Electronic Supplementary Information

Synthesis of cyclometalated platinum(II) complexes with benzoayrl-pyridines as C^N ligands for investigating their photophysical, electrochemical and electroluminescent properties

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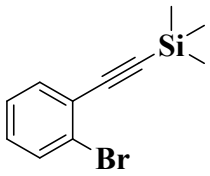
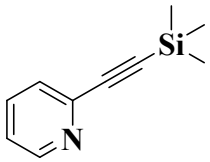
Contents

((2-bromophenyl)ethynyl)trimethylsilane (1)



Under a N_2 atmosphere, 1-bromo-2-iodobenzene (4.00 g, 14.14 mmol), trimethylethynylsilane (1.53 g, 15.55 mmol), dichlorobis(triphenylphosphine)palladium(II) (99 mg, 0.14 mmol) and copper(I) iodide (54 mg, 0.28 mmol) were mixed in triethylamine (50 mL) and the reaction mixture was left with stirring overnight at room temperature. Then the residue of the solvent was filtered and the filtrate was removed under vacuum. The crude product was purified by column chromatography using petroleum ether as the eluent to obtain the product as pale yellow oil (3.58 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (ddd, J = 8.0, 1.3, 0.4 Hz, 1H), 7.49 (ddd, J = 7.7, 1.8, 0.4 Hz, 1H), 7.24 (ddd, J = 7.7, 7.5, 1.3 Hz, 1H), 7.15 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.71, 132.47, 129.67, 127.00, 125.89, 125.37, 103.15, 99.77, 0.03.

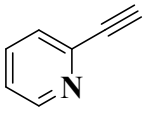
2-(trimethylsilylethynyl)pyridine (5)



Under a N_2 atmosphere, 2-bromopyridine (3.00 g, 18.99 mmol), trimethylethynylsilane (2.05 g, 20.89 mmol), dichlorobis(triphenylphosphine)palladium(II) (133 mg, 0.19 mmol) and copper(I) iodide (72 mg, 0.38 mmol) were mixed in triethylamine (40 mL) and the reaction mixture was left with stirring overnight at 50 °C. Then the residue of the solvent was filtered and the filtrate was removed under vacuum. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (5 : 1, v : v) as the eluent to obtain the product as oily liquid (3.22 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (dd, J = 4.7, 1.5 Hz, 1H), 7.57 (dd, J = 7.7, 1.7 Hz, 1H), 7.39

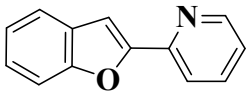
(ddd, J = 7.7, 7.7, 1.1 Hz, 1H), 7.16 (ddd, J = 7.7, 4.7, 1.7 Hz, 1H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.4, 142.6, 135.7, 126.8, 122.6, 103.3, 94.3, 0.7.

2-ethynylpyridine (6)



2-(trimethylsilylethynyl)pyridine (**5**) (3.00 g, 17.14 mmol) was dissolved in methanol (30 mL) followed by slow addition of 1 M KOH (1.10 g, 20 mL H_2O). The system was then stirred for 1h at room temperature. The resulting mixture was diluted with water and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The crude product was further purified via column chromatography using petroleum ether/ethyl acetate (3 : 1, v : v) as the eluent to obtain 6 as viscous liquid (1.67 g, 95%). ^{1}HNMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 3.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.59, 134.93, 129.20, 127.81, 117.84, 83.66, 75.06.

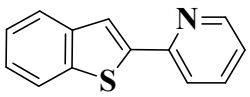
2-(benzo[*b*]furan-2-yl)pyridine (L-O)



Under a N_2 atmosphere, benzo[*b*]furan-2-ylboronic acid (0.38 g, 2.34 mmol), 2-bromopyridine (0.32 g, 2.04 mmol) and $Pd(PPh_3)_4$ (136 mg, 0.12 mmol) were mixed in 2M Na_2CO_3 and THF (20 mL, v:v = 2:1). The reaction mixture was heated to 100 ^{o}C with stirring overnight for 16 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4. Then the solvent was removed under vacuum and crude product was purified by column chromatography using petroleum ether/ethyl acetate (15 : 1, v:v) as the

eluent to obtain the product as white solid (0.36 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (d, *J* = 4.4 Hz, 1 H). 7.91 (d , *J* = 7.6 Hz, 1 H),7.78 (dt, *J* = 7.8, 1.6 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.44 (s, 1 H), 7.34 (dt, *J* = 7.6, 1.2 Hz, 1 H), 7.23-7.28 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.7, 155.5, 150.3, 149.7, 137.2, 129.3, 125.6, 123.6, 123.4, 122.1, 120.3, 112.0, 105.2.

2-(benzo[*b*]thiophen-2-yl)pyridine (L-S)



It follows the similar synthetic procedure to that of **L-O** using petroleum ether/ethyl acetate (15 : 1, v:v) as the eluent for purification. **L-S** was obtained as white solid with a yield of 89%.^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.63 (d, *J* = 4.8 Hz, 1H), 7.87 (dd, *J* = 8.1, 4.3 Hz, 1H), 7.84-7.74 (m, 3H), 7.74-7.64 (m, 1H), 7.41-7.30 (m, 2H), 7.24-7.14 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.47, 149.65, 144.77, 140.60, 140.43, 136.59, 125.02, 124.48, 124.09, 122.58, 122.56, 121.08, 119.55.

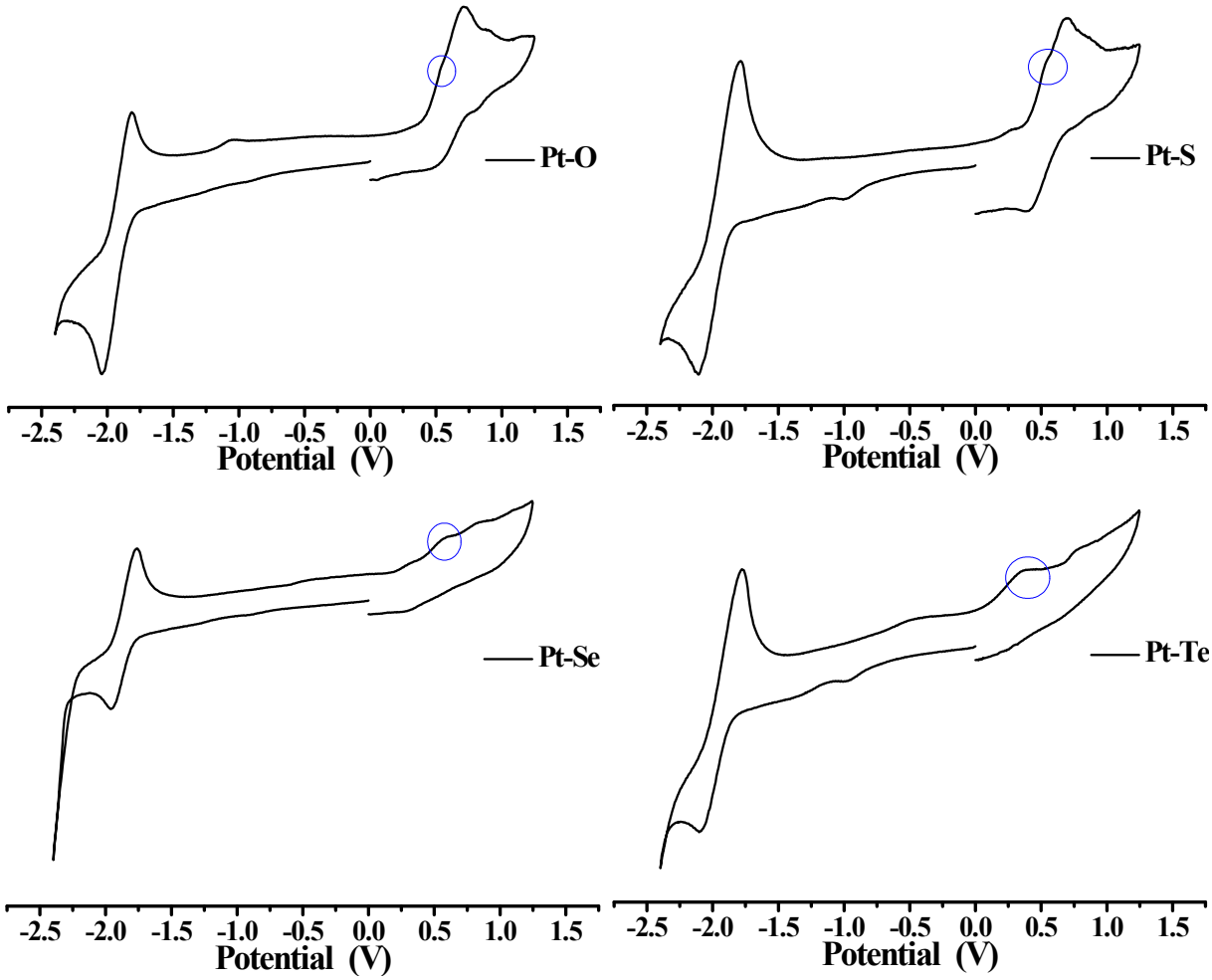


Figure S1. CV traces for these (C^N)Pt(acac)-type complexes.

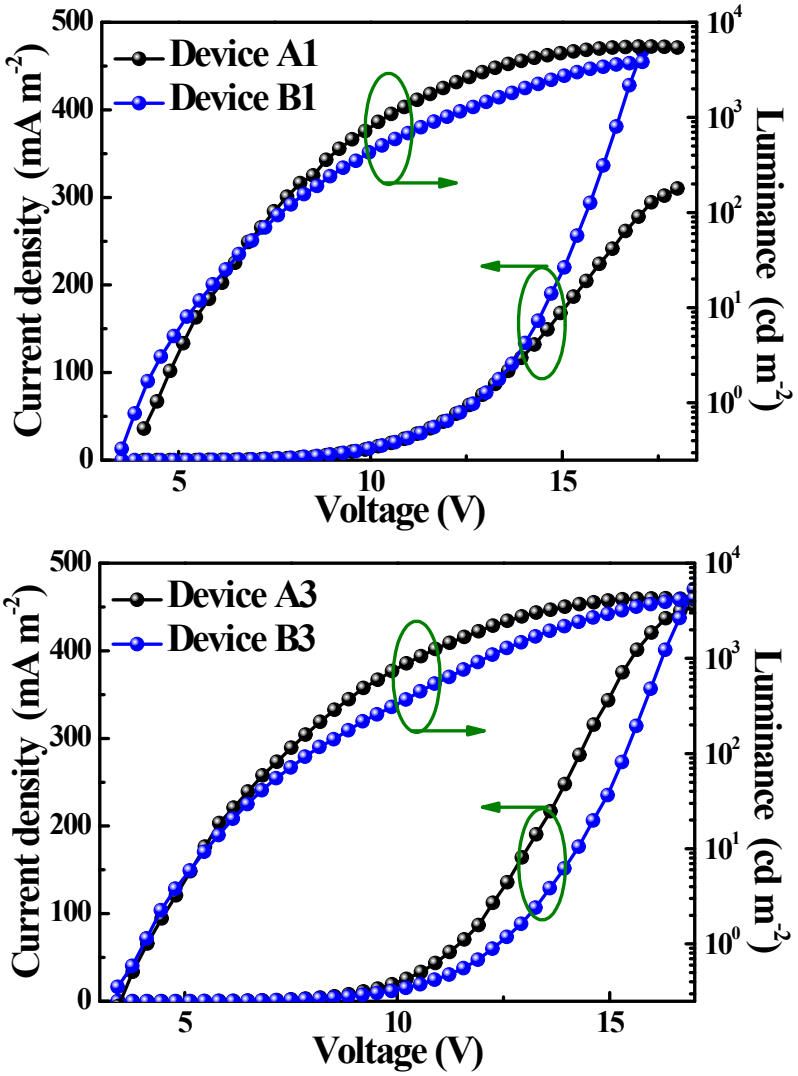


Figure S2. Current density–voltage–luminance (*J*–*V*–*L*) curves for the devices except the optimized ones.

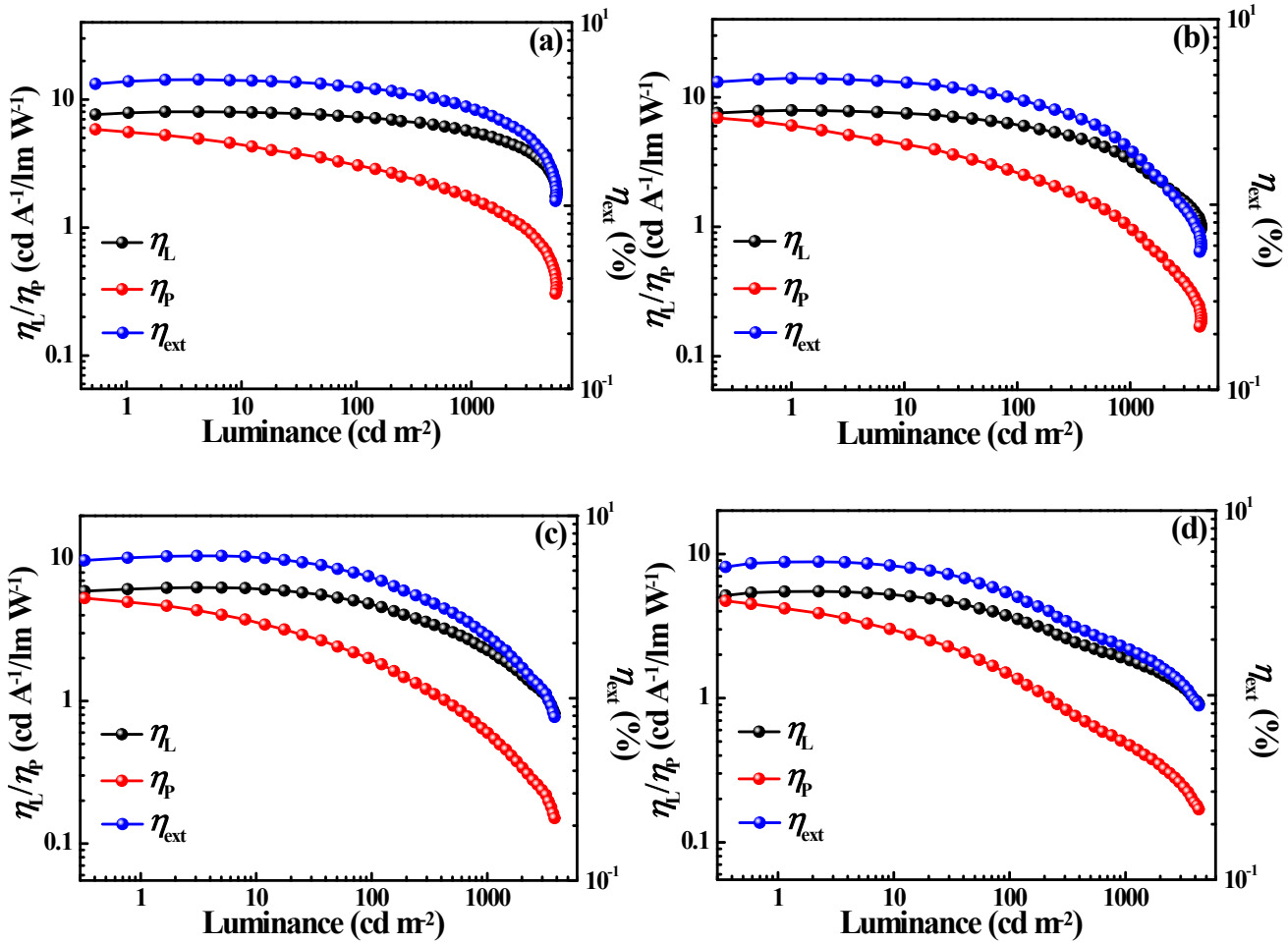


Figure S3. Relationship between EL efficiencies and luminance for the devices except the optimized ones. (a) Device **A1**, (b) Device **A3**, (c) Device **B1** and (d) Device **B3**.