_4 P Pt	C_{32} H_{25} Cl N_3 O_4 P Pt
Formula weight	450.78	777.06	777.06
Temperature, K	173(2)	173(2)	293(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	P2(1)/n	P-1	P-1
a, Å	9.7720(6)	9.4058(5)	9.1983(4)
b, Å	12.5346(7)	12.5485(7)	9.5114(4)
c, Å	11.1227(7)	13.1386(7)	16.4668(7)
α, deg	90.00	70.9460(10)	91.5660(10)
β, deg	99.4410(10)	73.1280(10)	92.5240(10)
γ, deg	90.00	79.9880(10)	92.9470(10)
Volume, $Å^3$	1343.94(14)	1397.30(13)	1436.73(11)
Z	4	2	2
Density (calculated), g cm^{-3}	2.317	1.847	1.796
Absorption coefficient, mm^{-1}	10.637	5.219	5.075
F(000)	880	760	760
Crystal dimensions, mm	0.30 × 0.24 × 0.22	0.32 × 0.22 × 0.20	0.32 × 0.24 × 0.22
θ range for data collection, deg	2.47 to 25.00	2.47 to 28.28	2.45 to 28.29
Limiting indices	11≤ h ≤11, -14 ≤ k ≤ 11, -13 ≤ l ≤ 7	2 ≤ h ≤ 12, -16 ≤ k ≤ 10, -17 ≤ l ≤ 17	2 ≤ h ≤ 11, -10 ≤ k ≤ 12, -21 ≤ l ≤ 20
Reflections collected	6192	8661	8805
Independent reflections (R_{int})	2313 (0.0260)	6468 (0.0197)	6595 (0.0166)
Completeness to θ = 25.00º, %	98.1	93.0	92.4
Observed reflections [I > 2α(I)]	2140	6261	6108
Absorption correction		Semi-empirical form equivalents	
Max. and min. transmission	1.0000 and 0.5128	1.0000 and 0.6620	1.0000 and 0.5795
Refinement method		Full-matrix least-squares equivalents	
Data / restraints / parameters	2313 / 0 / 181	6468 / 0 / 379	6595 / 0 / 379
Goodness-of-fit on F2	1.058	1.021	1.005
Final R indices [I > 2 α(I)]	= 0. 0277. wR2 = 0.0732	= 0.0205. wR2 = 0.0531	= 0.0274. wR2 = 0.0738
R indices (all data)	= 0.0241. wR2 = 0.0561	= 0.0382. wR2 = 0.0601	= 0.0430. wR2 = 0.0726
argest different peak and hole, $eÅ^{-3}$	0.996 and -1.010	1.085 and -1.581	1.328 and -1.373

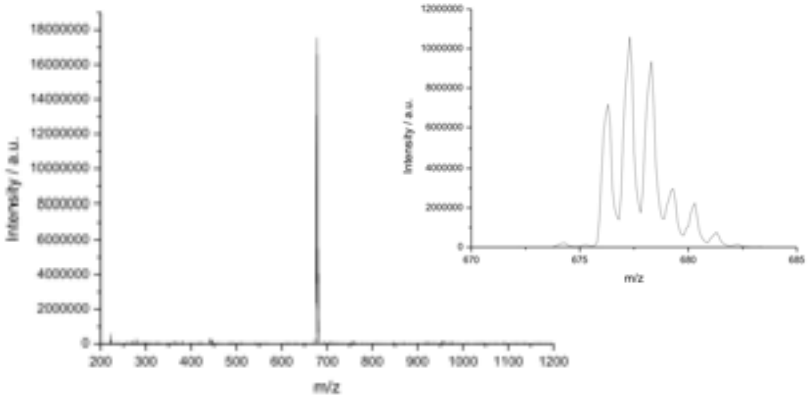
Table S2 Room-temperature UV-Vis absorption and emission data of the new cycloplatinated complexes in various solvents.

Complex	Media	UV-Vis absorption at 298 K λ/nm (ε_{max} / $dm^3\ mol^{-1}\ cm^{-1}$)	Emission at 298 K λ_{max}[b]/nm, τ_o[c], ϕ_{lum}[d]
[Pt(***L*****1**)Cl][a]	MeCN	249 (28585), 303 (17936), 345 (8598), 390 (3150), 430 (550)	514, 0.57 μs, 0.14
	MeOH	247 (36913), 263 (26982), 303 (22168), 335 (11603), 386 (3368)	511
	$CHCl_3$	252 (29783), 306 (18843), 343 (9903), 390 (3315)	514
	CH_2Cl_2	251 (31078), 305 (19259), 341 (9397), 392 (3278)	516
[Pt(***L*****2**)Cl] (**1**)	MeCN	279(17600), 312(11800), 354(6400), 400(2100), 445(430)	521, 1.28 μs, 0.18
	MeOH	279(18380), 313(12600), 353(7500), 397(1900), 440(570)	520
	Acetone	360(7400), 409(2700), 455(460)	523
	$CHCl_3$	284(10700), 317(7000), 362(4100), 412(1178), 445(510)	528
	CH_2Cl_2	283(5000), 317(3600), 363(2000), 413(800), 450(380)	531
[Pt(***L*****3**)Cl](**2**)	MeCN	306(12600), 335(6300), 346(5900), 378(2600), 425(400)	503, 2.36 μs, 0.10
	MeOH	305(14000), 331(7500), 347(6600), 376(2400), 425(450)	502
	Acetone	350(6000), 388(3000), 430(480)	506
	$CHCl_3$	311(8700), 341(4300), 355(3600), 382(1800), 430(240)	507
	CH_2Cl_2	309(10000), 339(4600), 353(4000), 385(2100), 425(230)	505
[Pt(***L*****2**)(PPh_3)](ClO_4) (**3**·ClO_4)	MeCN	320(6000), 332(5400), 346(4800), 410-440(~400)	510, 6.08 μs, 0.22
	MeOH	321(10800), 333(9800), 348(8700), 410-440(~700)	509
	$CHCl_3$	322(7730), 335(6800), 350(6500), 410-440(~600)	507
	CH_2Cl_2	323(11000), 335(9960), 349(9100), 410-440(~700)	509
[Pt(***L*****3**)(PPh_3)](ClO_4) (**4**·ClO_4)	MeCN	311(12200), 329(8300), 343(8600), 385-410(~1100)	491, 6.66 μs, 0.23
	MeOH	312(12100), 330(8100), 345(8600), 385-410(~1100)	492
	$CHCl_3$	316(16400), 334(10700), 348(12300), 385-410(~1200)	493
	CH_2Cl_2	314(12400), 322(8000), 346(8900), 385-410(~850)	493

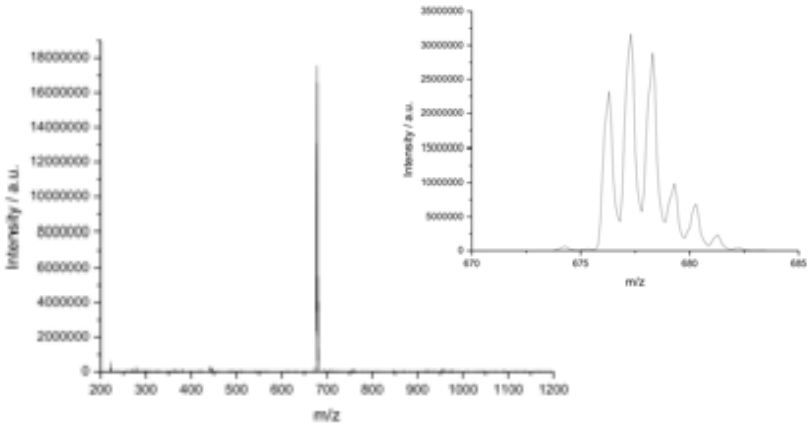
[a] From reference 7(c)

[b,c] Complex concentration = 5×10^{-5} M; excitation λ = 345 nm

(a)



(b)



(c)

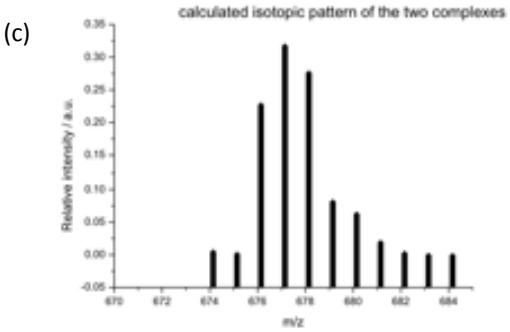


Figure S1 ESI-MS of complex **3** (S1a) and **4** (S1b) in 2:1 DMF / acetonitrile with their isotope distribution of the parent [M^+] ions shown in the corresponding insets. Both isotope distribution patterns correspond well with the theoretical pattern (shown in S1c) for [Pt(***L*****$_2$**)(PPh_3)]$^+$ and [Pt(***L*****$_3$**)(PPh_3)]$^+$ confirming that no displacement of the ancillary PPh3 ligand or the cyclometalating ***L*****$_2$** and ***L*****$_3$** ligands by DMF has taken place.

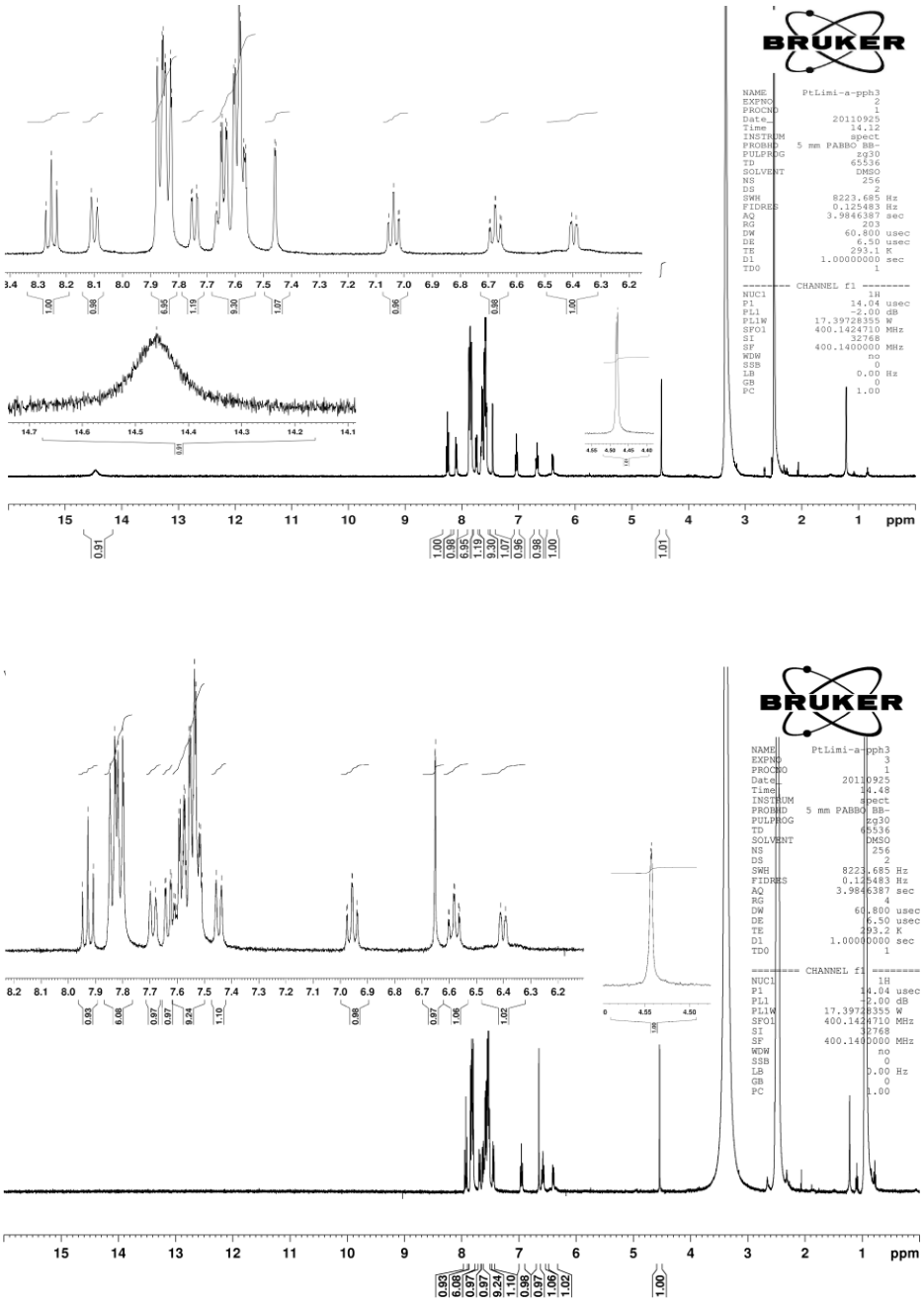


Figure S2 1H NMR spectra of complex **3** in *d*-DMSO, before (upper) and after (lower) the addition of triethylamine, showing the disappearance of the 1-imidazolyl-*NH* peak upon deprotonation.

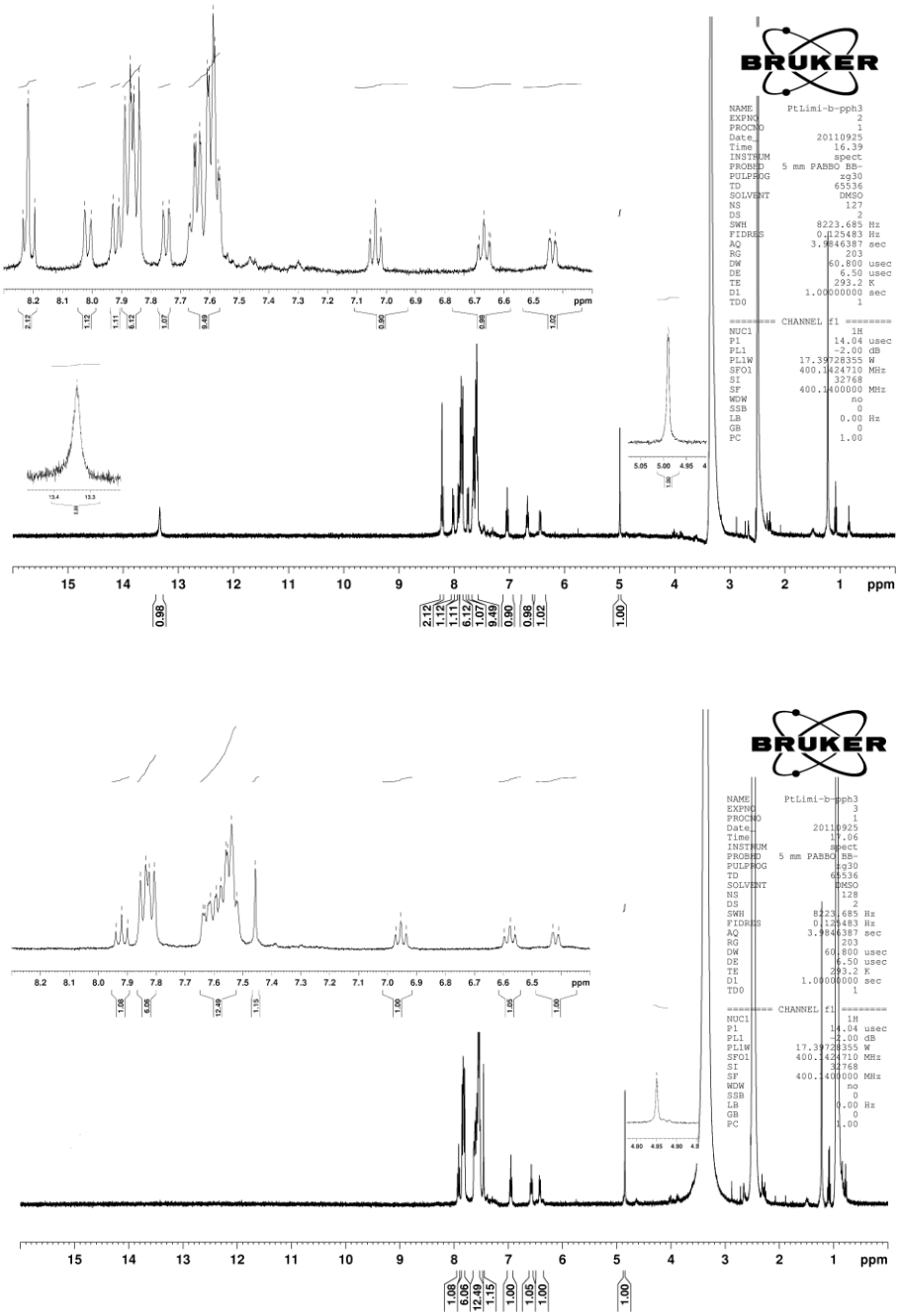


Figure S3 1H NMR spectra of complex **4** in *d*-DMSO, before (upper) and after (lower) the addition of triethylamine, showing the disappearance of the 1-imidazolyl-*NH* peak upon deprotonation.

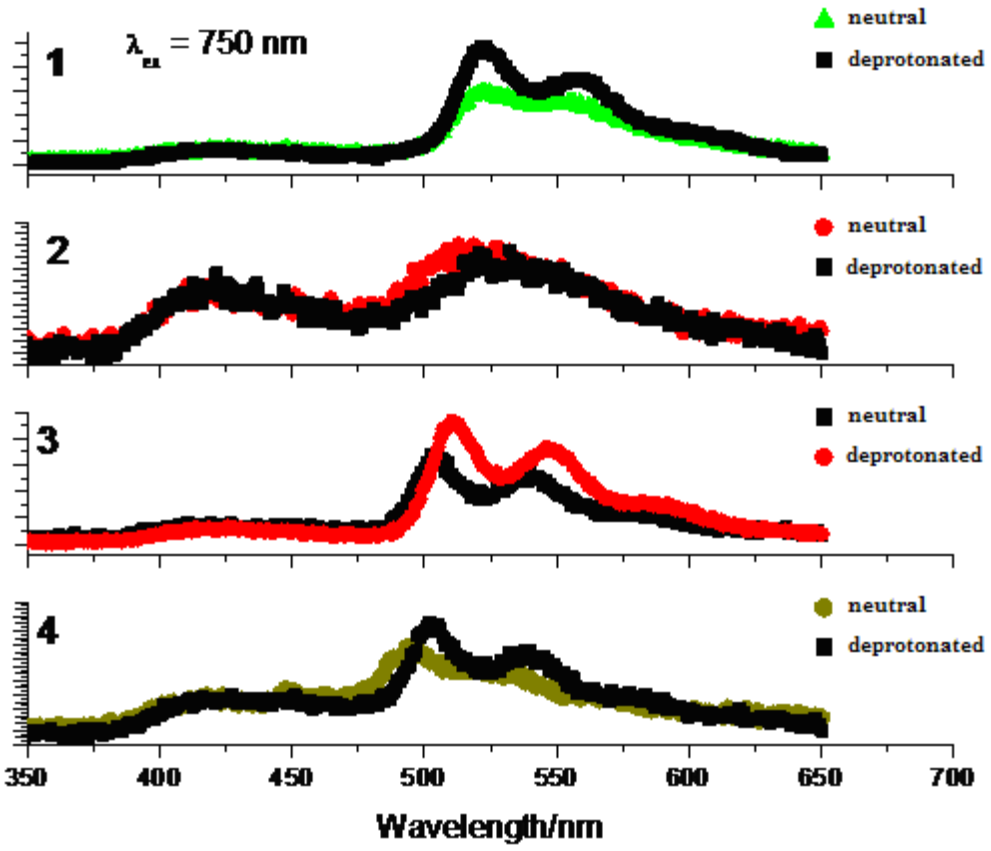


Figure S4 Two-photon excitation spectra of **1 - 4** (1×10^{-4} M) in neutral DMF as well as in the presence of 5% triethyamine at 298 K (λ_{ex} = 750 nm).