Electronic Supplementary Information

For

Effective phosphorescence quenching in borylated Pt^{II} ppy-type phosphors and their application as I^{-} ion sensors in aqueous medium

Xiaolong Yang, Zuan Huang, Jingshuang Dang, Cheuk-Lam Ho, Guijiang Zhou,* and Wai-Yeung Wong*

Experimental

General information: All reactions were performed under an inert nitrogen atmosphere. All the solvents were carefully dried and distilled from appropriate drying agents prior to use. All the commercially available chemicals were used directly with no further purification. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminium plates. Flash column chromatography and preparative TLC were carried out using silica gel from Shenghai Qingdao (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer and chemical shifts were quoted relative to the solvent residual peak at δ 7.26 for ^{1}H and 77.0 for ^{13}C, respectively. ESI-TOF mass spectral measurements were performed on micrOTOF-QII mass spectroscopy with a mild electrospray ionization (ESI) source in order to avoid the disassociation of the adducts as far as possible. The corresponding solution (ca. 0.2 mL) was added to methanol (ca. 0.2 mL). After mixing, the solution (20 μL) was injected into the instrument to get the mass spectra.

Physical measurements: The thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 409C instrument under a nitrogen atmosphere with the heating rate of 20 K/ min. Differential scanning calorimetry (DSC) was conducted on a NETZSCH DSC 200 PC unit under a nitrogen flow at a heating rate of 10 K/min. UV−vis spectra were recorded at room temperature on a Shimadzu UV-2250 spectrophotometer. Emission spectra and lifetimes of the complexes were measured using an Edinburgh Instruments Ltd (FLSP920) fluorescence spectrophotometer. The data analysis was conducted by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. The phosphorescence quantum yields (Φ_P) were determined in CH_2Cl_2 solutions at 298 K against *fac*-[Ir(ppy)$_3$] standard ($\Phi_P = 0.40$).[S1]

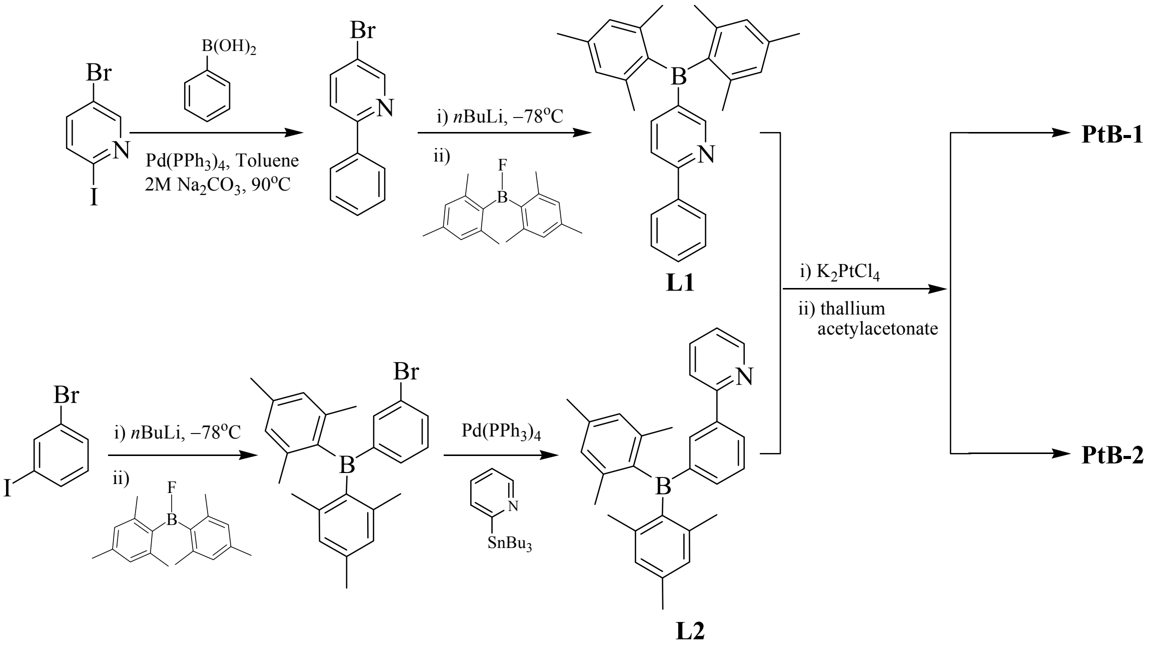
Emission and absorption titration: The THF solution of NBu_4I (ca. 1×10^{-3} M) was added to the THF solution of the platinum complex (ca. 1×10^{-5} M) in screw-capped UV or PL cell according to the target I^-:[Pt] ratio via a micro-syringe. The emission intensity data at 502 nm for **PtB-1** and 488 nm for **PtB-2** were taken to obtain their Stern–Volmer quenching constant (K_{sv}).[S2] The detection limit (D. L.) was also determined from the emission titration data based on the reported method.[S3]

^{1}H-NMR titration: After preparing the THF-d_8 solution for the concerned complexes with concentration ca. 6×10^{-3} M, 0.5 mL the as prepared was charged into a NMR tube. By adding 0.6 M THF solution of NBu_4I with a micro syringe into the NMR tube, the desired I^-:[Pt] ratio was achieved. After gently shaking the NMR tube for about two minutes, the corresponding NMR spectra were obtained.

Preparation of the sensing paper: A piece of filter paper with proper size was dipped into the THF solutions (ca. 10^{-5} M) of **PtB-1** and **PtB-2** for 3 s, respectively, and then taken out. It was dried at ca. 40 °C for 1 min and then can be employed for sensing I^- ions in water solution directly.

Preparation of the water solution for sensing: The NBu_4I (184.6 mg), NBu_4Cl (138.6 mg), NBu_4Br (160.6 mg), NBu_4BF_4 (164.6 mg), NBu_4I (193.7 mg), NBu_4Ac (150.6 mg), and K_3PO_4 (106.1 mg), NaClO (37.2 mg) and NBu_4ClO_4 (171.0 mg) were added to distilled water (50 mL) containing 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) (238.3 mg) as a buffer in a 200 mL volumetric flask. Then, distilled water was added until the solution surface reached the mark. After mixing the solution gently, the water solution containing various anions was obtained with a concentration of ca. 2.5×10^{-3} M. Then, the as-prepared solution (1 mL) was diluted to the ion concentration of ca. 1×10^{-5} M in a 250 mL volumetric flask. The resulting solution was employed for I^- sensing under aqueous condition. Another water reference solution (ca. 1 × 10^{-5} M) containing all the anions except I^- was also prepared at the same buffer concentration.

I^- sensing in water solution: The as-prepared sensing paper was dipped into the corresponding water solution for 3 s. Then, the sensing paper was taken out and put on a clean hot plate (ca. 50 °C) for 1.5 min. The sensing paper was then dipped into the water solution again. The whole process was repeated 2 times and the sensing paper was dried thoroughly on a clean hot plate at ca. 50 °C for 5 min. The change of emission colour was monitored by a UV lamp at 365 nm.



Scheme S1 Synthetic route for Pt^{II} complexes **PtB-1** and **PtB-2**.

The organic ligand (**L1**) was prepared according to the reference method.[8a]

Synthesis of PtB-1: Under a N_2 atmosphere, **L1** (0.50 g, 1.24 mmol) and K_2PtCl_4 (0.56 g, 1.35 mmol) were added to a mixture of 2-ethoxyethanol and water (3:1, v/v) (20 mL). The reaction mixture was heated to 85 °C for 19.5 h under stirring. After cooling the mixture to room temperature, saturated NaCl solution (35 mL) was added to the reaction mixture. The yellow precipitate formed was collected by filtration and dried under vacuum to give a yellow solid (0.67 g). Thallium acetylacetonate (0.47 g, 1.5 mmol) as well as the yellow solid were added to CH_2Cl_2 (25 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 15.5 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with hexane/CH_2Cl_2 (1:2, v/v). The product was obtained as an orange solid (0.44 g, 50.9 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.02 (d, J = 1.2 Hz, 1H, Ar), 7.86 (dd, J = 1.6, 8.0 Hz, 1H, Ar), 7.61 (d, J = 6.8 Hz, 1H, Ar), 7.56 (d, J = 8.0 Hz, 1H, Ar), 7.49 (d, J = 6.8 Hz, 1H, Ar), 7.21 (t, J = 7.2 Hz, 1H, Ar), 7.10 (t, J = 4.4 Hz, 1H, Ar), 6.86 (s, 4H, Ar), 5.39 (s, 1H, acac), 2.31 (s, 6H, CH_3), 2.08 (s, 12H, CH_3), 1.97 (s, 3H, acac), 1.65 (s, 3H, acac); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 185.86, 183.93 (acac), 170.51, 155.74, 146.07, 144.30, 141.05, 140.79, 140.24, 139.30, 130.89, 130.11, 128.48, 123.97, 123.61, 117.56 (Ar), 102.28, 27.46, 27.09 (acac), 23.65, 21.19 (CH_3). FAB-MS (*m/z*): 696 $[M]^+$. Anal. calcd. for $C_{34}H_{36}BPtNO_2$: C, 58.63; H, 5.21; N, 2.01; found: C, 58.27; H, 5.43; N, 2.16.

Synthesis of (3-bromophenyl)dimesitylborane: To a solution of 1-bromo-3-iodobenzene (1.10 g, 3.88 mmol) in dry ether (30 mL) cooled to –78 °C under stirring, 2.5 M *n*-BuLi (1.5 mL, 3.73 mmol) was added with a syringe dropwisely. Before fluorodimesitylborane (1.00g, 3.73 mmol) was added to the reaction mixture in one portion, the reaction mixture was stirred for 30 min at –78 °C. Then the reaction mixture was allowed to warm to room temperature slowly and stirred for 2 h before being quenched by adding water (15 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the combined organic phase was dried over $MgSO_4$. The residue was purified by column chromatography using hexane as eluent to give the product as a white solid (0.85 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.62-7.57 (m, 2H, Ar), 7.42-7.40 (m, 1H, Ar), 7.23 (t, *J* = 7.6 Hz, 1H, Ar), 6.82 (s, 4H, Ar), 2.31 (s, 6H, CH_3), 1.99 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.13, 139.09, 138.24, 134.55, 129.81, 128.30, 127.03, 122.90 (Ar), 23.43, 21.22 (CH_3). FAB-MS (*m/z*): 404, 406 $[M]^+$.

Synthesis of L2: To a stirred solution of (3-bromophenyl)dimesitylborane (1.0 g, 2.5 mmol) and 2-(tributylstannyl)pyridine (1.0 g, 2.7 mmol) in toluene (30 mL) was added $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol). The mixture was heated to 110 °C and stirred under a nitrogen atmosphere for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography using dichloromethane/hexane (v/v, 1:1) as eluent to give **L2** as a yellow jelly product (0.7 g, 69.4%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.67 (d, *J* = 4.8 Hz, 1H, Ar), 8.19 (d, *J* = 7.6 Hz, 1H, Ar), 8.03 (s, 1H, Ar), 7.72 (t, *J* = 8.0 Hz, 1H, Ar), 7.62 (d, *J* = 8.0 Hz, 1H, Ar), 7.56 (d, *J* = 6.0 Hz, 1H, Ar), 7.48 (t, *J* = 7.2 Hz, 1H, Ar), 7.24-7.20 (m, 1H, Ar), 6.83 (s, 4H, Ar), 2.32 (s, 6H, CH_3), 2.02 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.54, 149.39, 146.32, 141.61, 140.87, 138.82, 138.73, 137.04, 136.91, 134.29, 130.78, 128.62, 128.22, 122.04, 121.01(Ar), 23.50, 21.23(CH_3). FAB-MS (*m/z*): 403 $[M]^+$. Anal. calcd. for $C_{29}H_{30}BN$: C, 86.35; H, 7.50; N, 3.47; found: C, 86.20; H, 7.83; N, 3.27.

Synthesis of PtB-2: Under a N_2 atmosphere, **L2** (0.40 g, 1.00 mmol) and K_2PtCl_4 (0.37 g, 0.89 mmol) were added to a mixture of 2-ethoxyethanol and water (3:1, v/v) (30 mL). The reaction mixture was heated to 110 °C for 20 h under stirring. After the mixture was cooled to room temperature, saturated NaCl solution (35 mL) was added to the reaction mixture. The precipitate formed was collected by filtration and dried under vacuum to give a yellow solid (0.48 g). Thallium acetylacetonate (0.24 g, 0.79 mmol) together with the yellow solid were added to CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 18 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography eluting with hexane/CH_2Cl_2 (1:1, v/v). The product was obtained as a light greenish yellow solid (84 mg, 13.5 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.00 (dd, *J* = 6.0, 0.8 Hz, 1H, Ar), 7.75-7.66 (m, 2H, Ar), 7.57 (d, *J* = 0.8 Hz, 1H, Ar), 7.51 (d, *J* = 8.0 Hz, 1H, Ar), 7.33 (dd, *J* = 1.2, 7.6 Hz, 1H, Ar), 7.10 (t, *J* = 5.2 Hz, 1H, Ar), 6.82 (s, 4H, Ar), 5.48 (s, 1H, acac), 2.32 (s, 6H, CH_3), 2.05 (s, 12H, CH_3), 2.02 (s, 3H, acac), 2.00 (s, 3H, acac); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 185.97, 184.34 (acac), 168.10, 147.27, 147.22, 144.72, 141.95, 140.84, 138.35, 138.15, 138.10, 131.18, 130.32, 128.06, 121.20, 118.71 (Ar), 102.48, 28.25, 27.07(acac), 23.51, 21.22 (CH_3). FAB-MS (*m/z*): 696 $[M]^+$. Anal. calcd. for $C_{34}H_{36}BPtNO_2$: C, 58.63; H, 5.21; N, 2.01; found: C, 58.39; H, 5.40; N, 2.10.

Computational details: Density Functional Theory (DFT) calculations were performed using DMol^3 module (DMol^3 is available as part of Materials Studio) embedded in Material Studio program (Accelrys Software Inc.).[S4] Geometry optimizations were conducted with BLYP functional and DNP basis set under effective core potential. The solvent effects in THF (ε = 7.58) were considered as well. The frontier orbital (HOMO and LUMO) diagrams were illustrated based on the fully optimized structures.

References:

S1. K. A. King, P. J. Spellane and R.-J. Watts, *J. Am. Chem. Soc.*, 1985, **107**, 1431.

S2. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

S3. C. B. Murphy, Y. Zhang, T. Troxler, V. Ferry, J. J. Martin, W. E. Jr Jones, *J. Phys. Chem. B*, 2004, **108**, 1537.

S4. (a) B. Delley, *J. Chem. Phys.*, 1990, **92**, 508; (b) B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756.

Table S1 Photophysical and thermal data for the two Pt^{II} complexes.

	Absorption (298 K) [a]	Emission (298 K)	Φ_p [b]	τ_p [c]	τ_r [d]	$\Delta T_{5\%}/T_g$
	λ_{abs}/nm	λ_{em}/nm		μs	μs	°C
PtB-1	282 (4.47), 304 (4.53), 332 (4.57), 436 (3.99)	502, 535	0.45	1.49	1.59	262/125
PtB-2	270 (4.28), 322 (4.31), 344 (4.18), 402 (3.17)	482, 514	0.54	1.91	3.54	307/116

[a] Measured in THF at a concentration of 10 $^{-5}$ M, and log ε values are shown in parentheses. [b] In CH_2Cl_2 solution relative to *fac*-[Ir(ppy)$_3$] (Φ_p = 0.40), λ_{ex} = 360 nm. [c] Measured in degassed THF solutions at a concentration of ca. 10^{-5} M with a 370 nm excitation source. [d] The triplet radiative lifetimes (τ_r) were deduced from $\tau_r = \tau_P/\Phi_P$.

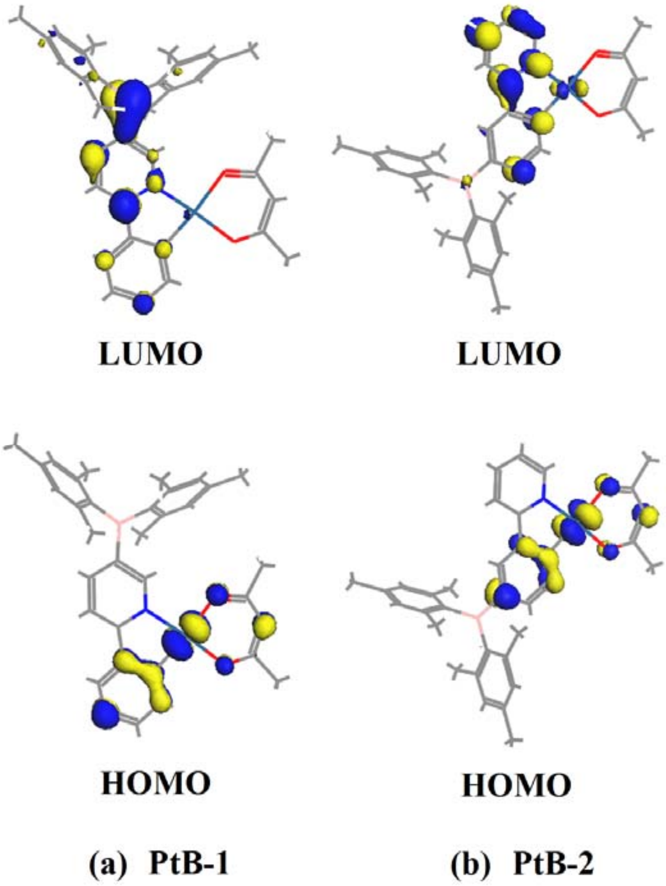


Fig. S1 The LUMO (top) and HOMO (bottom) patterns for **PtB-1** and **PtB-2**.

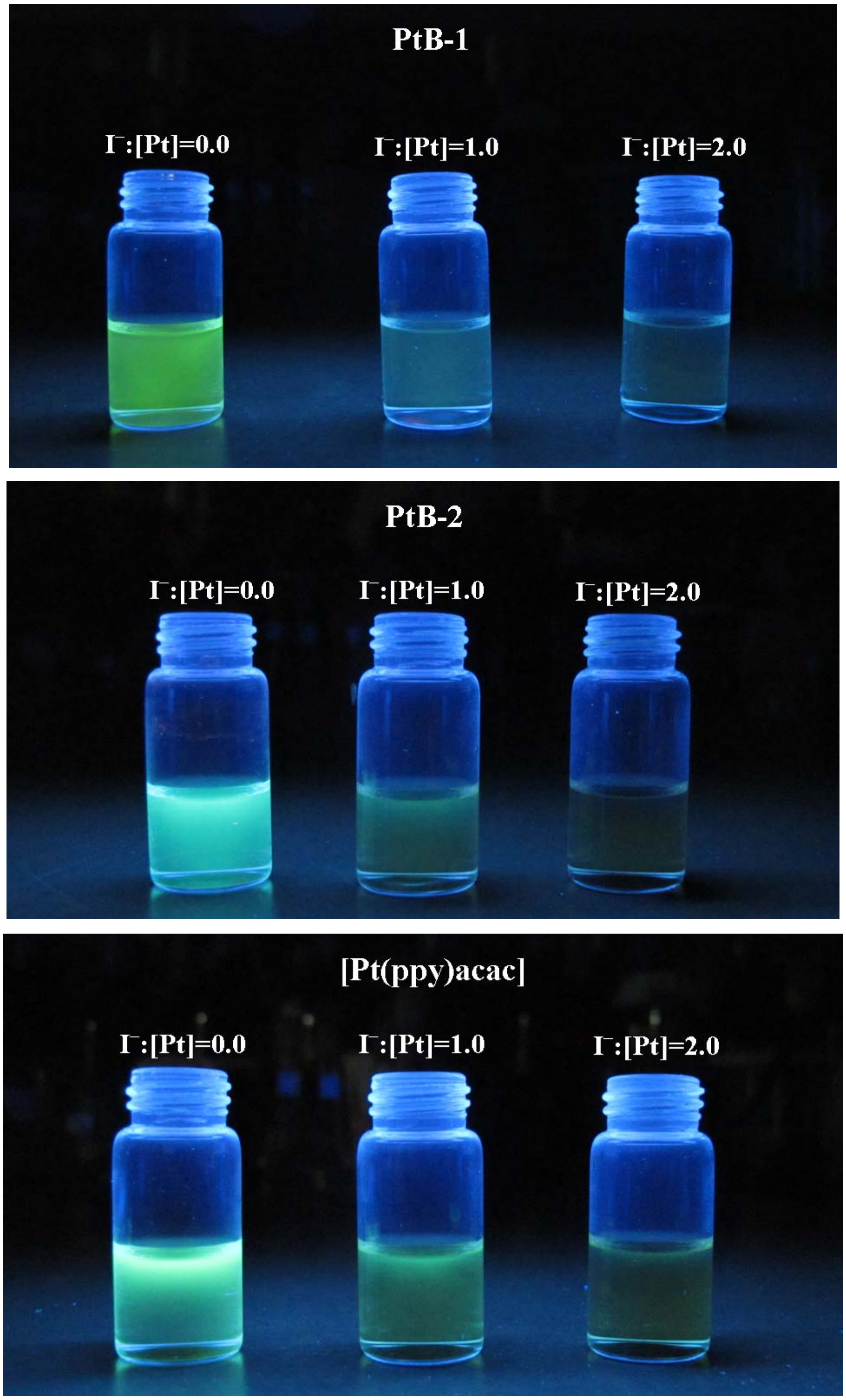


Fig. S2 The phosphorescence quenching of **PtB-1**, **PtB-2** and **[Pt(ppy)acac]** by adding I^- ions.

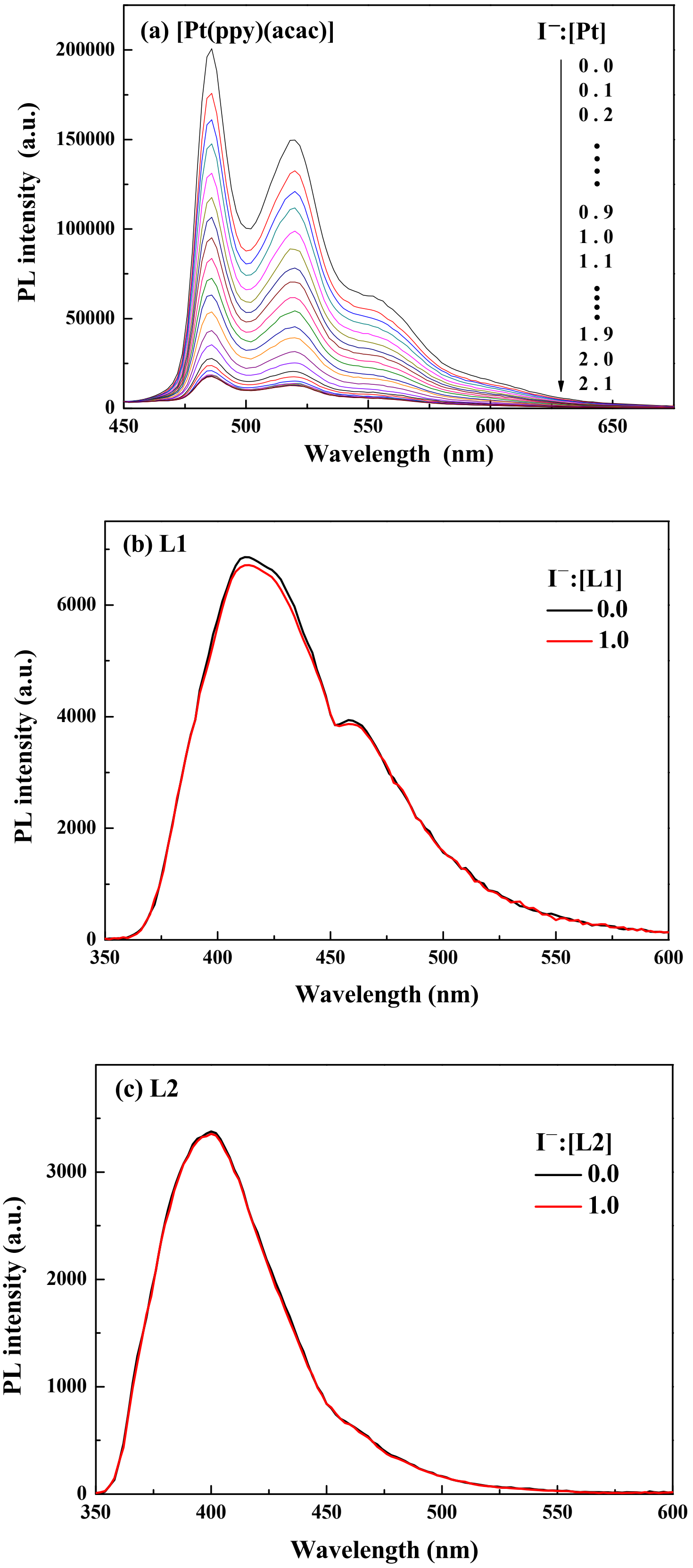


Fig. S3 The PL response for (a) **[Pt(ppy)acac]**, (b) **L1** and (c) **L2** to the external I⁻ ions.

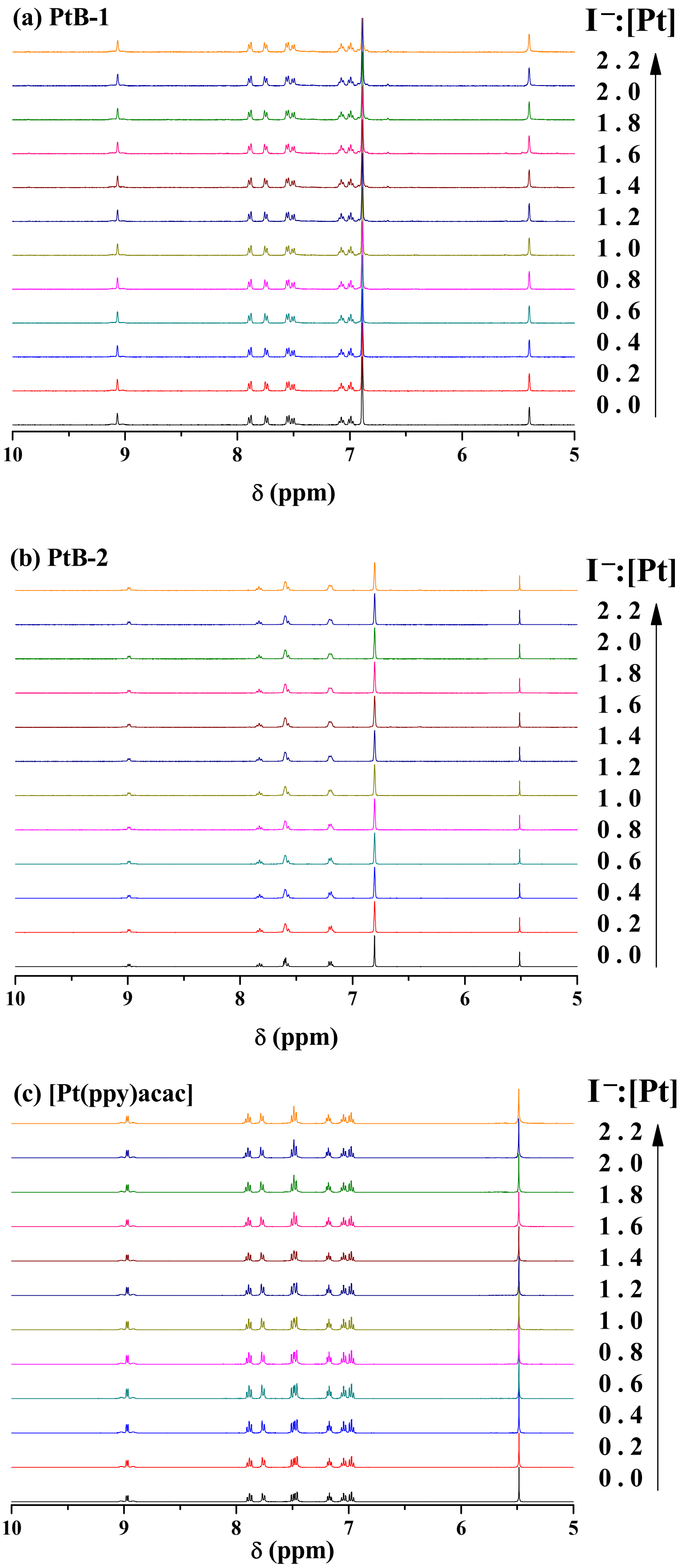
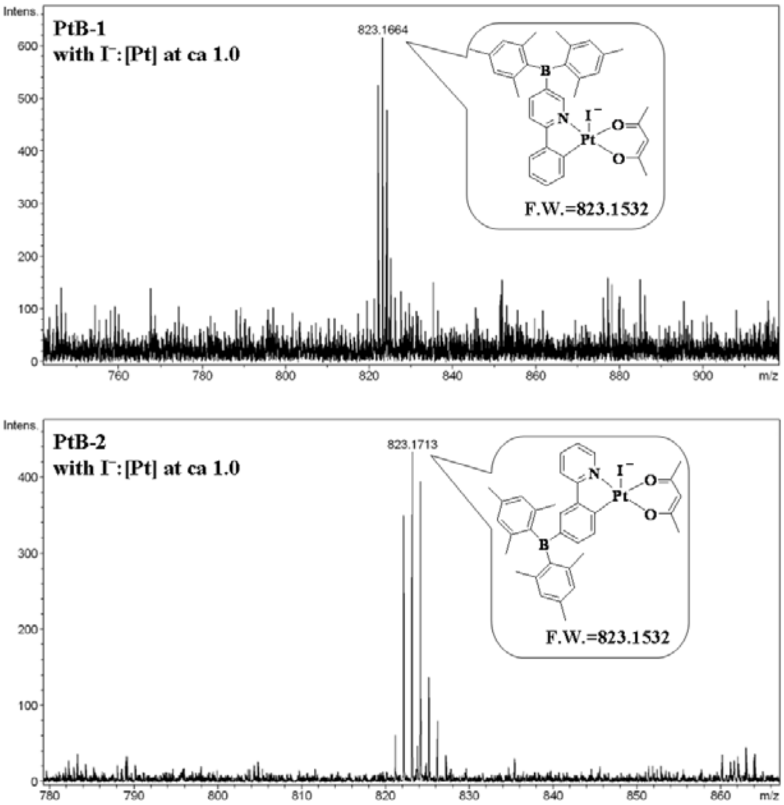
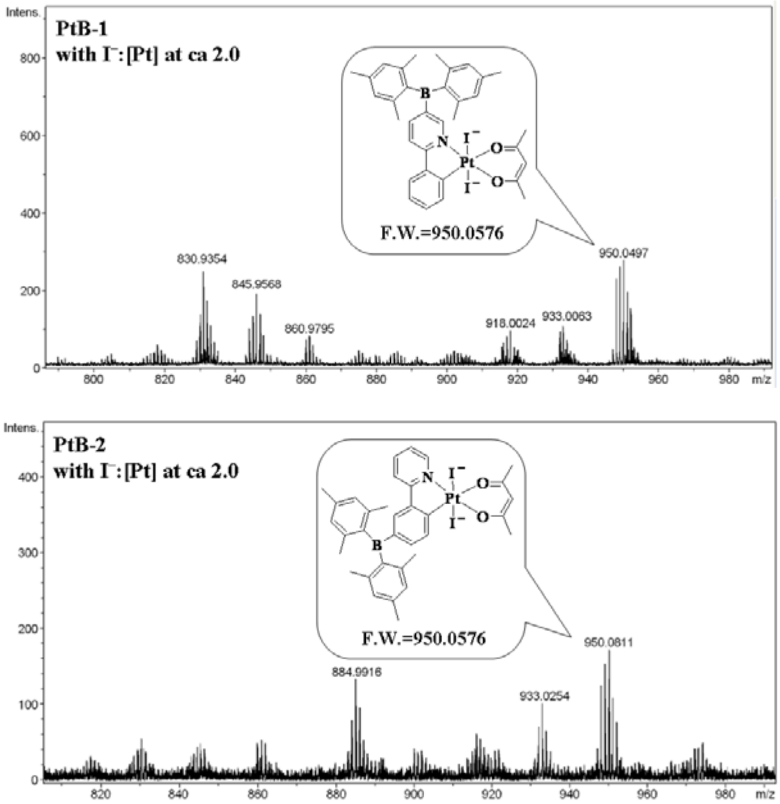


Fig. S4 The ^{1}H-NMR I⁻ ion titration results for (a) **PtB-1**, (b) **PtB-2** and (c) **[Pt(ppy)acac]**.



(a)



(b)

Fig. S5 The ESI-TOF mass spectra for the solutions of **PtB-1** and **PtB-2** with the I⁻:[Pt] ratio at (a) ca 1.0 and (b) 2.0.

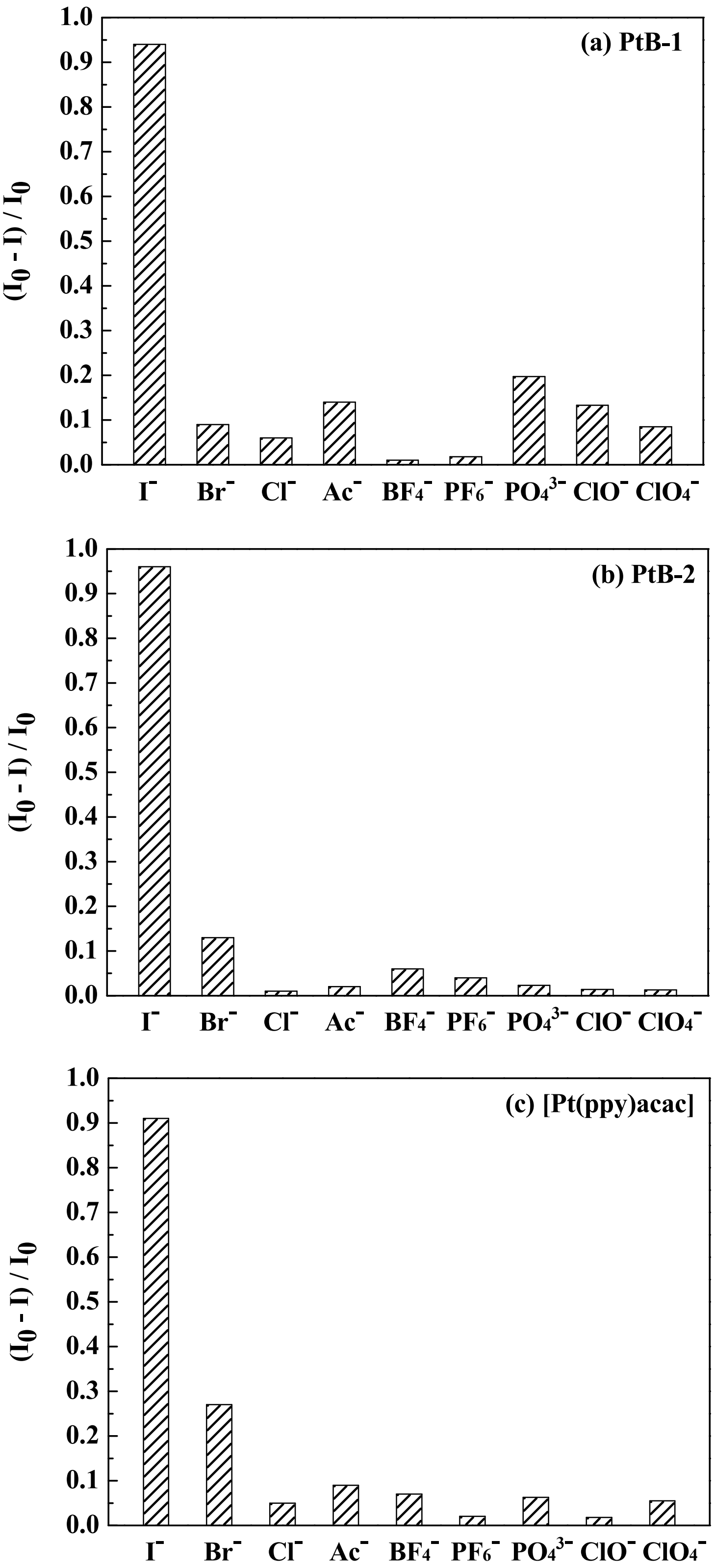


Fig. S6 The relative emission intensity variation at 502 nm for the **PtB-1** solution, 482 nm for the **PtB-2** solution and 486 nm for **[Pt(ppy)acac]** before and after adding different anions with the [anion]:[Pt] value of 2.1:1.

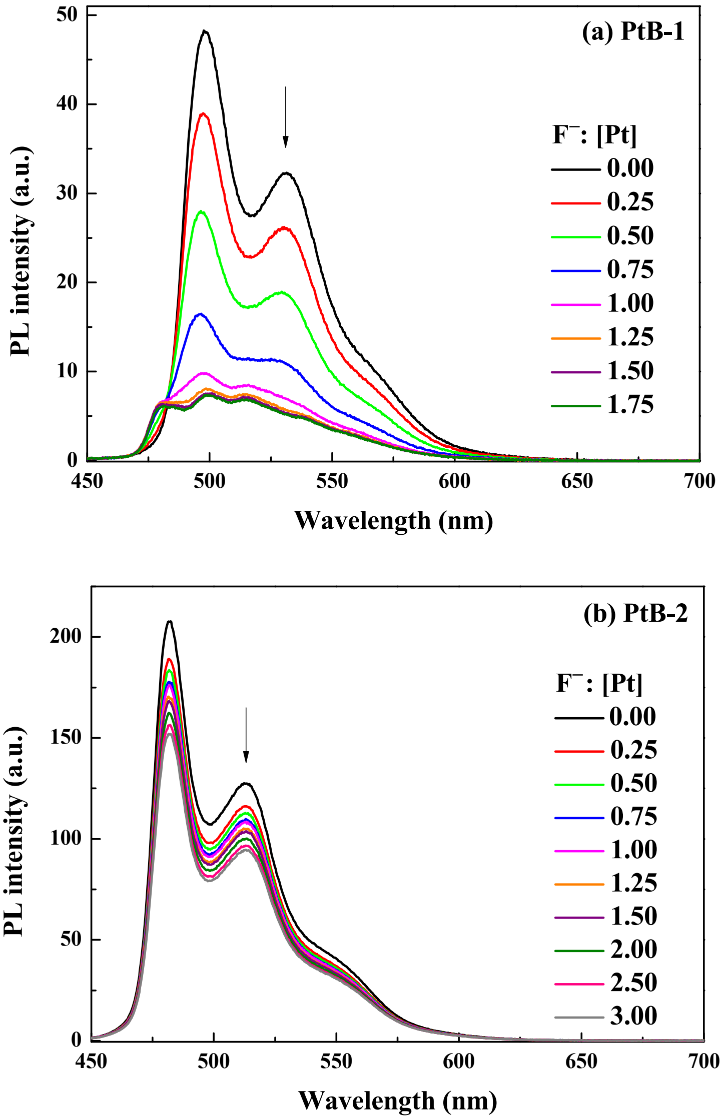


Fig. S7 The phosphorescence response of the (a) **PtB-1** and (b) **PtB-2** solutions to the added F⁻ ions.

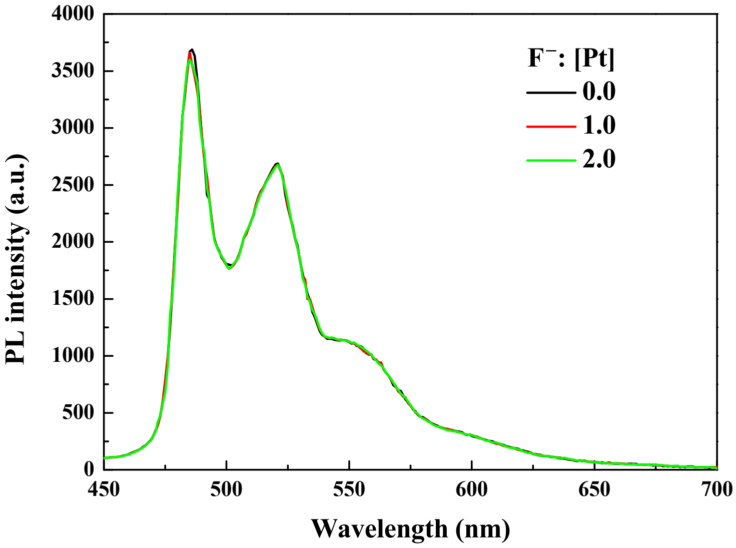
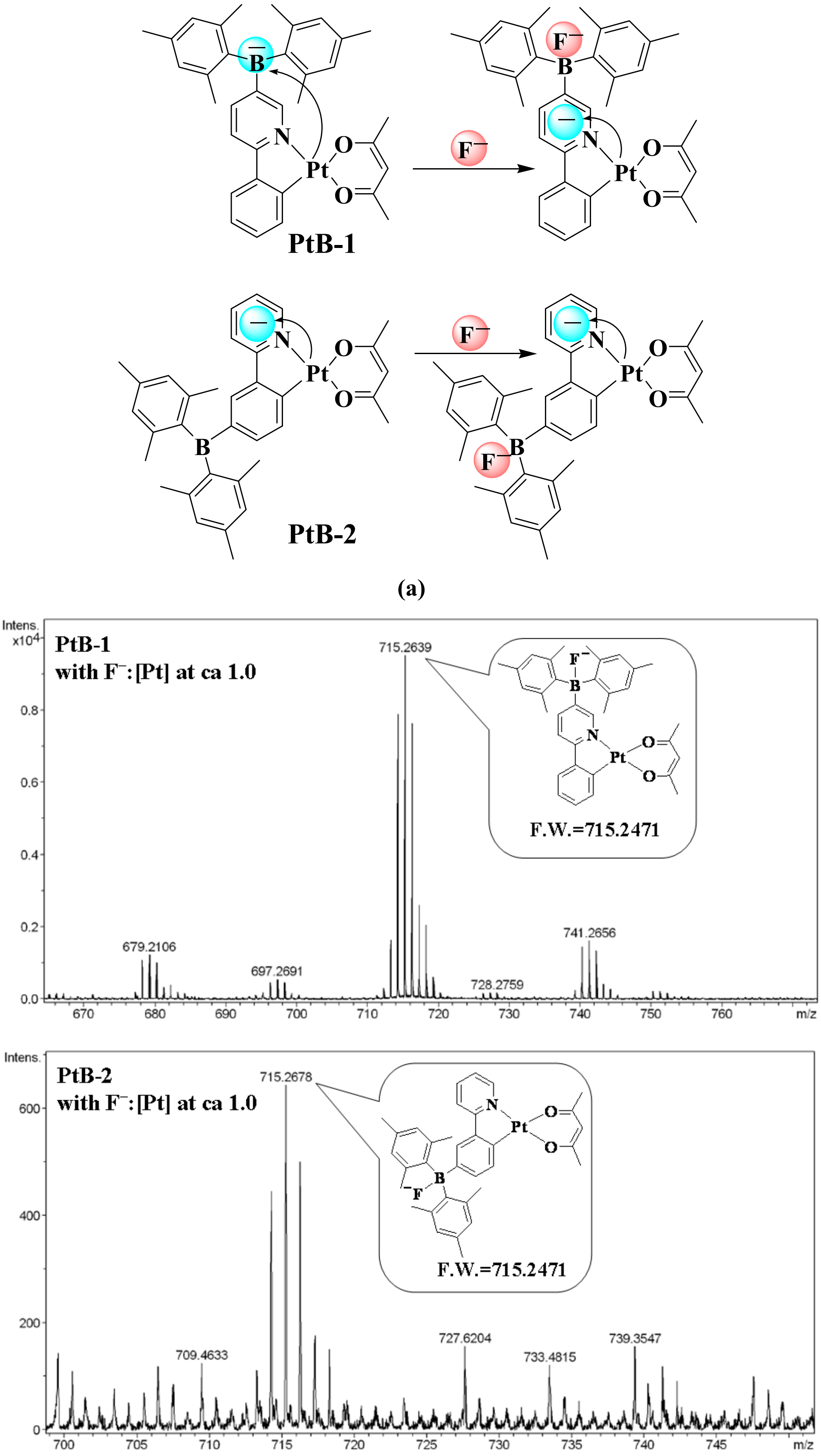


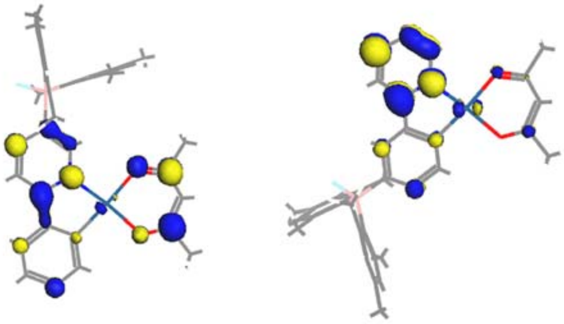
Fig. S8 The PL spectra for **[Pt(ppy)acac]** in THF solution before and after adding F^- ions.



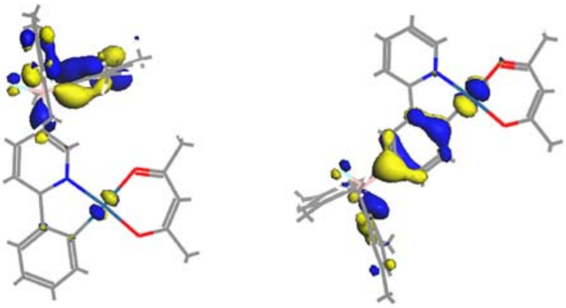
(a)

(b)

Fig. S9 The proposed binding mechanism between (a) the Pt^{II} complexes and F^- ion and (b) the corresponding ESI-TOF mass spectra.



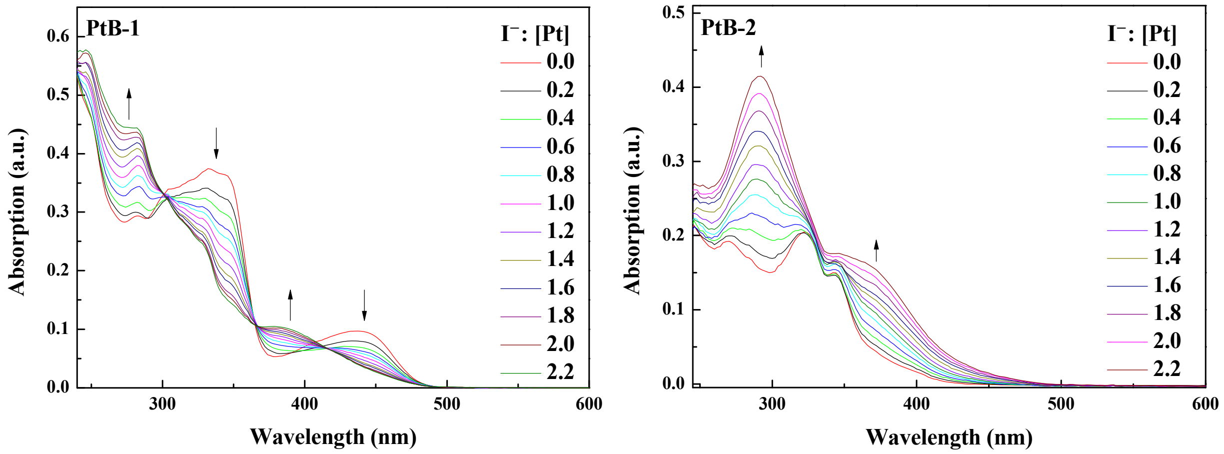
LUMO LUMO



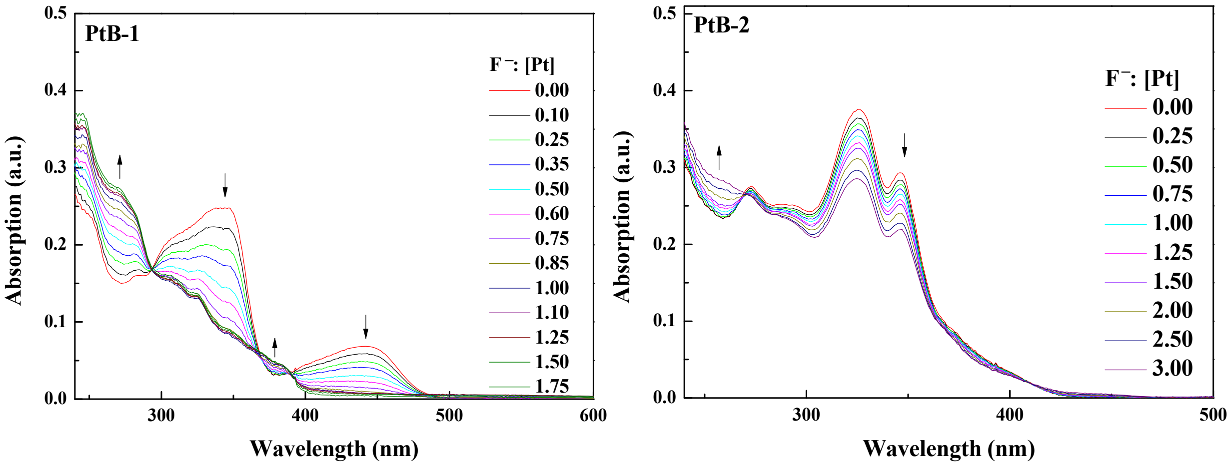
HOMO HOMO

(a) [PtB-1·F$^-$] (b) [PtB-2·F$^-$]

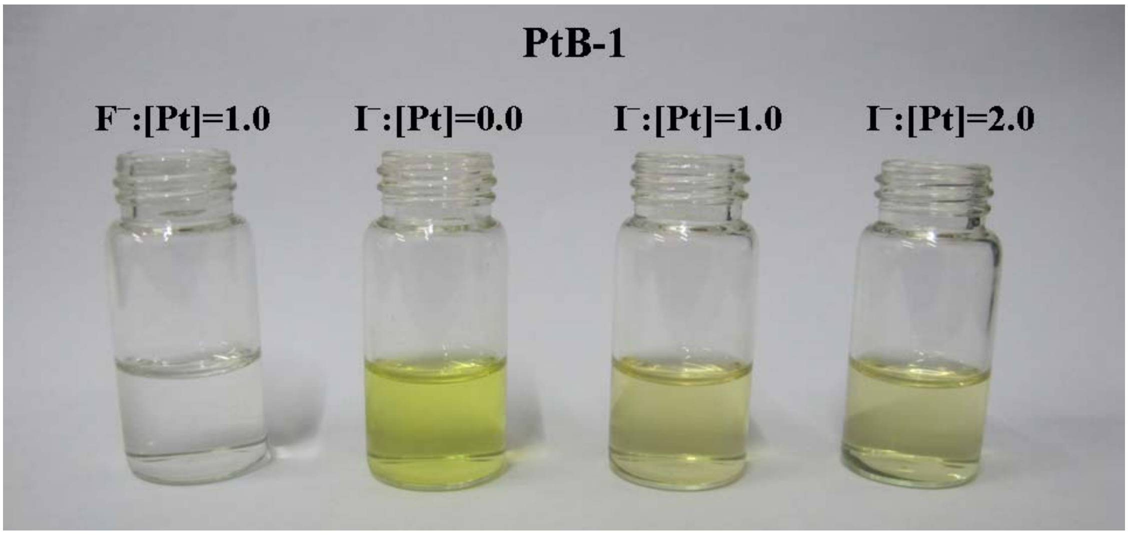
Fig. S10 The LUMO (top) and HOMO (bottom) patterns for adducts **PtB-1** and **PtB-2** with F$^-$ ion (a) **[PtB-1·F$^-$]**, (b) **[PtB-2·F$^-$]**.

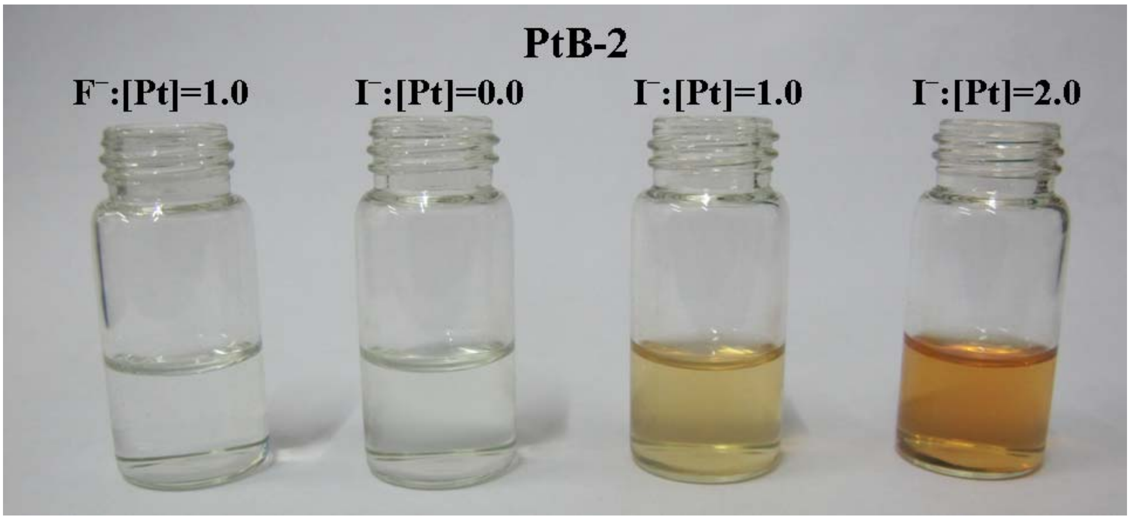

PtB-1
I^-: [Pt]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Absorption (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
300
400
500
600
Wavelength (nm)
PtB-2
I^-: [Pt]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Absorption (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
300
400
500
600
Wavelength (nm)

(a)


PtB-1
F^-: [Pt]
0.00
0.10
0.25
0.35
0.50
0.60
0.75
0.85
1.00
1.10
1.25
1.50
1.75
Absorption (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
300
400
500
600
Wavelength (nm)
PtB-2
F^-: [Pt]
0.00
0.25
0.50
0.75
1.00
1.25
1.50
2.00
2.50
3.00
Absorption (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
300
400
500
Wavelength (nm)

(b)


PtB-1
F^-:[Pt]=1.0
I^-:[Pt]=0.0
I^-:[Pt]=1.0
I^-:[Pt]=2.0



(c)

Fig. S11 The absorption responses of the **PtB-1** and **PtB-2** solutions to the added (a) I⁻ and (b) F⁻ ions and (c) the associated color variation.

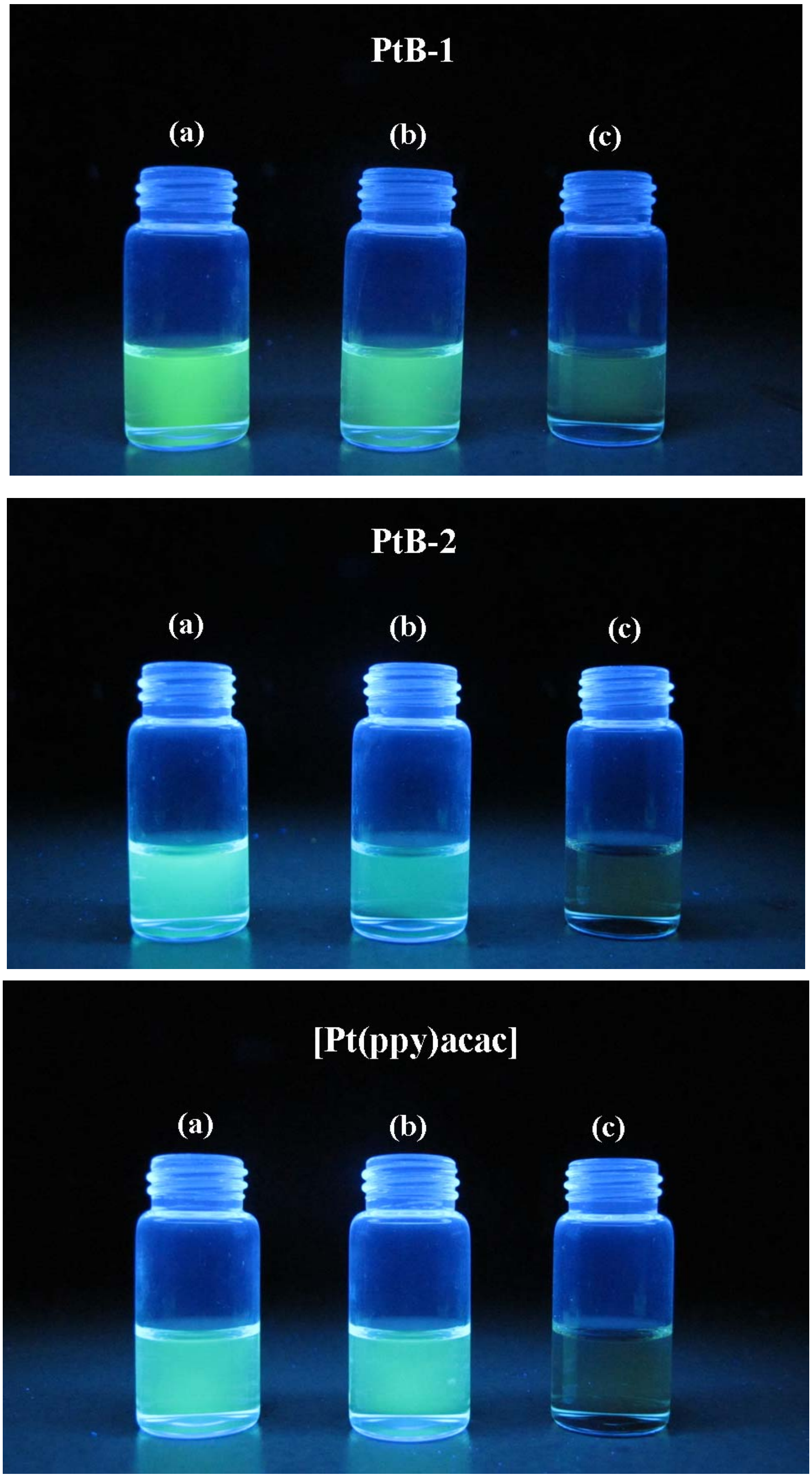


Fig. S12 The phosphorescent variation before and after adding one equivalent different ions to the solution of **PtB-1**, **PtB-2** and **[Pt(ppy)acac]**. (a) Before adding ions. (b) After adding ions of Cl^-, Br^-, Ac^-, BF_4^-, PF_6^-, PO_4^{3-}, ClO^- and ClO_4^-. (c) After adding ions of I^-, Cl^-, Br^-, Ac^-, BF_4^-, PF_6^-, PO_4^{3-}, ClO^- and ClO_4^-.