Supporting Information

Dual-Emissive Bis(diphenylphosphino)amine Platinum Complexes: Structural, Reactivity, Photophysical and Theoretical Investigations

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General remarks

The microanalyses were performed using Elementar CHN elemental analyzer. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^{1}H (300 MHz, TMS), ^{31}P (121 MHz, 85% H_3PO_4). The chemical shifts and coupling constants are in ppm and Hz, respectively. The UV-vis absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer in a cuvette with a 1 cm and/or 1 mm path length. Emission and excitation spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 steady-state fluorescence spectrometer at 298 and 77 K. This spectrometer was modified to allow for measurements of emission decay times. A PicoQuant FB-375 pulsed diode laser (λ_{exc} = 378 nm, pulse width 100 ps) was applied as the excitation source. The emission signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar card with a time resolution of 250 ps. Photoluminescence quantum yields were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C9920-02) equipped with an integrating sphere with a Spectralon inner surface coating. Polymer films containing about 1 weight% of the Pt complexes were obtained by dissolving the emitter and Poly(methyl methacrylate) (PMMA) in dichloromethane and spin-coating the solutions onto quartz glass substrates. All measurements were performed under a continuous flow of nitrogen gas in order to minimize emission quenching by oxygen. The monomeric precursors [Pt(C^N)Cl(DMSO)][1], C^N = bhq, **1a**; ppy, **1b**, [Pt(C^N)(CF_3CO_2)(SMe_2)][2], C^N = bhq, **1c**; ppy, **1d**, were synthesized as reported in the literature.

Computational Details

Density functional calculations were performed with the program suite Gaussian 09[3] using the B3LYP level of theory. The LANL2DZ basis set [4] was chosen to describe Pt. The 6-31G(d) basis set was used for other atoms. The geometries of complexes were fully optimized by employing the density functional theory without imposing any symmetry constraints. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. In all cases only real frequencies were obtained for the optimized structures. Solvent effects have been taken into account using the PCM model [5, 6].

X-ray Structure Determination

The X-ray diffraction measurements were carried out on STOE IPDS-II or IPDS-2T diffractometer with graphite-monochromated Mo Kα radiation. All single crystals were mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by a least-square refinement of the diffraction data. Diffraction data were collected in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA[7] software package. A numerical absorption correction was applied using X-RED[8] and X-SHAAPE[9] software. The data were corrected for Lorentz and polarizing effects. The structures were solved by direct methods[10] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[11] Atomic factors are from the International Tables for X-ray Crystallography[12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms

were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All refinements were performed using the XSTEP32 crystallographic software package.[13]

Atomic coordinates and displacement parameters are deposited with the Cambridge Crystallographic Data Centre. The CCDC 1964741 (**2a**), 1964742 (**2c**), 1964745 (**2d**), 1964744 (**3a**), 1964746 (**3b**), contain the supplementary crystallographic data for this paper. The crystal data of complexes **2a**, **2c**, **2d**, and **3a** are shown in Table S1.

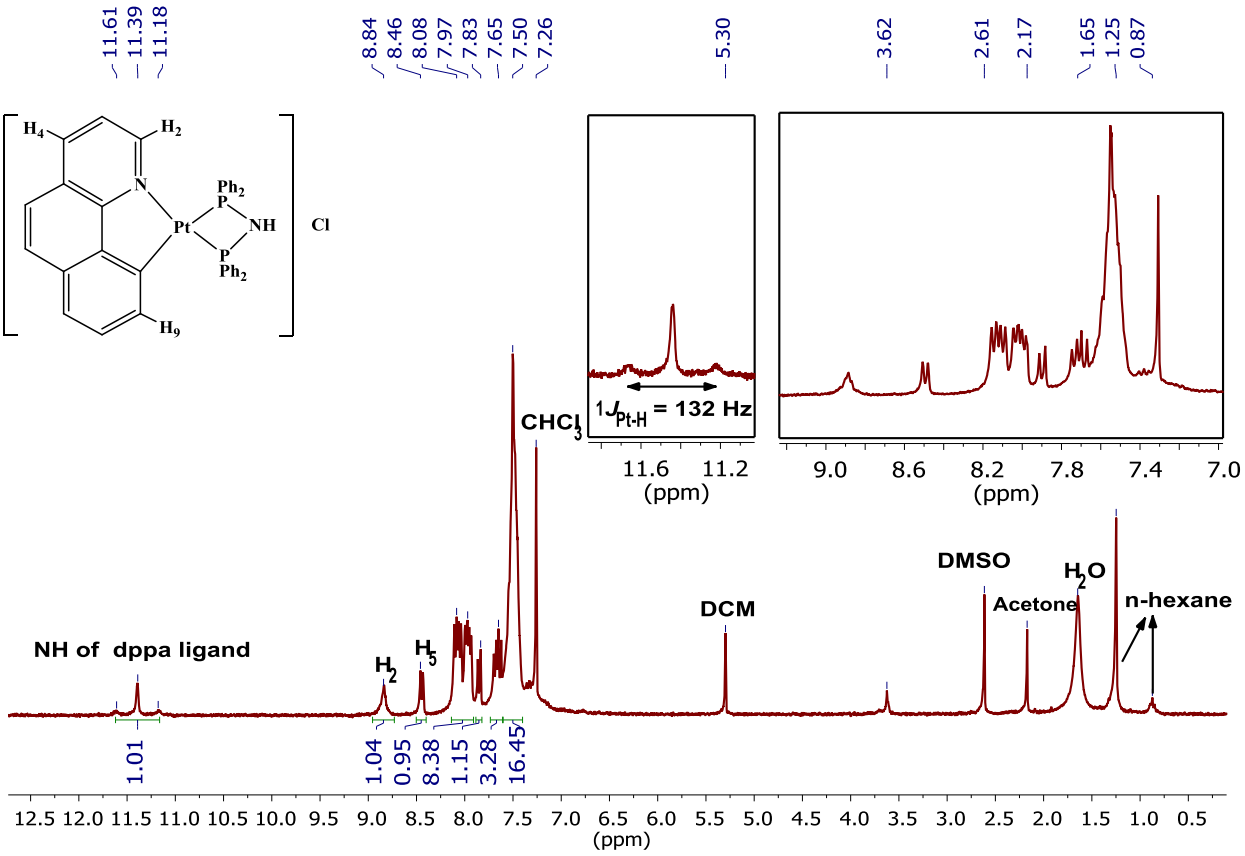


Figure S1. The ^{1}H NMR spectrum of [Pt(bhq)(dppa)]Cl, **2a**, in $CDCl_3$.

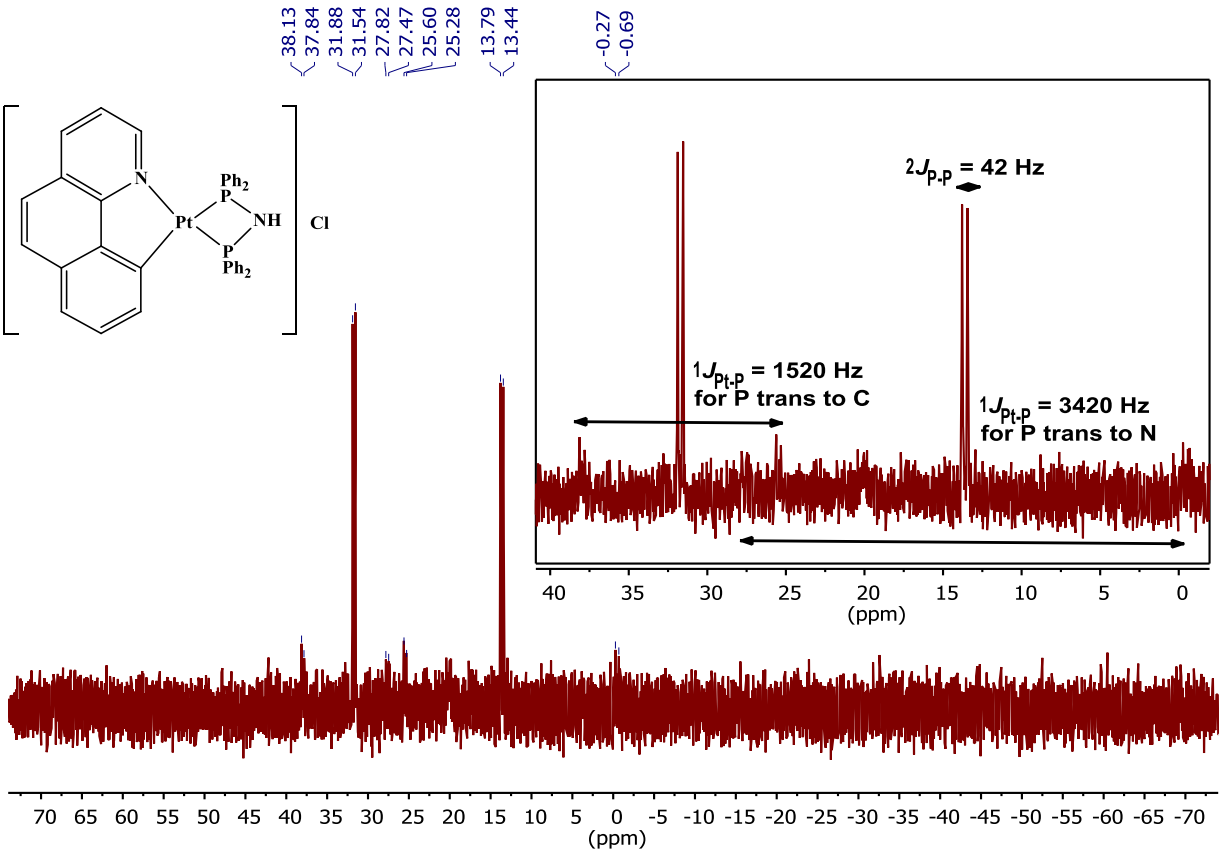


Figure S2. The ^{31}P NMR spectrum of [Pt(bhq)(dppa)]Cl, **2a**, in $CDCl_3$.

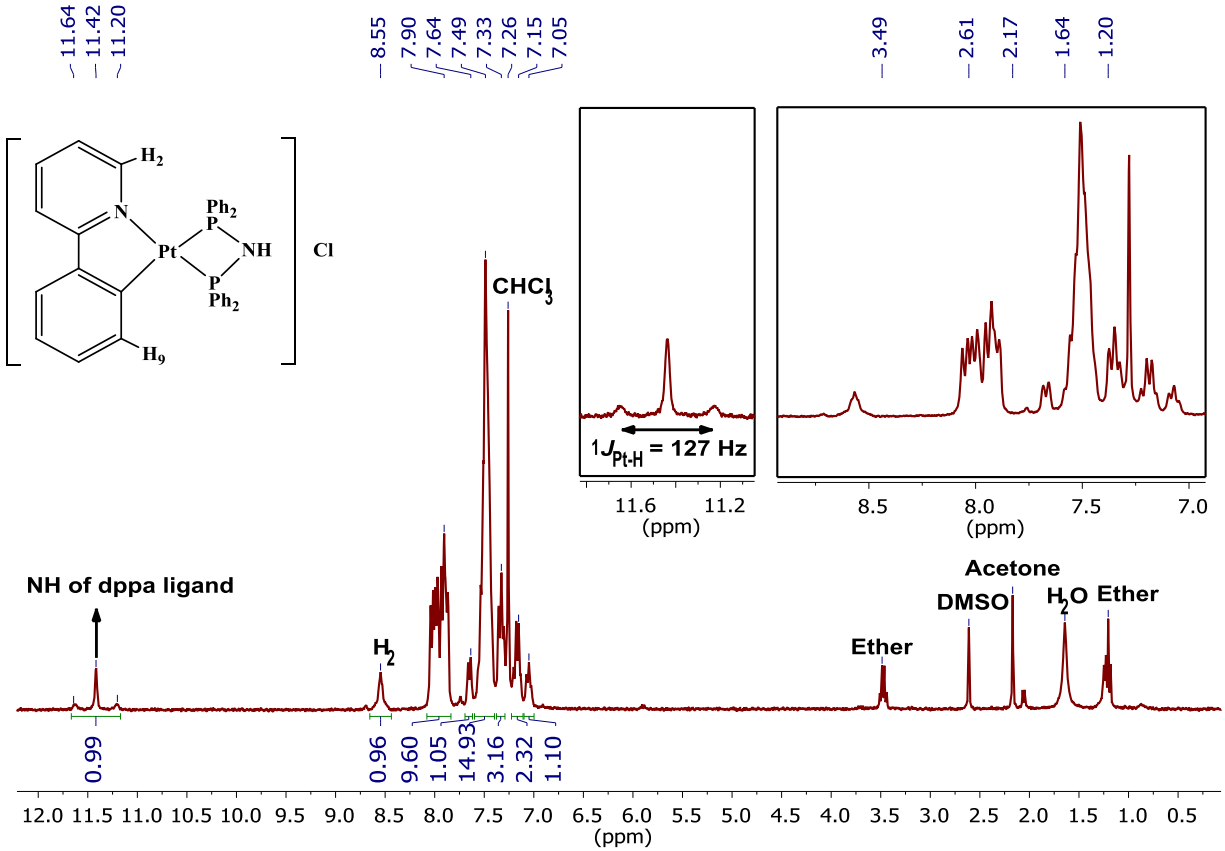


Figure S3. The ^{1}H NMR spectrum of [Pt(ppy)(dppa)]Cl, **2b**, in $CDCl_3$.

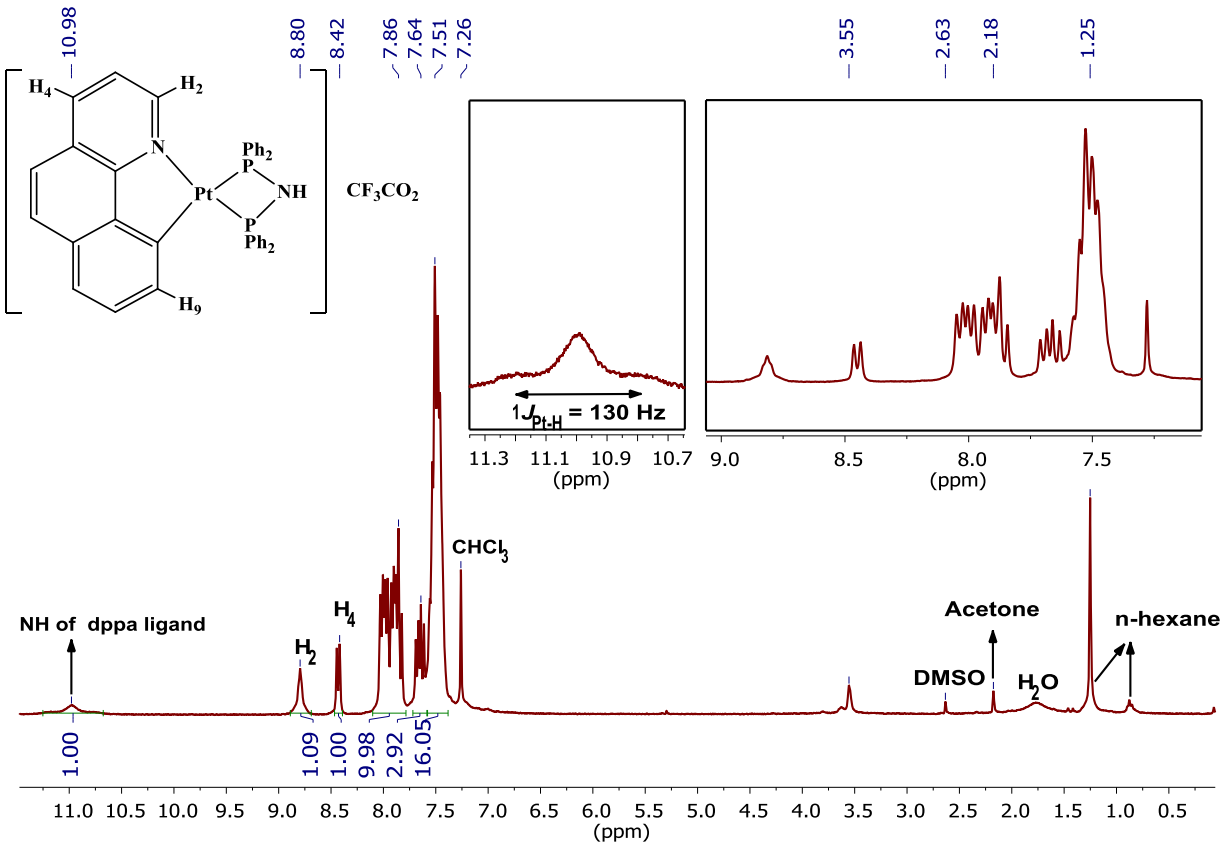


Figure S4. The ^{1}H NMR spectrum of [Pt(bhq)(dppa)]CF_3CO_2, **2c**, in $CDCl_3$.

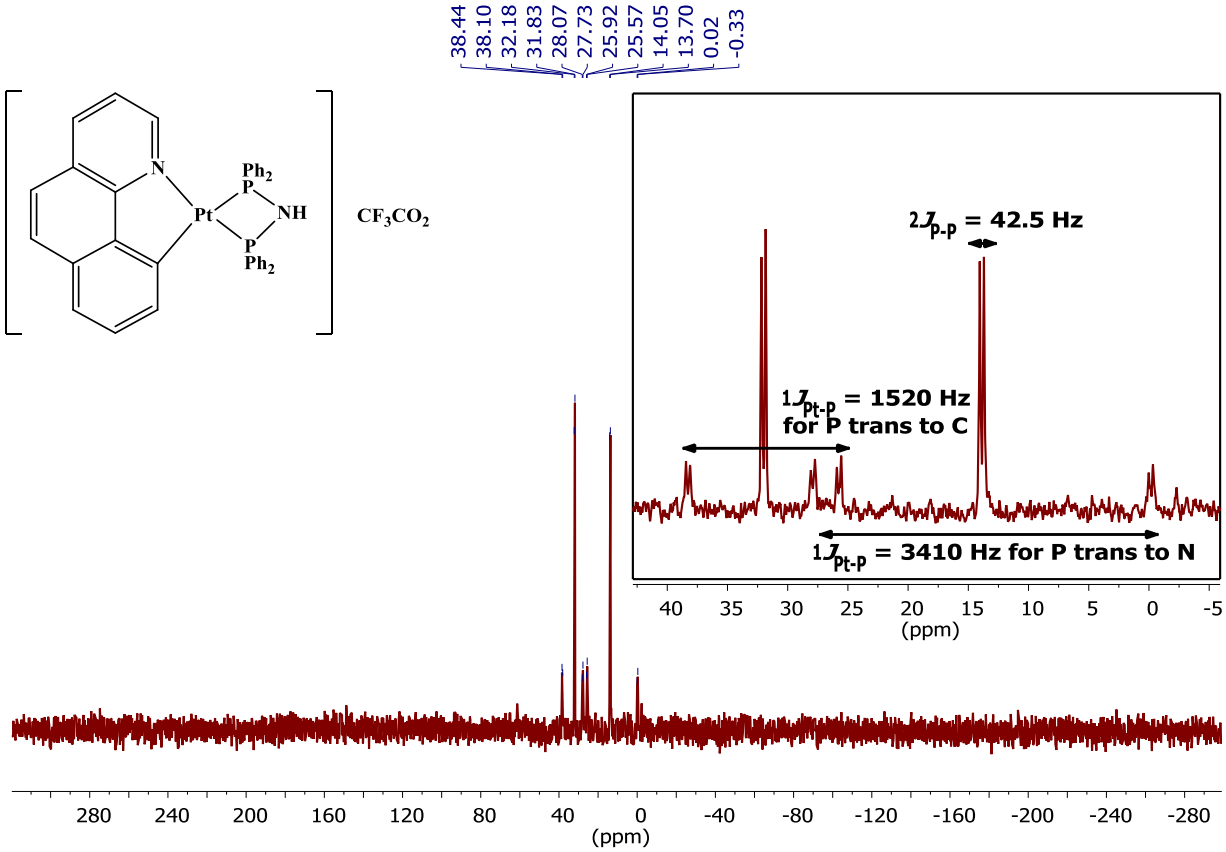


Figure S5. The ^{31}P NMR spectrum of [Pt(bhq)(dppa)]CF_3CO_2, **2c**, in $CDCl_3$.

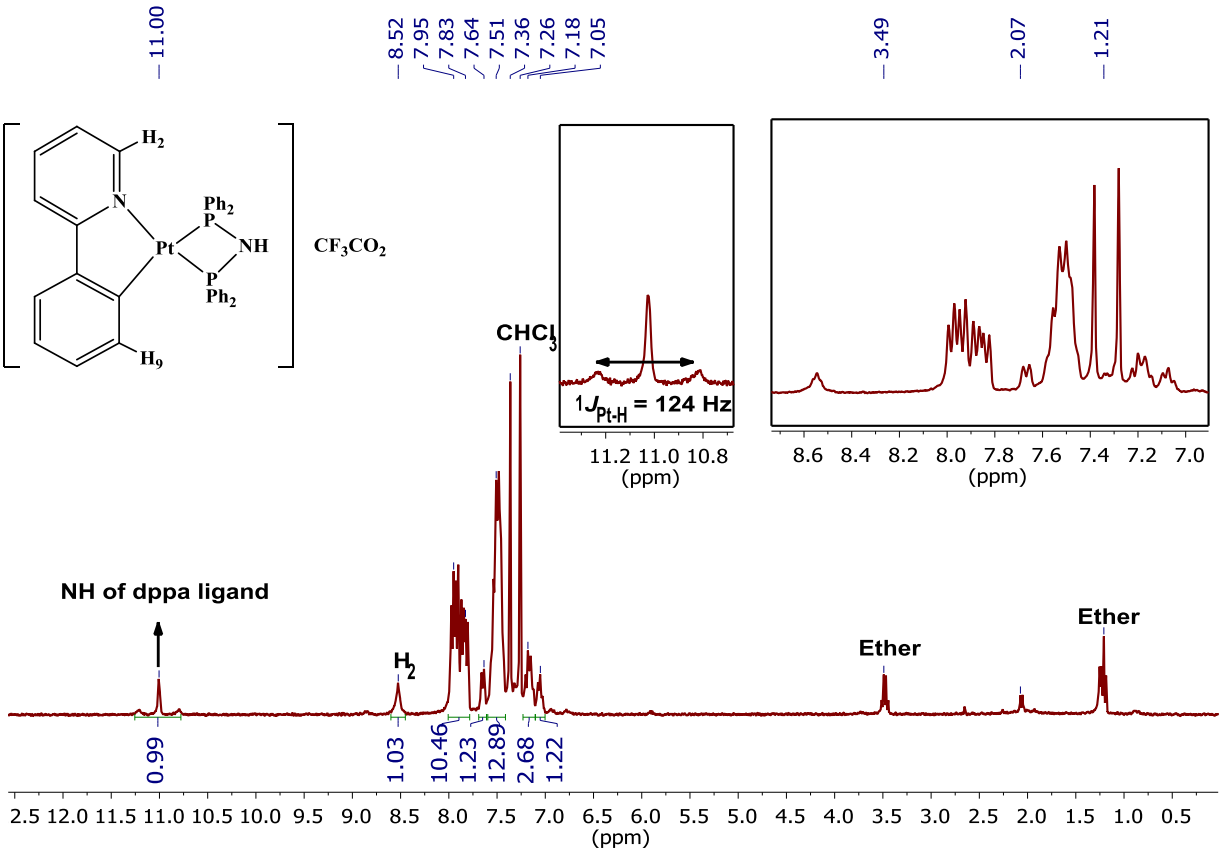


Figure S6. The ^{1}H NMR spectrum of [Pt(ppy)(dppa)]CF_3CO_2, **2d**, in $CDCl_3$.

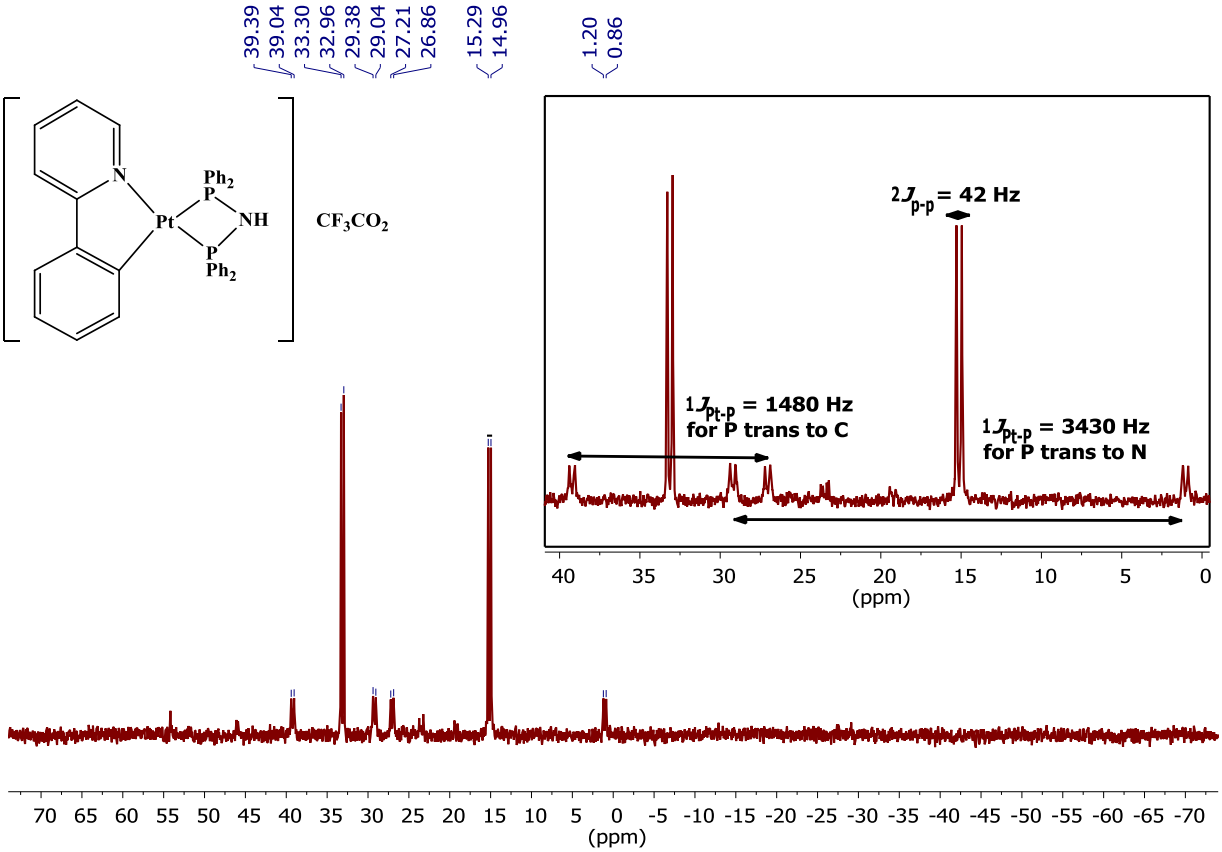


Figure S7. The ^{31}P NMR spectrum of [Pt(ppy)(dppa)]CF_3CO_2, **2d**, in $CDCl_3$.

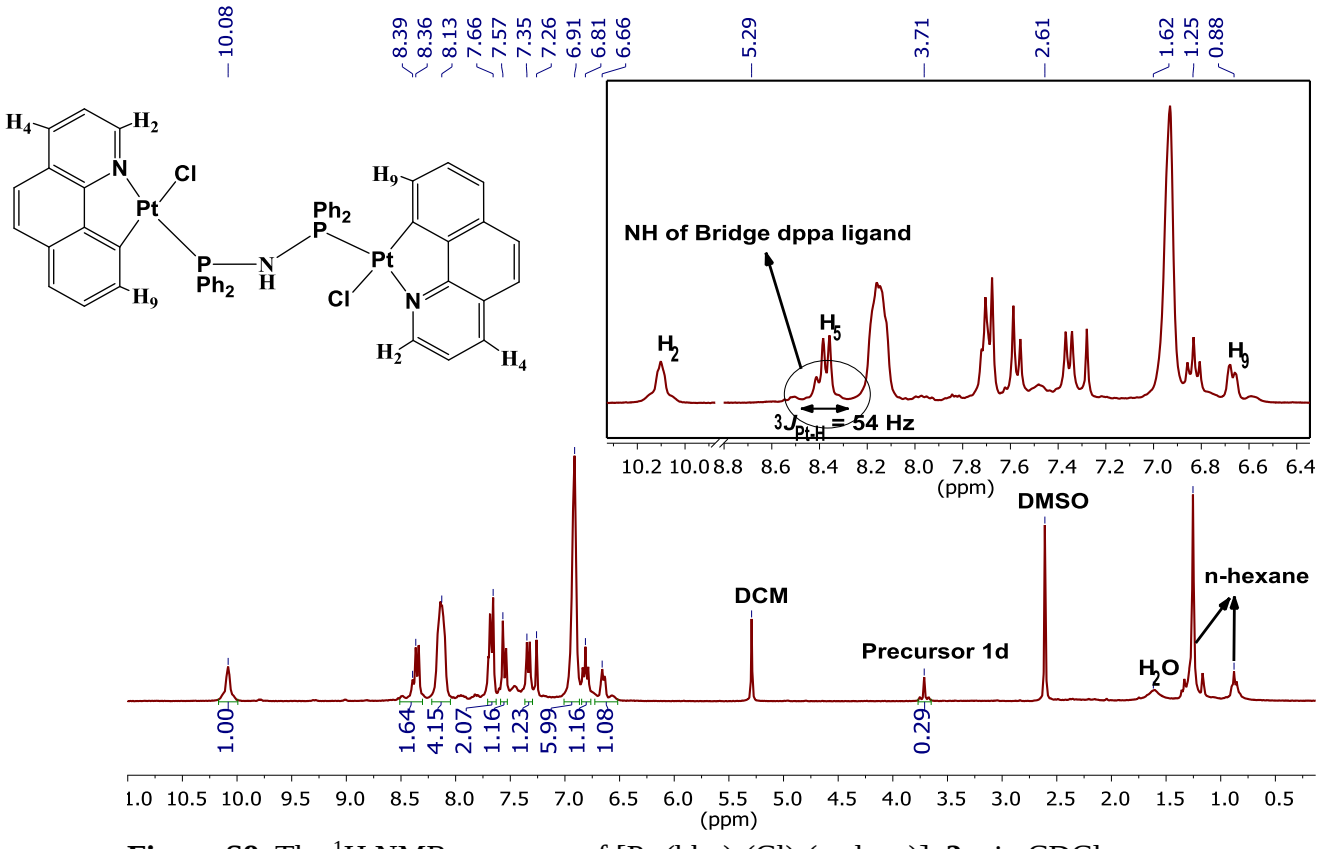


Figure S8. The ^{1}H NMR spectrum of [$Pt_2(bhq)_2(Cl)_2(\mu$-dppa)], **3a**, in $CDCl_3$.

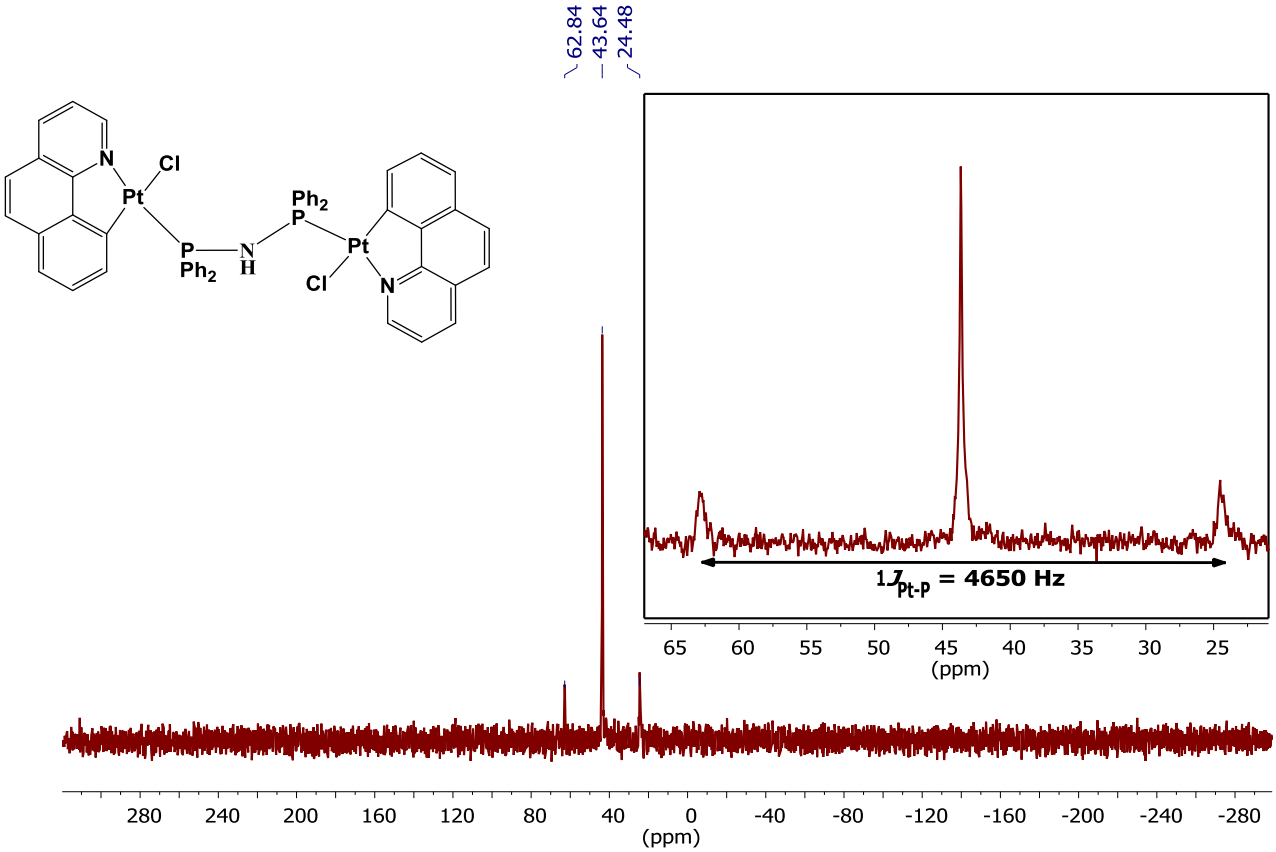


Figure S9. The ^{31}P NMR spectrum of [$Pt_2(bhq)_2(Cl)_2(\mu$-dppa)], **3a**, in $CDCl_3$.

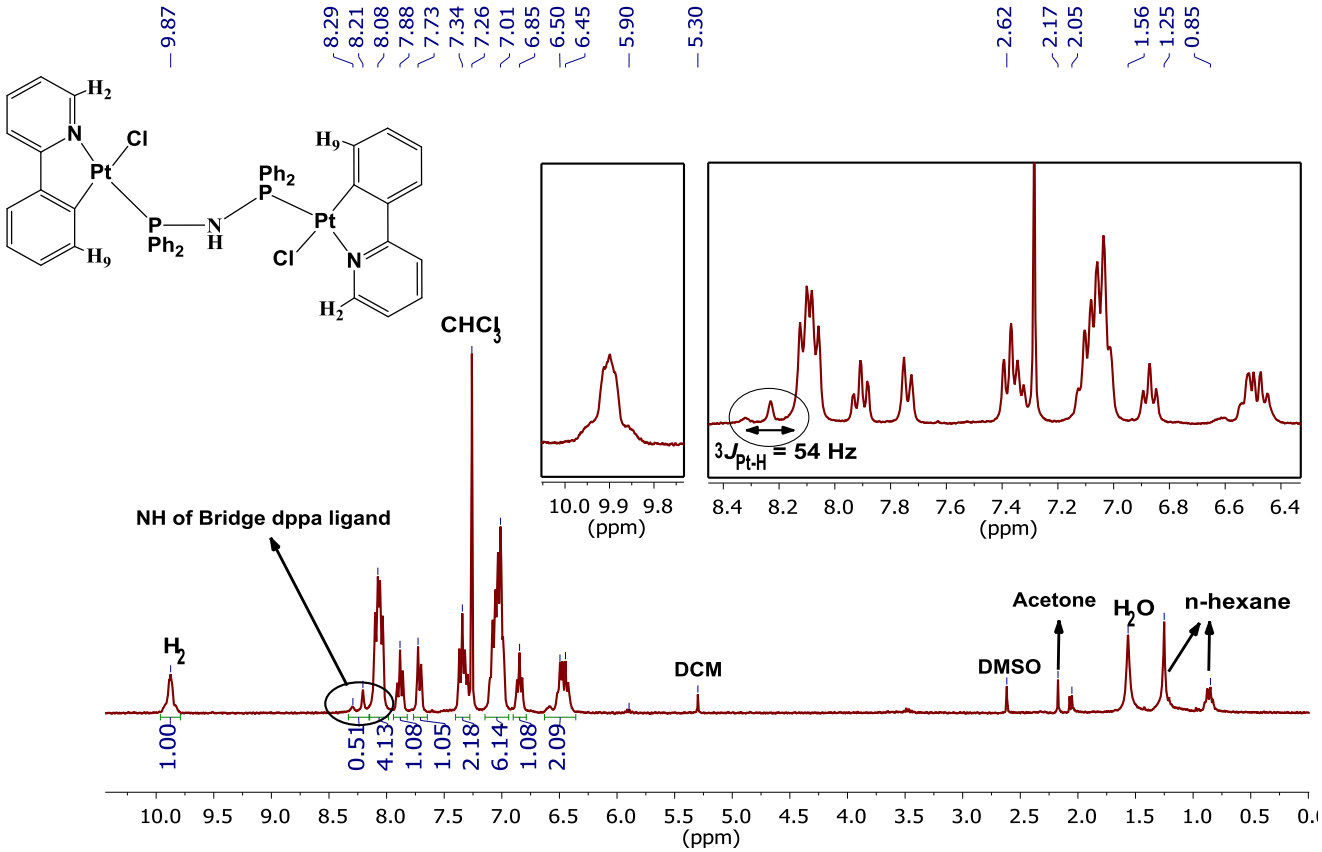


Figure S10. The ^{1}H NMR spectrum of [$Pt_2(ppy)_2(Cl)_2(\mu$-dppa)], **3b**, in $CDCl_3$.

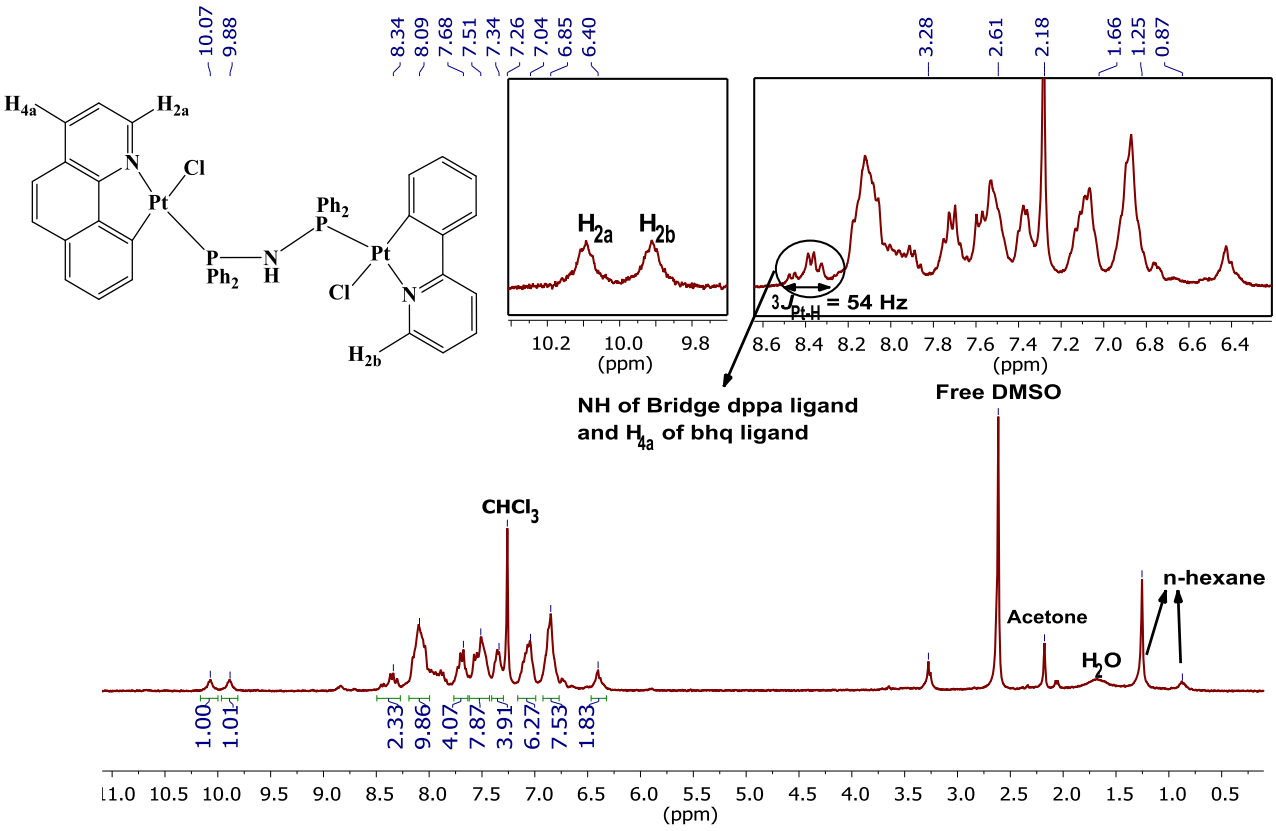


Figure S11. ^{1}H-NMR spectrum of Unsym-[$Pt_2(Cl)_2$(ppy)(bhq)(μ-dppa)], **3c**, in $CDCl_3$.

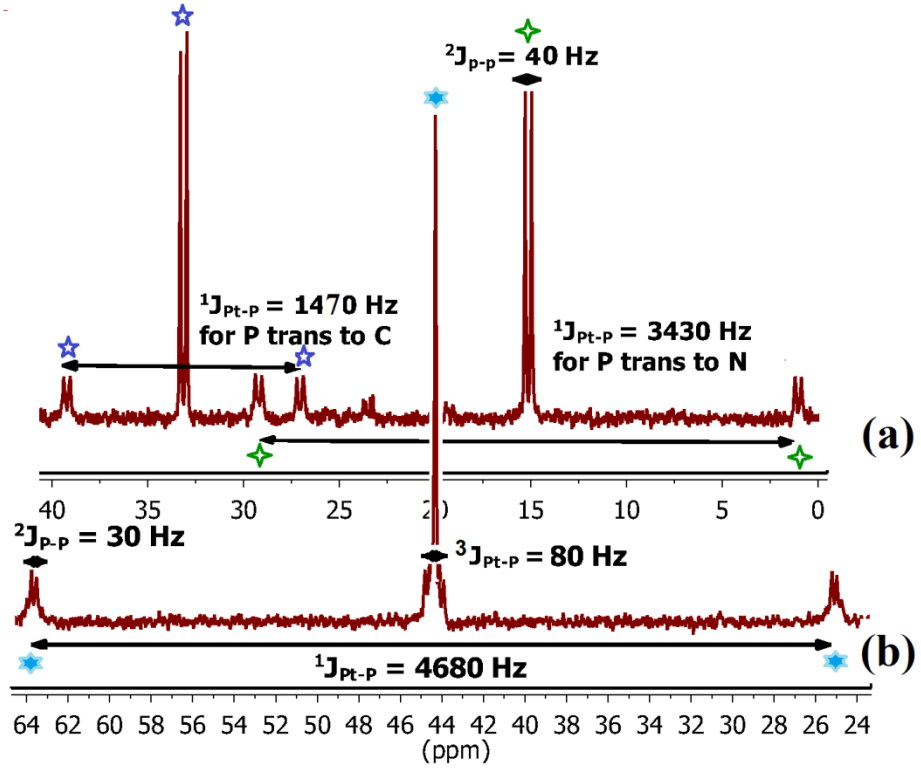


Figure S12. The ^{31}P{H}-NMR spectra of selected complexes: (a) **2b**, and (b) **3b**.

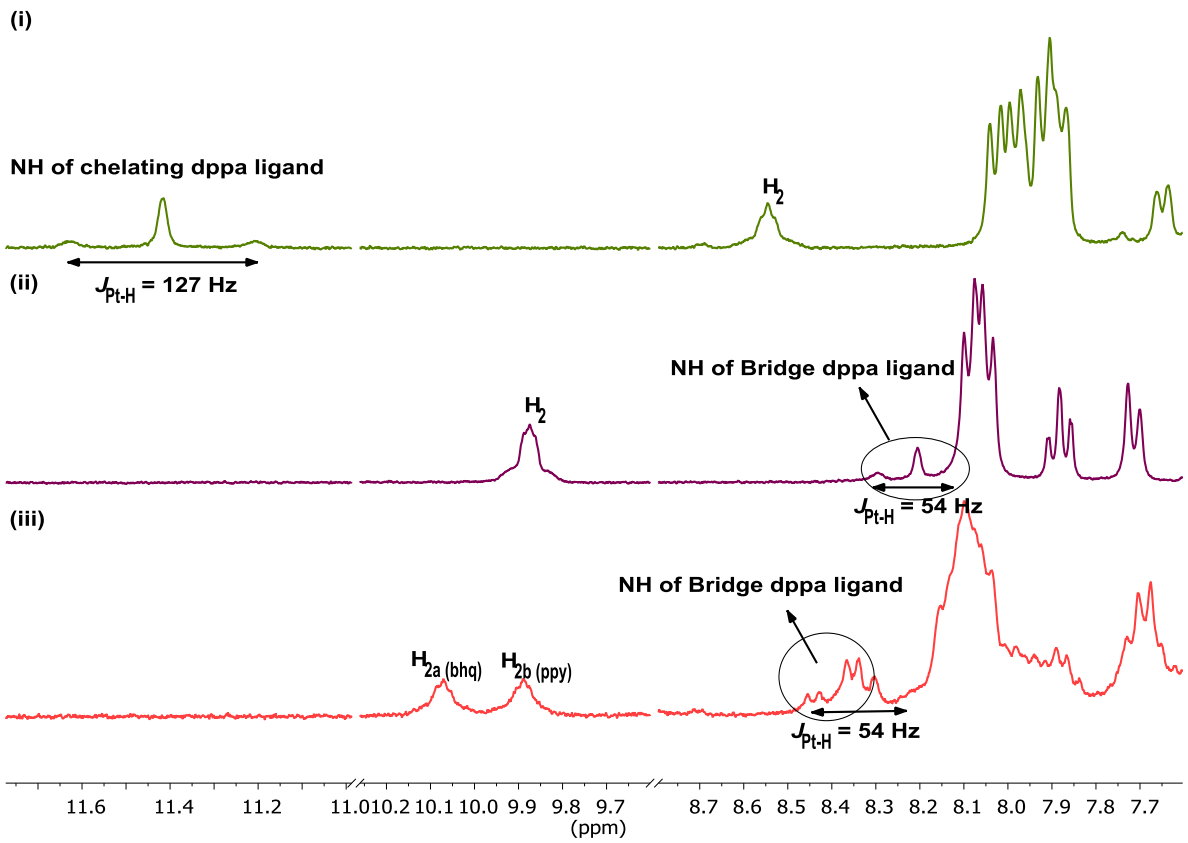


Figure S13. The aromatic region of ^{1}H-NMR spectra of selected complexes: (*i*) **2b,** (*ii*) **3b**, and (*iii*) **3c**.

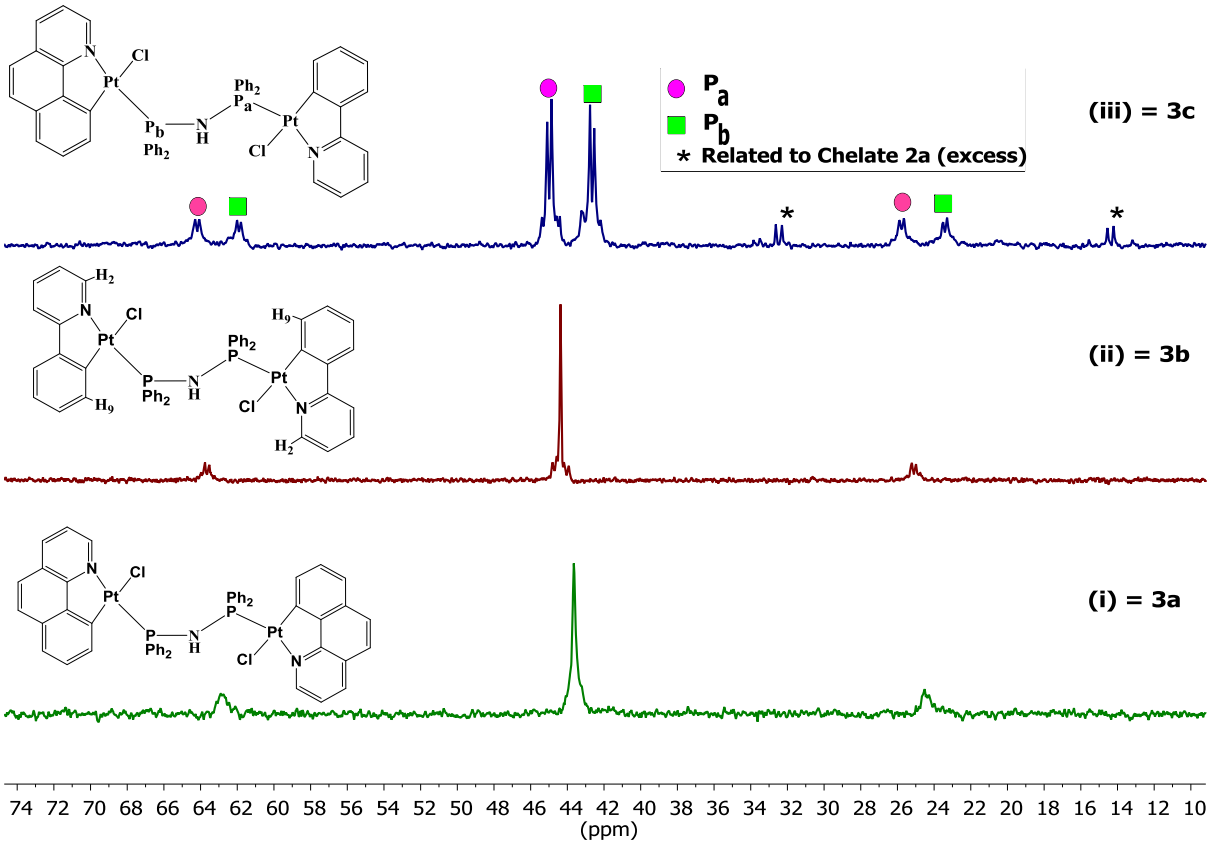


Figure S14. The ^{31}P{H}-NMR spectrum of (i) **3a**, (ii) **3b** and (iii) **3c** in $CDCl_3$.

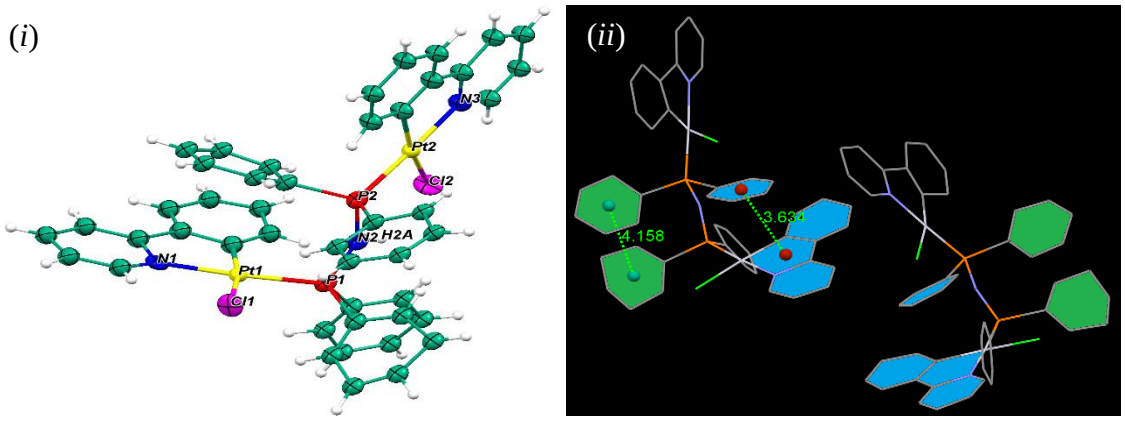


Figure S15. (*i*) ORTEP representation and (*ii*) π-π stacking interactions for $[Pt_2(ppy)_2(Cl)_2(\mu$-dppa)], **3b**. Ellipsoids are drawn at the 30% probability level, hydrogen atoms are shown as spheres of arbitrary radius. Selected geometrical parameters for **3b** (Å, °): Pt(1)-C(1) 2.00(3), Pt(1)-N(1) 2.08(3), Pt(1)-P(1) 2.221(8), Pt(1)-Cl(1) 2.374(7), Pt(2)-C(36) 1.99(3), Pt(2)-N(3) 2.05(2), Pt(2)-P(2) 2.220(9), Pt(2)-Cl(2) 2.398(6); C(1)-Pt(1)-N(1) 82.4(11), C(1)-Pt(1)-P(1) 95.9(9), N(1)-Pt(1)-P(1) 176.6(7), C(1)-Pt(1)-Cl(1) 170.1(9), N(1)-Pt(1)-Cl(1) 88.1(7), P(1)-Pt(1)-Cl(1) 93.5(3) ,C(36)-Pt(2)-N(3) 77.5(10), C(36)-Pt(2)-P(2) 98.3(8), N(3)-Pt(2)-P(2) 175.8(6), C(36)-Pt(2)-Cl(2) 167.4(9), N(3)-Pt(2)-Cl(2) 90.8(6), P(2)-Pt(2)-Cl(2) 93.3(3), P(1)-N(2)-P(2) 137.4(14).

Table S1. The crystal data and structure refinement for complexes **2a**, **2c**, **2d**, **3a,** and **3b.**

	2a.H_2O	**2c**	**2d**	**3a.**$2CH_2Cl_2.2H_2O$	**3b**
Formula	$C_{37}H_{31}ClN_2OP_2Pt$	$C_{39}H_{29}F_3N_2O_2P_2Pt$	$C_{37}H_{29}F_3N_2O_2P_2Pt$	$C_{52}H_{45}Cl_6N_3O_2P_2Pt_2$	$C_{46}H_{37}Cl_2N_3P_2Pt_2$
M_t [g mol^{-1}]	812.12	871.66	847.64	1408.73	1154.79
T [K]	120(2)	120(2)	298(2)	120(2)	298(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst syst	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	8.9146(18)	17.658(4)	9.2122(18)	10.824(2)	16.840(3)
b [Å]	15.405(3)	17.291(4)	16.750(3)	12.538(3)	13.547(3)
c [Å]	23.179(5)	21.870(4)	22.328(5)	19.399(4)	18.076(4)
α [deg]	90	90	90	108.08(3)	90
β [deg]	95.85(3)	90	99.90(3)	90.42(3)	91.72(3)
γ [deg]	90	90	90	102.08(3)	90
V [$Å^3$]	3166.6(11)	6677(2)	3394.0(12)	2439.9(10)	4121.7(14)
Z	4	8	4	2	4
ρ [Mg m^{-3}]	1.703	1.734	1.659	1.918	1.861
μ [mm^{-1}]	4.650	4.355	4.281	6.168	7.025
F(000)	1600	3424	1664	1364	2216
Cryst size (mm)	0.20 x 0.18 x 0.18	0.25 x 0.22 x 0.20	0.50 x 0.50 x 0.45	0.20 x 0.20 x 0.10	0.50 x 0.15 x 0.10
θ range [deg]	2.54 to 25.00	2.49 to 25.00	2.22 to 25.00	1.75 to 25.00	2.22 to 25.00
Limiting indices	-10<=h<=10	-18<=h<=20	-10<=h<=10	-12<=h<=12	-20<=h<=18
	-16<=k<=18	-18<=k<=20	-17<=k<=19	-14<=k<=14	-16<=k<=14
	-27<=l<=27	-22<=l<=26	-26<=l<=26	-23<=l<=21	-21<=l<=21
Collected Data	14870	19590	15561	18220	18989
Unique Data	5555	5876	5937	8576	7209
R(int)	0.1122	0.1311	0.0990	0.1581	0.2387
Absorption	Numerical	Numerical	Numerical	Numerical	Numerical
correction	0.907	0.946	0.974	0.819	0.852
GOF on F^2 [S]	0.0530,0.0836	0.0575,0.0820	0.0536,0.1210	0.0700,0.1055	0.1110,0.2544
R_1, wR_2 [I > 2δ (I)]	0.1070,0.0933	0.1228,0.0945	0.0881,0.1345	0.1592,0.1248	0.1852,0.2785
R_1, wR_2 (all data)					

Table S2. Experimental absorption parameters for complexes **2** and **3** in CH_2Cl_2 and benzene.

	Media [a]	**$\lambda_{abs-exp}$ /nm ($\varepsilon/10^2$ $M^{-1}cm^{-1}$)**
2a	CH_2Cl_2	404 (28.03), 383 (28.03), 347 (31.86), 300 (215.89), 252 (362.21)
	Benzene	410 (5.48), 389 (5.75), 345 (11.56), 302 (39.41), 284 (43.26)
2b	CH_2Cl_2	375 (17.43), 329 (51.46), 273 (238.17), 250 (316.31)
	Benzene	381 (15.81), 330 (62.35), 317 (71.08), 280 (186.56)
2c	CH_2Cl_2	402(28.73), 383(29.83), 345(29.83), 300(220.96), 288(213.35), 256(368.63)
	Benzene	407(17.12), 389(17.48), 349(20.35), 303(118.43), 288(115.56)
2d	CH_2Cl_2	369 (23.35), 330 (63.49), 316 (68.27), 253 (340.74)
	Benzene	375 (20.89), 331 (61.63), 318 (65.17), 280 (202.58)
3a	CH_2Cl_2	406(62.28), 328(159.54), 304(299.97), 261(482.56), 247(460.86)
	Benzene	417(67.04), 399(61.14), 331(161.15), 307(289.50), 269(440.11)
3b	CH_2Cl_2	379(58.03), 328(110.91), 315(127.02), 284(258.11), 250(349.96)
	Benzene	385(55.89), 330(105.85), 319(124.63), 289(236.77)
3c	CH_2Cl_2	386(34.63), 328(85.93), 304(147.86), 258(320.95)
	Benzene	421(19.38), 393(33.59), 330(88.89), 307(138.74), 284(166.43)

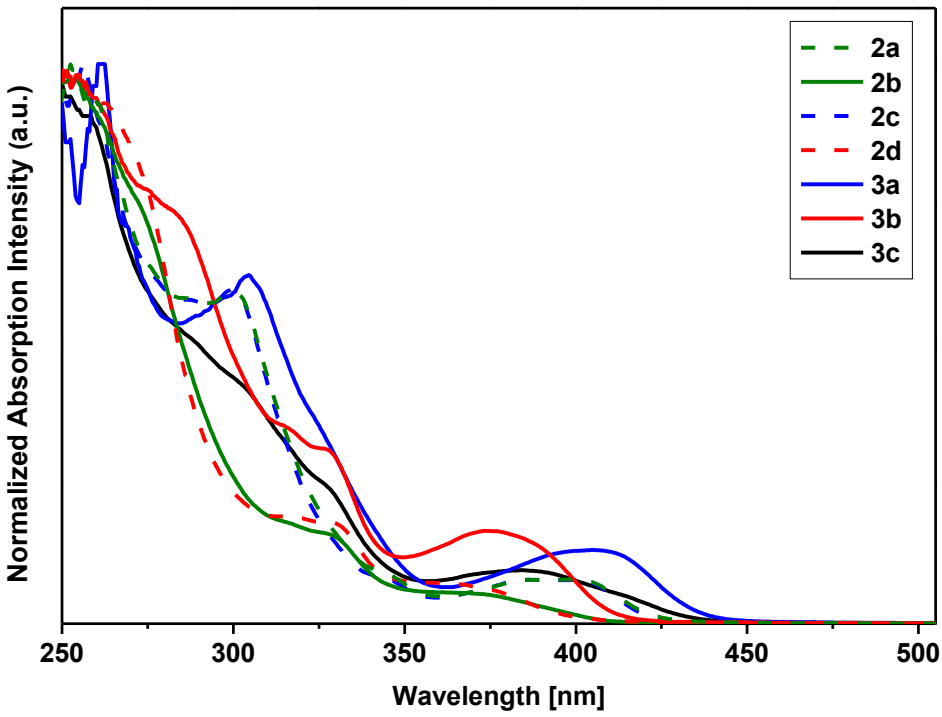


Figure S16. Normalized absorption spectra of complexes **2** and **3** in CH_2Cl_2 at 298 K.

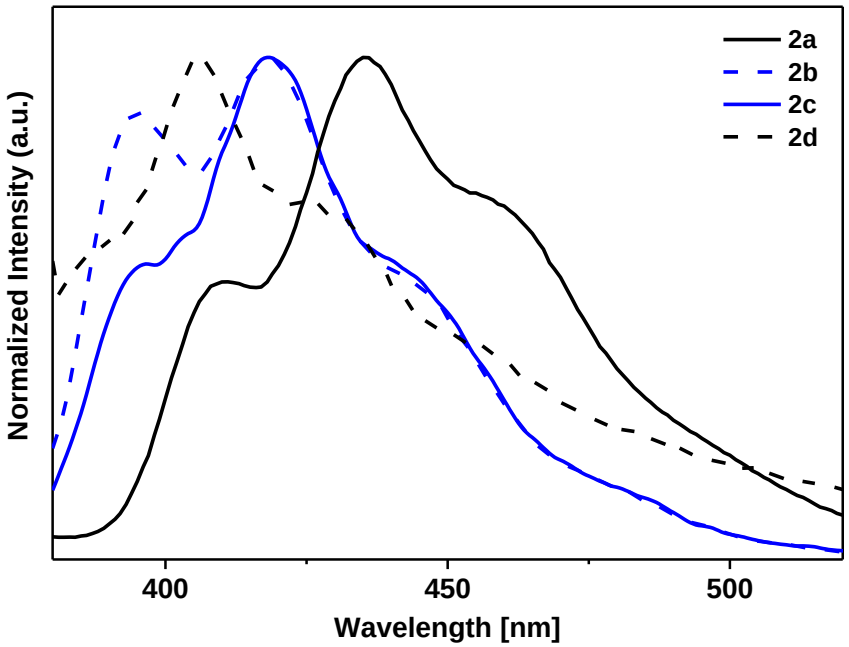


Figure S17. Normalized emission spectra of complexes in CH_2Cl_2 (10^{-4} M) at 298 K.

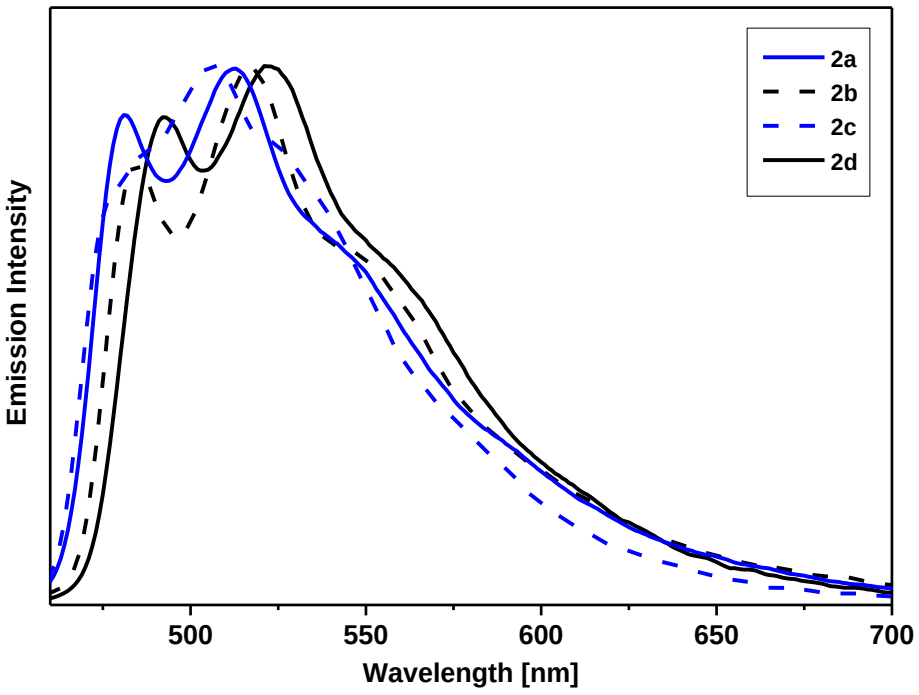


Figure 18. Normalized emission spectra of complexes **2** in powder at 298 K.

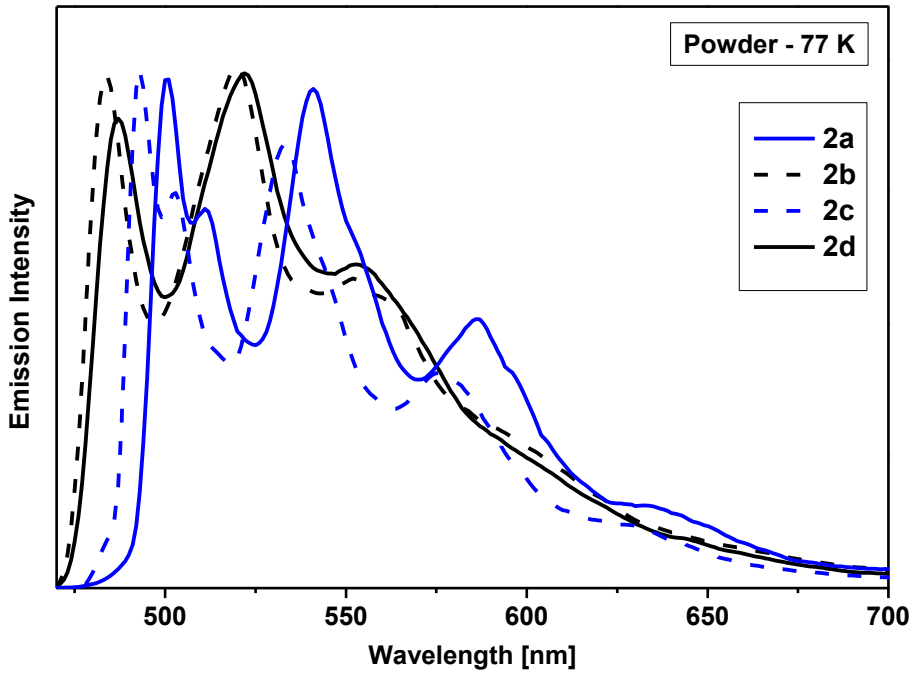
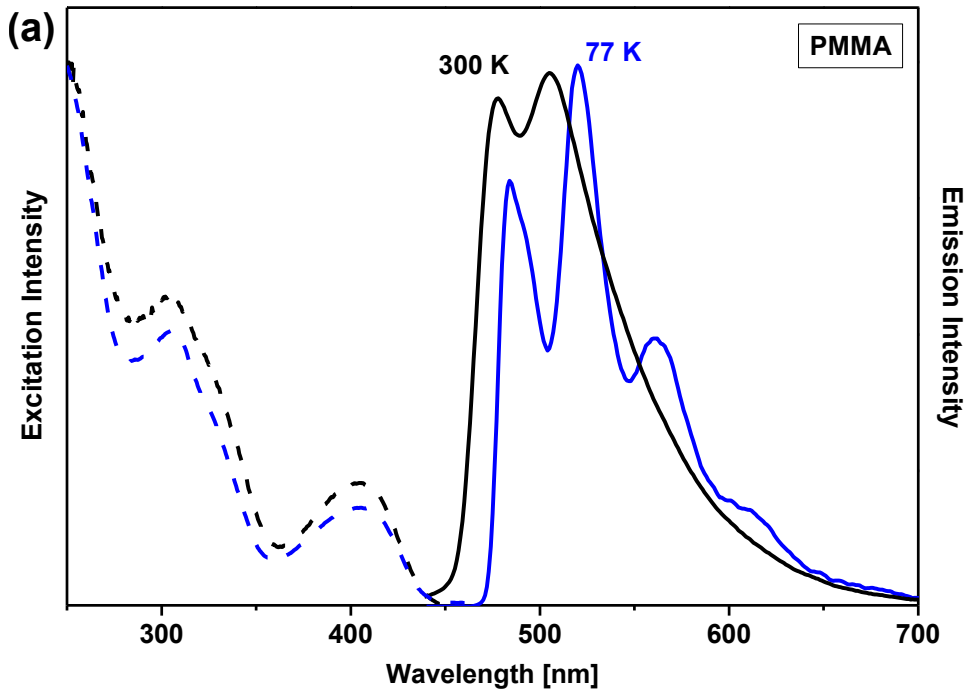
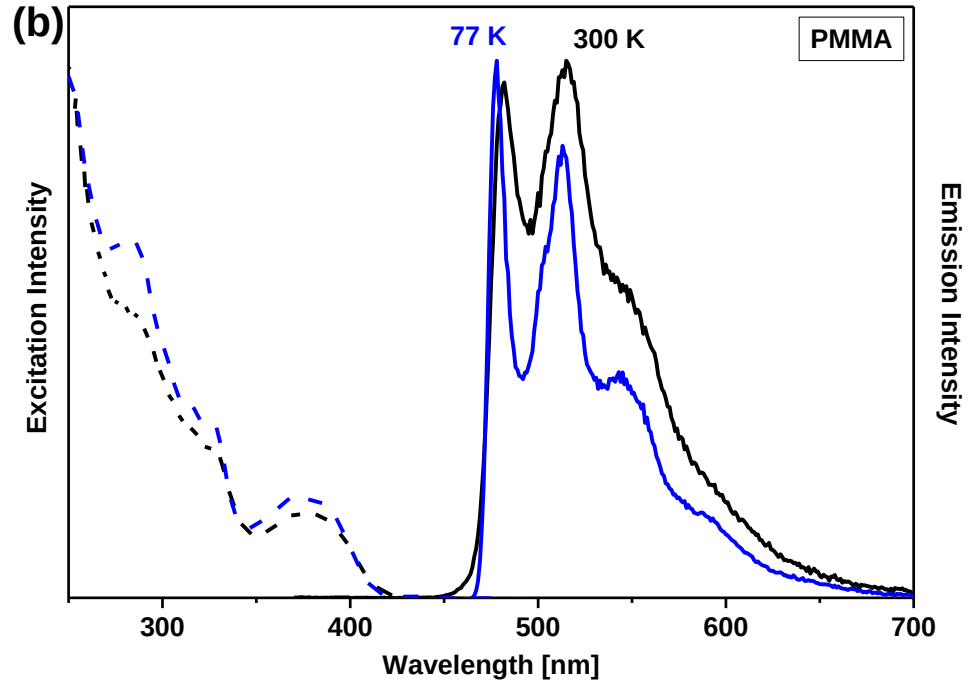


Figure S19. Normalized emission spectra of complexes **2** in powder form at 77 K.


(a)
PMMA
300 K
77 K
Excitation Intensity
Emission Intensity
300
400
500
600
700
Wavelength [nm]


(b)
PMMA
77 K
300 K
Excitation Intensity
Emission Intensity
300
400
500
600
700
Wavelength [nm]

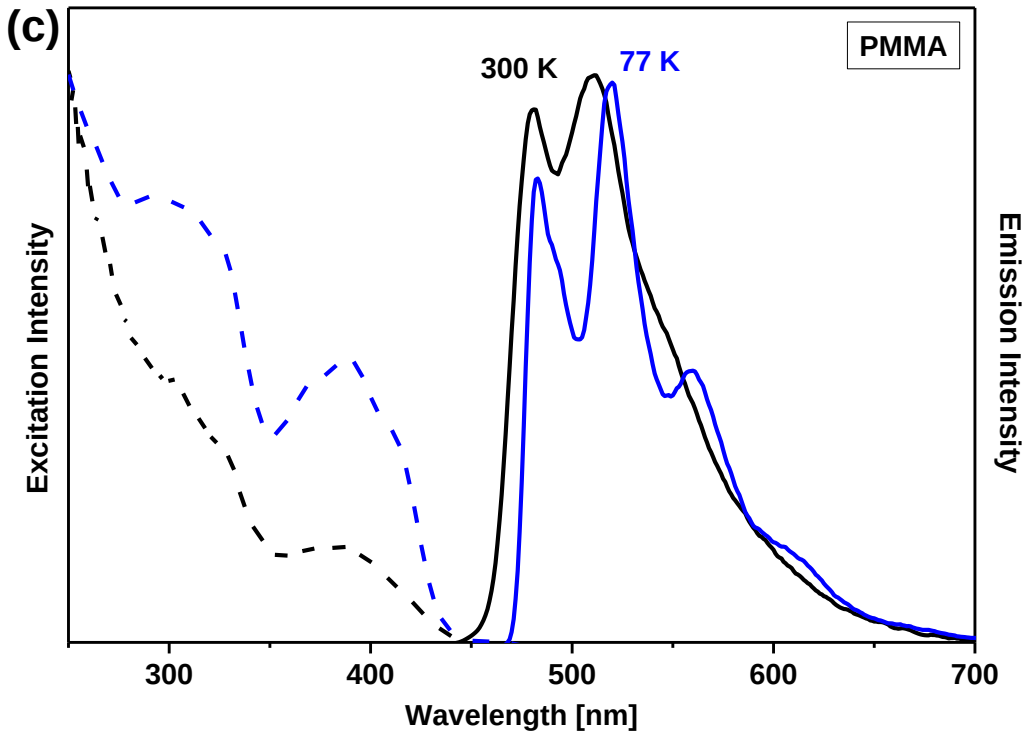


Figure S20. Normalized excitation (dash lines) and emission (solid lines) spectra of (a) **3a**, (b) **3b**, and (c) **3c** in PMMA at 77 K (blue) and 298 K (black).

References:

1. Esmaeilbeig, A.; Samouei, H.; Abedanzadeh, S.; Amirghofran, Z., Synthesis, characterization and antitumor activity study of some cyclometalated organoplatinum (II) complexes containing aromatic N-donor ligands. *J. Organomet. Chem.* **2011,** *696* (20), 3135-3142.
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