

Electronic Supporting Information

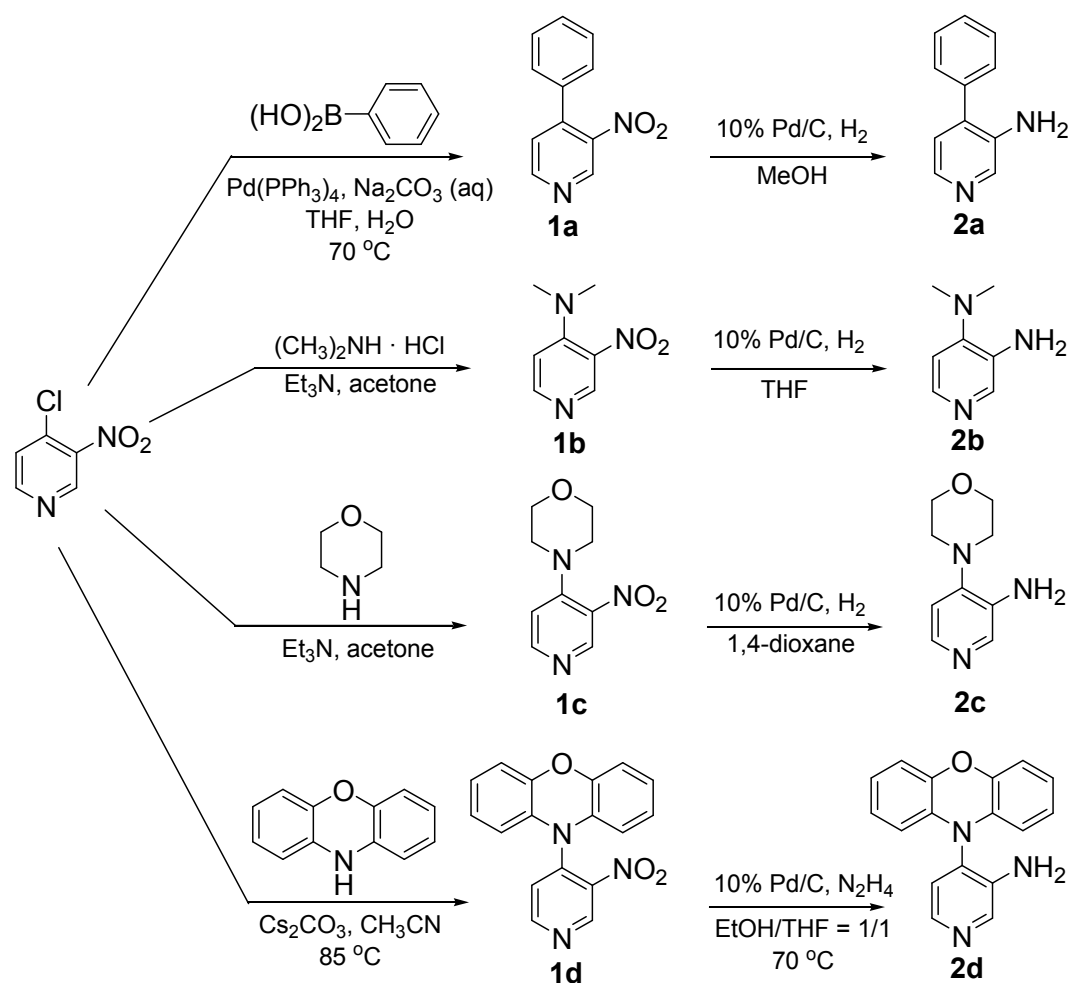
New platinum complexes exhibiting host dependent photoluminescence as single dopants in double emitting layer, hybrid white electroluminescence devices

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Synthesis procedure

Synthesis of pyridylamine derivatives



3-Nitro-4-phenylpyridine (1a).¹ A solution of 4-chloro-3-nitropyridine (6.0 g, 37.9 mmol), phenylboronic acid (5.08 g, 41.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (2.20 g, 1.90 mmol) in THF (120 mL) was stirred under nitrogen atmosphere at rt. After 12 mL of 2N Na_2CO_3 was delivered, the reaction mixture was heated at 70°C for 2 h. The cooled crude mixture was poured onto water and extracted with CH_2Cl_2 (100 mL \times 3 times) then dried over anhydrous magnesium sulphate. The mixture was purified over silica gel using CH_2Cl_2 as the eluent to afford the pale yellow powder (7.0 g, 92%). ^1H NMR (400 MHz, CDCl_3) : δ 9.08 (s, 1H), 8.81 (d, 1H, $J = 4.8$ Hz), 7.49-7.48 (m, 3H), 7.42 (d, 1H, $J = 4.8$ Hz), 7.36-7.34 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.88, 145.28, 144.01, 134.57, 129.74, 129.16, 127.73, 125.89. EI-MS: calcd. 200.1, $m/z = 200.1$ (M^+).

***N,N*-Dimethyl-3-nitropyridin-4-amine (1b).** A mixture of 4-chloro-3-nitropyridine (10.0 g, 63.1 mmol), dimethylamine hydrochloride (6.64 g, 82.0 mmol) was dissolved in 210 mL of acetone and was subsequently treated with triethylamine (11 mL, 75.7 mmol). The reaction mixture was stirred under nitrogen atmosphere at rt for 24 h. The white precipitate was filtered off. The organic phase was then extracted with ethyl acetate (100 mL × 3 times) then dried over anhydrous magnesium sulphate. The crude was purified by column chromatography (silica gel, ethyl acetate/dichloromethane: 1/1(v/v)) to afford a yellow liquid (7.44 g, 70%). ¹H NMR (400 MHz, CDCl₃) : δ 8.79 (s, 1H), 8.28 (d, 1H, *J* = 6.0 Hz), 6.80 (d, 1H, *J* = 6.0 Hz), 3.01 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 151.63, 149.40, 148.35, 135.26, 110.91, 41.80. FAB-MS: calcd. 167.1, *m/z* = 168.1 (M+H⁺).

4-(3-Nitropyridin-4-yl)morpholine (1c). A mixture of 4-chloro-3-nitropyridine (10.0 g, 63.1 mmol), morpholine (7.14 g, 82.0 mmol) was dissolved in 210 mL of acetone and was subsequently treated with triethylamine (11 mL, 75.7 mmol). The reaction mixture was stirred under nitrogen atmosphere at rt for 24 h. The white precipitate was filtered off. The organic phase was then extracted with ethyl acetate (100 mL × 3 times) then dried over anhydrous magnesium sulphate. The crude was purified by flash column chromatography (silica gel, ethyl acetate/dichloromethane: 1/1(v/v)) to afford an orange powder (12.66 g, 96%). ¹H NMR (400 MHz, CDCl₃) : δ 8.83 (s, 1H), 8.38 (d, 1H, *J* = 6.0 Hz), 6.03(d, 1H, *J* = 6.0 Hz), 3.82 (t, 4H, *J* = 4.8 Hz), 3.20 (t, 4H, *J* = 4.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.13, 140.94, 148.37, 136.79, 112.73, 66.27, 50.06. EI-MS: calcd. 209.1, *m/z* = 209.1 (M⁺).

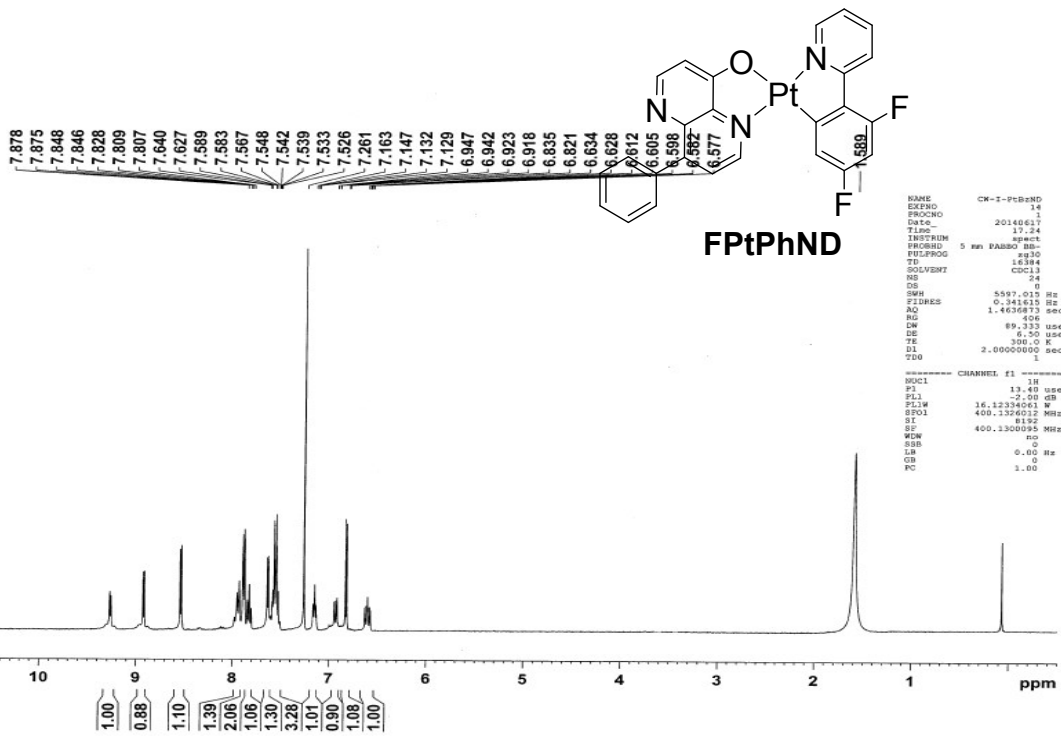
10-(3-Nitropyridin-4-yl)-10*H*-phenoxazine (1d). A mixture of 4-chloro-3-nitropyridine (2.00 g, 12.7 mmol), phenoxazine (1.62 g, 8.86 mmol) and cesium carbonate (3.30 g, 10.1 mmol) in 20 mL of acetonitrile was stirred under nitrogen atmosphere at 85 °C for 24 h. After cooling to room temperature, the reaction mixture was removed by vacuum distillation. The resulting residue was then extracted with CH₂Cl₂ (75 mL × 3 times) then dried over anhydrous magnesium sulphate. The crude was finally purified by flash column chromatography over silica gel using CH₂Cl₂ as the eluent to afford a drak brown solid (2.40 g, 62%). ¹H NMR (400 MHz, CDCl₃) : δ 9.40 (s, 1H), 9.05 (d, 1H, *J* = 4.8 Hz), 7.58 (d, 1H, *J* = 5.2 Hz), 6.80-6.75 (m, 4H), 6.66 (td, 2H, *J* = 6.8 Hz, *J* = 2.8 Hz), 5.93 (d, 2H, *J* = 8.0 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 156.49, 148.43, 145.34, 144.12, 141.02, 131.43, 128.48, 123.65, 123.44, 116.62, 113.03. EI-MS: calcd. 305.1, *m/z* = 305.1 (M⁺).

3-Nitro-4-phenylpyridine (2a). A solution of 4-phenylpyridin-3-amine (**1a**) (4.00 g, 20.0 mmol) and 10% Pd/C (0.4 g, 3.8 mmol) in methanol (50 mL) was stirred under H₂ atmosphere at rt for 72 h. The reaction mixture was filtered and then concentrated under reduced pressure to provide the product (3.00 g, 88%). ¹H NMR (400 MHz, CDCl₃) : δ 8.22 (s, 1H), 8.06 (d, 1H, *J* = 4.8 Hz), 7.52-7.41 (m, 5H), 7.08 (d, 1H, *J* = 4.8 Hz), 3.95 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.06, 139.82, 137.97, 136.91, 133.62, 129.11, 128.38, 128.28, 124.19. EI-MS: calcd. 170.1, *m/z* = 170.1 (M⁺).

N⁴,N⁴-Dimethylpyridine-3,4-diamine (2b). A solution of *N,N*-dimethyl-3-nitropyridin-4-amine (**1b**) (10.0 g, 59.9 mmol) and 10% Pd/C (1.0 g, 9.4 mmol) in THF (150 mL) was stirred under H₂ atmosphere at rt for 24 h. The reaction mixture was filtered and then concentrated under reduced pressure to provide the product (8.05 g, 98%). ¹H NMR (400 MHz, CDCl₃) : δ 7.98 (s, 1H), 7.95 (d, 1H, *J* = 5.6 Hz), 6.77 (d, 1H, *J* = 5.6 Hz), 3.69 (s, 2H), 2.73 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.25, 141.48, 137.55, 136.65, 113.26, 41.94. FAB-MS: calcd. 137.1, *m/z* = 138.1 (M+H⁺).

4-Morpholinopyridin-3-amine (2c). A solution of 4-(3-nitropyridin-4-yl)morpholine (**1c**) (6.00 g, 28.7 mmol) and 10% Pd/C (0.6 g, 5.6 mmol) in 1,4-dioxane (120 mL) was stirred under H₂ atmosphere at rt for 72 h. The reaction mixture was filtered and then concentrated under reduced pressure to provide the product (3.91 g, 76%). ¹H NMR (400 MHz, CDCl₃) : δ 8.04 (s, 1H), 8.00 (d, 1H, *J* = 5.2 Hz), 6.80 (d, 1H, *J* = 5.2 Hz), 3.86 (t, 4H, *J* = 4.8 Hz), 3.71 (s, 2H), 3.01 (t, 4H, *J* = 4.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 145.14, 140.91, 137.30, 113.29, 66.96, 49.63. EI-MS: calcd. 179.1, *m/z* = 179.1 (M⁺).

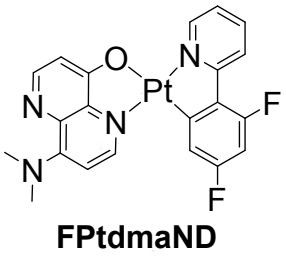
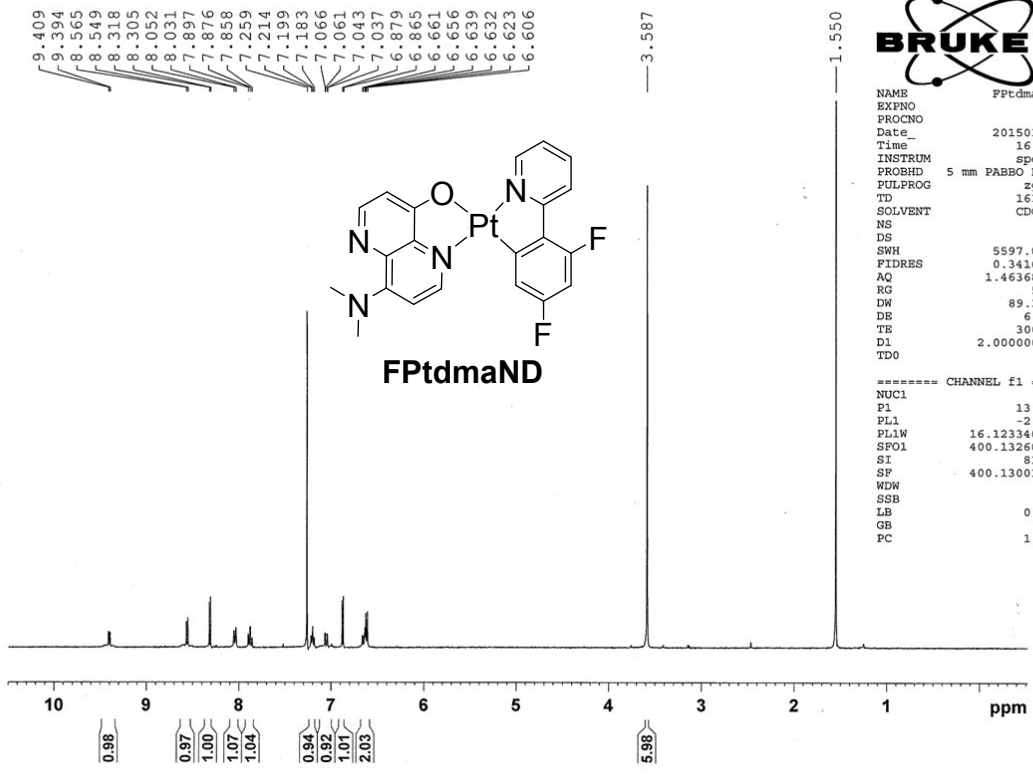
4-(10*H*-Phenoxazin-10-yl)pyridin-3-amine (2d). The mixture of 10-(3-nitropyridin-4-yl)-10*H*-phenoxazine (**1d**) (1.50 g, 4.9 mmol), 10% Pd/C (0.15 g, 1.4 mmol) and 1.4 mL of hydrazine in mixed solvent of THF/EtOH 1:1(v/v) (58 mL) was stirred under nitrogen atmosphere at 70 °C for 20 h. The reaction mixture was filtered and then concentrated under reduced pressure to provide the product (1.20 g, 89%). ¹H NMR (400 MHz, MeOD) : δ 8.30 (s, 1H), 7.97 (d, 1H, *J* = 4.8 Hz), 7.19 (d, 1H, *J* = 4.8 Hz), 6.72-6.64 (m, 6H), 5.97 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (100 MHz, MeOD) δ 144.28, 142.06, 141.54, 140.32, 131.71, 130.12, 125.63, 123.89, 122.55, 116.13, 113.23. EI-MS: calcd. 275.1, *m/z* = 275.1 (M⁺).



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ZD0           1
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FPtPhND



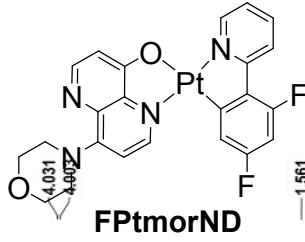
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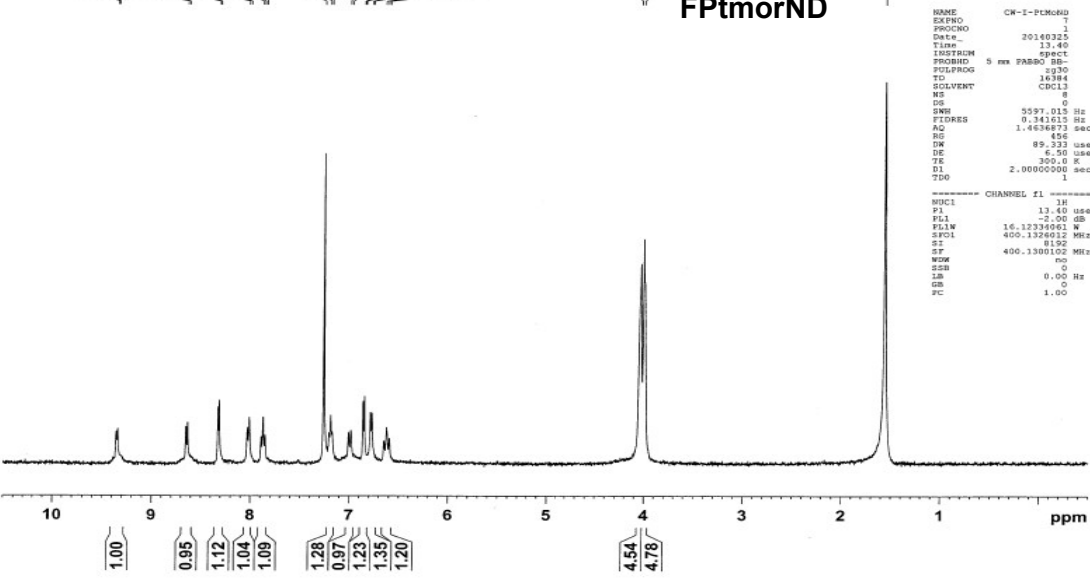
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DF            6.50 usec
TE            300.0 K
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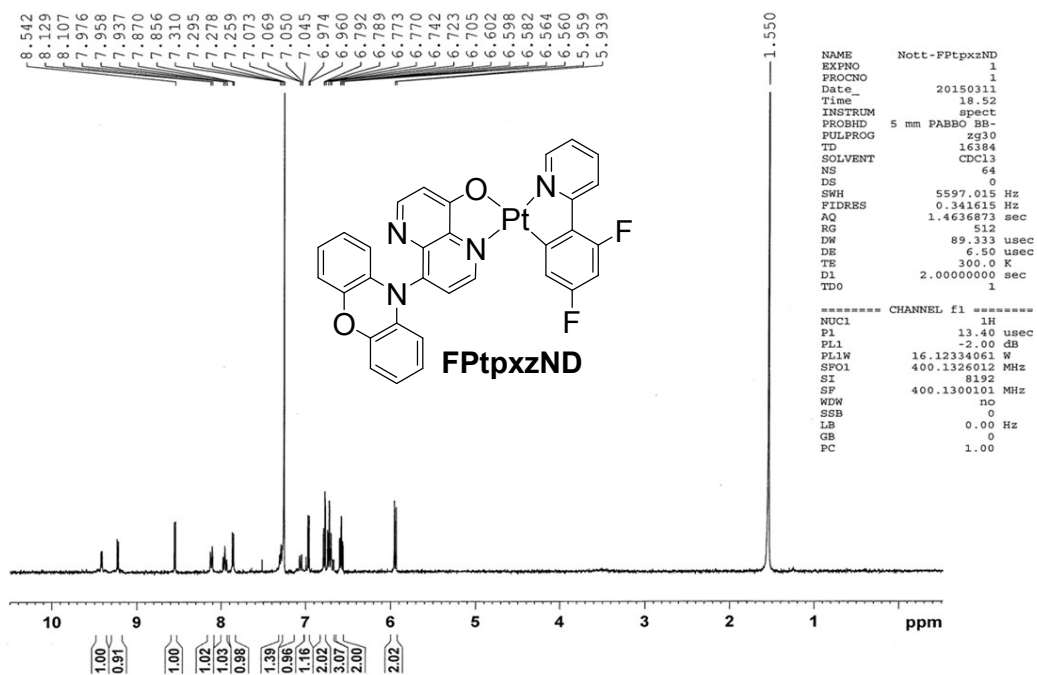


Figure S1 ^1H NMR spectrum of FPtXND.

Excitation spectra

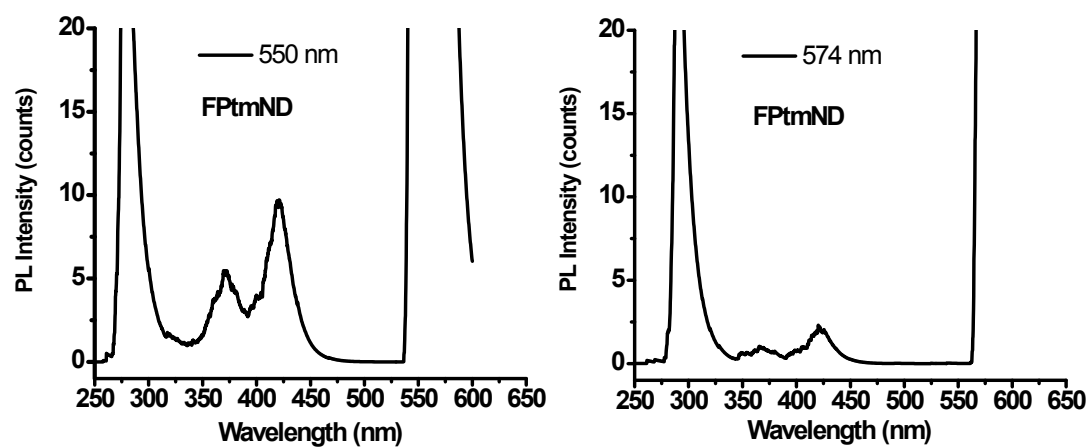


Figure S2 Excitation spectra of FPtmND.

Phosphorescence lifetime

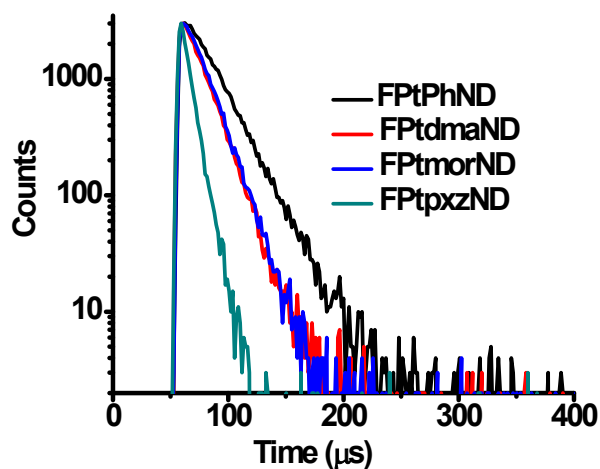


Figure S3 Solution PL decay profile of FPtXND.

The estimation of HOMO-LUMO optical gap energy (E_g)

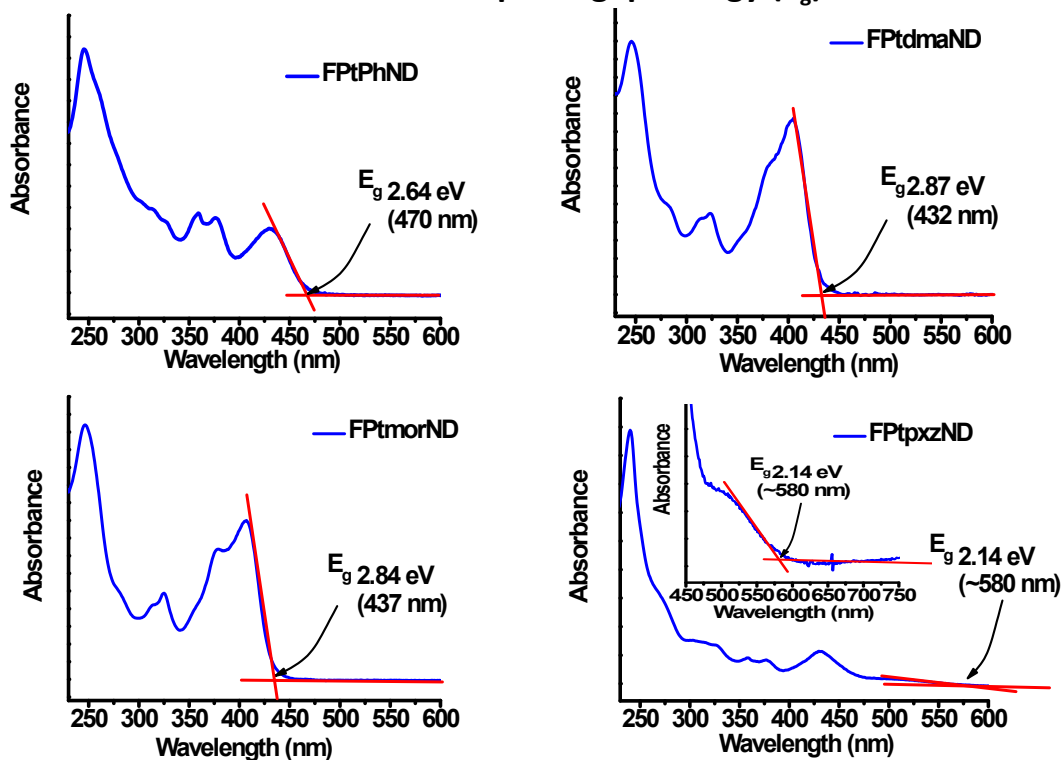


Figure S4 UV-visible absorption spectra of FPtXND in CH_2Cl_2 (1×10^{-5} M) used to determine the onset wavelength (λ_{onset}).

Electroluminescence data

CBP hosted single EML devices (Device A and B)

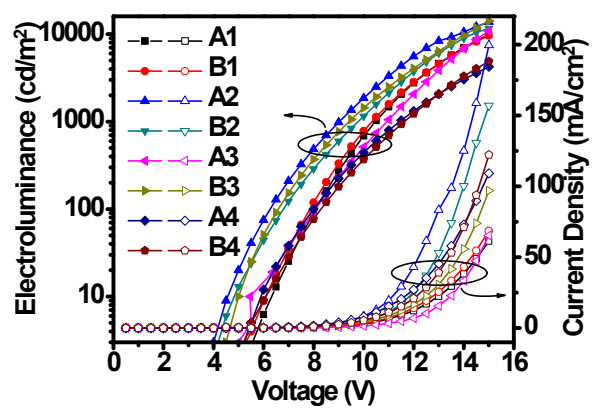


Figure S5 Electroluminescence-voltage-current density characteristics of Device A and B.

Reference

1. T. Hirose, F. Helmich and E. W. Meijer, *Angew. Chem. Int. Ed.*, 2013, **52**, 304.