

Highly efficient single emitter white phosphorescent organic light-emitting diodes based on Pt (II) complexes

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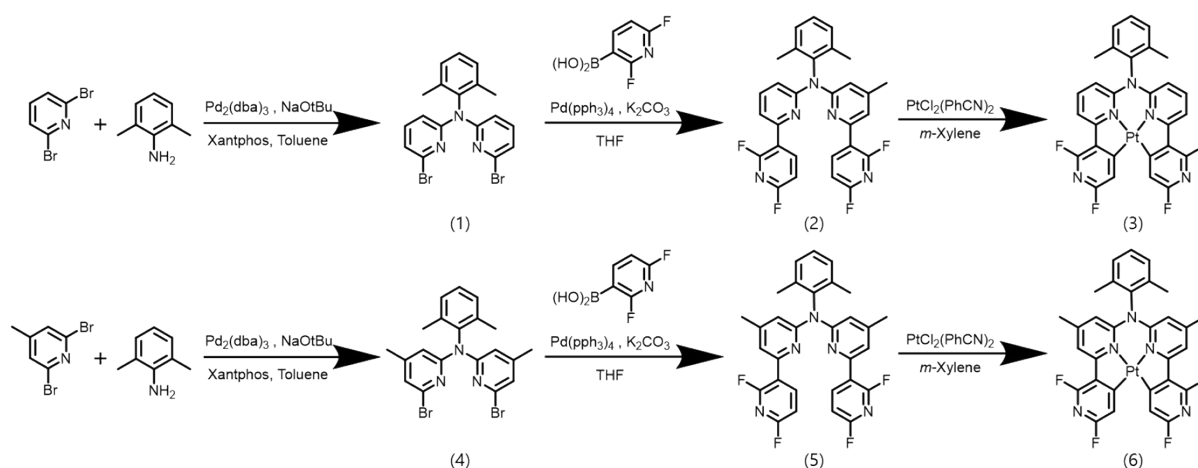
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Scheme 1. Synthetic Route of XA-H-Pt (3) / XA-CH₃-Pt (6)

Synthetic Materials: All reactions were performed in a N₂ atmosphere. All solvents and reagents were purchased from Aldrich, Alfa Aesar, and TCI. All commercial materials were used without further purification. The (2,6-difluoropyridin-3-yl)boronic acid and PtCl₂(PhCN)₂ were obtained from provided from Furuya Metal.

Measurement: ¹H NMR data were recorded using a Bruker DRX 300 MHz spectrometer and ¹³C NMR data were measured on a Bruker DRX 500 MHz spectrometer. High resolution mass (HRMS) analysis was measured using a Jeol JMS-700. UV-visible absorption spectra were obtained in methylene chloride on a PerkinElmer LAMBDA-900 UV-vis-IR spectrophotometer. The photoluminescence spectra were obtained in methylene chloride on a LS-50B luminescence spectrophotometer. The thermal analysis measurements were performed using a TA 2050 TGA thermogravimetric analyzer under a nitrogen atmosphere. The samples were heated at 10 °C/min. Differential scanning calorimetry was conducted under nitrogen using a TA Instruments 2100 DSC. The samples were heated at 10 °C/min from 0 °C to 300 °C. Absorption spectra were measured using a PerkinElmer LAMBDA-900 UV/vis/IR spectrophotometer. Photoluminescence spectra were measured using a LS-50B luminescence spectrophotometer. Cyclic voltammograms of materials were measured on an epsilon E3 at a room temperature in a 0.10 M solution of tetrabutylammonium perchlorate (Bu₄NClO₄) in CH₂Cl₂ at a scanning rate of 50 mV/s. A Pt wire was used as the counter electrode and an Ag/Ag⁺ electrode as the reference electrode.

Synthesis of 6-bromo-N-(6-bromopyridin-2-yl)-N-(2,6-dimethylphenyl)pyridin-2-amine, (1):

To a three-neck round bottom flask were added 2,6-dibromopyridine (6.45 g, 27.23 mmol), 2,6-dimethylaniline (1.5 g, 12.37 mmol), sodium tert-butoxide (3.56 g, 37.11 mmol), xantphos (0.71 g, 1.23 mmol), and toluene (85 mL). The flask was backfilled with nitrogen for three times and Pd₂(dba)₃ (0.55 g, 0.61 mmol) was added. The reaction mixture was stirred at 100 °C under nitrogen atmosphere for 6 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water and dried over MgSO₄. After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (ethyl acetate:hexane=1:20) to afford the desired product as white solid (2.46 g, 46%). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 7.48-7.42 (t, 2 H), 7.33-7.28 (m, 1 H), 7.25-7.22 (m, 2 H), 7.13-7.10 (d, *J* = 7.56 Hz, 2 H), 7.01-6.98 (d, *J* = 8.21 Hz, 2 H), 2.07 (s, 6 H). ¹³C NMR (300 MHz, CD₂Cl₂): δ (ppm) = 155.3, 139.9, 139.6, 139.3, 137.6, 129.0, 128.2, 121.1, 112.7, 17.9; HRMS (EI⁺, *m/z*): calcd for C₁₈H₁₅Br₂N₃ 430.9633, found 430.9634.

Synthesis of N-(2',6'-difluoro-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-[2,3'-bipyridin]-6-amine, (2):

To a three-neck round bottom flask were added compound (1) (2.4 g, 5.54 mmol), (2,6-difluoropyridin-3-yl)boronic acid (3.52 g, 22.16 mmol), potassium carbonate (2.29 g, 16.62 mmol), THF (48 mL), and water (16 mL). The flask was backfilled with nitrogen for three times and Pd(PPh₃)₄ (0.63 g, 0.55 mmol) was added. The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 12 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with methylene chloride. The organic layer was washed with water and dried over MgSO₄. After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (ethyl acetate:hexane=1:20) to afford the desired product as white solid (2.15 g, 76%). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) = 8.42-8.33 (m, 2 H), 7.76-7.70 (t, 2 H), 7.55-7.52 (dd, *J* = 7.59 Hz, 2 H), 7.35-7.23 (m, 3 H), 7.18-7.15 (d, *J* = 8.30 Hz, 2 H), 6.91-6.87 (m, 2 H), 2.13 (s, 6 H). ¹³C NMR (300 MHz, CD₂Cl₂): δ (ppm) = 155.5, 148.2, 148.1, 145.7, 145.7, 145.6, 145.6, 140.8, 138.3, 137.8, 128.8, 127.8, 117.1, 116.9, 113.8, 106.9, 106.8, 106.5, 106.4, 18.0; HRMS (EI⁺, *m/z*): calcd for C₂₈H₁₉F₄N₅ 501.1577, found 501.1576

Synthesis of XA-H-Pt (3):

To a three-neck round bottom flask were added compound (2) (2 g, 3.98 mmol), $\text{PtCl}_2(\text{PhCN})_2$ (2.26 g, 4.75 mmol), *m*-xylene (36 mL). The flask was backfilled with nitrogen for three times. the reaction mixture was stirred at 160°C under nitrogen atmosphere for 24 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with methylene chloride. The organic layer was washed with water and dried over MgSO_4 . After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (methylene chloride 100%) to afford the desired product as yellow solid (1.13 g, 41%). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.14-8.11 (d, $J = 8.17$ Hz, 2 H), 7.99-7.94 (t, 2 H), 7.77-7.53 (m, 3 H), 7.48-7.45 (d, $J = 7.56$ Hz, 2 H), 6.70-6.64 (m, 2 H), 2.02 (s, 6 H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) = 150.8, 148.3, 139.9, 136.9, 136.7, 130.7, 130.4, 129.5, 123.4, 122.2, 121.7, 113.0, 112.9; HRMS (FAB+, m/z): calcd for $\text{C}_{28}\text{H}_{17}\text{F}_4\text{N}_3\text{Pt}$ 694.1068, found 695.1139

Synthesis of 6-bromo-N-(6-bromo-4-methylpyridin-2-yl)-N-(2,6-dimethylphenyl)-4-methylpyridin-2-amine, (4):

To a three-neck round bottom flask were added 2,6-dibromo-4-methylpyridine (9.11 g, 36.31 mmol), 2,6-dimethylaniline (2.00 g, 16.50 mmol), sodium tert-butoxide (4.75 g, 49.51 mmol), Xantphos (0.95 g, 1.65 mmol) and Toluene(110 mL). The flask was backfilled with nitrogen for three times and $\text{Pd}_2(\text{dba})_3$ (0.75 g, 0.82 mmol) was added. the reaction mixture was stirred at 100°C under nitrogen atmosphere for 6 hours. After cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water and dried over MgSO_4 . After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (ethyl acetate:hexane=1:20) to afford the desired product as white solid (2.8 g, 37%). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 7.52-7.16 (m, 3 H), 6.91 (s, 2 H), 6.73 (s, 2 H), 2.23 (s, 6 H), 2.05 (s, 6 H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) = 155.4, 151.4, 140.1, 139.3, 137.6, 128.9, 128.0, 122.0, 113.4, 20.6, 18.0; HRMS (EI+, m/z): calcd for $\text{C}_{20}\text{H}_{19}\text{Br}_2\text{N}_3$ 458.9946, found 458.9940

Synthesis of N-(2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-amine, (5):

To a three-neck round bottom flask were added compound (4) (2.7 g, 5.85 mmol), (2,6-difluoropyridin-3-yl)boronic acid (3.72 g, 23.41 mmol), potassium carbonate (2.42 g, 17.55 mmol), THF (54 mL) and Water (18 mL). The flask was backfilled with nitrogen for three times and $\text{Pd}(\text{PPh}_3)_4$ (0.67 g, 0.58 mmol) was added. the reaction mixture was stirred at 80°C under nitrogen atmosphere for 12 h. After cooling to room temperature, the reaction mixture

was diluted with water and extracted with methylene chloride. The organic layer was washed with water and dried over MgSO_4 . After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (ethyl acetate:hexane=1:20) to afford the desired product as white solid (2.48 g, 80%). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.41-8.32 (m, 2 H), 7.37 (s, 2 H), 7.31-7.21 (m, 3 H), 6.98 (s, 2 H), 6.89-6.85 (m, 2 H), 2.38 (s, 6 H), 2.12 (s, 6 H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) = 155.8, 149.5, 147.9, 147.8, 145.8, 145.7, 145.7, 145.6, 141.0, 137.8, 128.7, 127.6, 118.4, 118.2, 114.2, 106.8, 106.7, 106.3, 106.3, 21.2, 18.1; HRMS (EI+, m/z): calcd for $\text{C}_{30}\text{H}_{23}\text{F}_4\text{N}_5$ 529.1890, found 529.1894.

Synthesis of XA-CH₃-Pt (6):

To a three-neck round bottom flask were added compound (5) (2.4 g, 4.53 mmol), $\text{PtCl}_2(\text{PhCN})_2$ (2.56 g, 5.43 mmol), m-xylene (36 mL). The flask was backfilled with nitrogen for three times. the reaction mixture was stirred at 160 °C under nitrogen atmosphere for 24 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with methylene chloride. The organic layer was washed with water and dried over MgSO_4 . After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (methylene chloride 100%) to afford the desired product as yellow solid (1.21 g, 38%). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.93 (s, 2 H), 7.74-7.44 (m, 5 H), 6.40 (s, 2 H), 2.35 (s, 6 H), 2.02 (s, 6 H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ (ppm) = 152.1, 147.4, 139.9, 136.9, 130.6, 130.2, 118.1, 117.8, 113.6, 113.1, 112.9, 112.8, 111.2, 110.9, 110.8, 110.4, 22.3, 17.2; HRMS (FAB+, m/z): calcd for $\text{C}_{30}\text{H}_{21}\text{F}_4\text{N}_5\text{Pt}$ 722.1381, found 723.1438

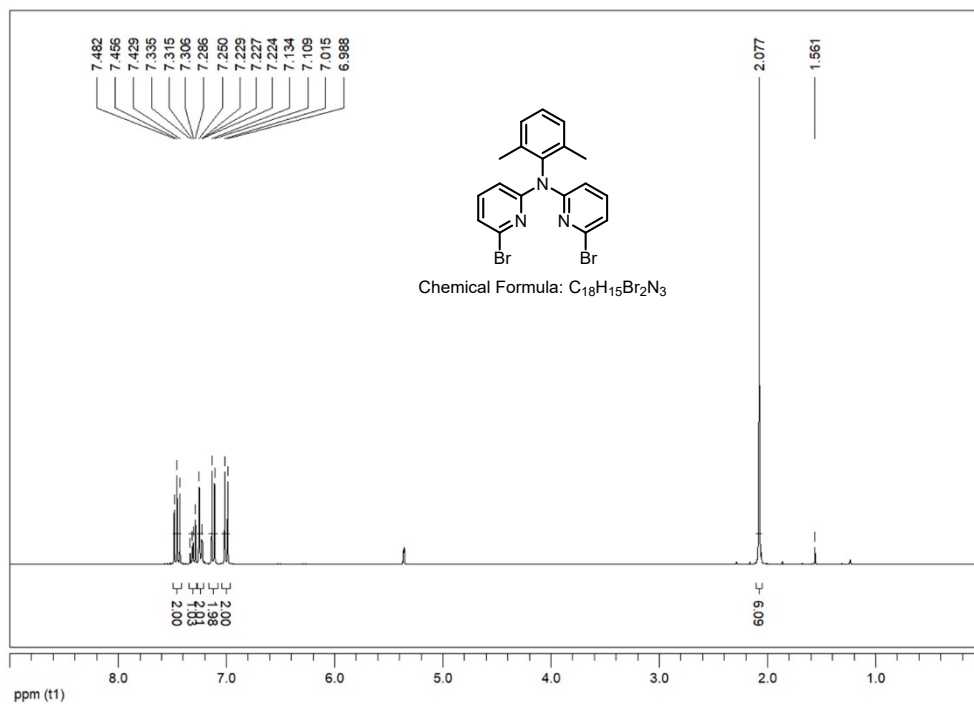


Figure S1. 1H NMR data of 6-bromo-N-(6-bromopyridin-2-yl)-N-(2,6-dimethylphenyl)pyridin-2-amine (1)

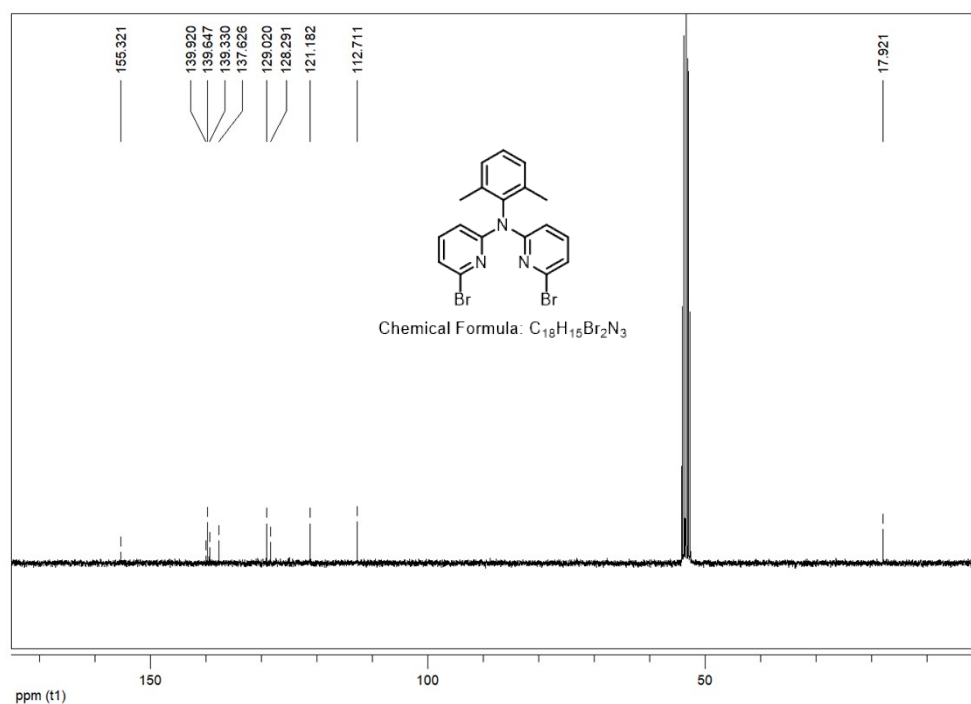


Figure S2. ^{13}C NMR data of 6-bromo-N-(6-bromopyridin-2-yl)-N-(2,6-dimethylphenyl)pyridin-2-amine (1)

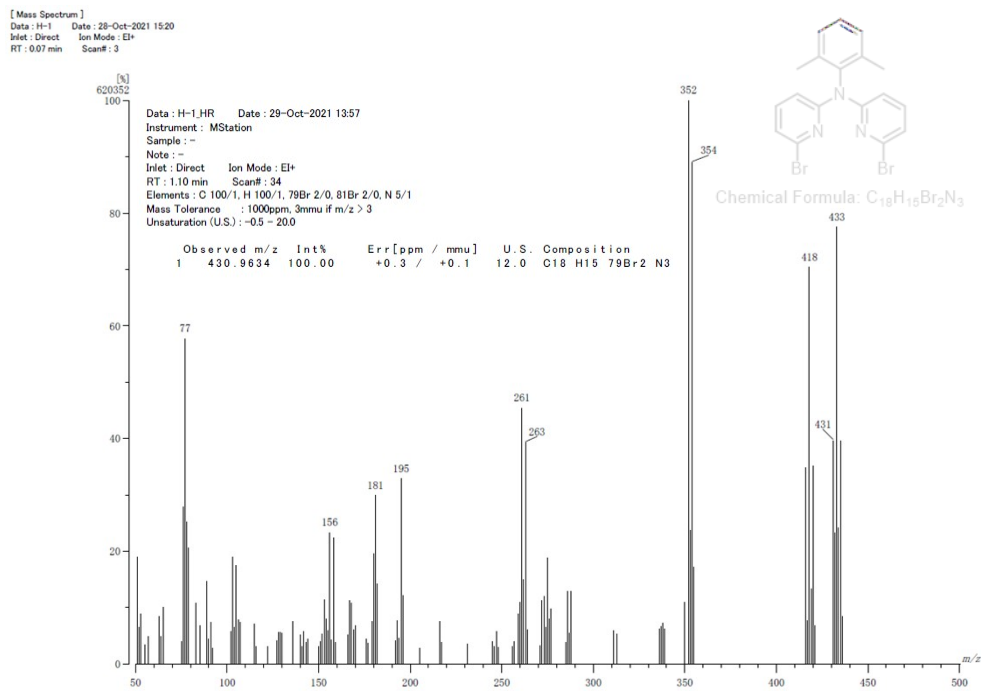


Figure S3. EI Mass data of 6-bromo-N-(6-bromopyridin-2-yl)-N-(2,6-dimethylphenyl)pyridin-2-amine (1)

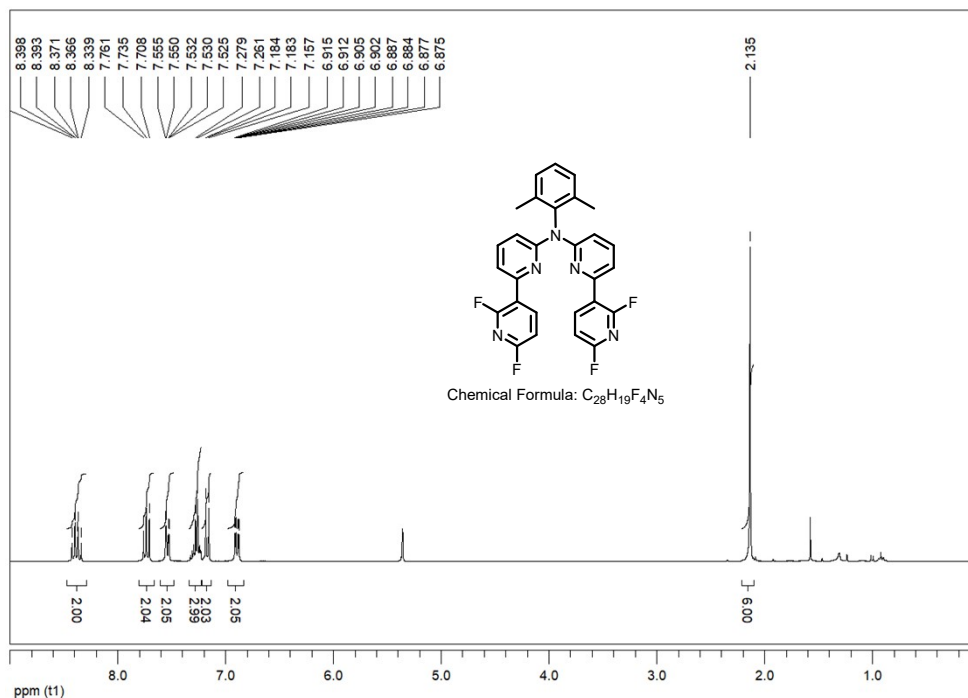


Figure S4. ¹H NMR data of N-(2',6'-difluoro-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-[2,3'-bipyridin]-6-amine (2)

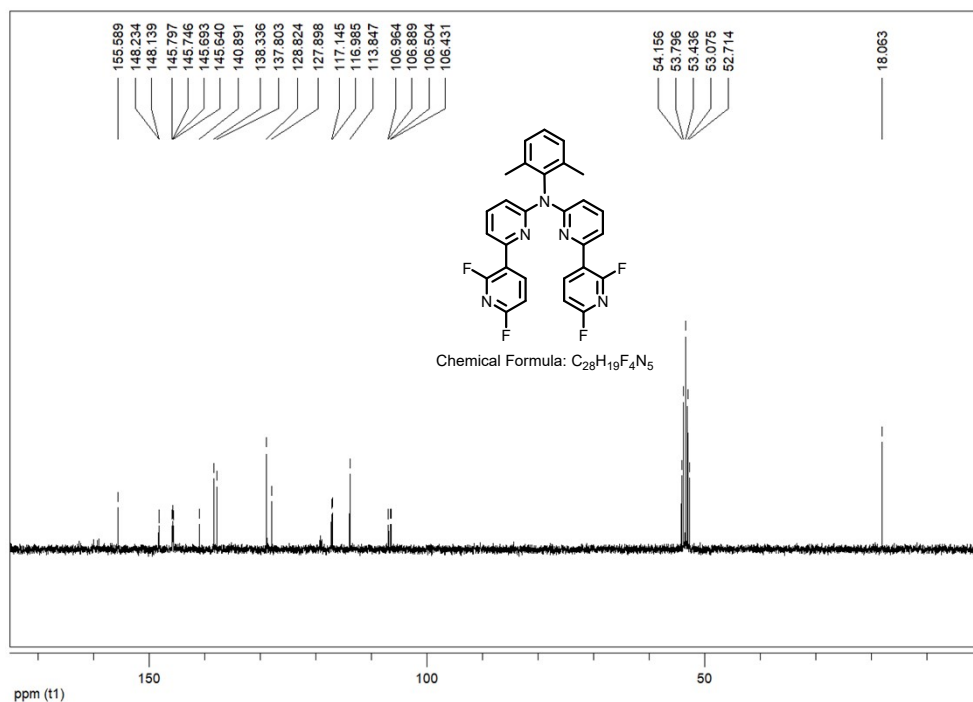


Figure S5. ^{13}C NMR data of N-(2',6'-difluoro-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-[2,3'-bipyridin]-6-amine (2)

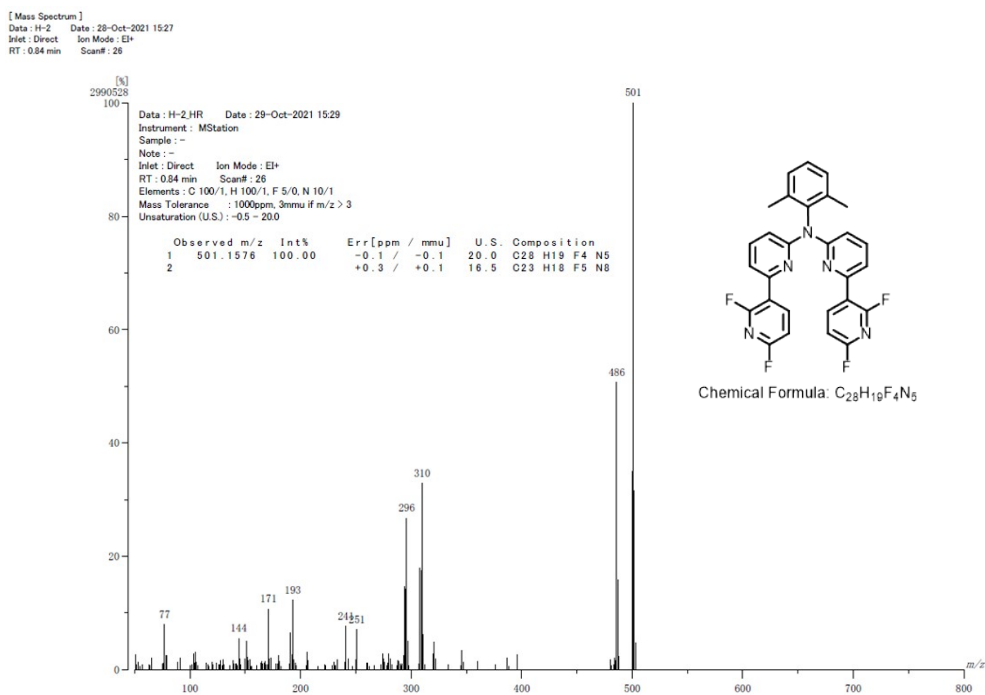


Figure S6. EI Mass data of N-(2',6'-difluoro-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-[2,3'-bipyridin]-6-amine (2)

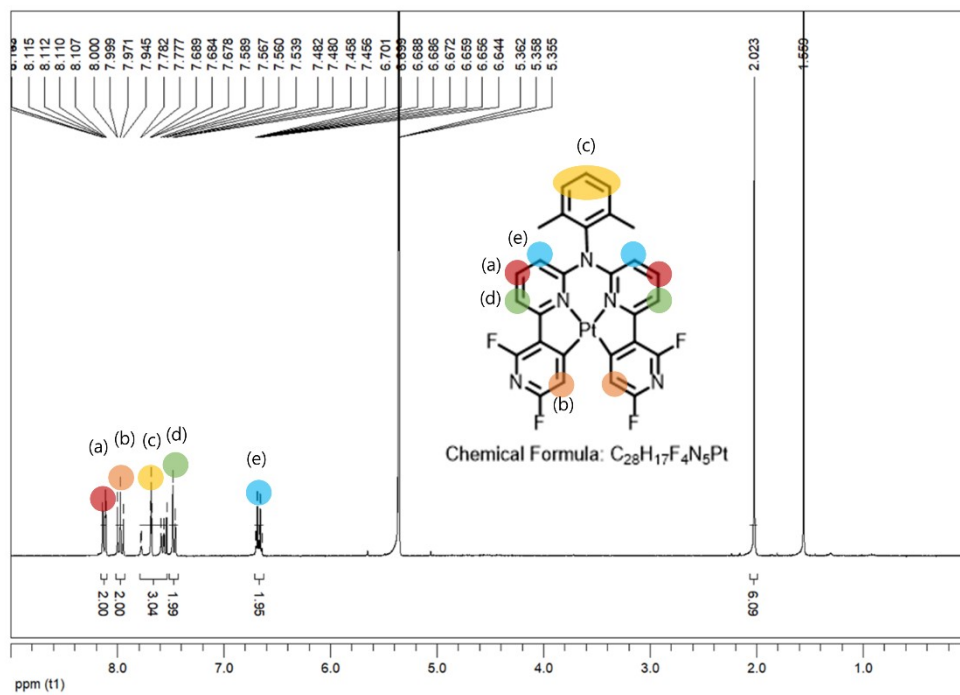


Figure S7. ^1H NMR data of XA-H-Pt (3)

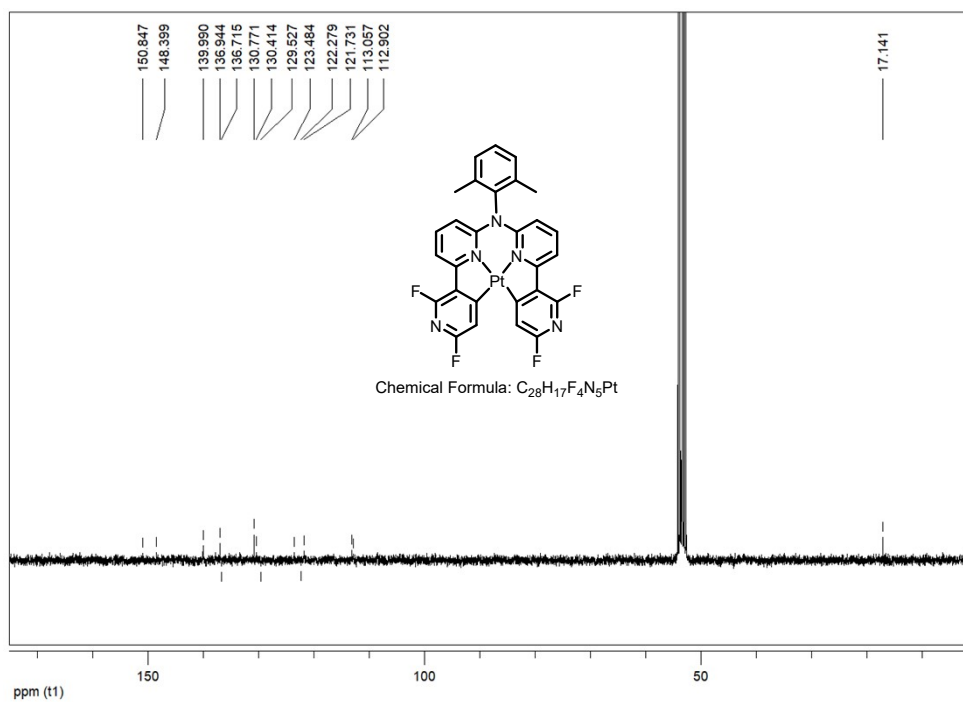


Figure S8. ^{13}C NMR data of XA-H-Pt (3)

[Mass Spectrum]
 Data: Meth-H-Pt Date: 26-Apr-2022 13:37
 Inlet: Direct Ion Mode: FAB+
 RT: 0.14 min Scan#: 5

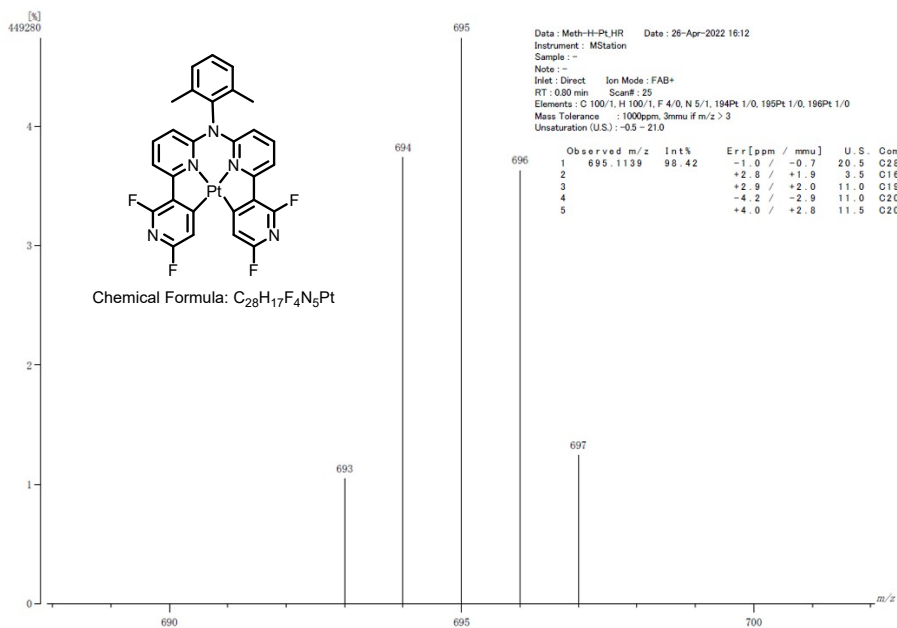


Figure S9. FAB Mass data of XA-H-Pt (3)

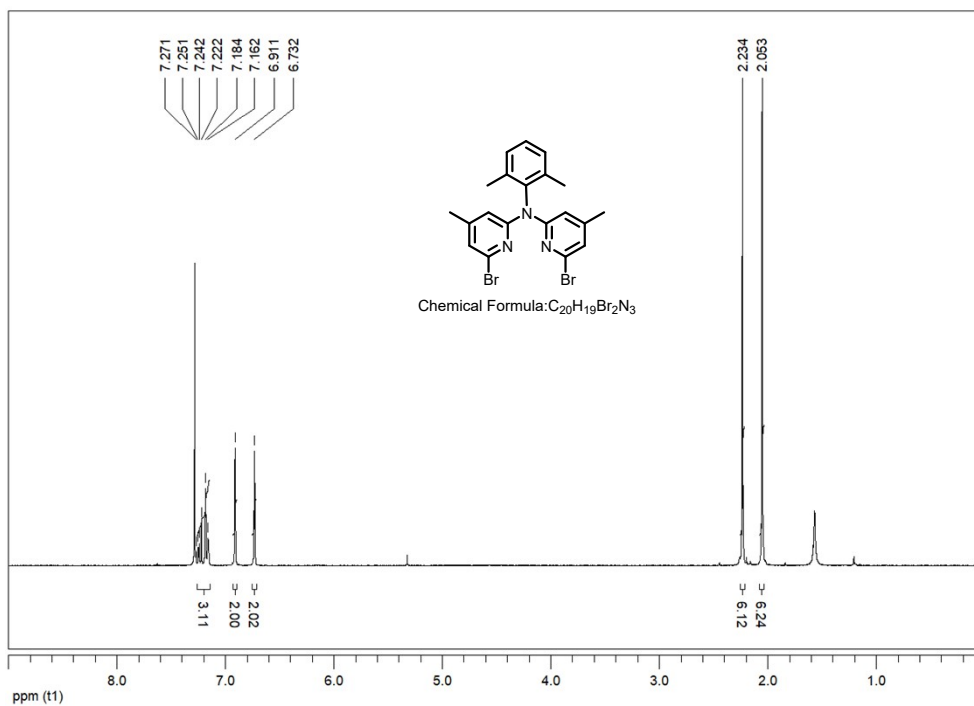


Figure S10. 1H NMR data of 6-bromo-N-(6-bromo-4-methylpyridin-2-yl)-N-(2,6-dimethylphenyl)-4-methylpyridin-2-amine (4)

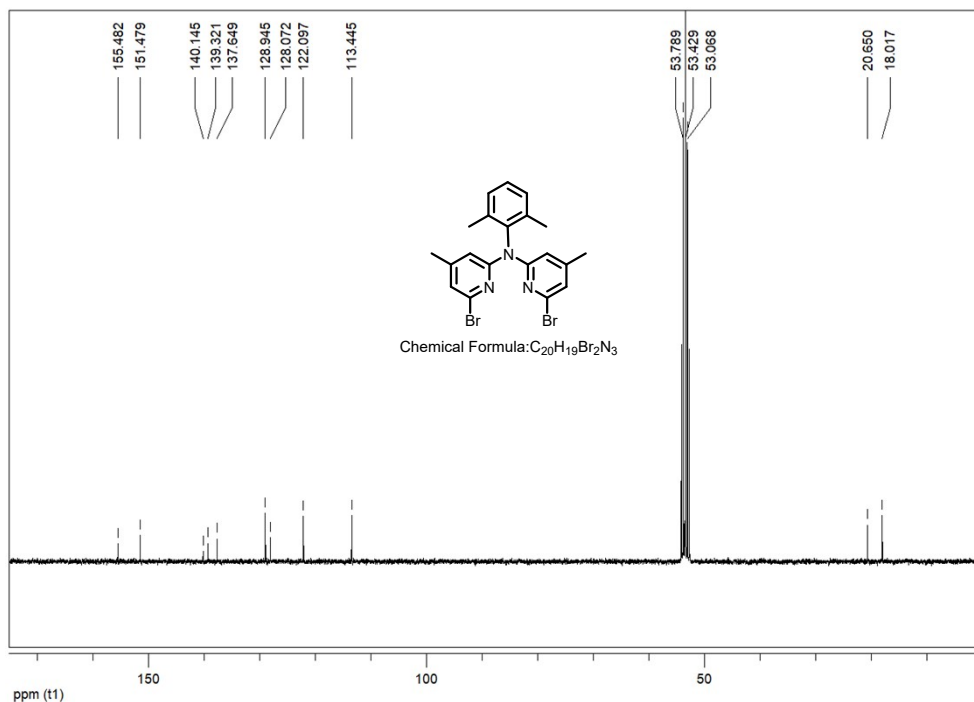


Figure S11. ^{13}C NMR data of 6-bromo-N-(6-bromo-4-methylpyridin-2-yl)-N-(2,6-dimethylphenyl)-4-methylpyridin-2-amine (4)

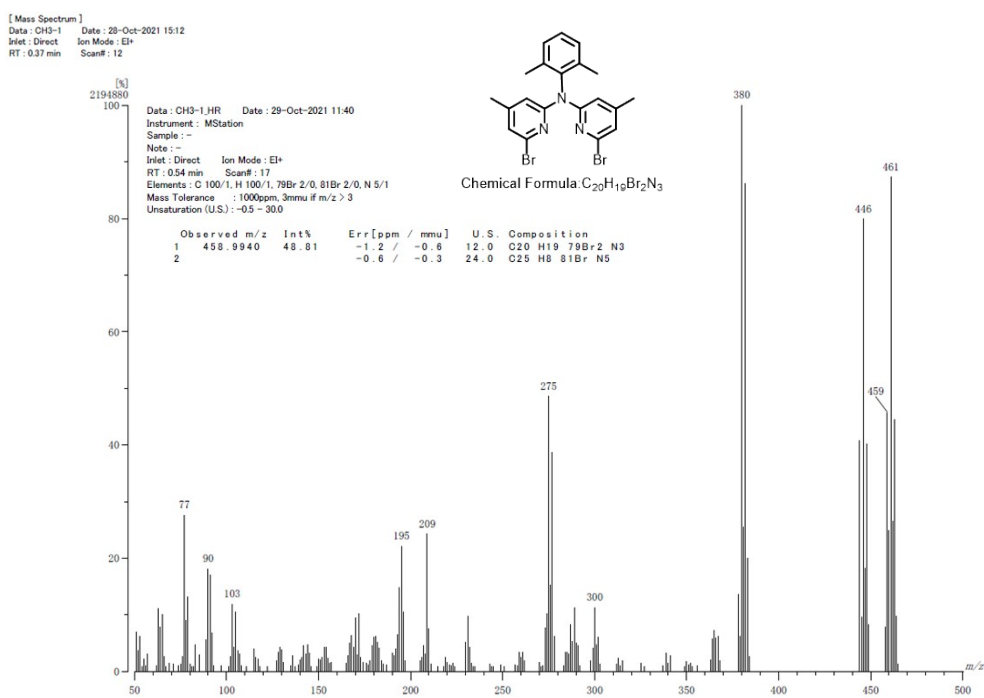


Figure S12. EI Mass data of 6-bromo-N-(6-bromo-4-methylpyridin-2-yl)-N-(2,6-dimethylphenyl)-4-methylpyridin-2-amine (4)

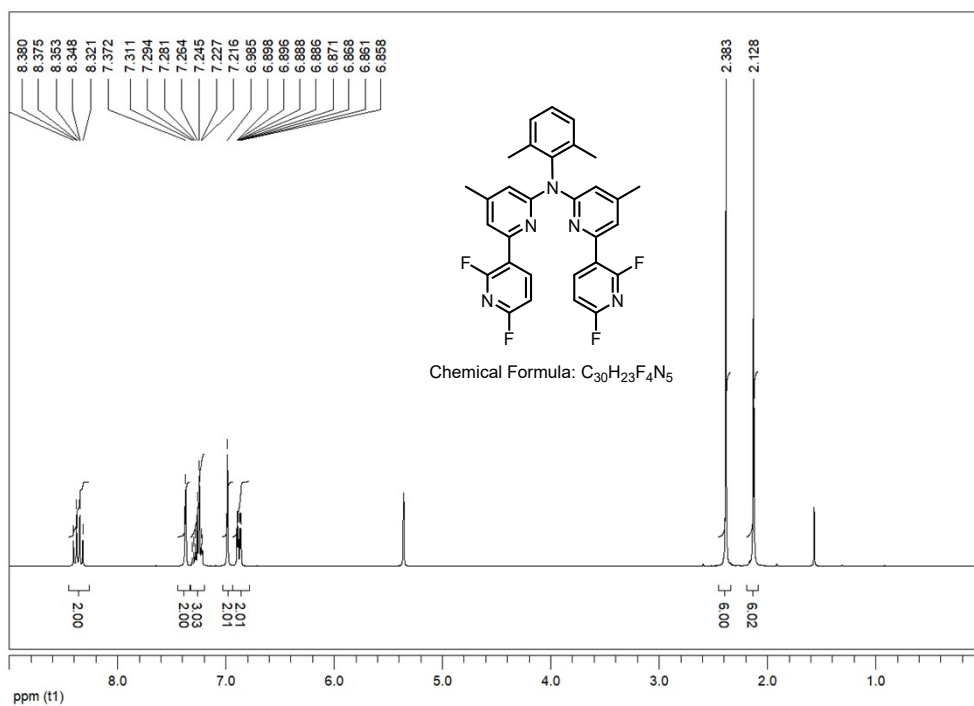


Figure S13. 1H NMR data of N-(2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-amine (5)

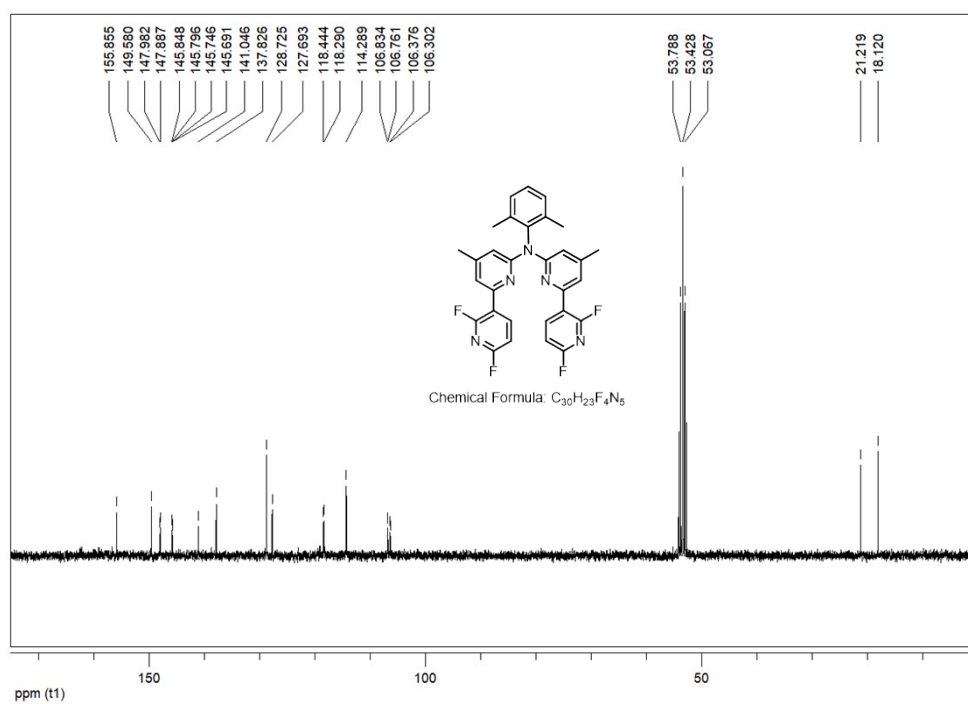


Figure S14. ^{13}C NMR data of N-(2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-amine (5)

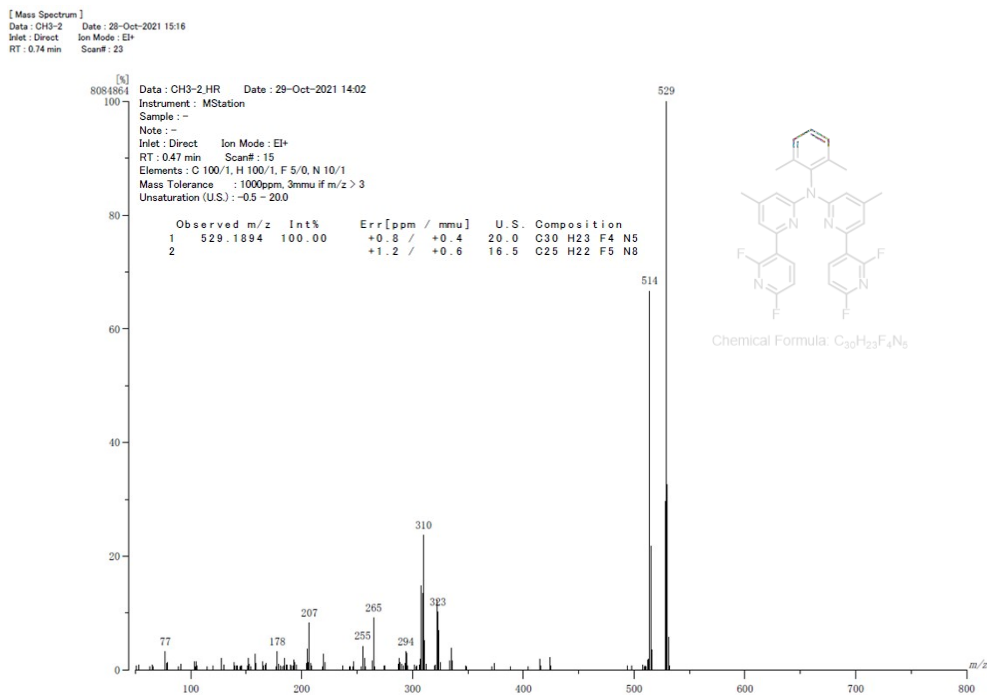


Figure S15. EI Mass data of N-(2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-yl)-N-(2,6-dimethylphenyl)-2',6'-difluoro-4-methyl-[2,3'-bipyridin]-6-amine (5)

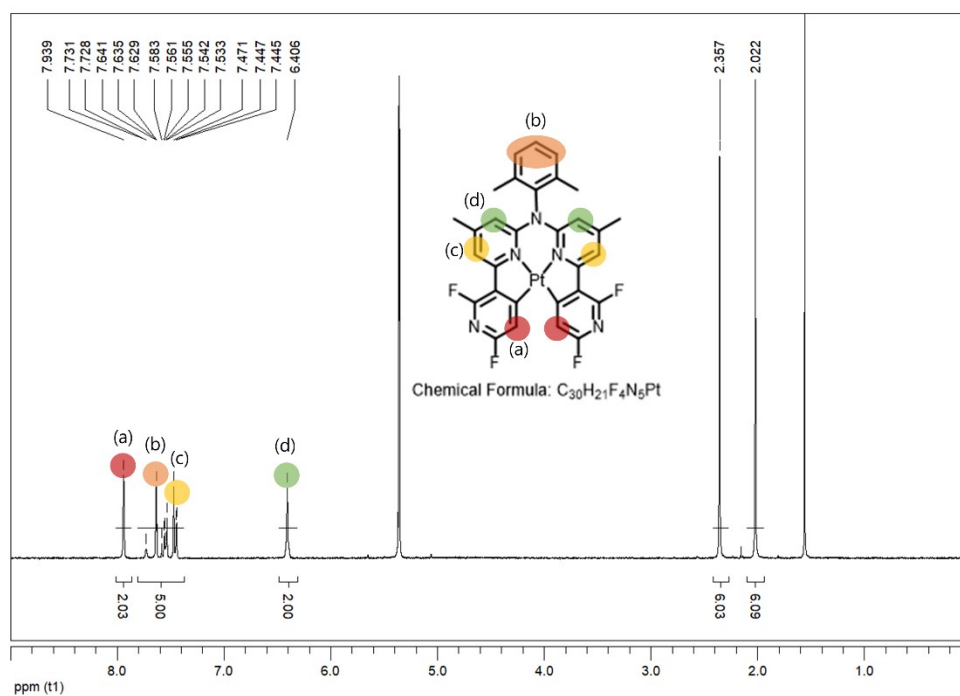


Figure S16. ¹H NMR data of XA-CH₃-Pt (6)

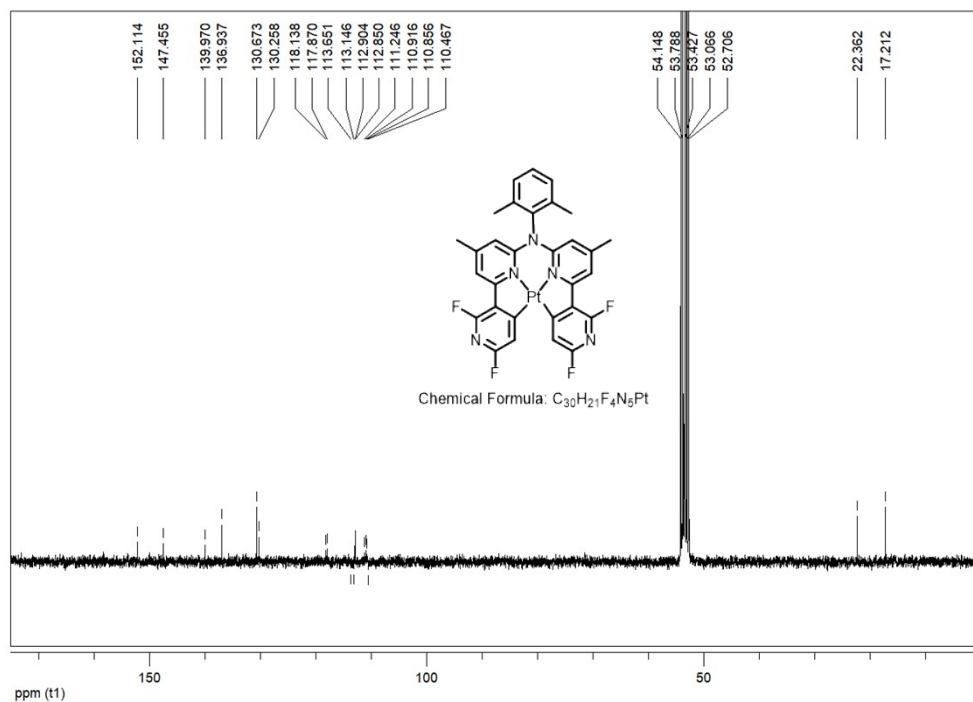


Figure S17. ¹³C NMR data of XA-CH₃-Pt (6)

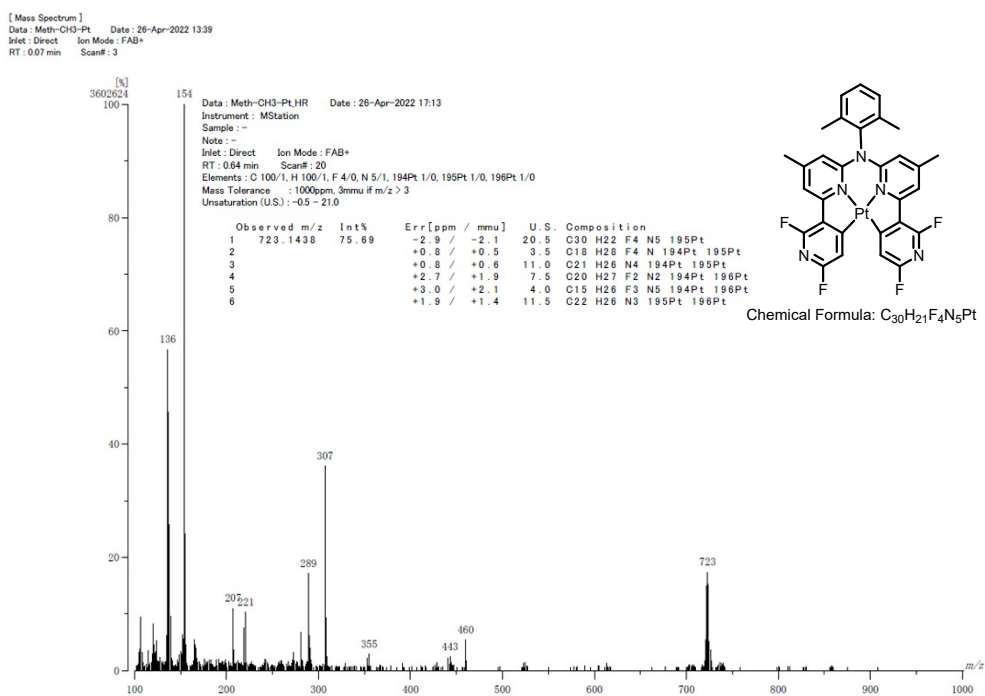


Figure S18. FAB Mass data of XA-CH₃-Pt (6)

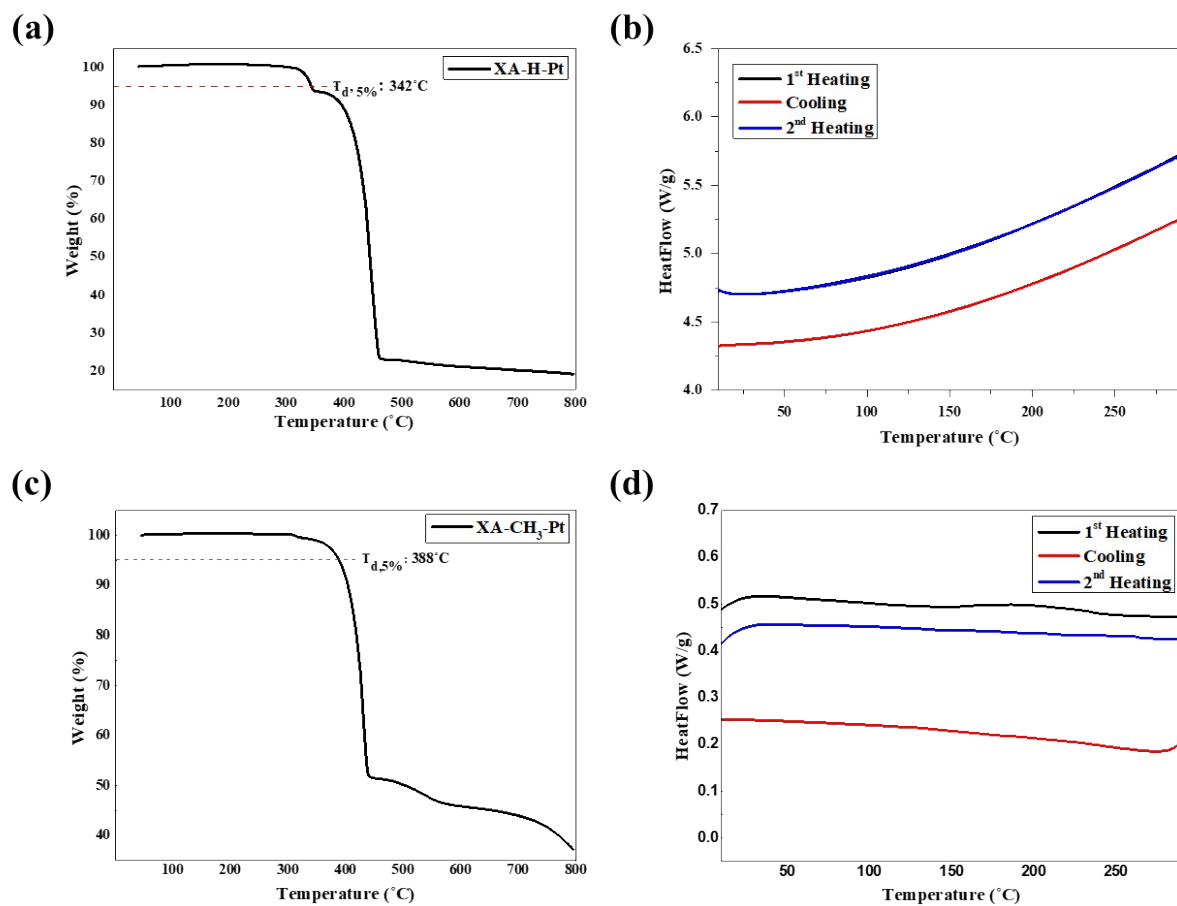


Figure S19. Differential scanning calorimetry (DSC) scan and thermogravimetric analysis data of XA-H-Pt (a, b) and XA-CH₃-Pt (c, d)

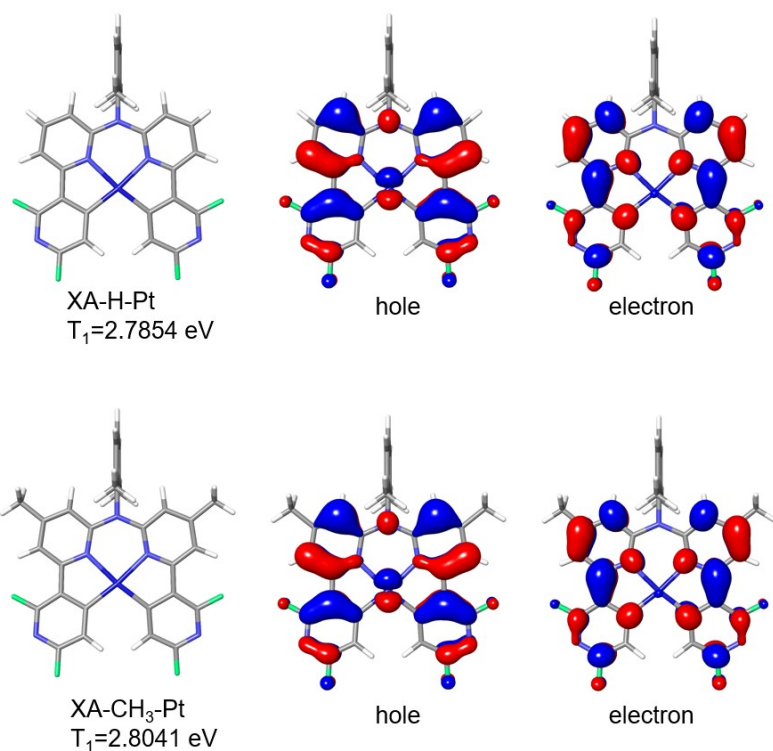


Figure S20. Molecular structure and T_1 natural transition orbital (NTO) distribution of the Pt complex.

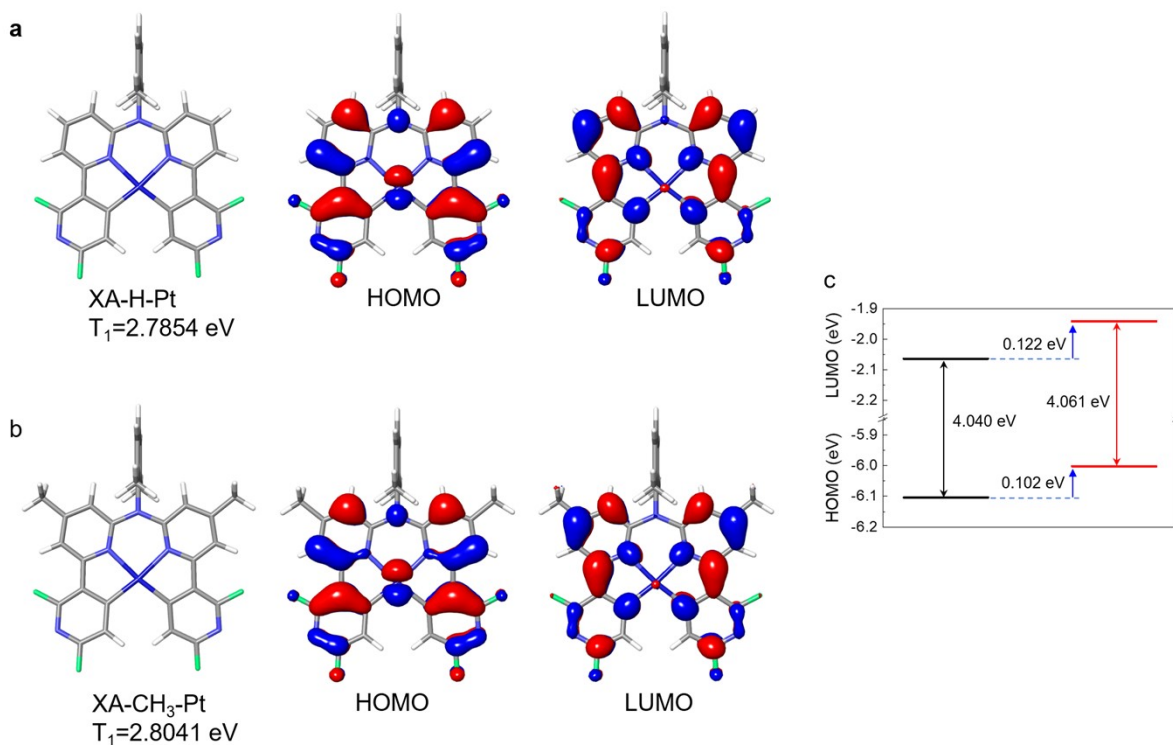


Figure S21. Molecular structure, HOMO, LUMO, and energy diagram of the Pt complexes.

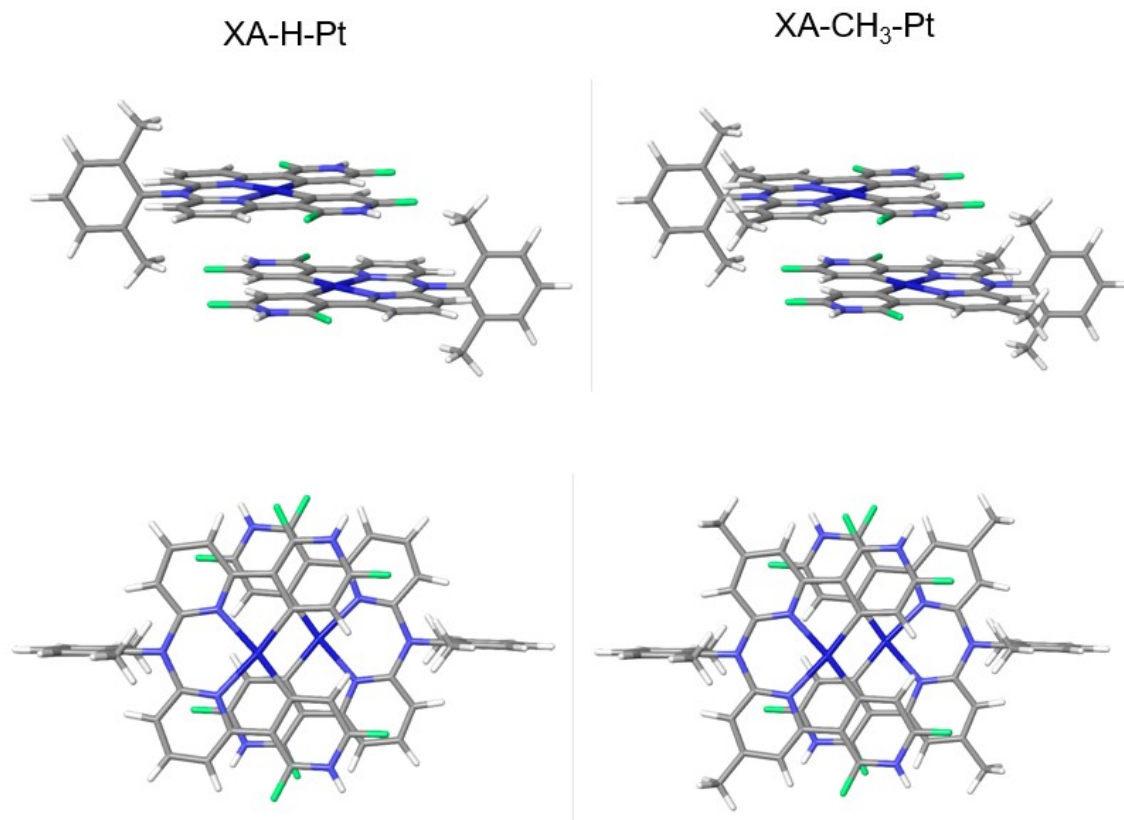
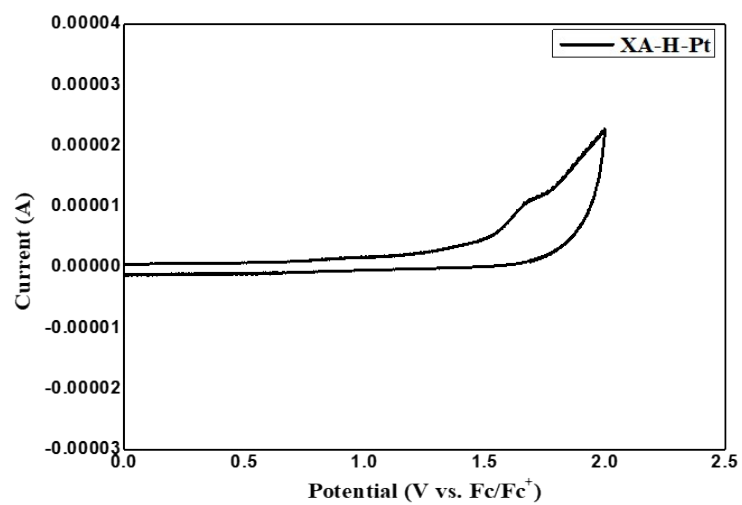


Figure S22. Dimer structure of Pt complexes.

(a)



(b)

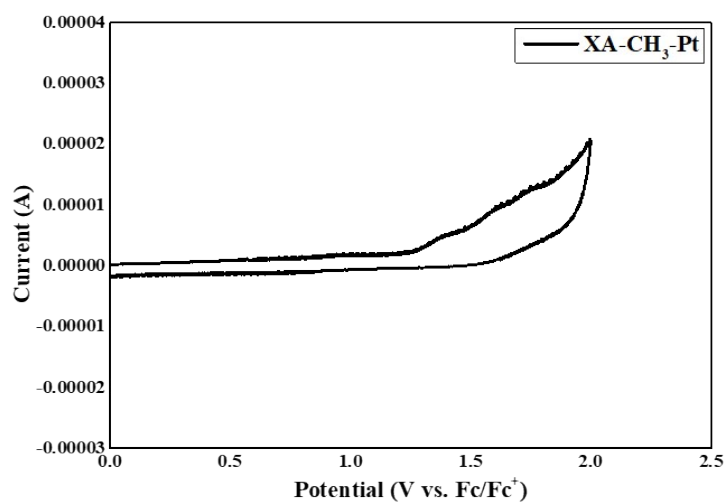


Figure S23. Cyclic voltammetry measurement results of XA-H-Pt (a) and XA-CH₃-Pt (b)

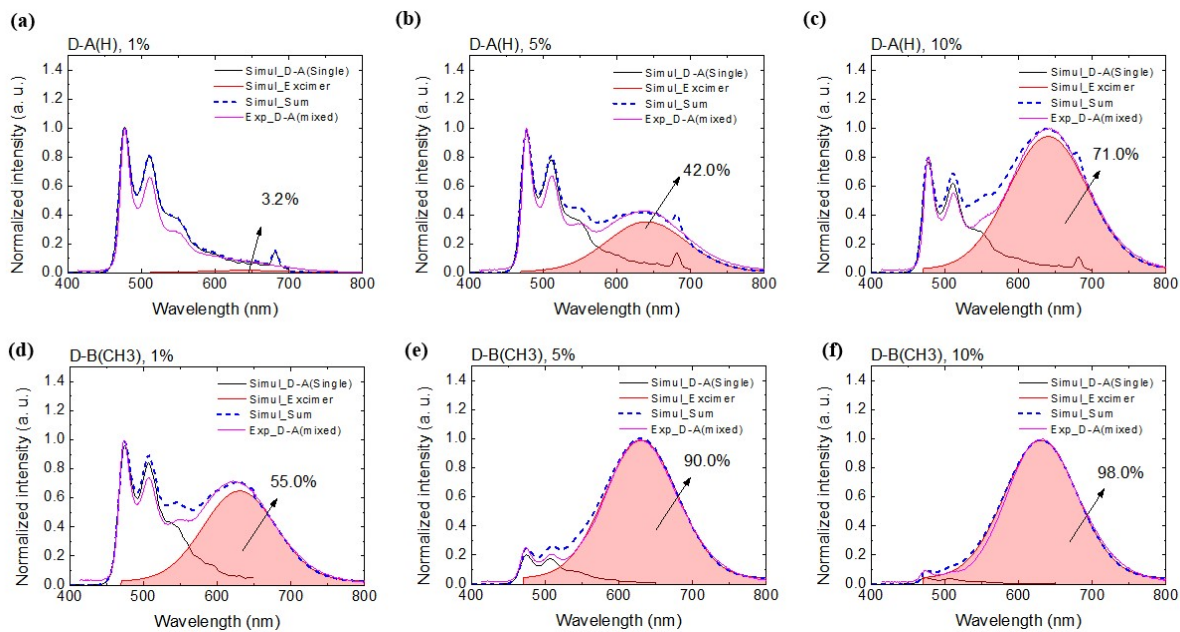


Figure S24. Photoluminescence spectrum (PL spectrum) at 1, 3, 5% concentrations of XA-H-Pt (a-c) and XA-CH₃-Pt (d-f)

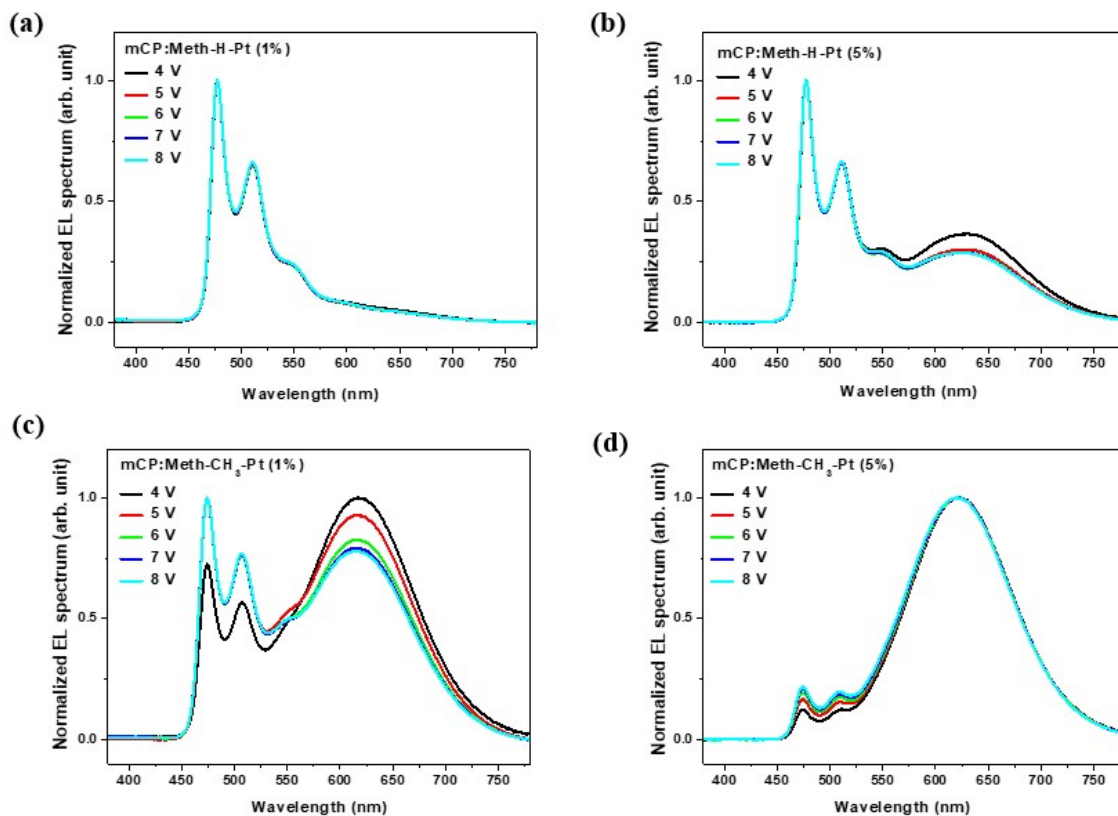


Figure S25. Voltage-dependent electroluminescence spectrum (EL spectrum) at 1, 5% concentration of (a, b) XA-H-Pt, (c, d) XA-CH₃-Pt

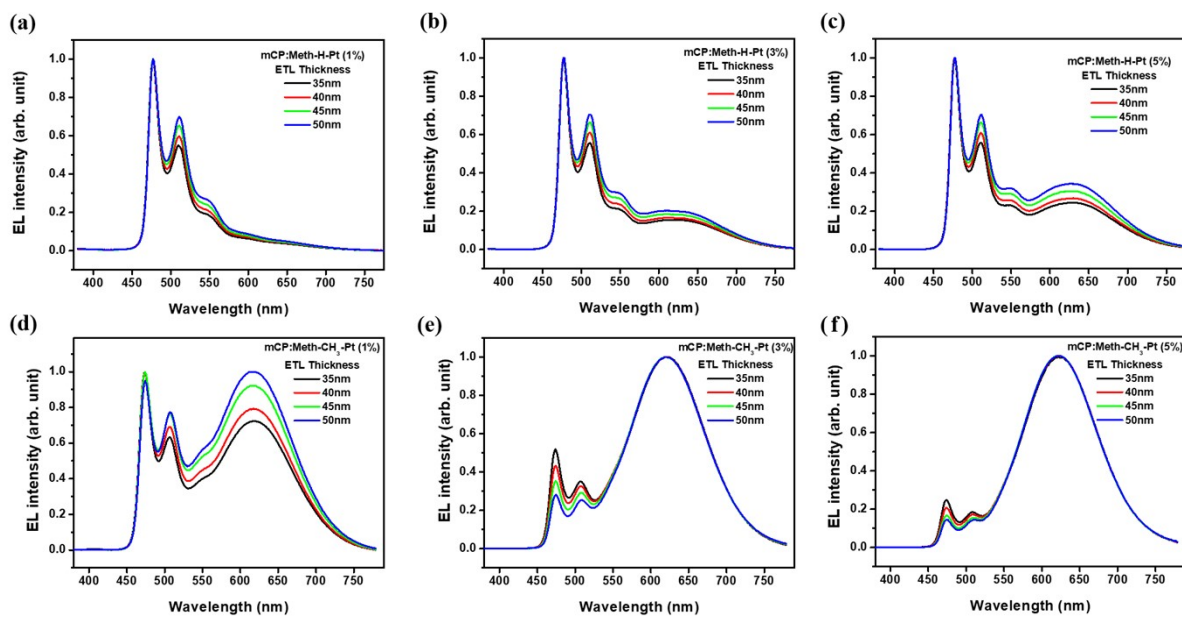
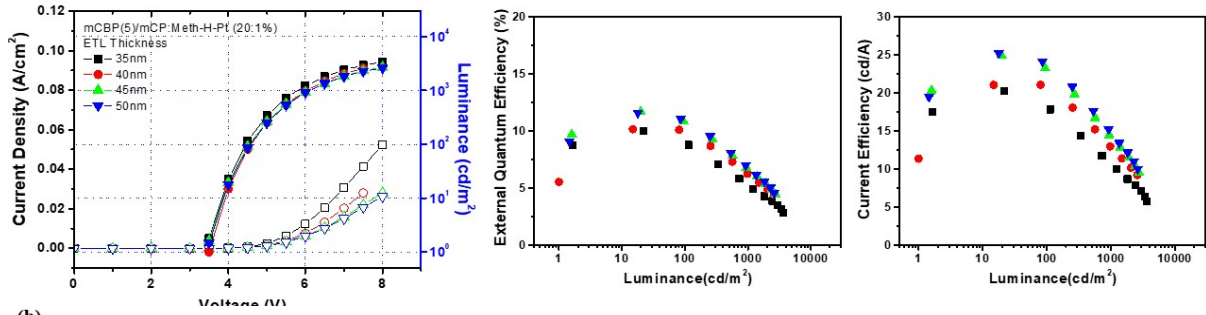
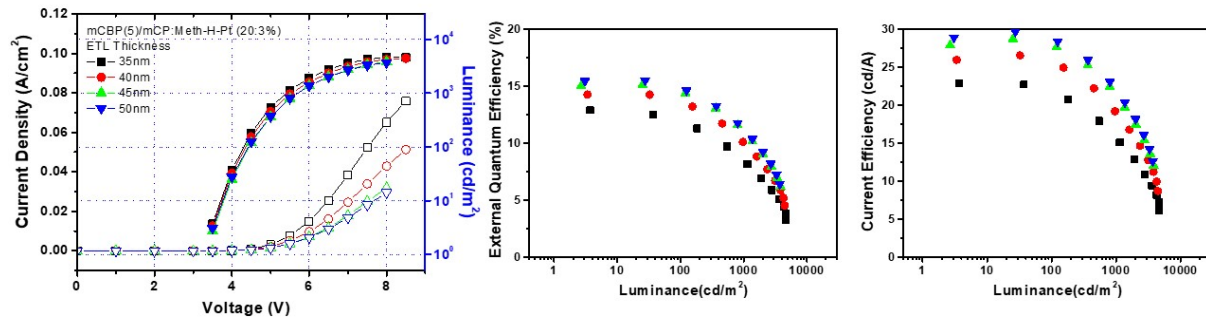


Figure S26. Electroluminescence (EL) spectra of (a-c) XA-H-Pt and (d-f) XA-CH₃-Pt based PhOLEDs depending on the ETL Thickness variations

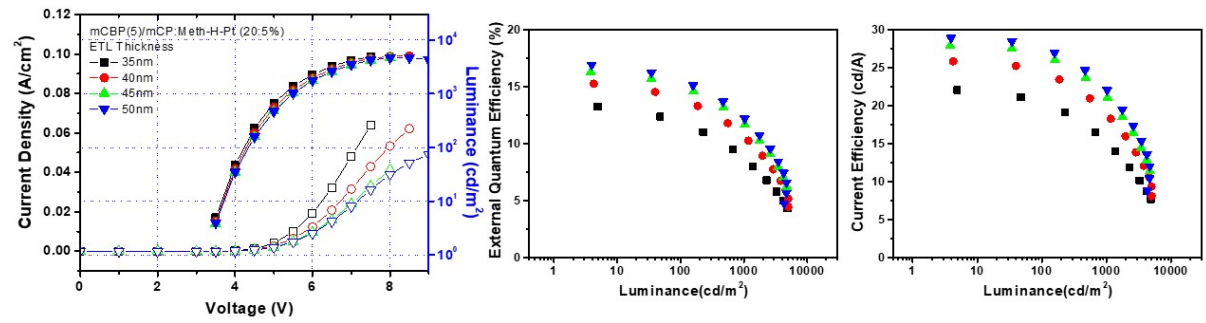
(a)



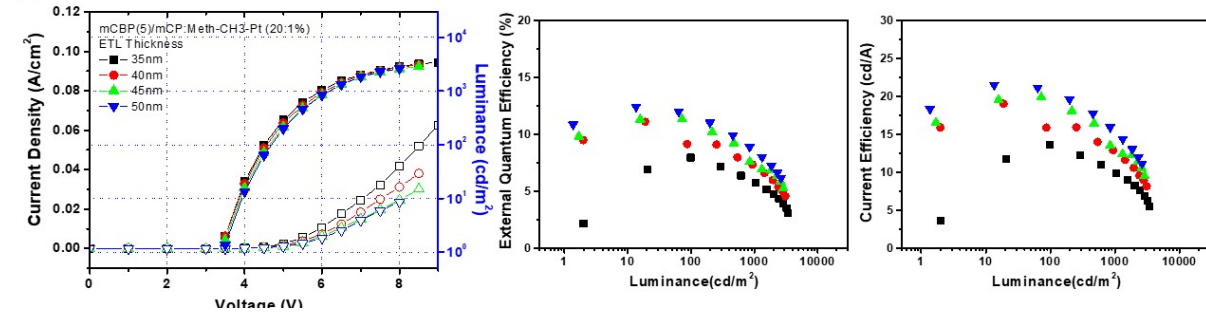
(b)



(c)



(d)



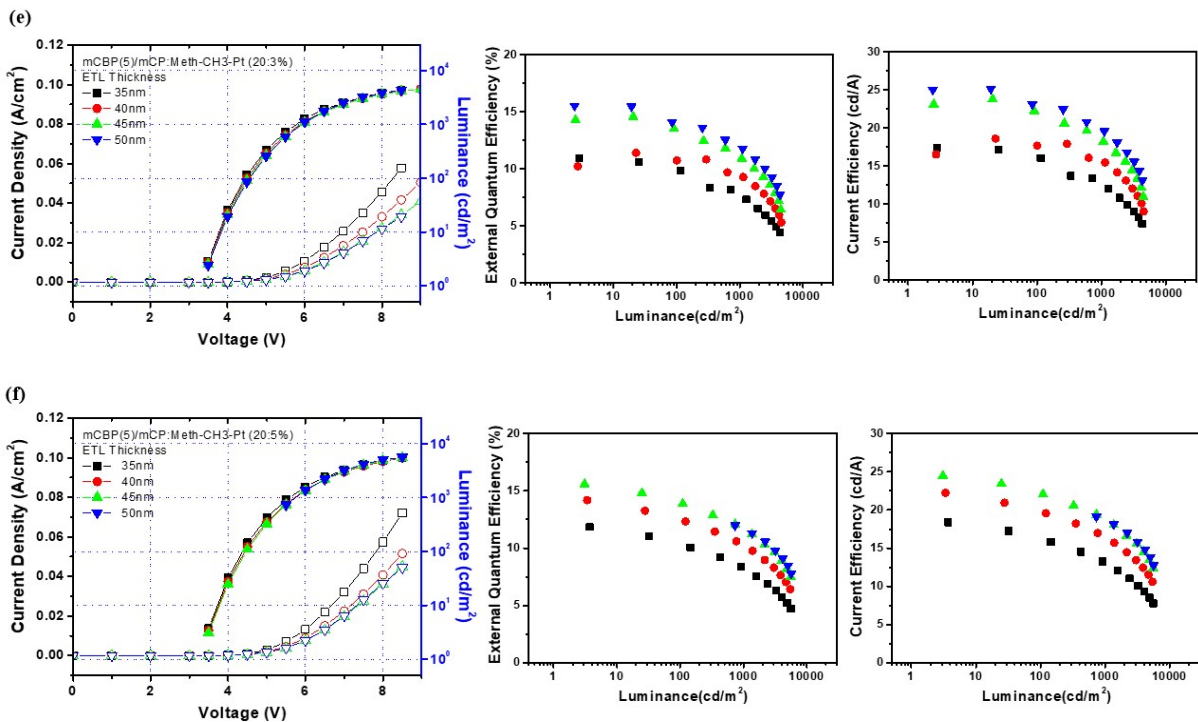


Figure S27. Current density (J) - voltage (V) - luminance (L), external quantum efficiency (EQE) and current efficiency (cd/A) of electron transport layer (ETL) thickness-dependent OLEDs, (a) XA-H-Pt, 1%, (b) XA -H-Pt, 3%, (c) XA -H-Pt, 5%, (d) XA -CH₃-Pt, 1%, (e) XA -CH₃-Pt, 3%, (f) XA -CH₃-Pt, 5%,

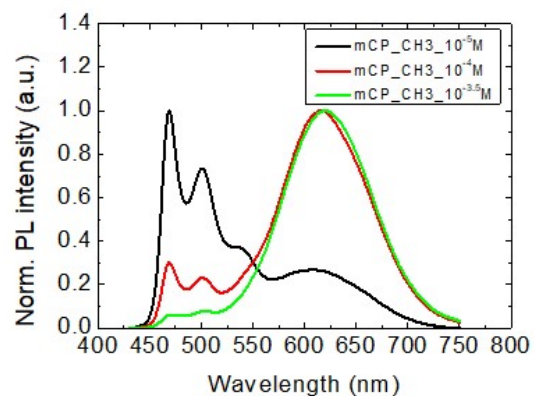
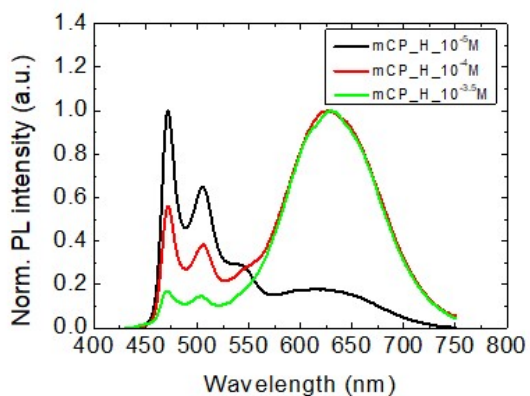


Figure S28. Photoluminescent spectra of XA-H-Pt (left) and XA-CH₃-Pt (right) in solution at different concentrations.

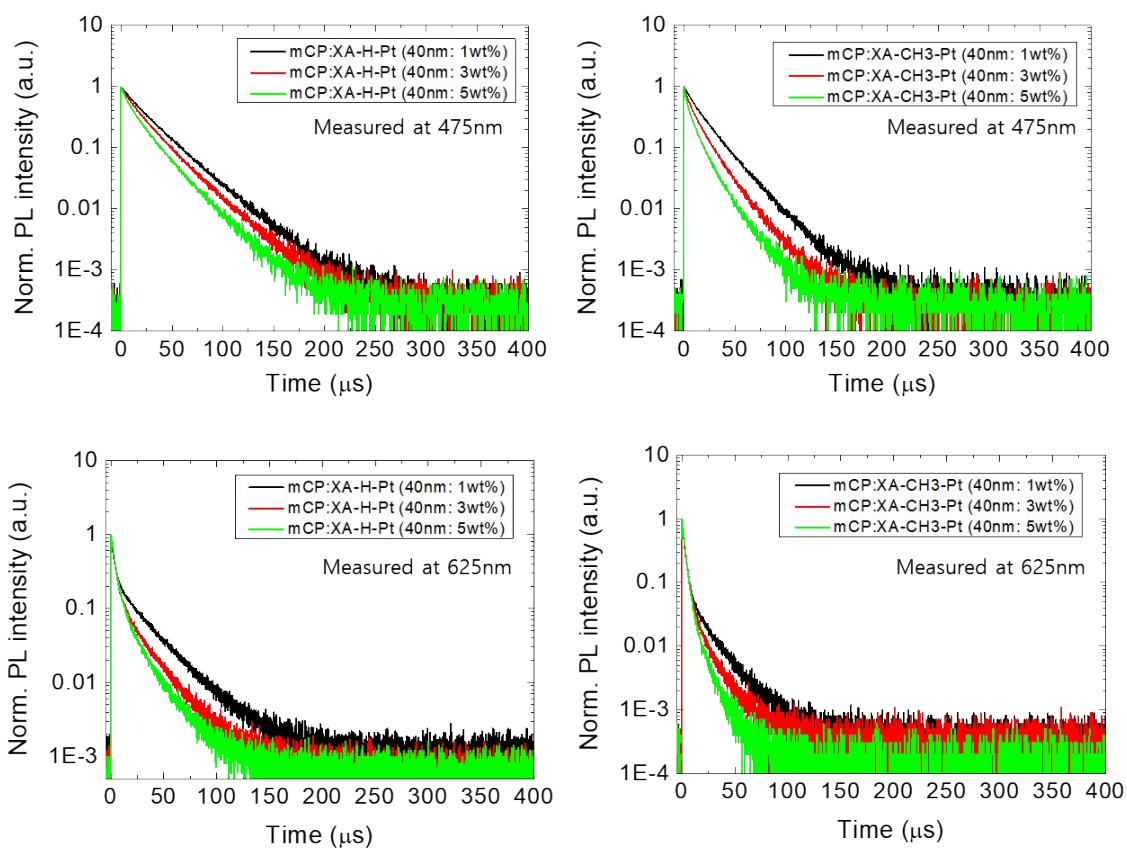


Figure S29. TRPL decay curves of mCP films with different concentrations of Pt-complex measured at 475 nm and 625nm at room temperature.