

Supplementary data for

Diphenylamino-Modified Neutral Pt(II) Complexes: Their Aggregation-Induced Phosphorescent Emission and Picric Acid-Sensing Properties

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Photophysical properties

The UV-vis absorption spectra of **1–3** in THF at room temperature are presented in Figure S1a, and the detailed photophysical data are listed in Table S1. All complexes exhibit the strong absorption bands below 300 nm, which are assigned to a typical ligand-centered ¹LC (¹π–π*) transition. The lower energy absorption bands at about 350–450 nm are derived from mixing among metal-to-ligand ¹MLCT/³MLCT and ligand-to-ligand charge transfer ¹LLCT/³LLCT together with ligand-centered ³LC (³π–π*) transitions, which are similar to the previously reported literature [1].

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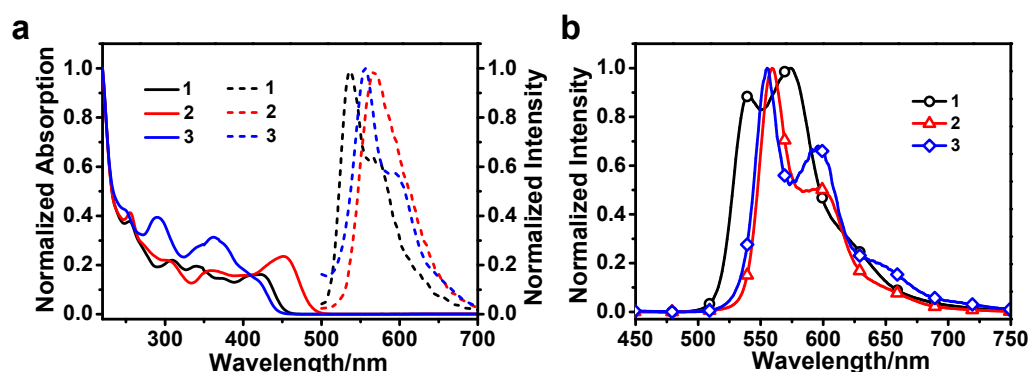


Figure S1. (a) Normalized absorption (solid trace) and emission (dash trace) spectra of **1–3** at room temperature ($c = 50 \mu\text{M}$ in THF). (b) Normalized emission spectra of **1–3** in the solid state. The excitation wavelength was 400 nm.

Figure S1a presents the emission spectra of **1–3** in THF. Efficient phosphorescence emission peaks of 536, 567, and 556 nm are observed for **1–3**. In comparison to **1**, the maximum emission wavelengths of **2** and **3** are red-shifted due to the presence of trifluoromethyl and triphenylamine group. In the solid state, the emission maxima of **1–3**

are determined as 573, 559, and 555 nm, respectively (Figure S1b). The phosphorescence quantum yields of **1–3** are 11%, 14%, and 4%, respectively. The results display that the structures of cyclometalating ligands have a substantial impact on the photophysical properties of the complexes.

Table S1. Photophysical data of **1–3**.

Complexes	λ_{abs}^a (nm)	λ_{em}^b (nm)	λ_{em}^c (nm)	Φ_{PL}^d
1	254(1.42), 309(0.82), 340(0.72), 422(0.59)	536 , 568	540, 573	11%
2	256(1.63), 306(0.84), 357(0.68), 451(0.92)	567	559 , 600	14%
3	250(1.76), 290(1.64), 361(1.29), 420(0.50)	556 , 596	555 , 595	4%

^a Measured in THF at a concentration of 50 μM and extinction coefficients ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are shown in parentheses. ^b The emission maxima of the complexes in THF. ^c The emission maxima of the complexes in the solid state. ^d The quantum yields (Φ_{PL}) in deoxygenated CH_2Cl_2 were measured with $[\text{Ir}(\text{ppy})_2(\text{acac})]$ ($\Phi_{\text{PL}} = 0.34$) as a standard. All results were measured at ambient temperature.

Molecular packing modes of complexes 1–3

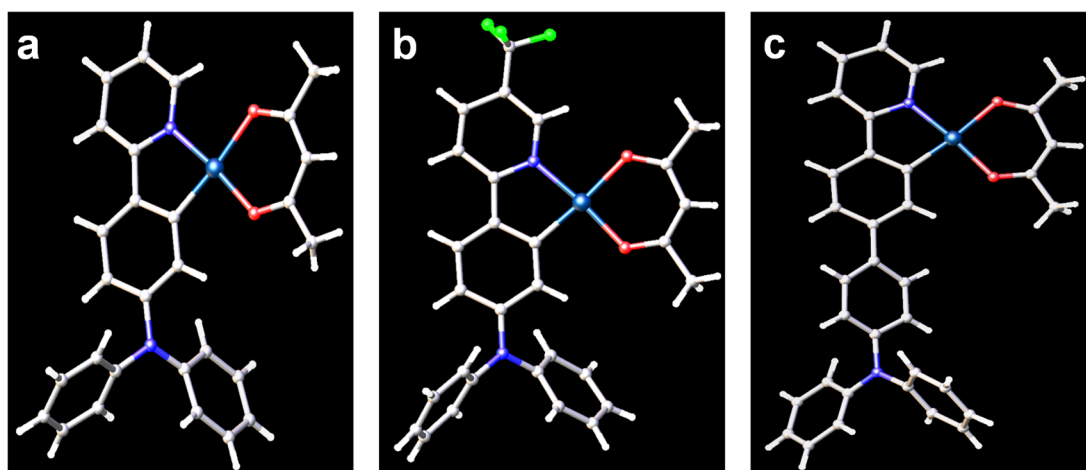


Figure S2. Crystal structures of **1** (a), **2** (b), and **3** (c).

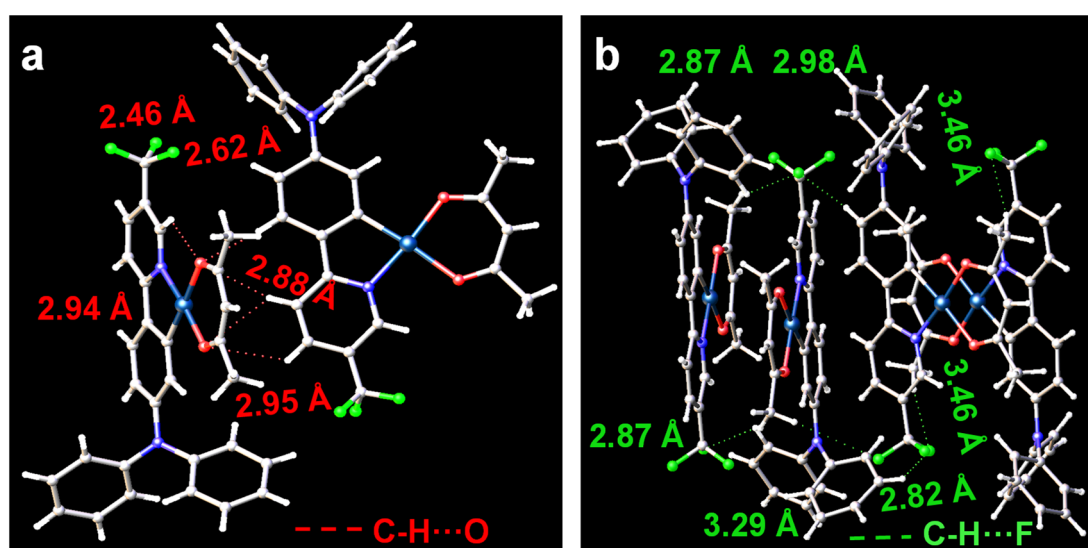


Figure S3. (a) Intermolecular C-H...O hydrogen bonds and (b) intermolecular C-H...F hydrogen bonds of **2**.

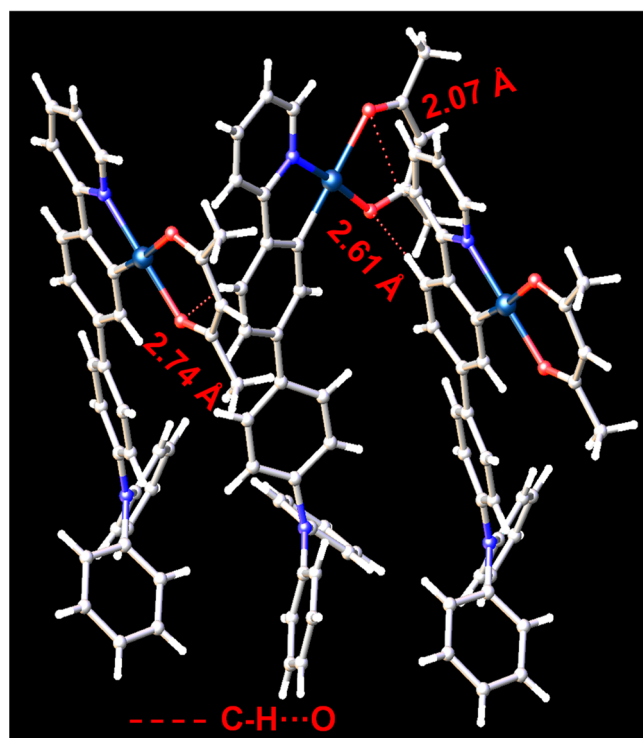


Figure S4. Intermolecular C-H...O hydrogen bonds of **3**.

Table S2. Crystal data for complexes **1–3**.

Complexes	1	2	3
Formula	C ₂₈ H ₂₄ O ₂ N ₂ Pt	C ₂₉ H ₂₃ O ₂ N ₂ F ₃ Pt	C ₃₄ H ₂₈ O ₂ N ₂ Pt
Crystal System	Monoclinic	Triclinic	Triclinic
Temperature	296 K	296 K	293 K
Space group	P2(1)/c	P-1	P-1
Cell lengths (Å)	a = 13.446(4) b = 9.606(3) c = 18.330(6) α = 90 β = 103.229(4) γ = 90	a = 12.1092(4) b = 12.7133(4) c = 18.3191(6) α = 78.388(3) β = 72.068(2) γ = 89.806(2)	a = 10.4098(14) b = 15.594(2) c = 16.792(2) α = 90.110(2) β = 93.084(2) γ = 91.575(2)
Cell volume (Å ³)	2304.6(13)	2623.08(15)	2720.8(6)
Z	4	2	2
Density (g/cm ³)	1.774	1.731	1.689
F (000)	1200.0	1328.0	1360.0
hmax, kmax, lmax	17, 12, 23	14, 15, 21	12, 15, 18
Absorption coefficient (mm ⁻¹)	6.117	5.399	5.192
R (int)	0.0255	0.0581	0.0831
Data/restraints/ parameters	5144/0/300	9219/54/671	9443/48/703
Goodness-of-fit on F ²	1.049	1.030	0.921
R ₁ ^a [I > 2σ(I)]	0.0224	0.0478	0.0729
wR ₂ ^b [I > 2σ(I)]	0.0502	0.0725	0.1119
R ₁ ^a (all data)	0.0313	0.0945	0.1628
wR ₂ ^b (all data)	0.0532	0.0806	0.0930
CCDC number	2071354	918648	762460

$$^{[a]}R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

$$^{[b]}wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

PA detection of complexes 1–3

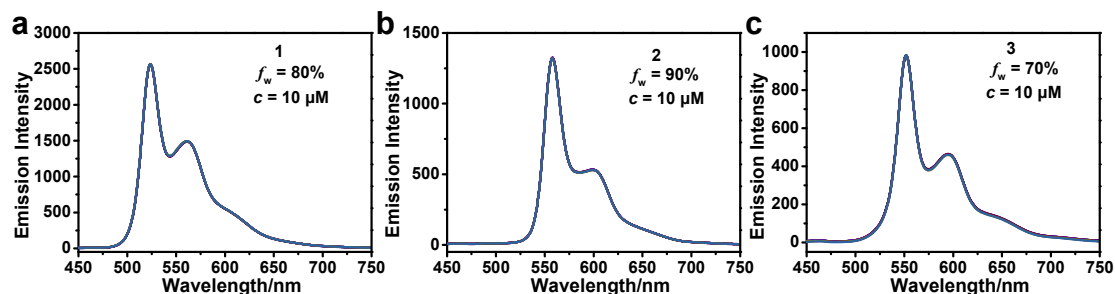


Figure S5. The emission spectra of **1** (a), **2** (b), and **3** (c) in 11 blank samples. The excitation wavelength was 400 nm.

Table S3. The emission intensities of **1** at 523 nm, **2** at 558 nm, and **3** at 552 nm in 11 blank samples.

Complexes	1	2	3
X ₁	2560.8	1316.8	979.5
X ₂	2560.4	1316.9	979.8
X ₃	2560.2	1316.7	980.0
X ₄	2562.1	1317.9	980.3
X ₅	2560.5	1318.4	981.0
X ₆	2561.9	1318.9	981.3
X ₇	2559.8	1319.4	981.7
X ₈	2559.8	1317.7	980.4
X ₉	2558.6	1317.4	980.8
X ₁₀	2559.6	1317.5	981.2
X ₁₁	2560.6	1316.7	981.5
X	2560.4	1317.7	980.8

The values of σ for **1–3** were calculated according to the following equation:

$$\sigma = [\sum (X_i - X)^2 / (n-1)]^{0.5}$$

X_i ($i = 1, 2, 3 \dots 11$) represents the emission intensity of each blank sample, X represents the mean value of the emission intensity, n represents the number of blank samples.

According to the above formula, the values of σ for **1–3** were calculated to be 0.9529, 0.8752, and 0.7041.

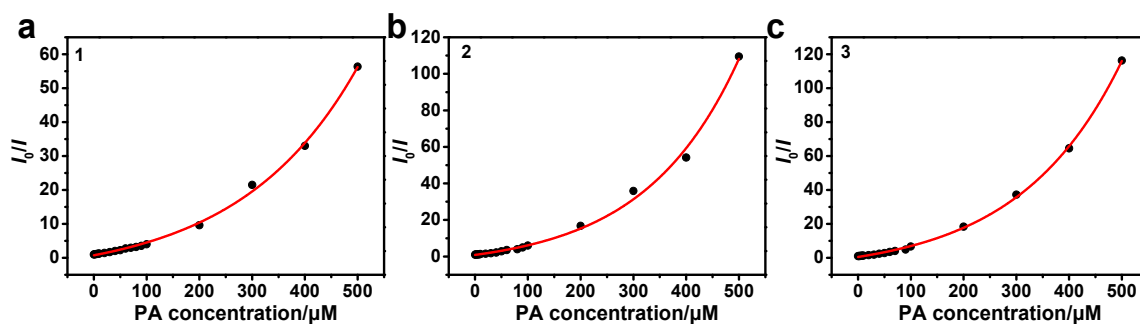


Figure S6. The Stern–Volmer plots of **1** (a), **2** (b), and **3** (c) for PA.

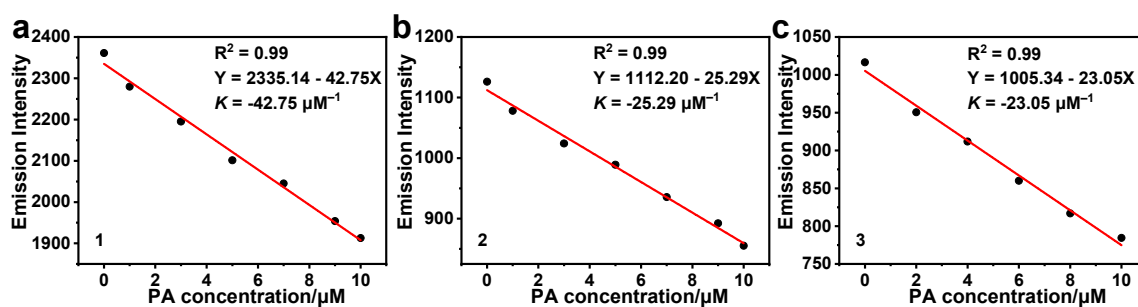


Figure S7. The linear graphs of the emission intensities of **1** (a), **2** (b), and **3** (c) vs. the concentration of PA.

Table S4. Some reported sensors for the detection of PA.

Probes	Solvent	LOD	$K_{\text{SV}}/\text{M}^{-1}$	References
	$\text{CH}_2\text{Cl}_2/\text{DMF}$ (v/v, 4:1)	-	4.8×10^4	[2]
	$\text{CHCl}_3/\text{CH}_3\text{OH}$ (v/v, 1:1)	-	5.0×10^6	[3]
	DMF	-	5.0×10^4	[4]
	CHCl_3	-	3.6×10^4	[5]
	Micellar media	1.0 μM	1.1×10^4	[6]
	CH_3CN	2.3 μM	6.8×10^4	[7]
	THF/ H_2O 1: (v/v, 2:8) 2: (v/v, 1:9) 3: (v/v, 3:7)	1: 70 nM 2: 100 nM 3: 90 nM	1: 2.3×10^4 2: 2.8×10^4 3: 3.0×10^4	This work

- no values reported.

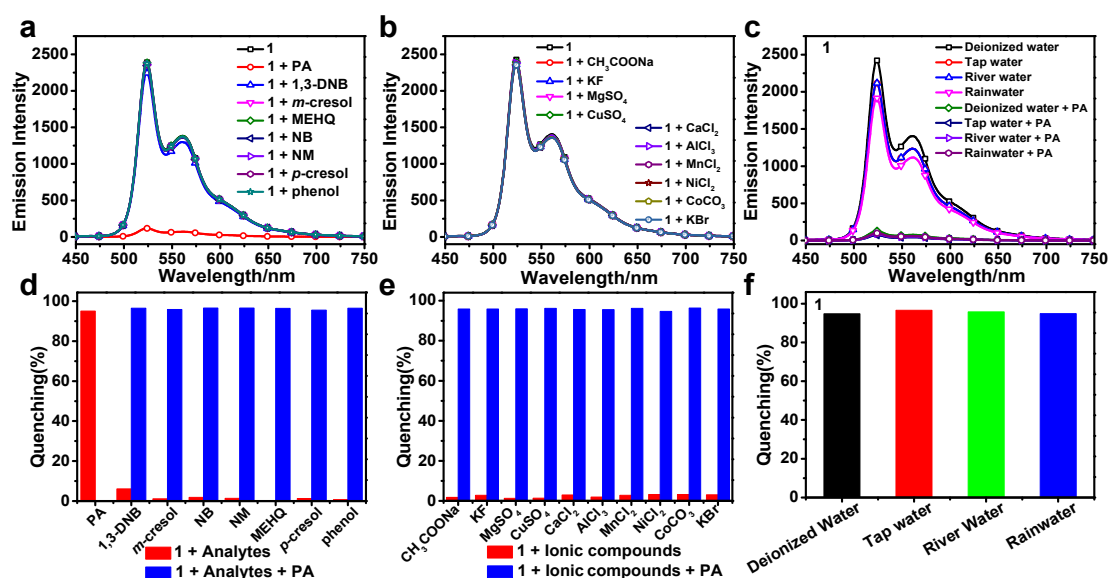


Figure S8. The emission spectra of **1** in THF/H₂O (v/v = 2:8, 10 μ M) with different analytes (a), ionic compounds (b), and common water samples (c) present. Quenching percentages of **1** with different analytes (d), ionic compounds (e) before (red) and after (blue) the addition of PA. (f) Quenching percentage of **1** towards PA in common water samples. The excitation wavelength was 400 nm.

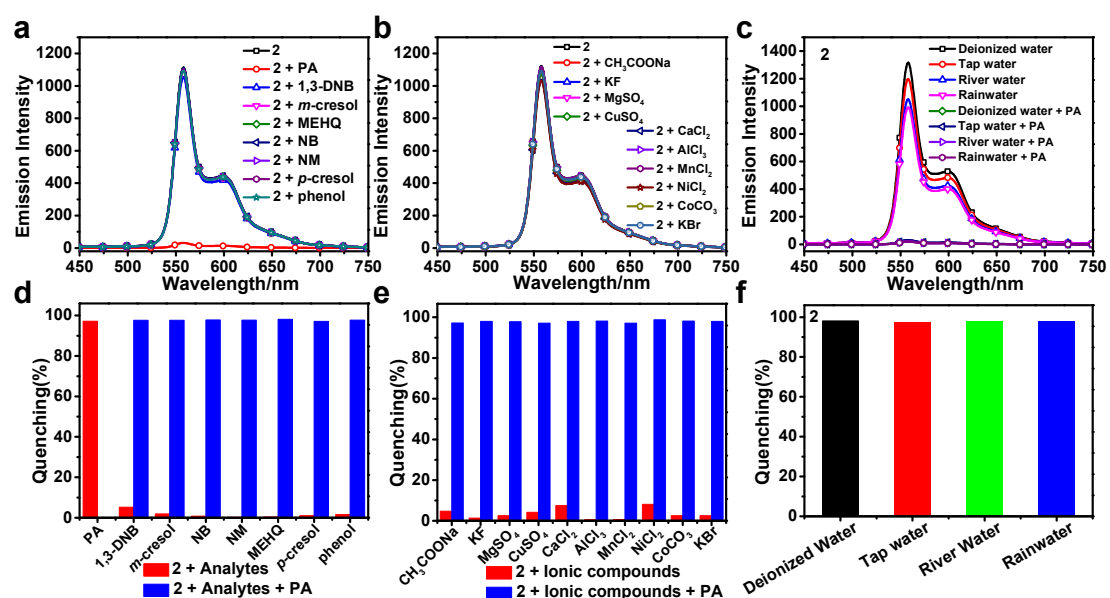


Figure S9. The emission spectra of **2** in THF/H₂O (v/v = 1:9, 10 μ M) with different analytes (a), ionic compounds (b), and common water samples (c) present. Quenching percentages of **2** with different analytes (d), ionic compounds (e) before (red) and after (blue) the addition of PA. (f) Quenching percentage of **2** towards PA in common water samples. The excitation wavelength was 400 nm.

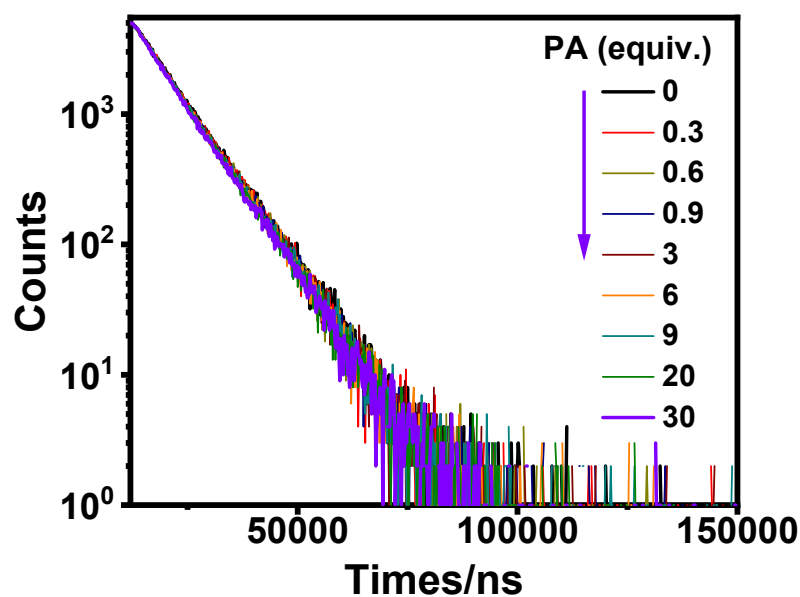
Phosphorescence decay traces of **3** in detecting PA

Figure S10. Phosphorescence decay traces of **3** in THF/H₂O (v/v = 3:7, 10 μM) after addition of PA at different concentrations.

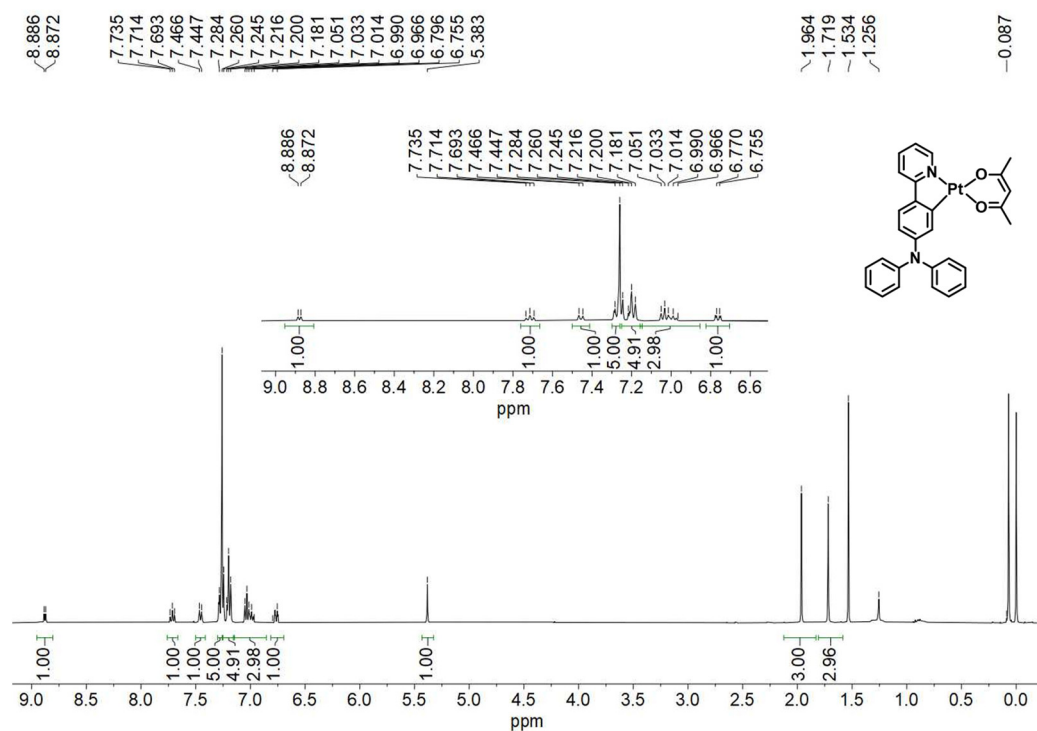
NMR spectra and HRMS of complexes **1–3**

Figure S11. The ¹H NMR spectrum of **1** in CDCl₃.

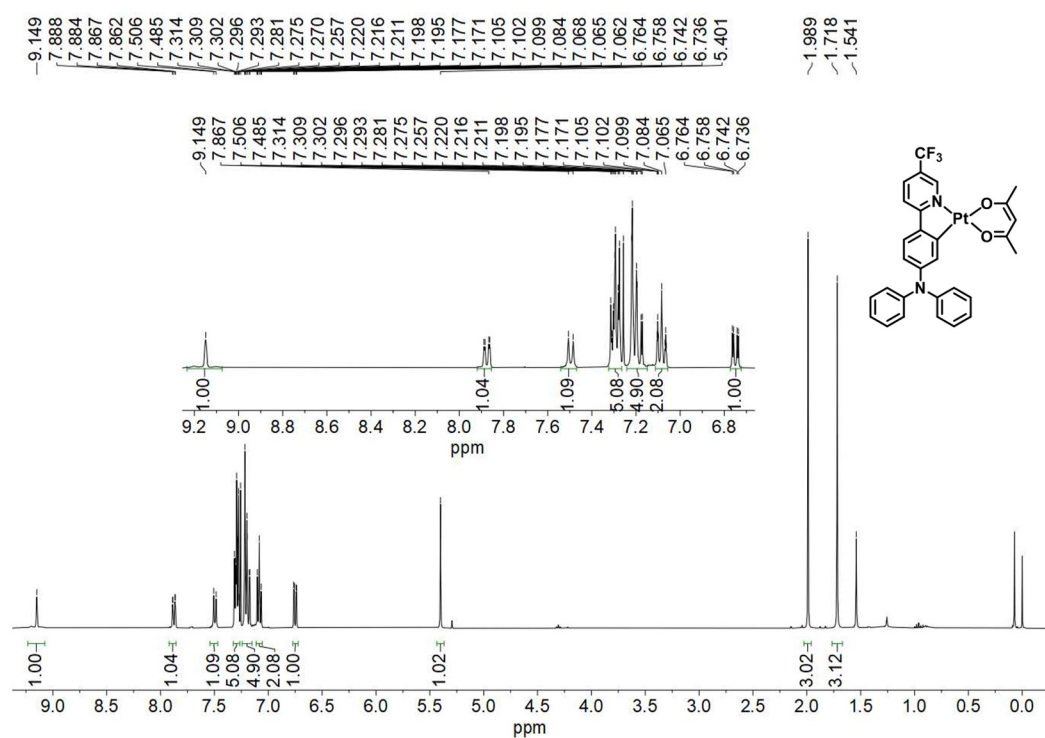


Figure S12. The ¹H NMR spectrum of 2 in CDCl₃.

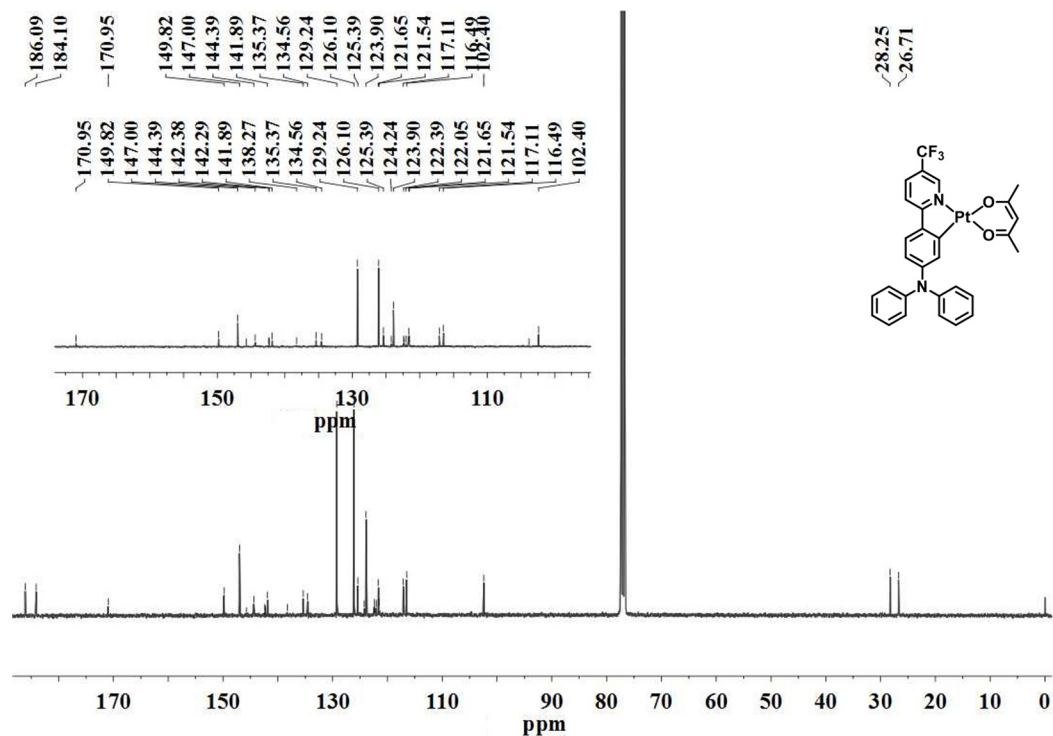


Figure S13. The ¹³C NMR spectrum of 2 in CDCl₃.

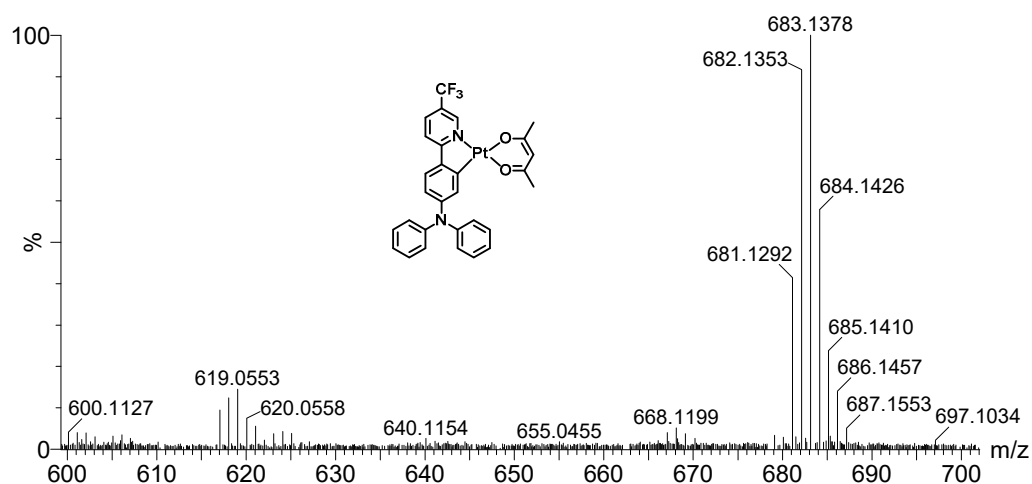
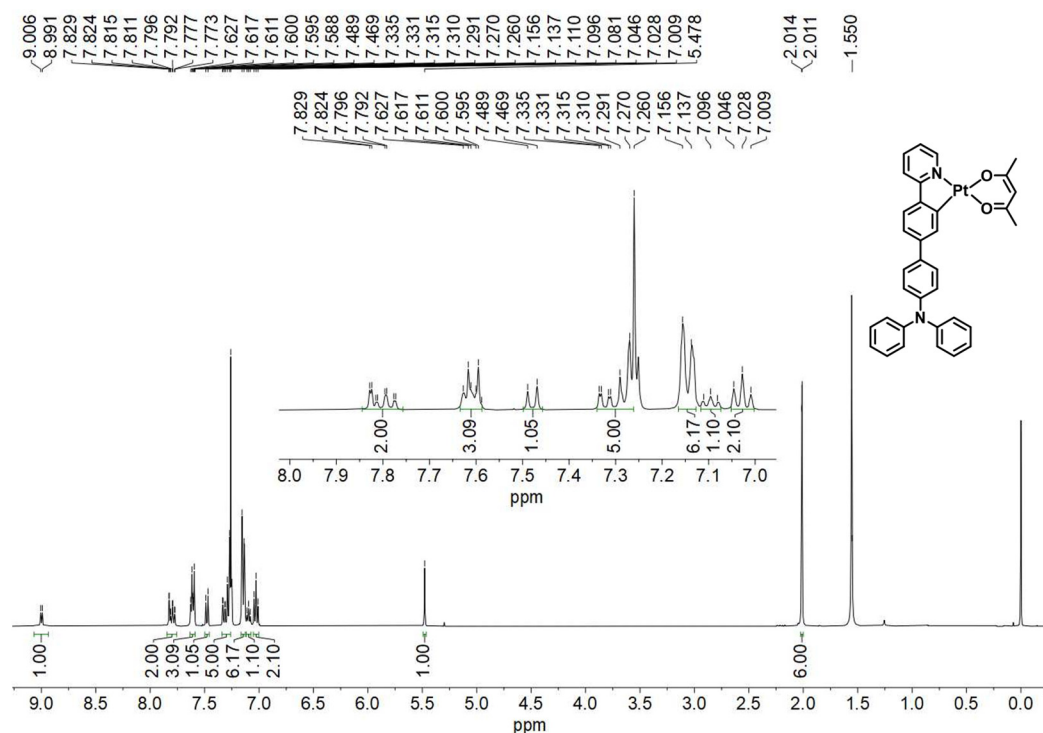


Figure S14. The HRMS of 2.

Figure S15. The ¹H NMR spectrum of 3 in CDCl₃.

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