Electronic Supplementary Information

Pt^{II}(C^N)(N-donor ligand)Cl-type complexes showing highly sensitive aggregation-induced phosphorescent emission (AIPE) behavior fulfilled by long-size ligands and distorted molecular configuration

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Contents

Synthesis

Procedures for the Synthesis of CN1-Br

Under the N_2 atmosphere, 2-bromo-9,9-diethyl-7-iodo-9H-fluorene (5.0 g, 11.7 mmol), diphenylamine (2.2 g, 12.9 mmol), CuI (0.25 g, 1.29 mmol) were heated in *p*-xylene (35 mL) at 100 ^{o}C for 20 min. Then, KOH (5.00 g, 88.90 mmol) was added and the reaction mixture was heated to 130 ^{o}C for 48 h. After cooling to room temperature, the reaction was poured into ice water (50 mL). The mixture was extracted with CH_2Cl_2 (3×30 mL). The organic phase was dried over anhydrous Na_2SO_4. After removing solvent, the residue was purified on silica column with petroleum ether as eluent to obtain the product as white solid (3.8 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.52 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.44-7.41 (m, 3H), 7.26-7.24 (m, 4H), 7.12 (d, J = 7.6 Hz, 4H), 7.08-7.02 (m, 3H), 1.96-1.84 (m, 4H), 0.34 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.03, 151.12, 147.99, 147.53, 140.48, 135.69, 130.30, 129.54, 129.36, 129.11, 126.14, 124.44, 124.08, 123.85, 123.77, 123.66, 122.95, 122.75, 122.48, 120.59, 120.45, 120.25, 119.14, 56.42, 32.66, 8.64.

Procedures for the Synthesis of CN2-Br

Following the same procedure for synthesis of **CN1-Br** with starting material of bis(4-methoxyphenyl)amine. The yield of this reaction is 69%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 9.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 4H), 6.95 (s, 1H), 6.90-6.87 (m, 1H), 6.83 (d, J = 8.8 Hz, 4H), 3.89 (s, 6H), 1.95-1.82 (m, 4H), 0.33 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.44, 151.74, 150.66, 148.47, 141.22, 140.46, 133.41, 129.72, 125.92, 125.82, 120.44, 120.00, 119.89, 119.48, 115.94, 114.46, 56.28, 32.61, 8.66.

Procedures for the Synthesis of CN1-1

Under the N_2 atmosphere, **CN1-Br** (2.1 g, 4.5 mmol), 2-(tributylstannyl)pyridine (1.81 g, 4.9 mmol), $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol) were heated in toluene (25 mL) at 110 ^{o}C for 20 min. The reaction mixture was heated to 110 ^{o}C for 18 h. After cooling to room temperature, the solvent as removed under reduced pressure and the residue was purified on silica column with CH_2Cl_2:petroleum ether (1:1, v:v) as eluent to obtain the product as pale yellow solid (1.3 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.71 (d, J = 4.6 Hz, 1H), 7.99-7.60 (m, 6H), 7.29-6.98 (m, 13H), 2.09-1.94 (m, 4H), 0.39 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.03, 151.12, 147.99, 147.53, 140.48, 135.69, 130.30, 129.54, 129.36, 129.11, 126.14, 124.44, 124.08, 123.85, 123.77, 123.66, 122.95, 122.75, 122.48, 120.59, 120.45, 120.25, 119.14, 56.42, 32.66, 8.64.

Procedures for the Synthesis of CN1-2

Following the same procedure for synthesis of **CN1-1** with starting material of **CN2-Br**. The yield of this reaction is 62%.^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.71 (d, J = 4.6 Hz, 1H), 7.96-7.91 (m, 2H), 7.81-7.76 (m, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.08 (d, J = 8.8 Hz, 4H), 6.98 (s, 1H), 6.93-6.82 (m, 5H), 3.82 (s, 6H), 2.09-1.89(m, 4H), 0.38 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.77, 155.34, 151.66, 150.18, 149.47, 148.39, 142.59, 141.30, 136.88, 136.54, 134.21, 125.90, 125.74, 121.55, 120.99, 120.36, 120.31, 118.81, 116.22, 114.56, 56.77, 55.51, 32.75, 8.69.

Procedures for the Synthesis of CN1-3

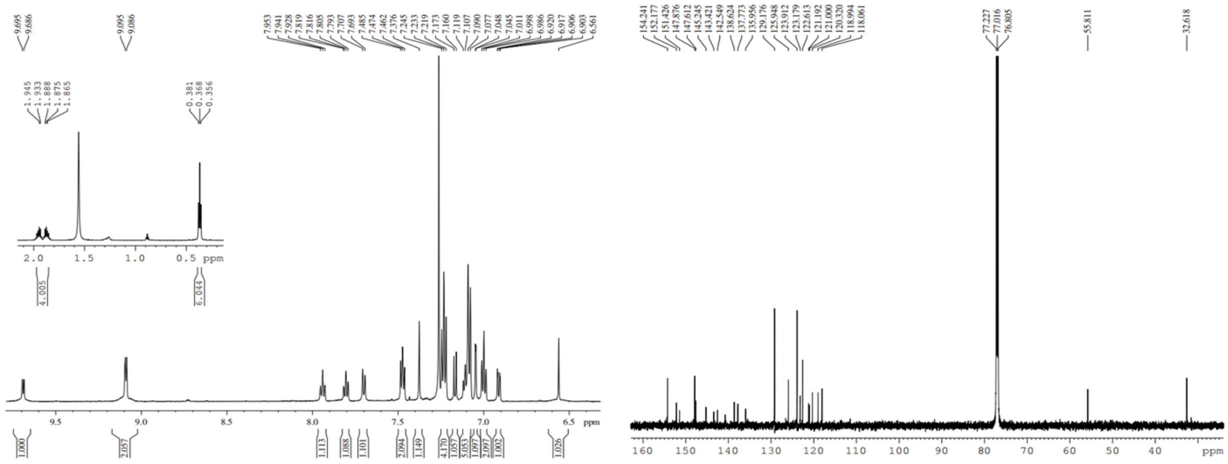
Under the N_2 atmosphere, **CN1-Br** (1.5 g, 2.9 mmol), 4-pyridylboronic acid (0.68 g, 3.5 mmol), $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol) were heated in toluene (15 mL) and 2M K_2CO_3 (15 mL) at 110 ^oC for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3×25 mL). The organic phase was dried over anhydrous Na_2SO_4. After removing solvent, the residue was purified on silica column with CH_2Cl_2:EA (5:1, v:v) as eluent to obtain the product as white solid (1.1 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75 (d, J = 4.4 Hz, 2H), 7.99-7.60 (m, 5H), 7.29-6.98 (m, 13H), 2.11-1.96 (m, 4H), 0.38 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.14, 148.09, 147.83, 140.58, 136.19, 131.20, 129.66, 129.15, 127.34, 125.26, 124.33, 123.59, 123.36, 123.12, 122.82, 122.36, 121.79, 120.95, 120.31, 120.02, 119.52, 57.44, 32.61, 8.67.

Procedures for the Synthesis of CN2-1

Under the N_2 atmosphere, **CN1-Br** (2.0 g, 4.3 mmol), bis(pinacolato)diboron (1.2 g, 4.7 mmol), $Pd(dppf)Cl_2$ (0.24 g, 0.21 mmol) and AcOK (1.26g, 12.8 mmol) were heated in dioxane (30 mL) at 110 ^oC for 18 h. After cooling to room temperature, the solvent as removed under reduced pressure and the residue was purified on silica column with CH_2Cl_2:petroleum ether (1:3, v:v) as eluent to obtain the crude intermediate compound as white solid (1.33 g, 64%). Under the N_2 atmosphere, crude intermediate compound (0.8 g, 1.5 mmol), 1-chloroisoquinoline (0.26 g, 1.6 mmol), $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol) were heated in toluene (15 mL) and 2M K_2CO_3 (15 mL) at 110 ^oC for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4. After removing solvent, the residue was purified on silica column with CH_2Cl_2: petroleum ether (4:1, v:v) as eluent to obtain the product as pale yellow solid (0.6 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.65 (d, J = 6.0 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.73-7.61 (m, 5H), 7.58-7.54 (m, 1H), 7.28-7.26 (m, 3H), 7.24 (s, 1H), 7.16 (d, J = 8.0 Hz, 5H), 7.07 (d, J = 4.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 2H), 2.06-1.89 (m, 4H), 0.43 (t, J = 7.4 Hz, 6H).

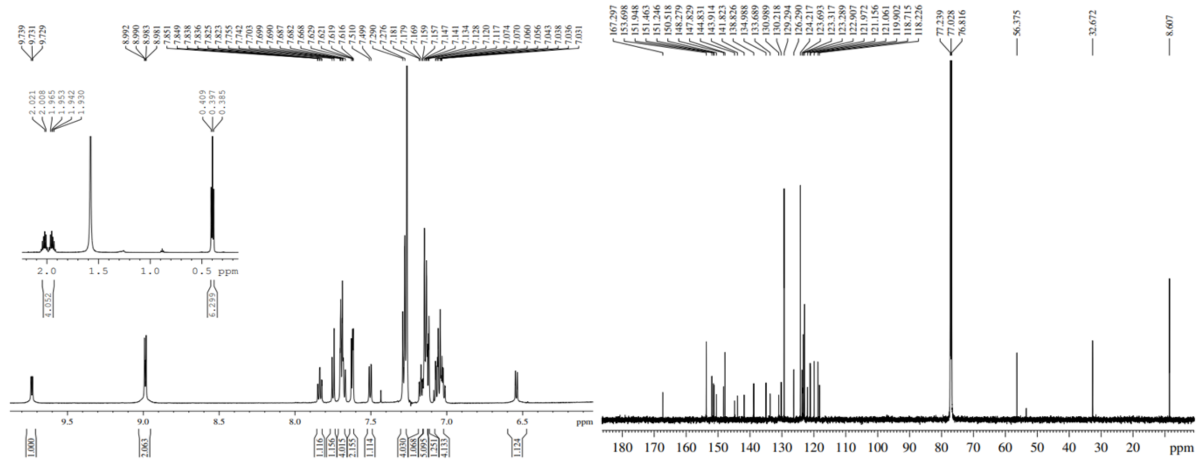
Procedures for the Synthesis of CN2-2

Following the same procedure for synthesis of **CN2-1** with starting material of **CN2-Br**. The yield of this reaction is 62%.^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.64 (d, J = 6.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.72-7.53 (m, 6H), 7.11-7.09 (m, 4H), 7.02 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 4.4 Hz, 1H), 6.86-6.84 (m, 4H), 3.83 (s, 6H), 2.05-1.87 (m, 4H), 0.43 (t, J = 7.4 Hz, 6H).



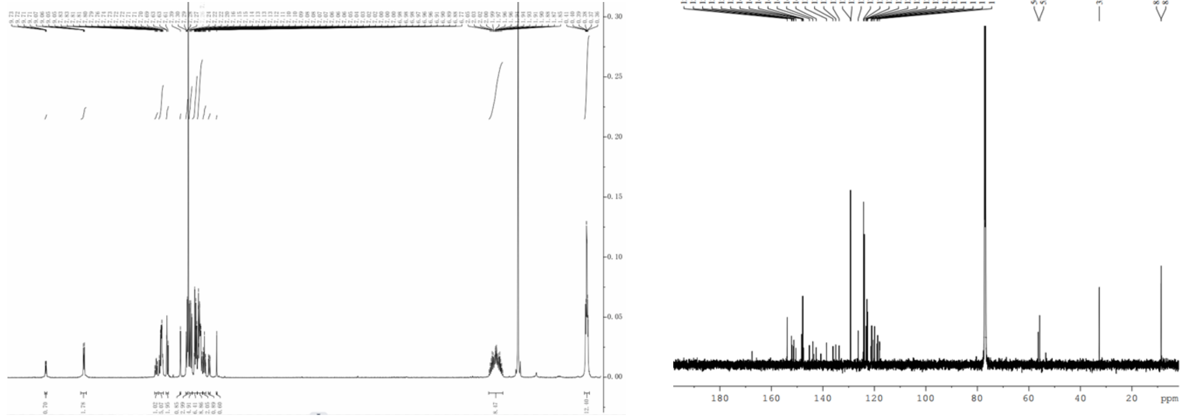
^{1}H-NMR ^{13}C-NMR

(a) P1



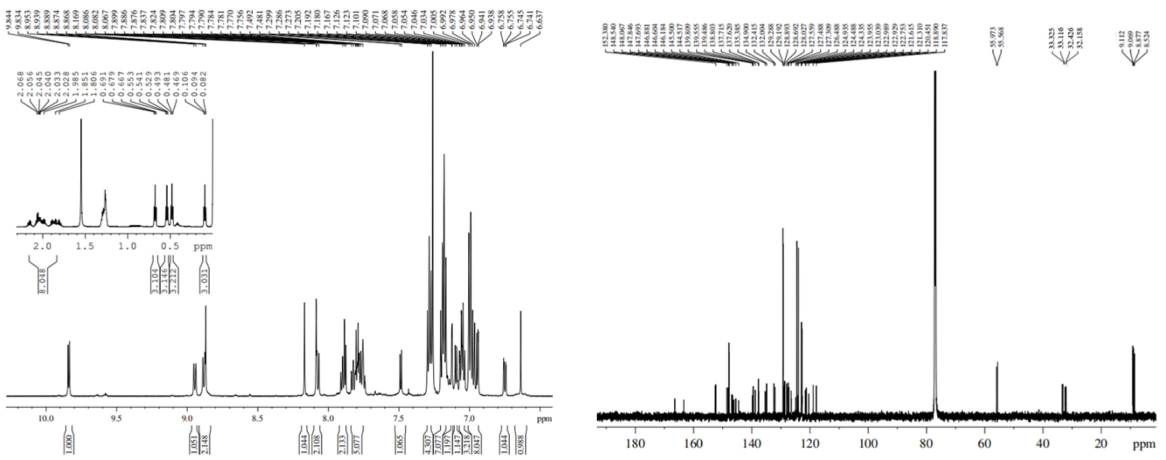
^{1}H-NMR ^{13}C-NMR

(b) P2



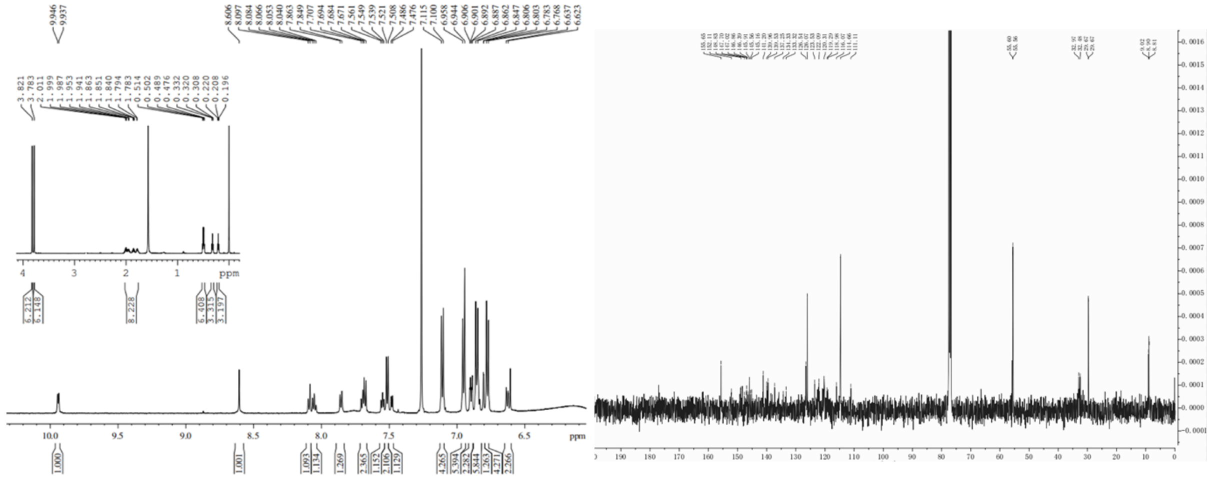
^{1}H-NMR ^{13}C-NMR

(c) P3



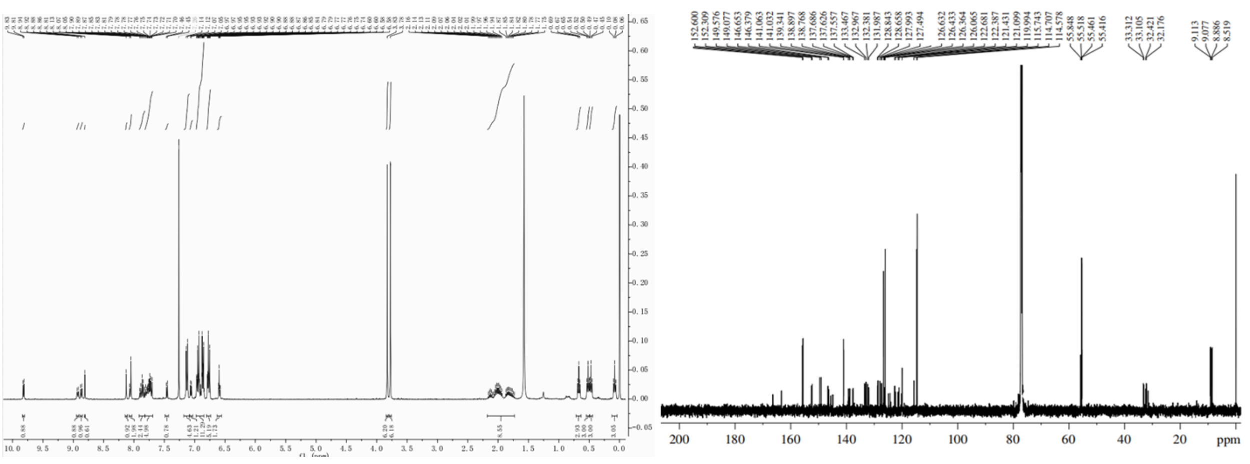
^{1}H-NMR ^{13}C-NMR

(d) P4



^{1}H-NMR ^{13}C-NMR

(e) P5



^{1}H-NMR ^{13}C-NMR

(f) P6

Figure S1. NMR spectra for the Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.

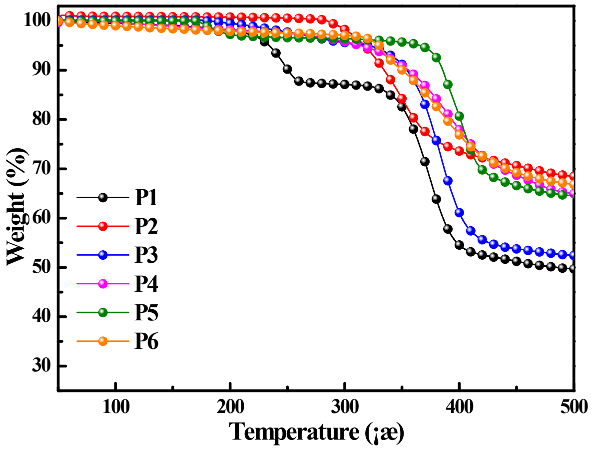
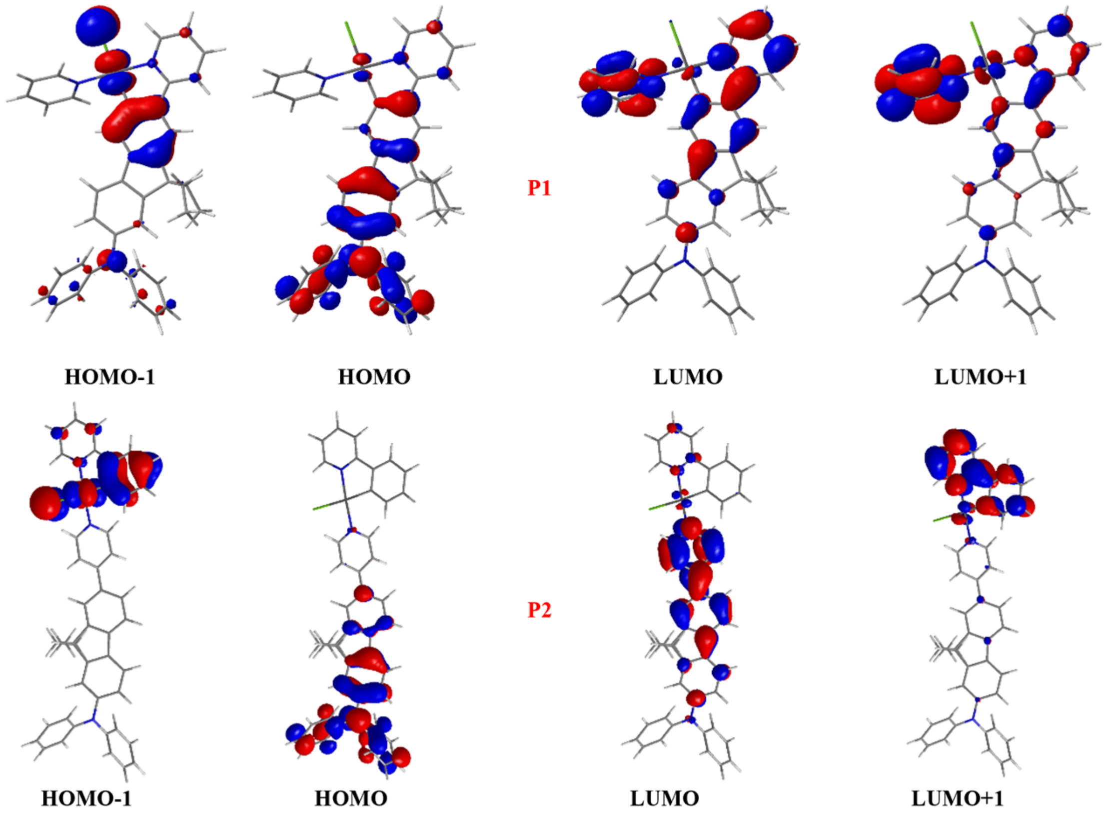


Figure S2. TGA curves for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.



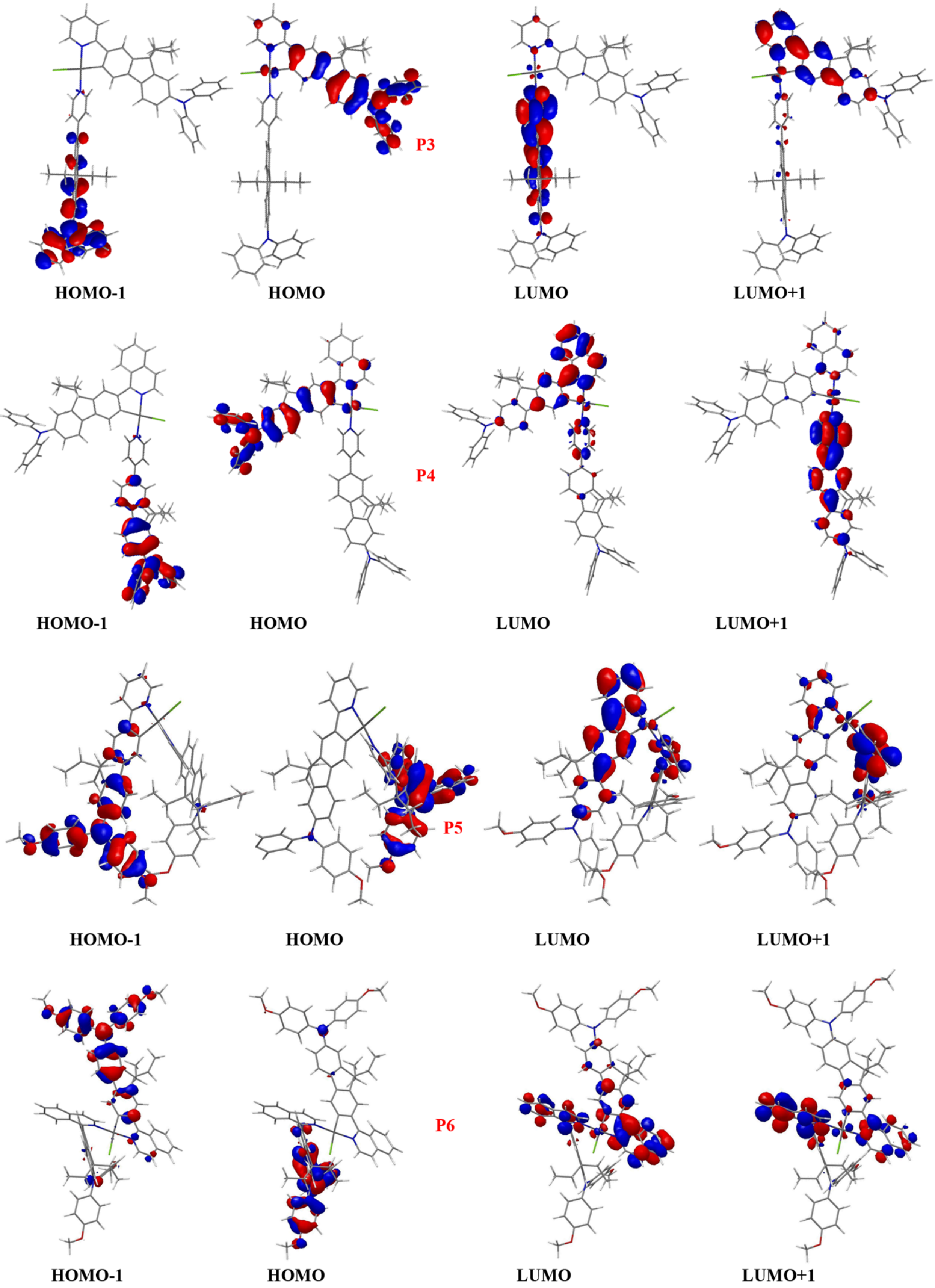


Figure S3. Patterns of the key MOs for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.

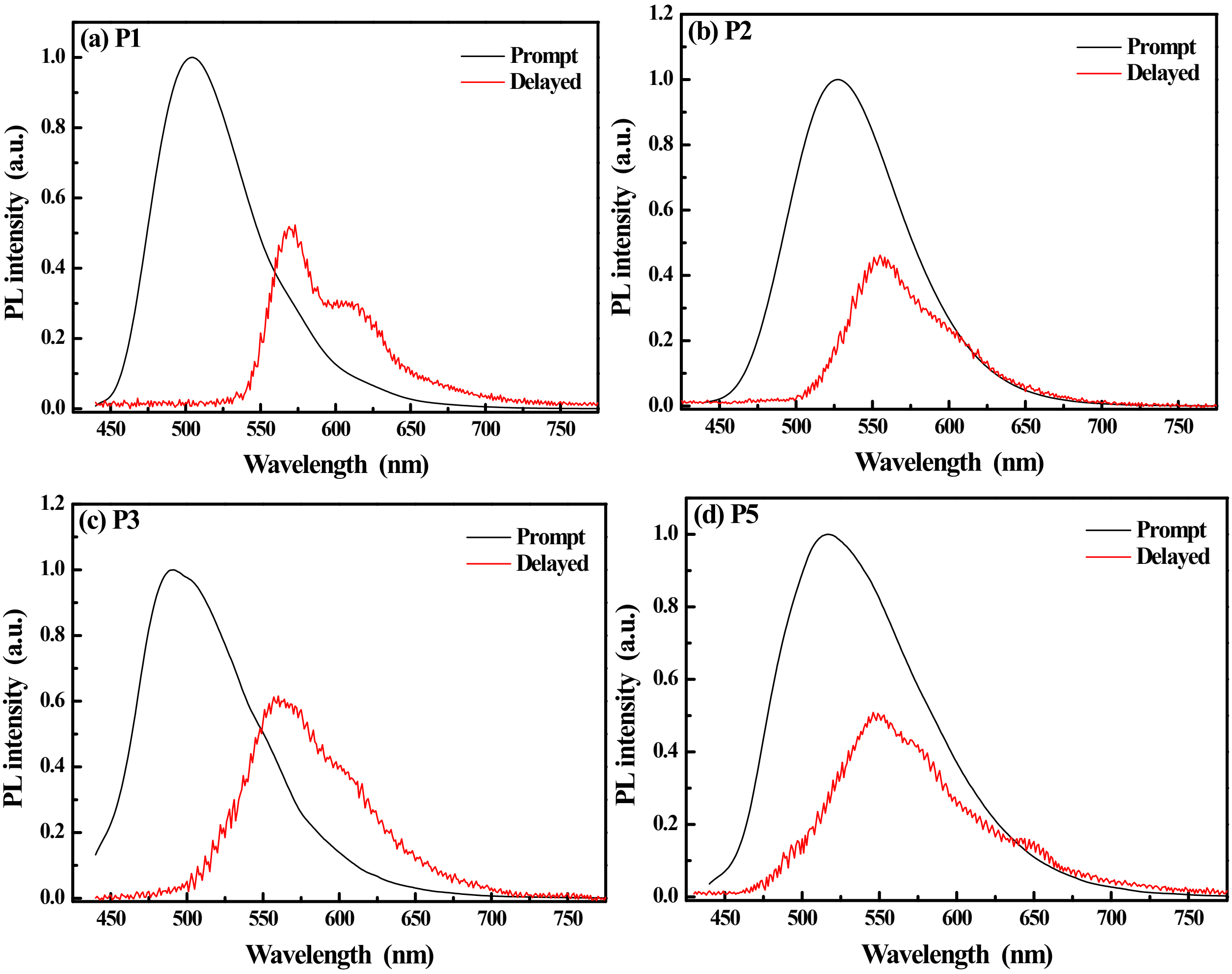


Figure S4. Prompt and delayed (50 ns) PL spectra in CH_2Cl_2 for **P1**, **P2**, **P3** and **P5** at 293 K.

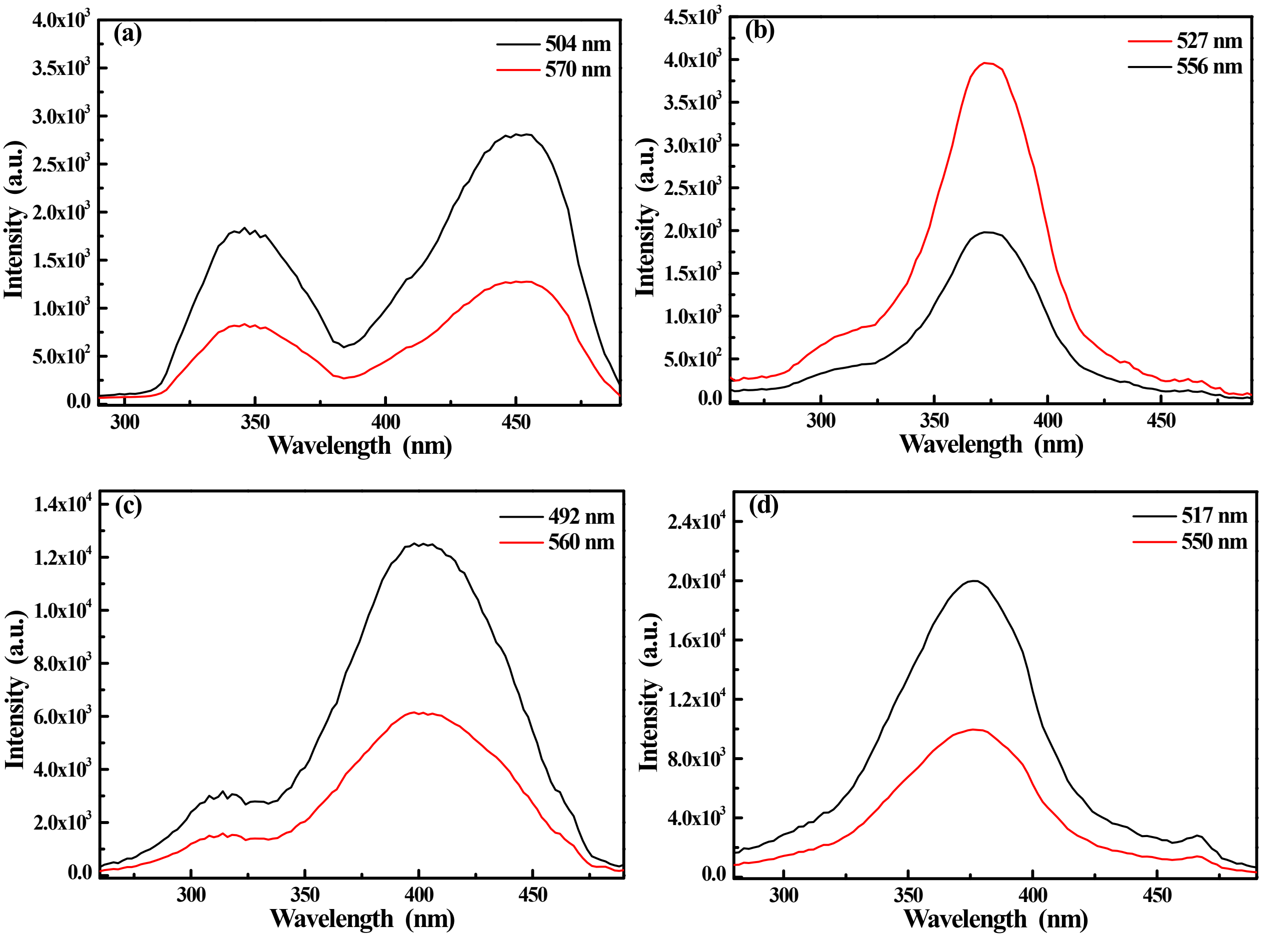


Figure S5. Excitation spectra at different emission wavelengths for **P1**, **P2**, **P3** and **P5** inCH_2Cl_2 at 293 K.

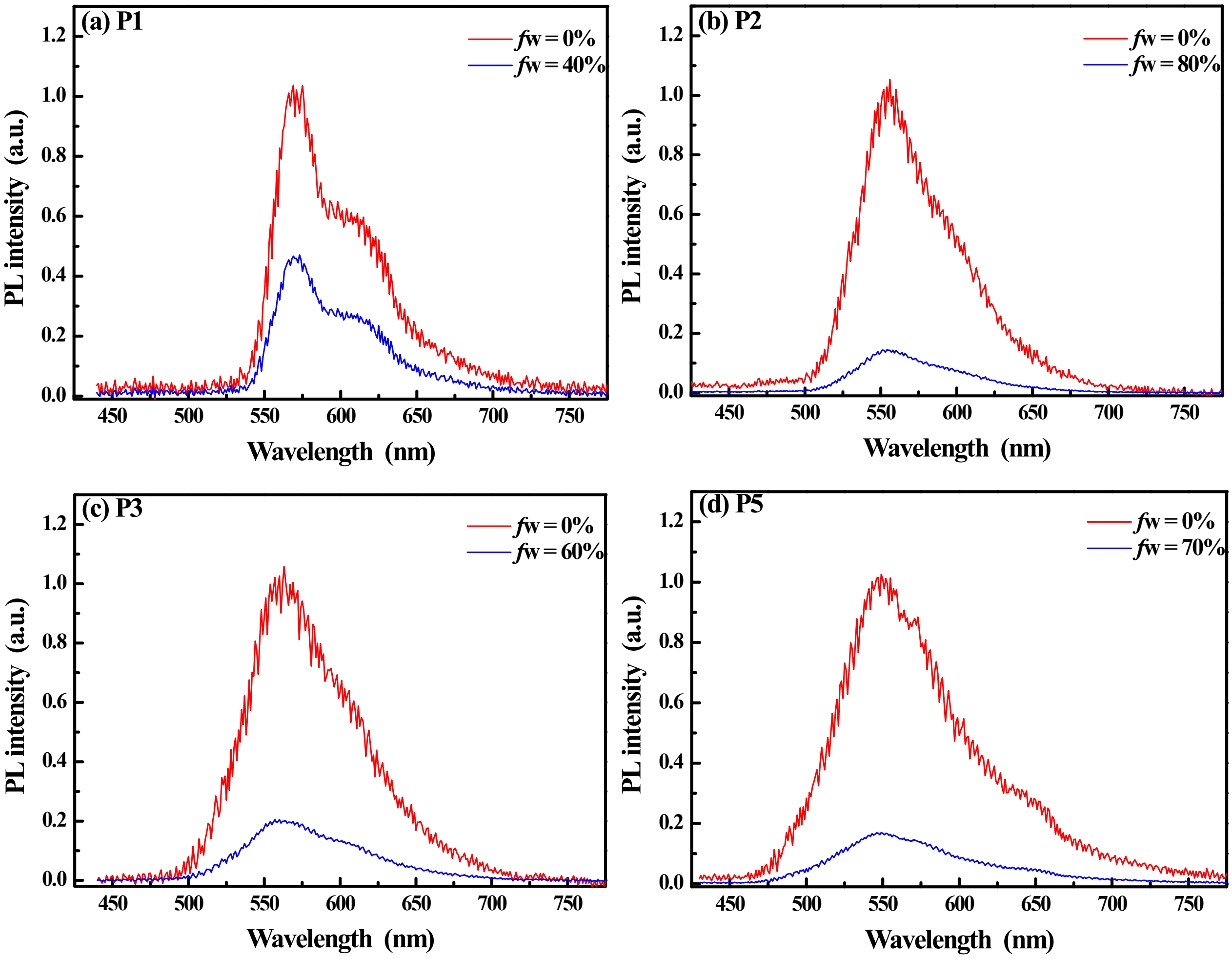


Figure S6. Delayed (50 ns) PL spectra in THF-H_2O mixture for **P1**, **P2**, **P3** and **P5** at 293 K.

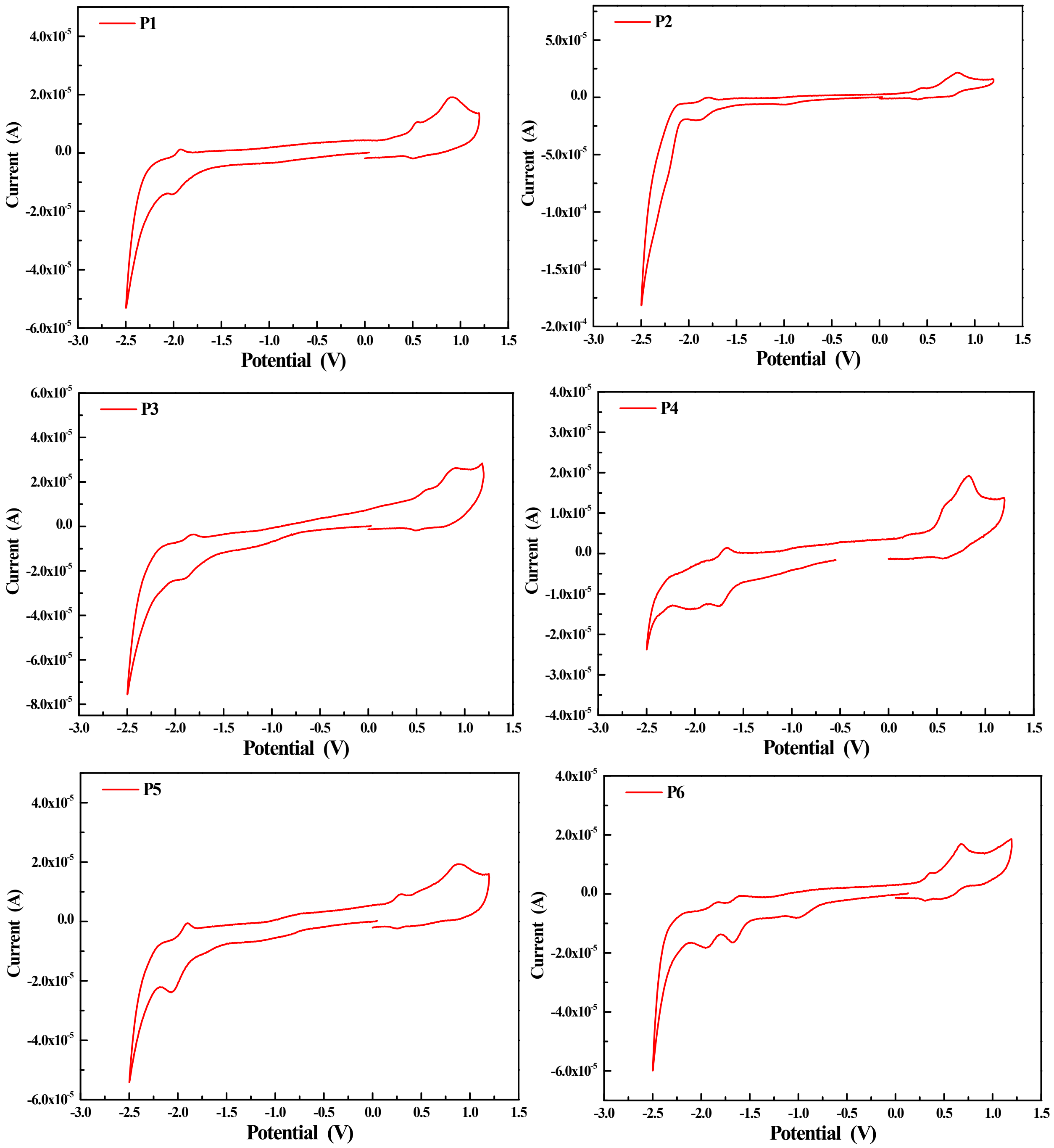


Figure S7. CV curves for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.

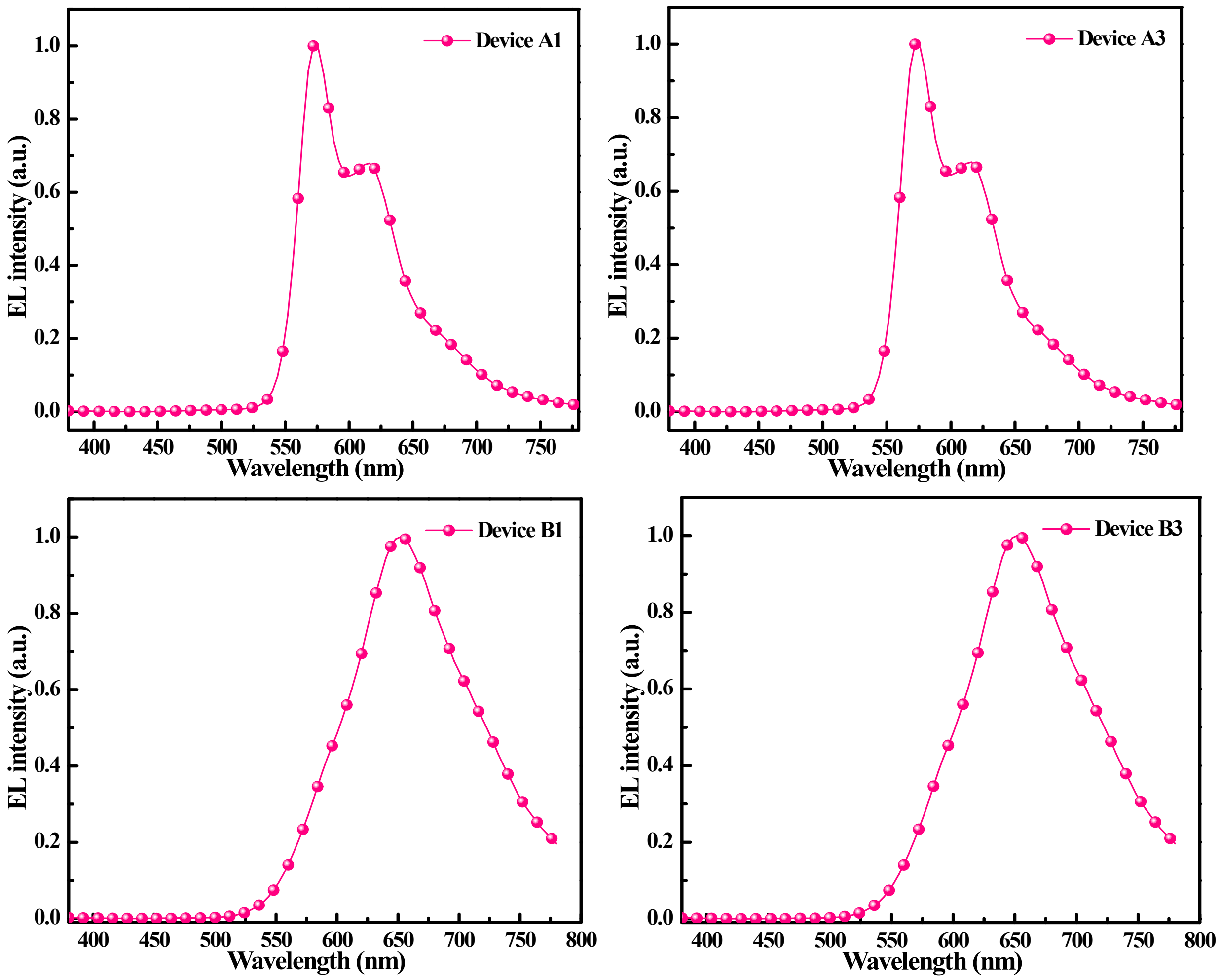


Figure S8. EL spectra for devices **A1**, **A3**, **B1** and **B3** at *ca.* 10 V.

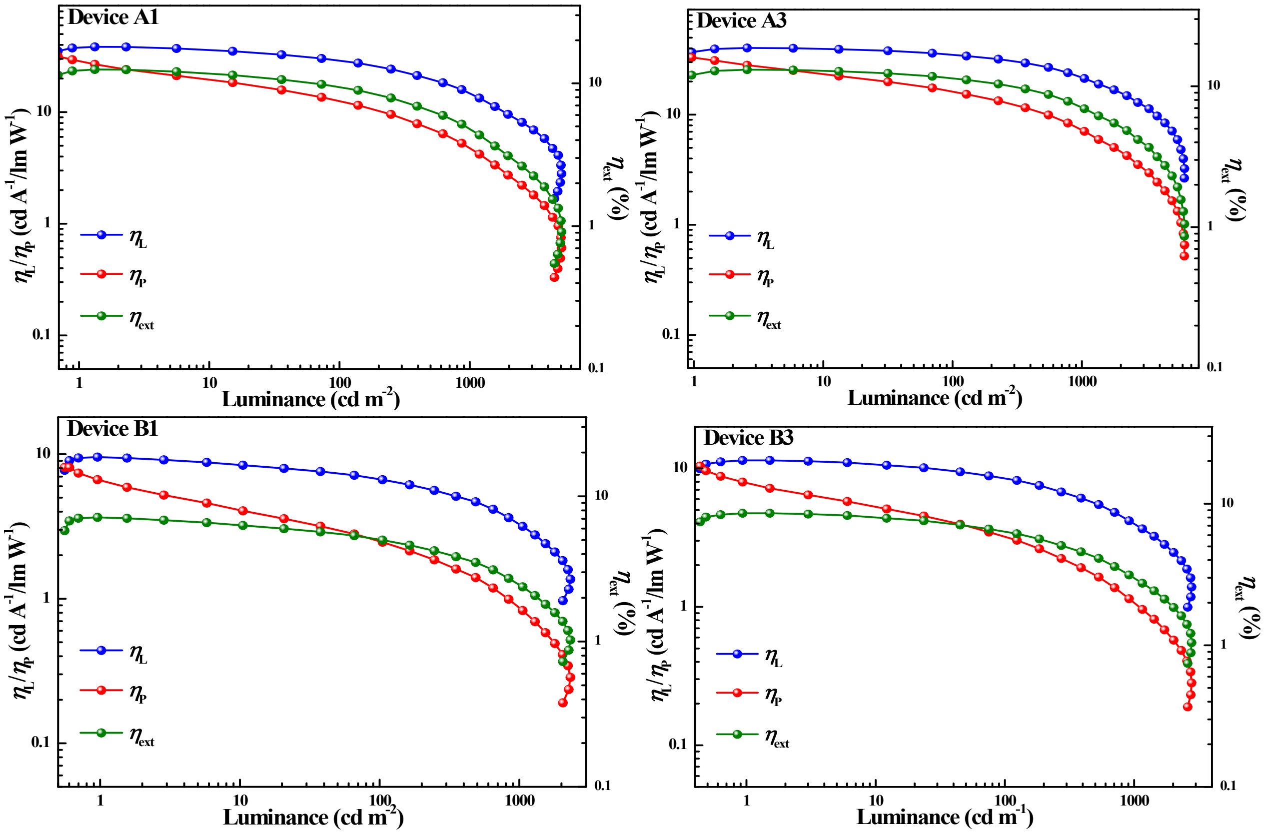


Figure S9. EL efficiencies *vs.* luminance curves for devices **A1**, **A3**, **B1** and **B3**.