Electronic Supplementary Information

Aggregation-Induced Phosphorescent Emission (AIPE) Behaviors in Pt^{II}(C^N)(N-donor ligand)Cl-type Complexes Through Restrained D_{2d} Deformation of the Coordinating Skeleton and Their Optoelectronic Properties

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Contents

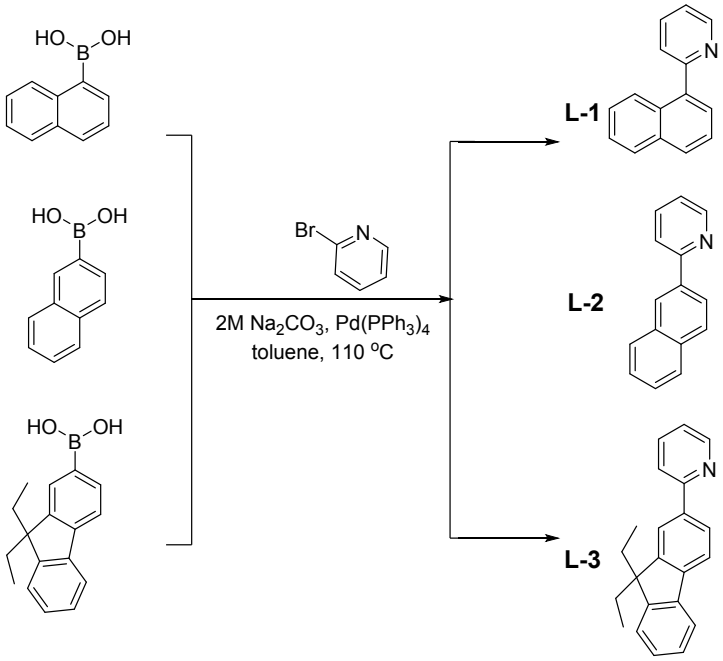
Procedures for the Synthesis of C^N-type ligands

Synthetic scheme for C^N-type ligands are shown in Scheme S1. Under the N_2 atmosphere, 1-naphthaleneboronic acid, 2-naphthaleneboronic acid or 9,9-diethyl-9H-fluorene-2-boronic acid (1.0 equiv.), 2-bromopyridine (1.2 equiv.) and $Pd(PPh_3)_4$ (5 mol%) were heated to 110 ^oC in a mixture of 5 mL of 2M K_2CO_3 and 15 mL of degassed THF for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane, the organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The residue was obtained as a crude product, which was chromatographed on a silica column to produce the pure product.[1,2]

L-1: yellowish oil; yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.79 (dd, J = 4.8, 1.7 Hz, 1 H), 8.08 (dd, J =7.1, 2.9 Hz, 1 H), 7.91 (d, J = 8.1, 2 H), 7.82 (dt, J = 7.7, 1.7 Hz, 1 H), 7.56 (m, 5H), 7.33 (ddd, J = 7.7, 4.8, 1.1 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.5, 149.7, 138.7, 136.5, 134.2, 131.4, 129.0, 128.5, 127.6, 126.6, 126.0, 125.8, 125.4, 125.2, 122.1.

L-2: white solid; yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.75 (d, J = 4.2 Hz, 1 H), 8.49 (s, 1H), 8.14 (dd, J = 8.6, 1.5 Hz, 1 H), 7.90 (m, 4H), 7.80 (td, J = 7.5, 1.8 Hz, 1 H), 7.50 (m, 2H), 7.26 (dd, J = 7.5, 4.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 157.3, 149.7, 136.7, 133.5, 133.4, 128.6, 128.3, 127.6, 126.4, 126.2, 124.5, 122.1, 120.7.

L-3: white solid; yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): d 8.71 (dd, J = 0.8, 4.9 Hz, 1 H), 8.06 (d, J = 1.6 Hz, 1H), 7.59 (dd, J = 1.6, 7.8 Hz, 1H), 7.78–7.61 (m, 4H), 7.33–7.29 (m, 3H), 7.15–7.10 (m, 1H), 2.17–1.99 (m, 4H), 0.35 (t, J = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 157.38, 150.20, 150.10, 149.30, 142.23, 140.71, 137.93, 136.36, 127.10, 126.63, 125.62, 122.66, 121.58, 121.02, 120.29, 119.71, 119.59, 56.15, 32.68, 8.55.



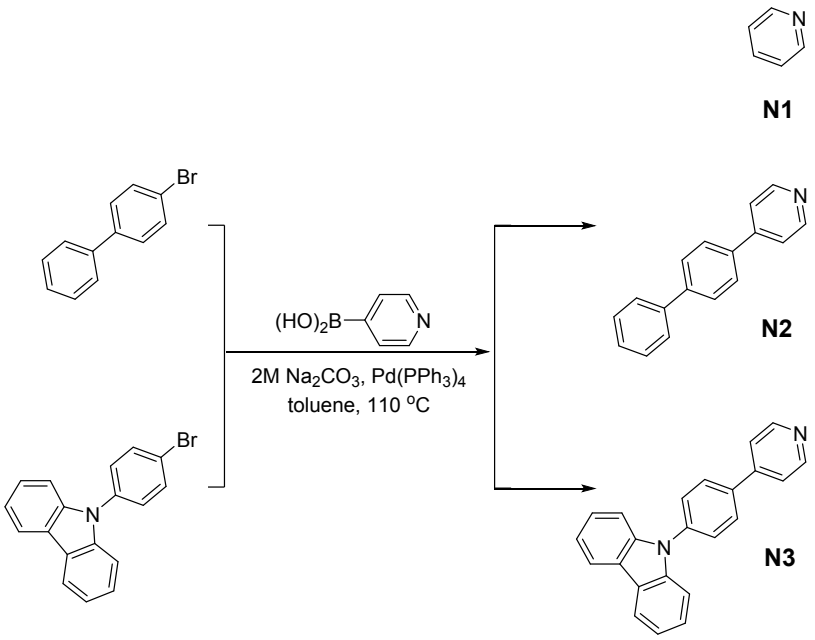
Scheme S1 Synthetic scheme for the C^N-type ligands.

Procedures for the Synthesis of N-Donor Ligands

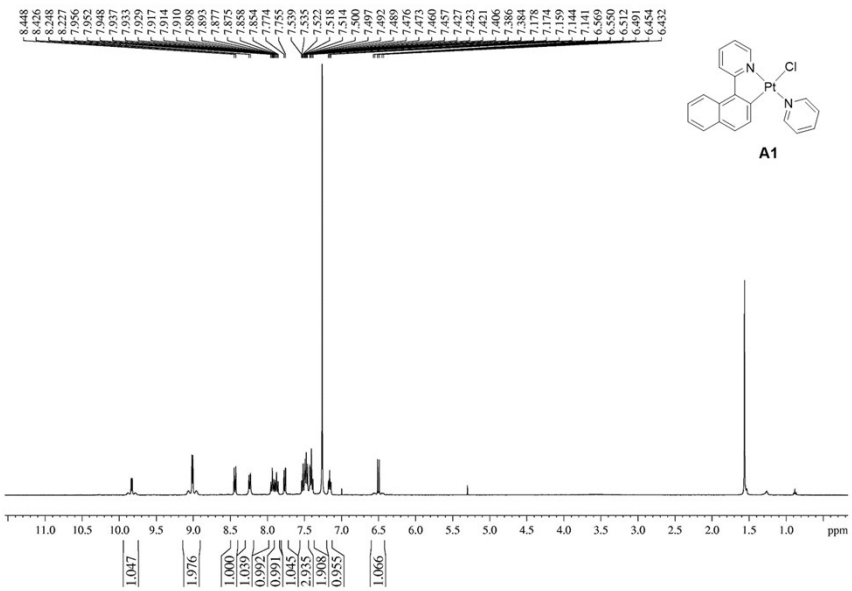
Synthetic scheme for N-donor ligands are shown in Scheme S2. Under the N_2 atmosphere, the corresponding borate compound or boronic acid (1.0 equiv.), pyridine-4-boronic acid (1.2 equiv.) and $Pd(PPh_3)_4$ (5 mol%) were heated to 110 °C in a mixture of 5 mL of 2M K_2CO_3 and 15 mL of degassed THF for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane, the organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The residue was obtained as a crude product, which was chromatographed on a silica column to produce the pure product.[3,4]

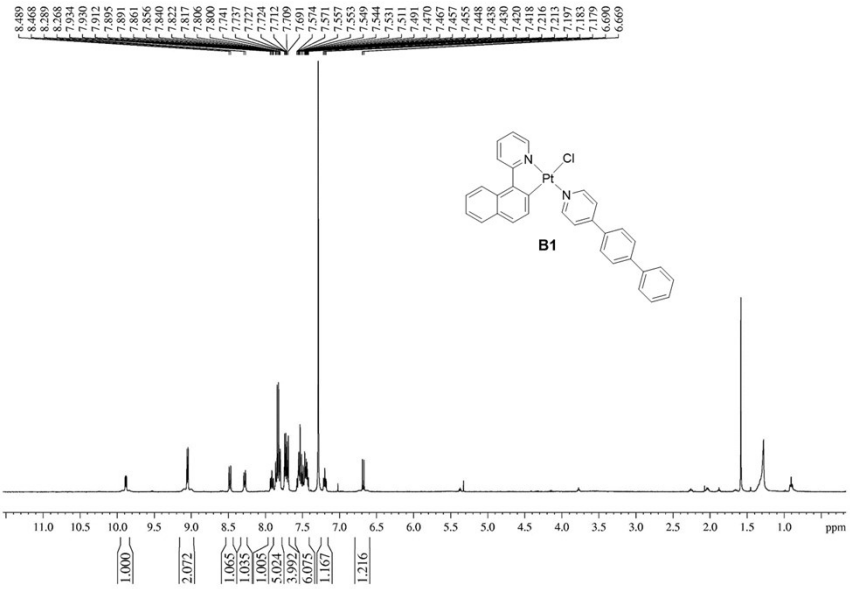
N2: white solid; yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.68 (d, J = 5.5 Hz, 2H), 7.72 (s, 4H), 7.64 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 6.0 Hz, 2H), 7.48 (dd, J = 7.6, 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.2, 148.1, 142.1, 140.3, 136.9, 129.0, 127.9, 127.8, 127.5, 127.2, 121.6.

N3: white solid; yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.76-8.72 (m, 2H), 8.20-8.14 (m, 2H), 7.90-7.85 (m, 2H), 7.74- 7.69 (m, 2H), 7.62-7.59 (m, 2H), 7.50-7.41 (m, 4H), 7.35-7.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.6, 147.5, 140.8, 138.8, 137.2, 128.6, 127.7, 126.2, 123.7, 121.7, 120.6, 120.4, 109.9.



Scheme S2 Synthetic scheme for the N-donor ligands.

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Cl
Pt
N
N
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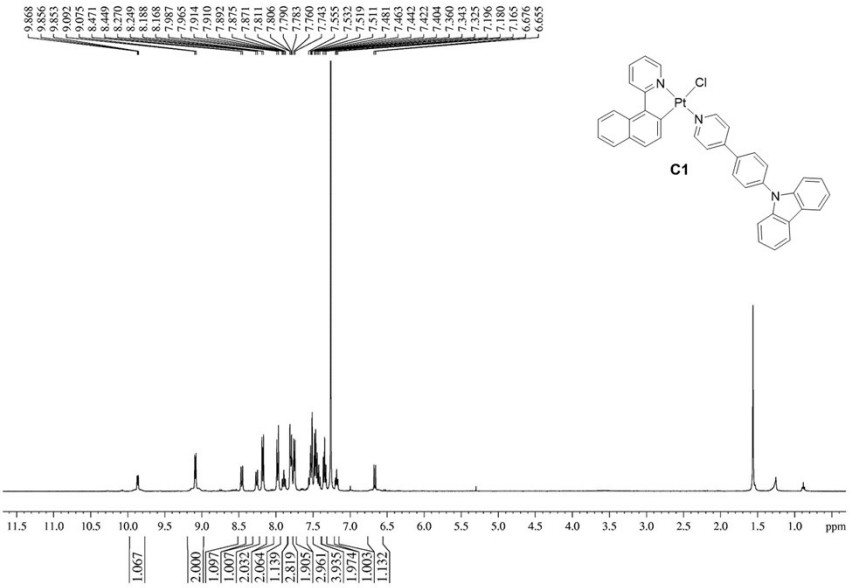
1.000
2.072
1.065
1.035
1.005
5.024
3.992
6.075
1.167
1.216


C1
Cl
Pt
N
N
N
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1.067
2.000
1.097
1.007
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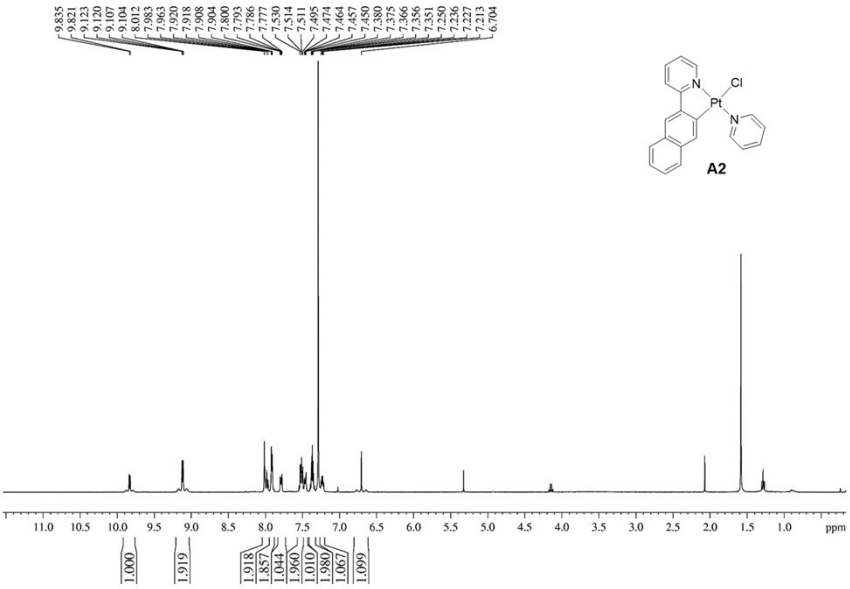
2.064
1.139
2.819
1.905
2.961
3.935
1.974
1.003
1.132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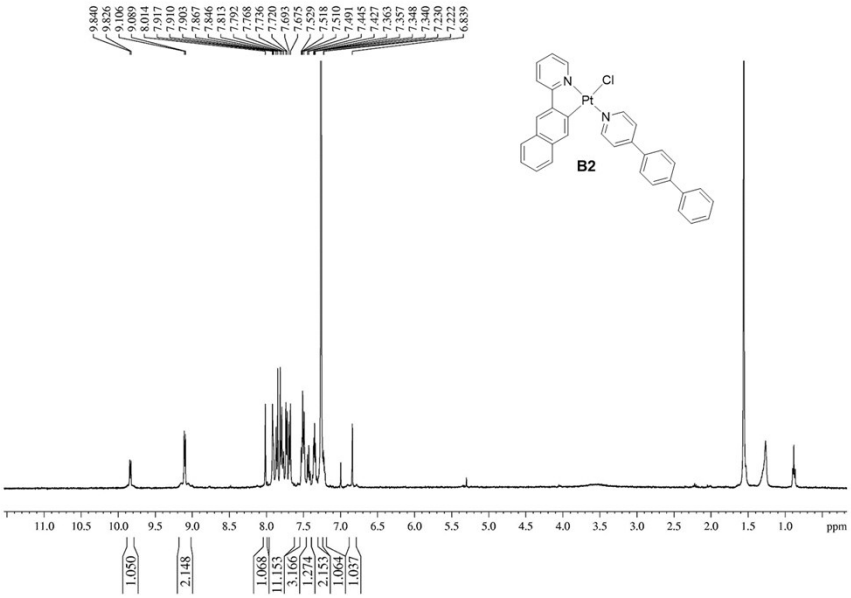
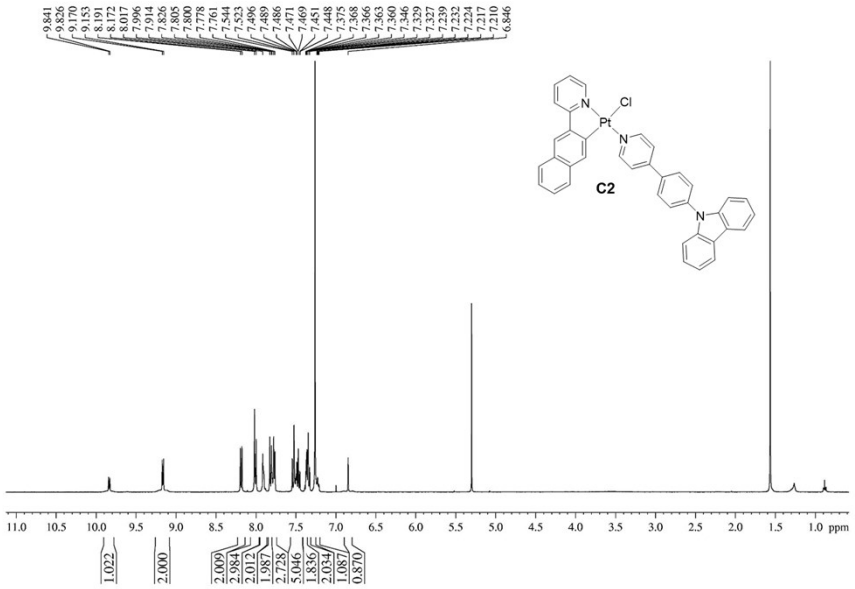
Pt
N
N
ppm


B2
Cl
Pt
N
N
ppm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Cl
Pt
N
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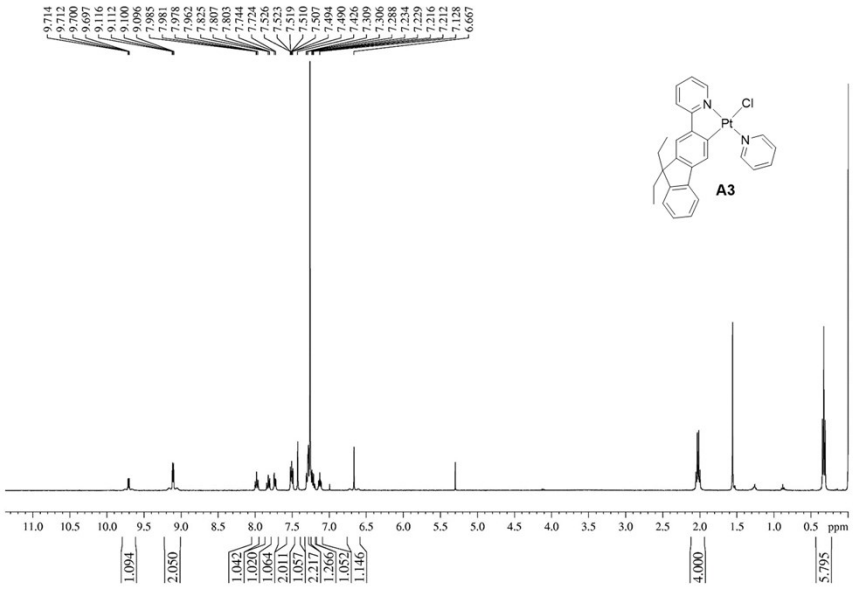
2.012
1.987
2.728
5.046
1.836
2.034
1.087
0.870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Cl
Pt
N
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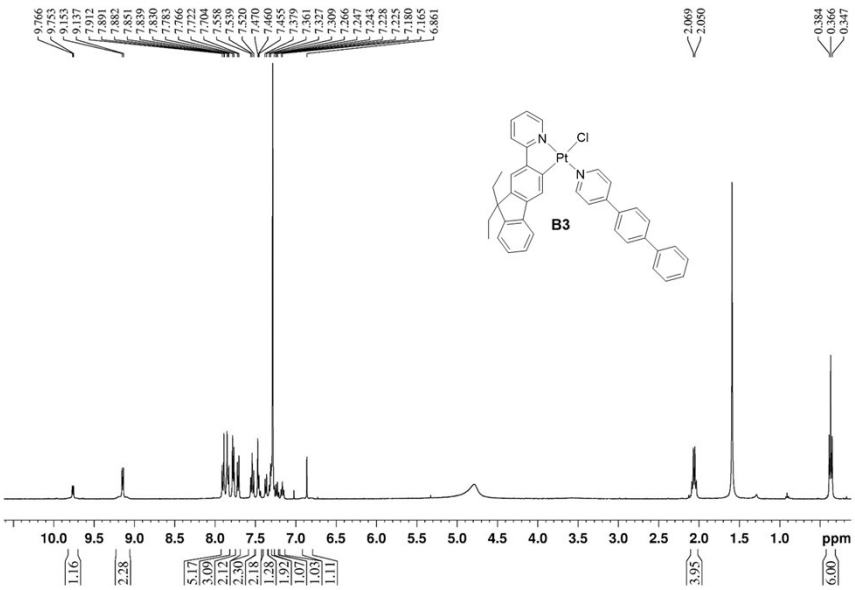
1.094
2.050
1.042
1.020
1.064
2.011
1.057
2.217
1.266
1.052
1.146
4.000
5.795



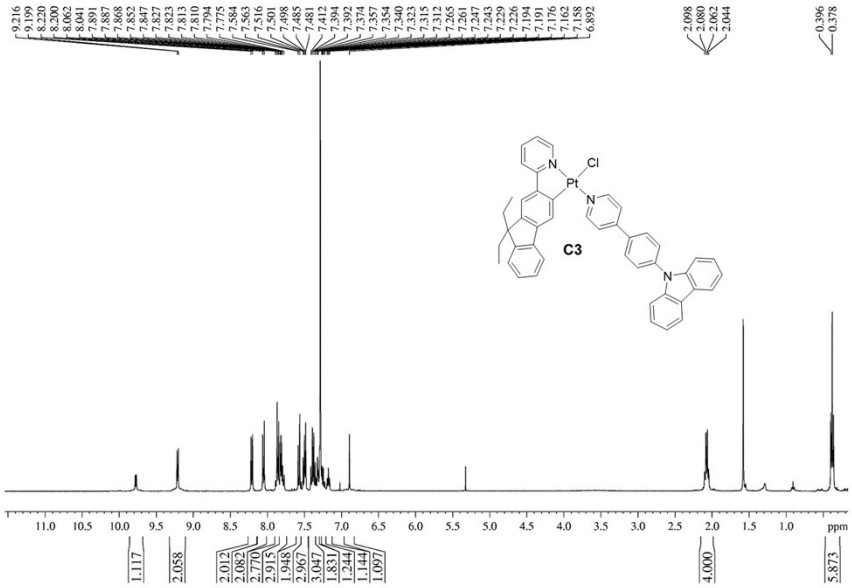
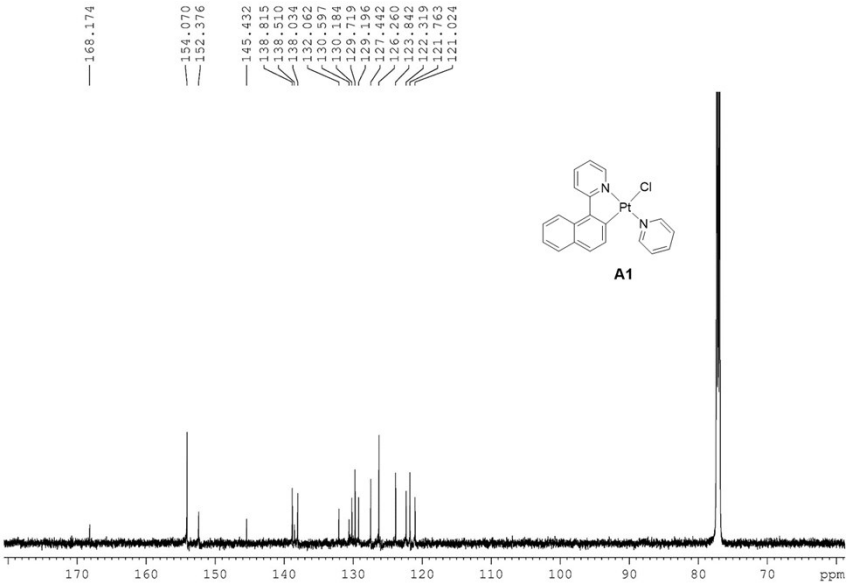


Fig. S1 ^{1}H NMR spectra for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.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154.070
152.376
145.432
138.815
138.510
138.034
132.062
130.597
130.184
129.719
129.196
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122.319
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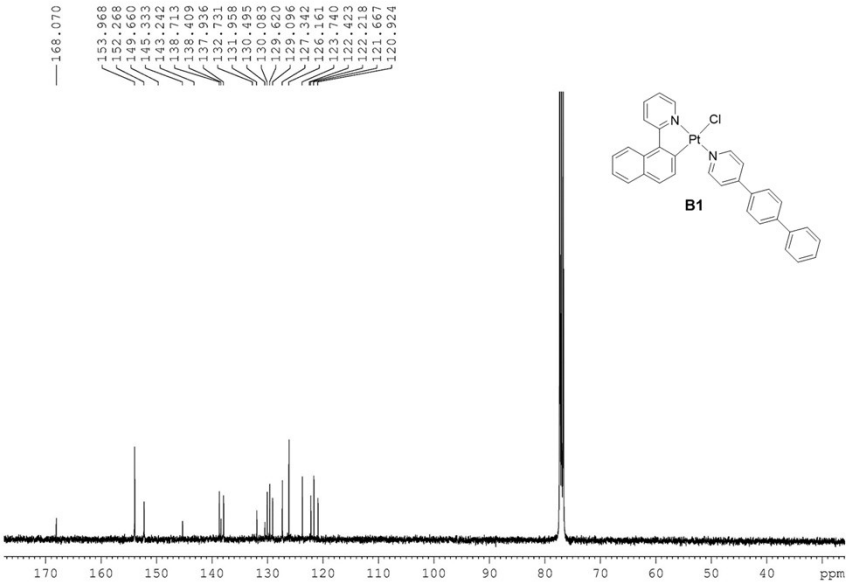
N
Cl
Pt
N
A1
170 160 150 140 130 120 110 100 90 80 70 ppm


168.070
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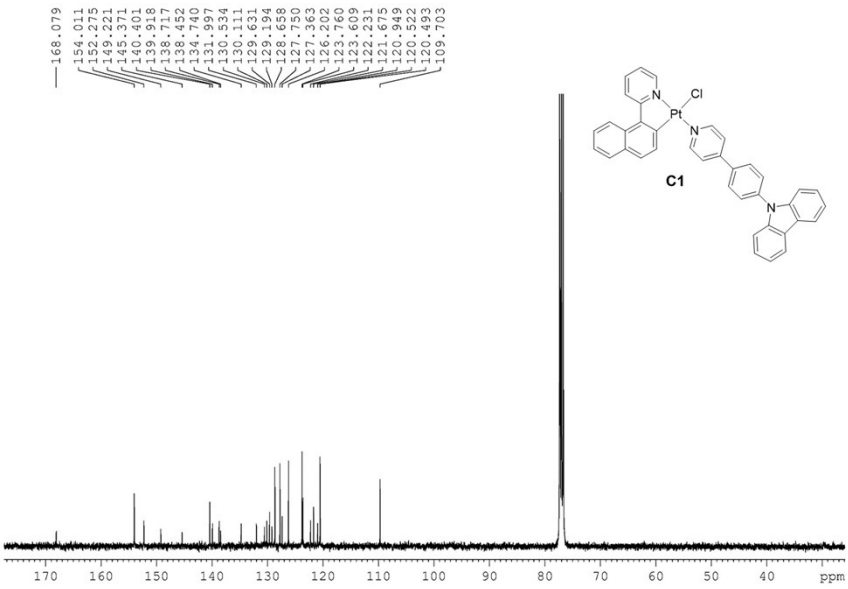
149.660
145.333
143.242
138.713
138.409
137.936
132.731
131.958
130.495
130.083
129.620
129.096
127.342
126.161
123.740
122.423
122.218
121.667
120.924
N
Cl
Pt
N
B1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm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152.275
149.221
145.371
140.401
139.918
138.717
138.452
134.740
131.997
130.534
130.111
129.631
129.194
128.658
127.750
127.363
126.202
123.760
123.609
122.231
121.675
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120.522
120.493
109.703
C1
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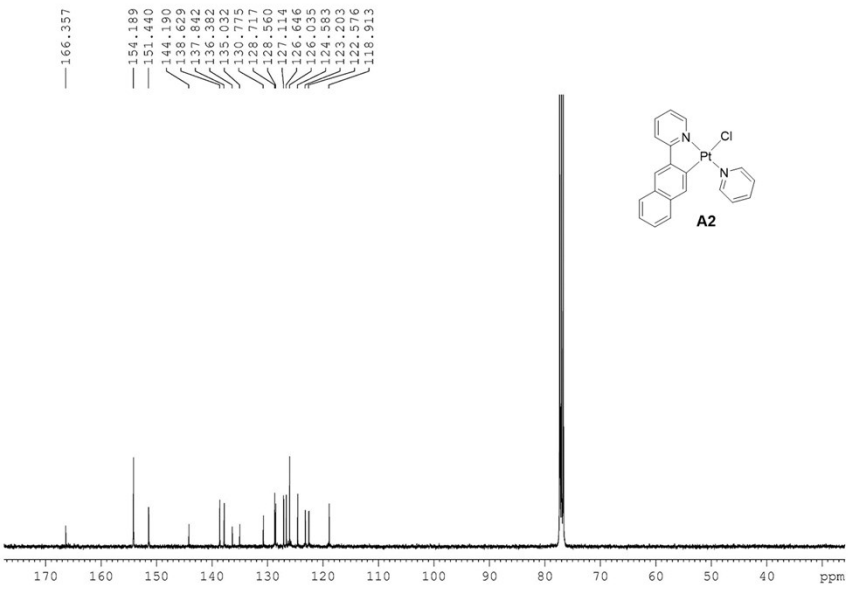
166.357
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151.440
144.190
138.629
137.842
136.382
135.032
130.775
128.717
128.560
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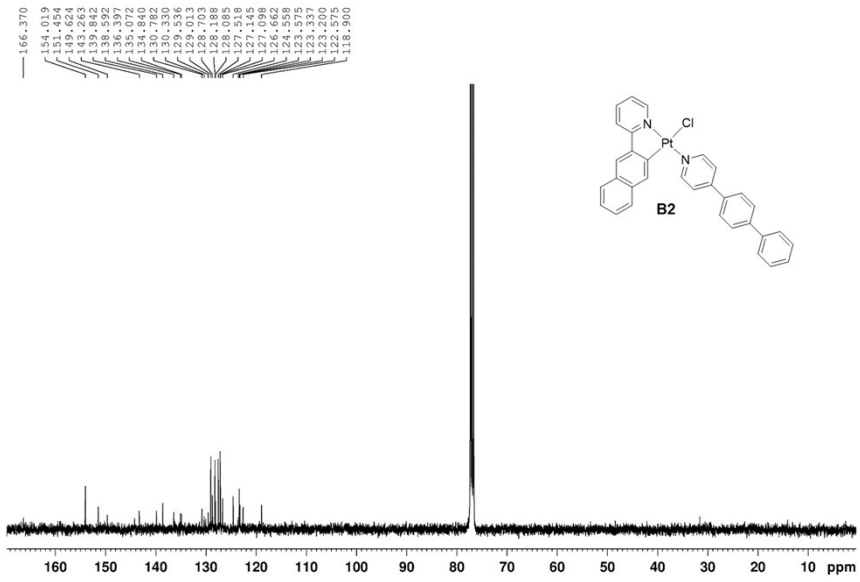
126.035
124.583
123.203
122.576
118.913
A2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


166.370
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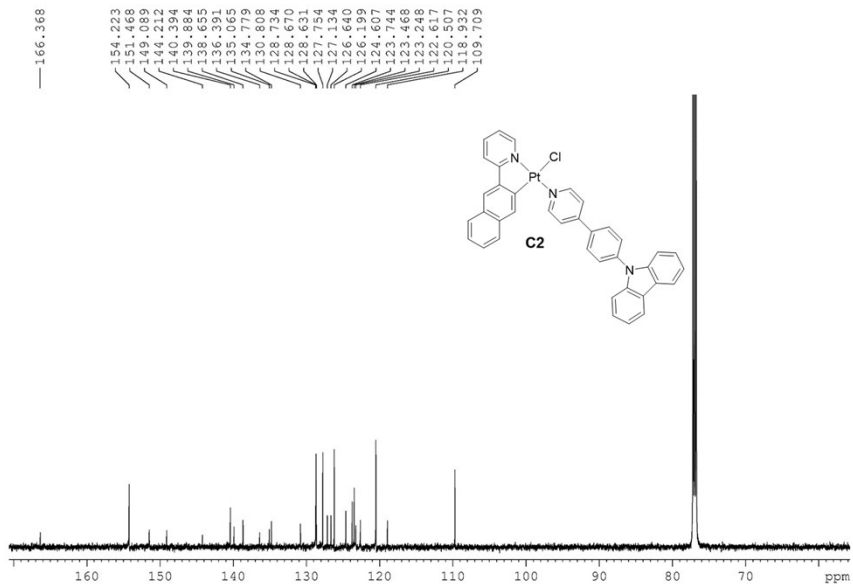
151.454
149.624
143.263
139.842
138.592
136.397
135.072
134.140
134.082
130.330
129.536
129.013
128.703
128.188
128.085
127.518
127.145
127.098
126.662
124.558
123.575
123.337
122.500
122.575
118.900
N
Cl
Pt
N
B2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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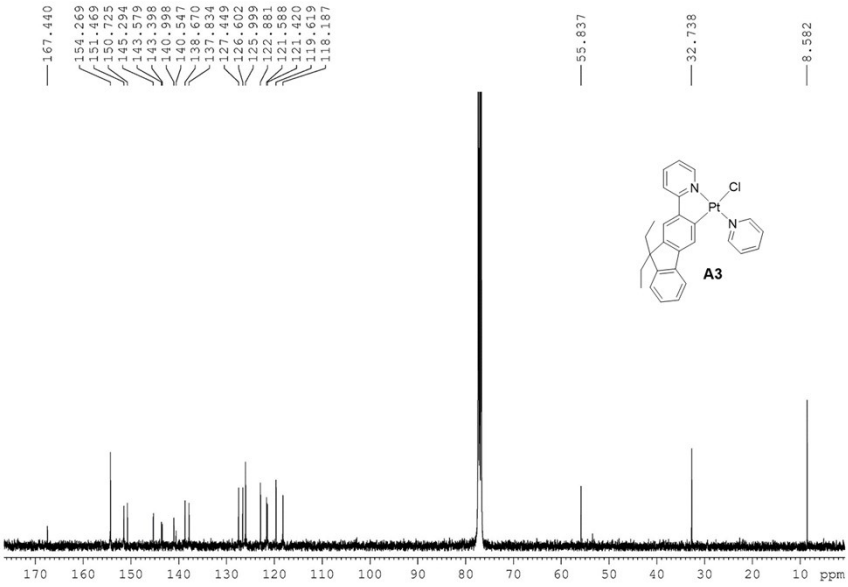
128.670
128.631
127.754
127.134
126.640
126.199
124.607
123.744
123.468
123.248
122.617
122.507
118.932
109.709
N
Cl
Pt
N
C2
N
160 150 140 130 120 110 100 90 80 70 ppm


167.440
154.269
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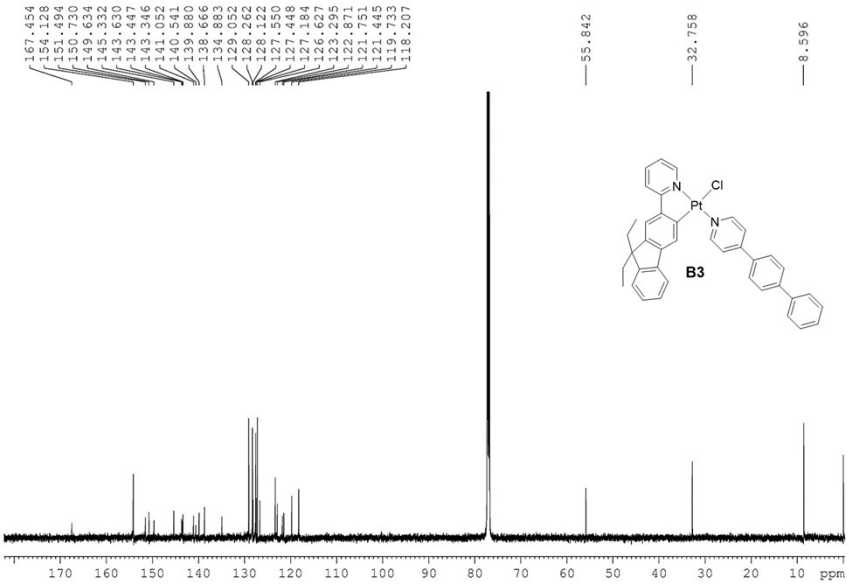
145.294
143.579
143.398
140.998
140.547
138.670
137.834
127.449
126.602
125.999
122.881
121.588
121.420
119.619
118.187
55.837
32.738
8.582
A3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


167.454
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145.332
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141.052
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134.883
129.052
128.262
128.122
127.550
127.448
127.184
126.627
123.295
122.871
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121.445
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118.207
55.842
32.758
8.596
B3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

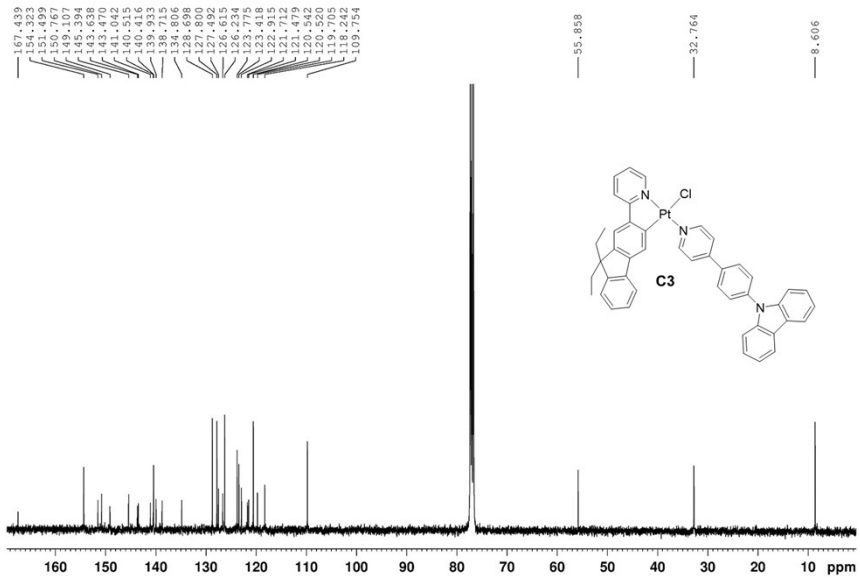


Fig. S2 ^{13}C NMR spectra for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.

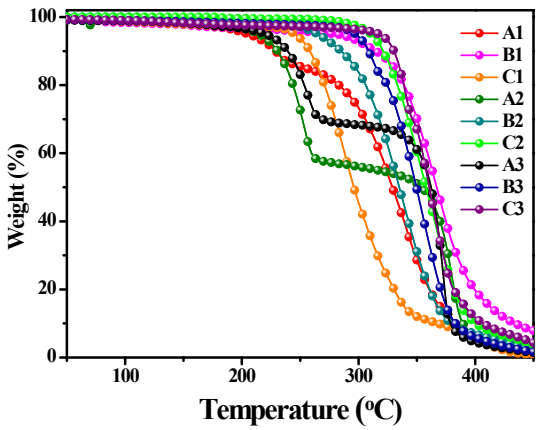


Fig. S3 The TGA curves for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes.

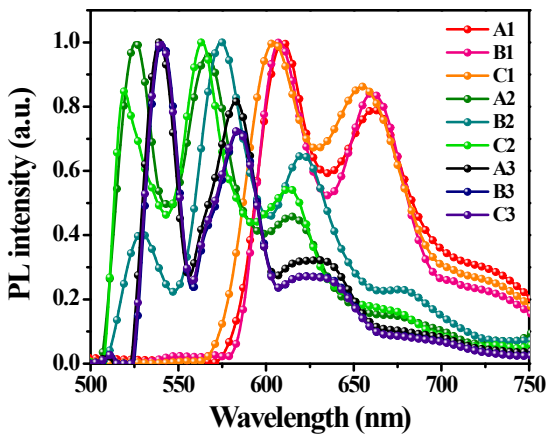
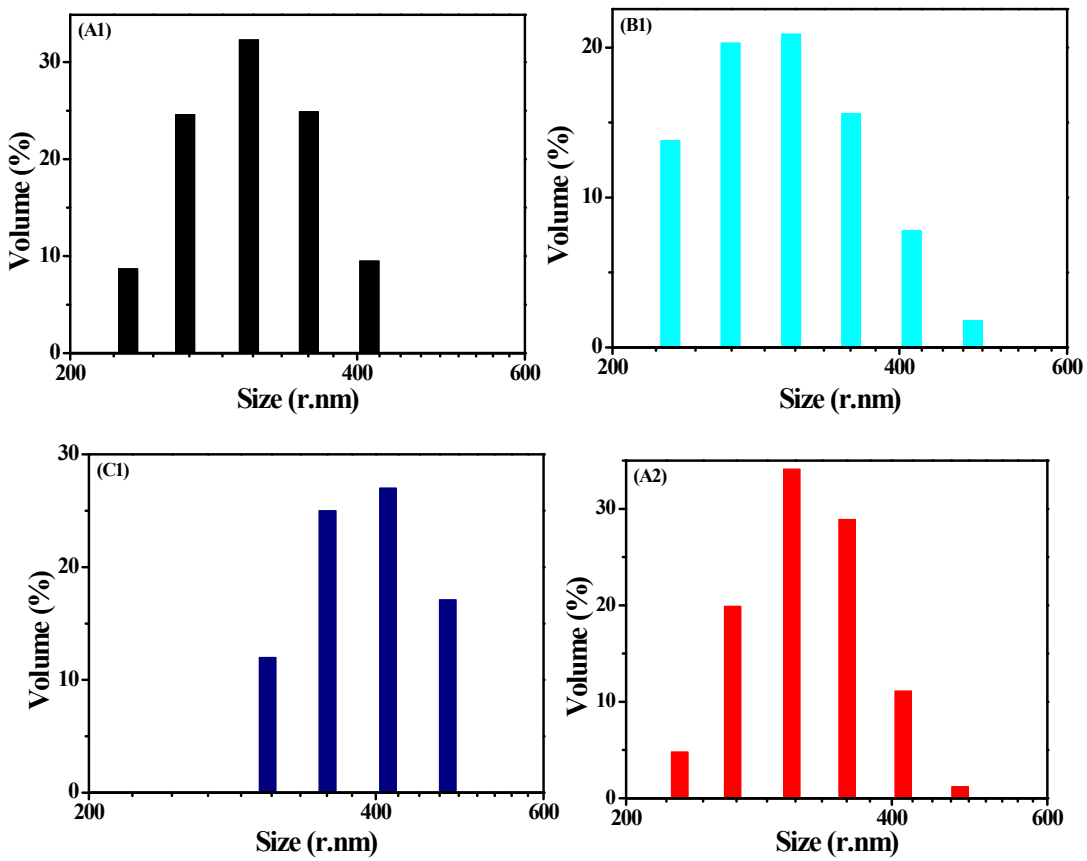


Fig. S4 Photoluminescent spectra for these Pt^{II}(C^N)(N-donor ligand)Cl-type complexes at 77K.



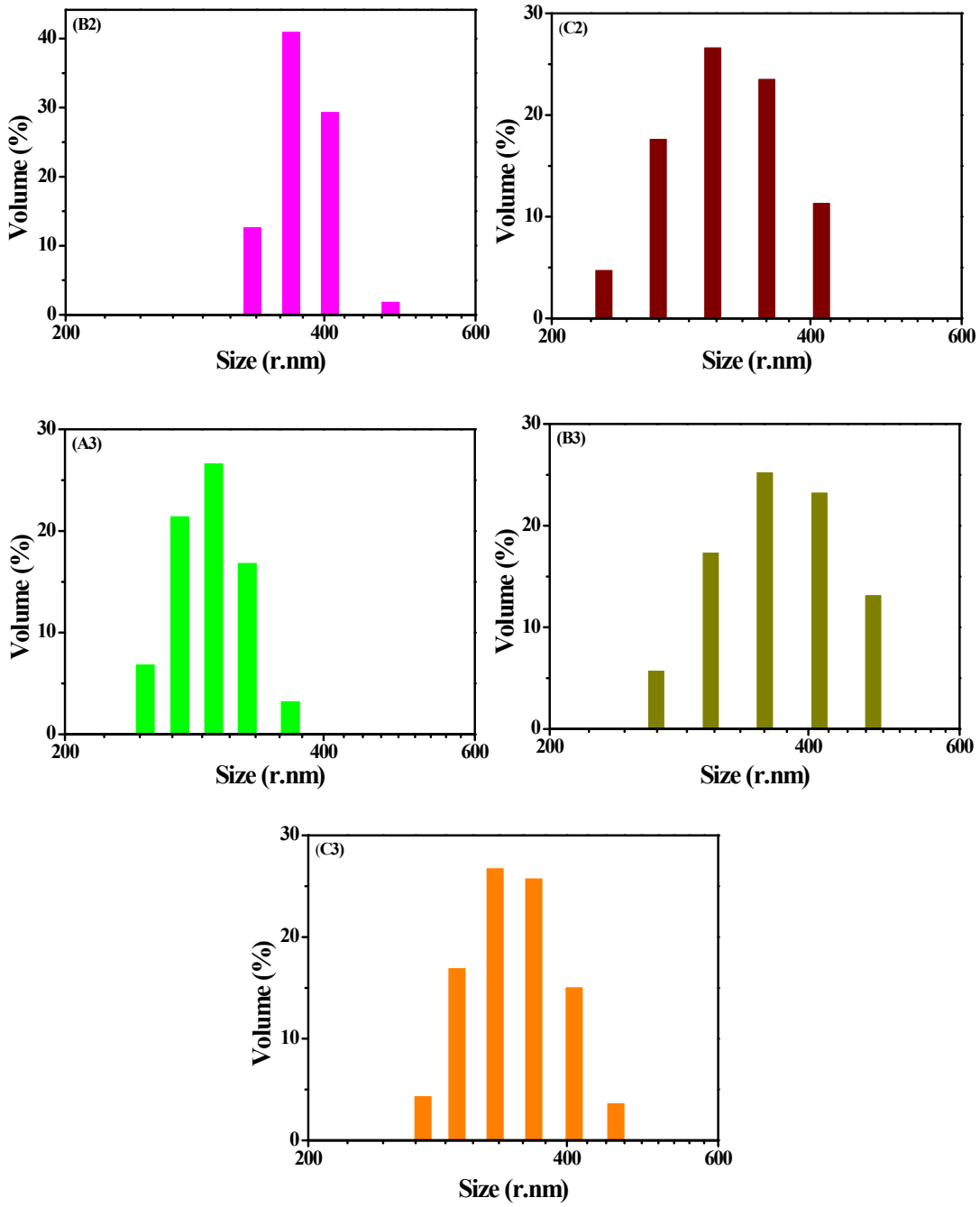


Fig. S5 Particle size distribution of these Pt^{II}(C^N)(N-donor ligand)Cl-type obtained from the THF : H_2O mixture at f_w^c.

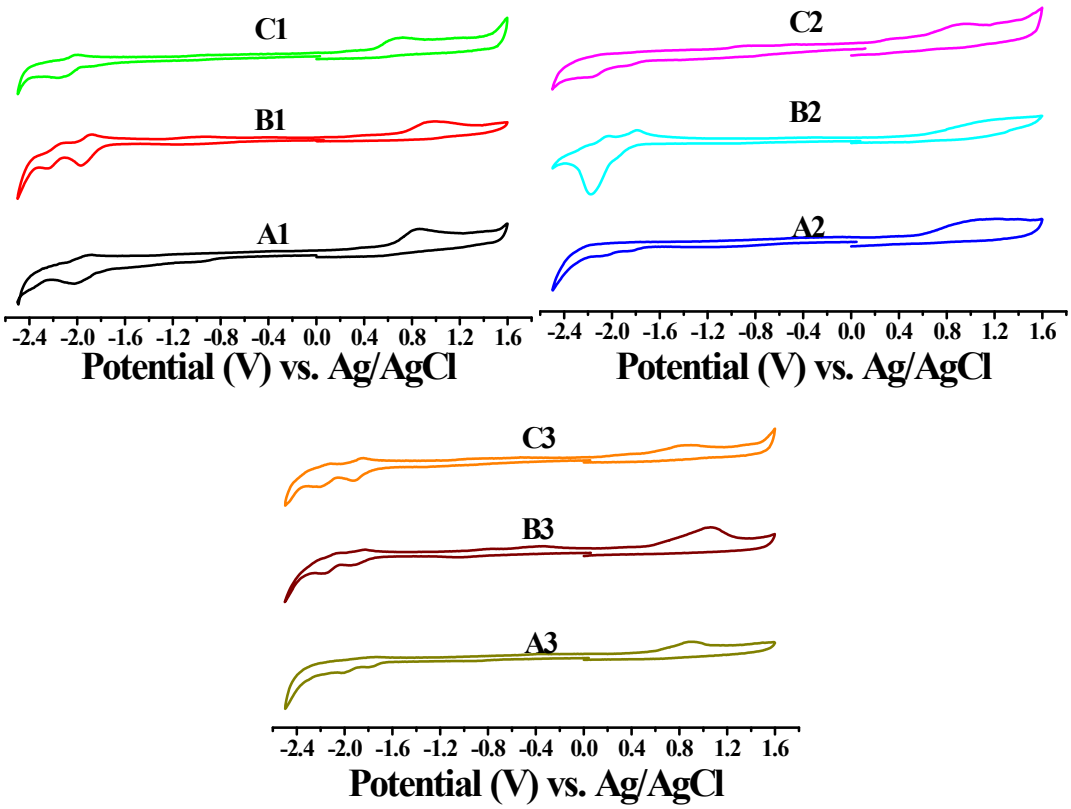
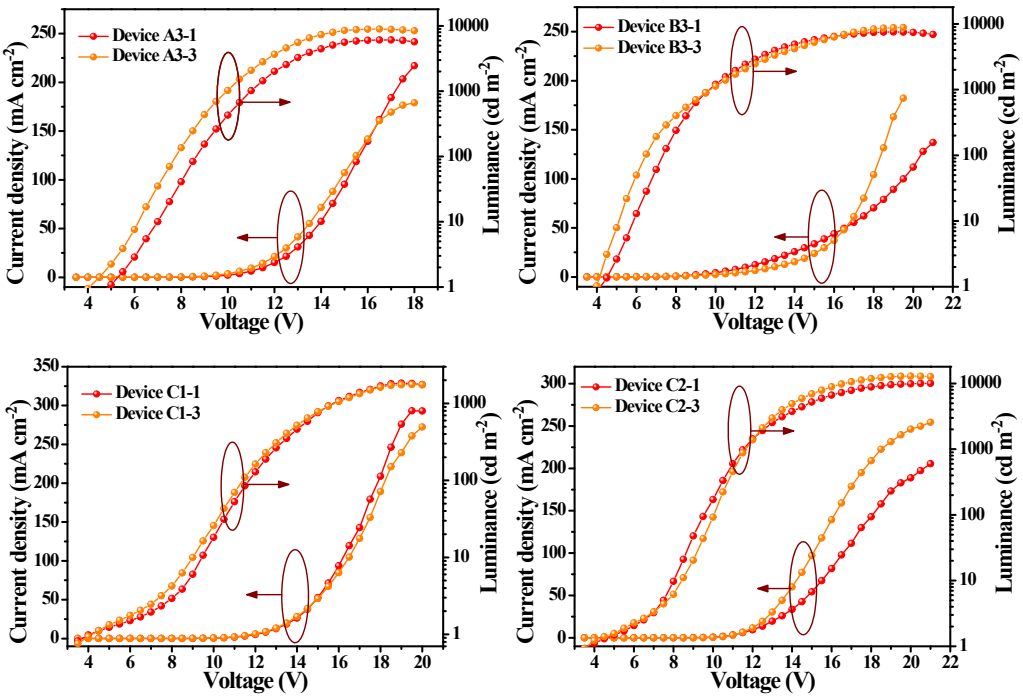


Fig. S6 CV carves for **A1**, **B1**, **C1**, **A2**, **B2**, **C2**, **A3**, **B3** and **C3**



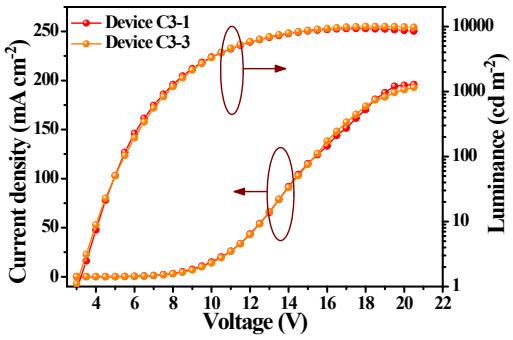
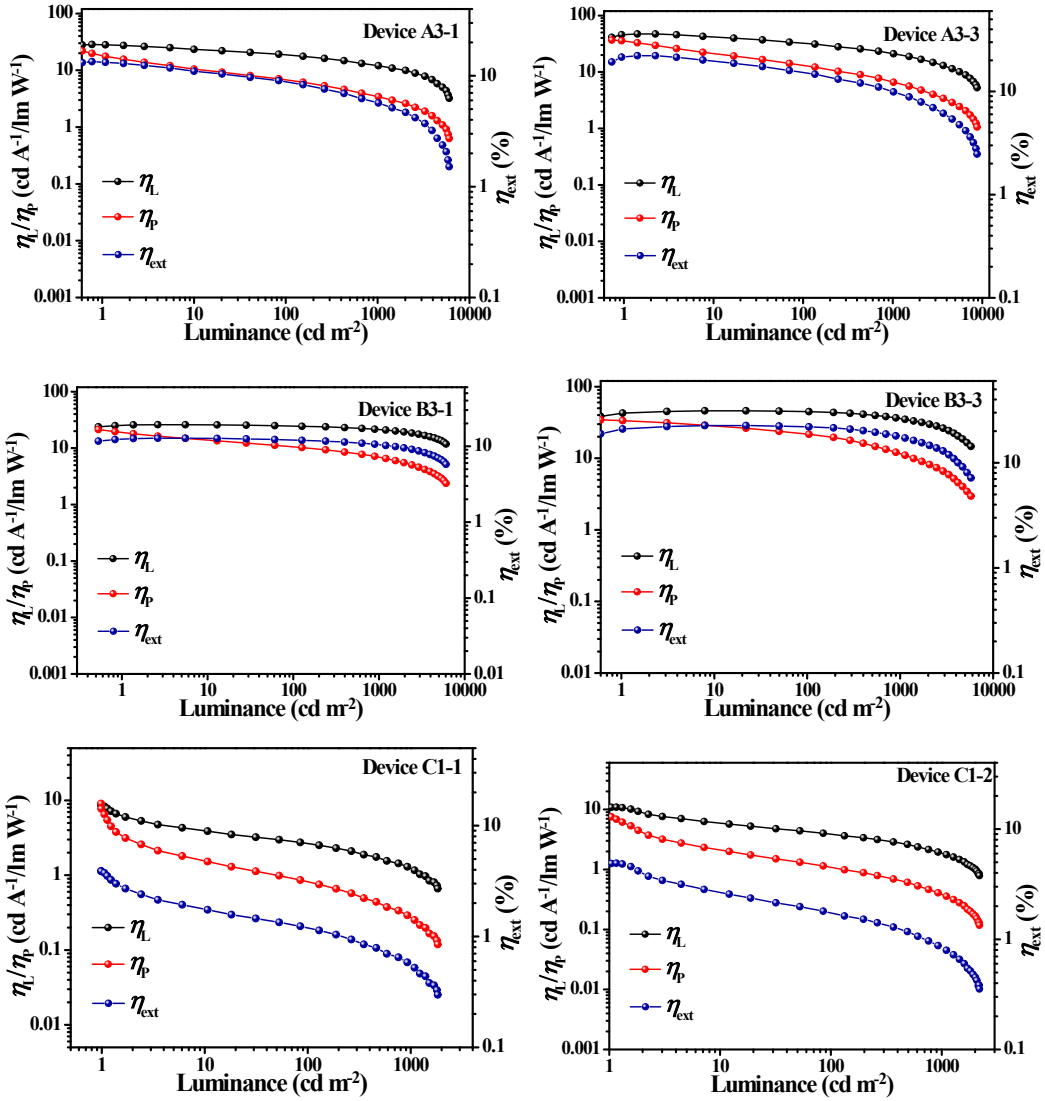


Fig. S7 Current density–voltage–luminance (J–V–L) relationships of the OLEDs.



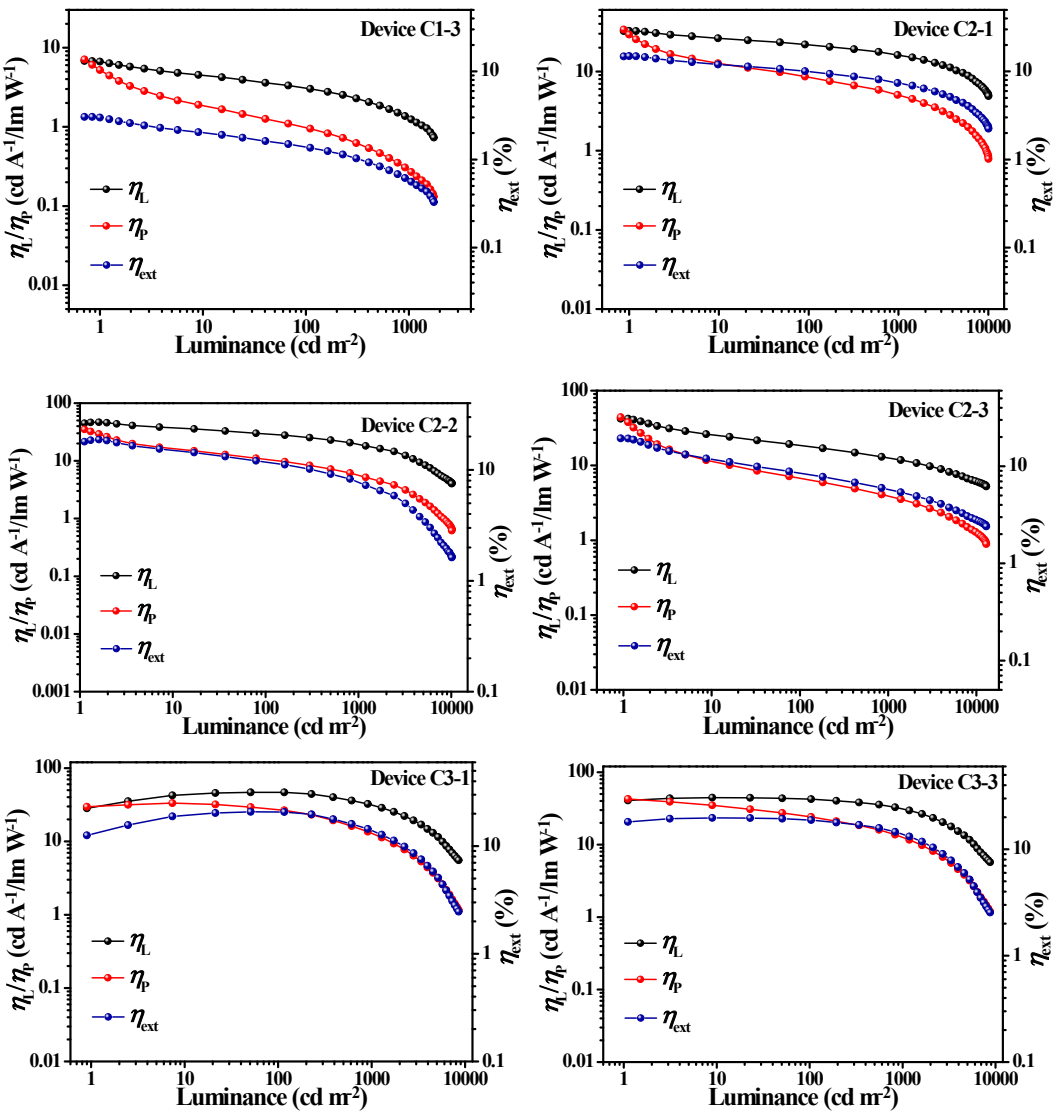


Fig. S8 EL efficiencies *vs.* luminance curves for the OLEDs.

References

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3 O. Kobayashi, D. Uraguchi, T. Yamakawa, *Org. Lett.*, 2009, **11**, 2679-2682.

4 K. Leduskrasts, A. Kinens, E. Suna, *Chem. Commun.*, 2019, **55**, 12663-12666.