Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2013

Highly emissive platinum(II) complexes bearing carbene and cyclometalated ligands.

Haruka Uesugi, Toshiaki Tsukuda, Koichiro Takao, Taro Tsubomura*

Supporting information

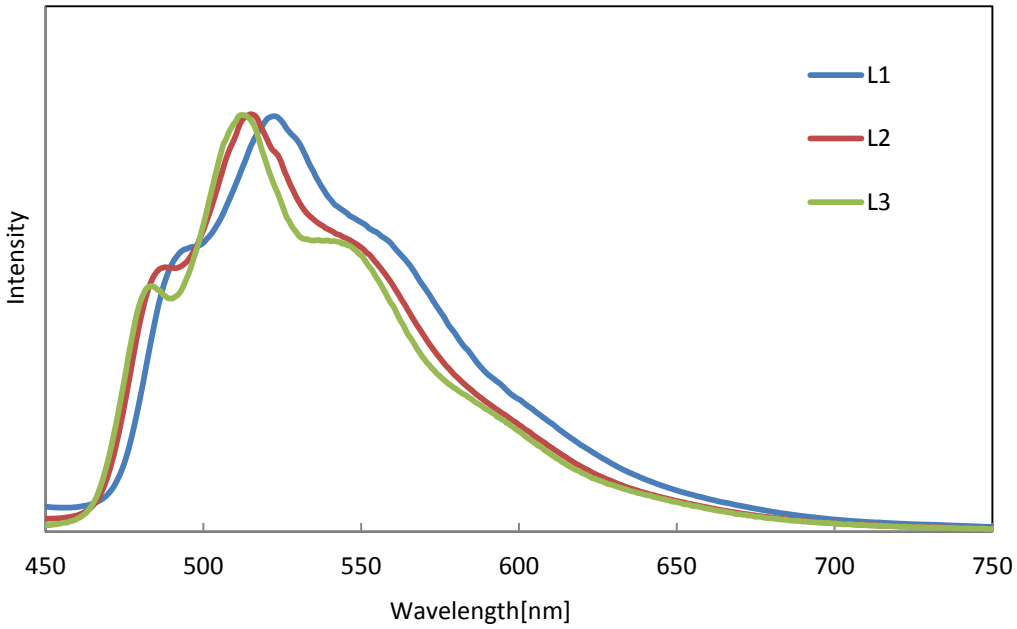



Fig.S1a. Emission spectra of [Pt(ppy)(Ln)]$PF_6$ (**1a**$PF_6$, **2a**$PF_6$, and **3a**$PF_6$) in the solid state.

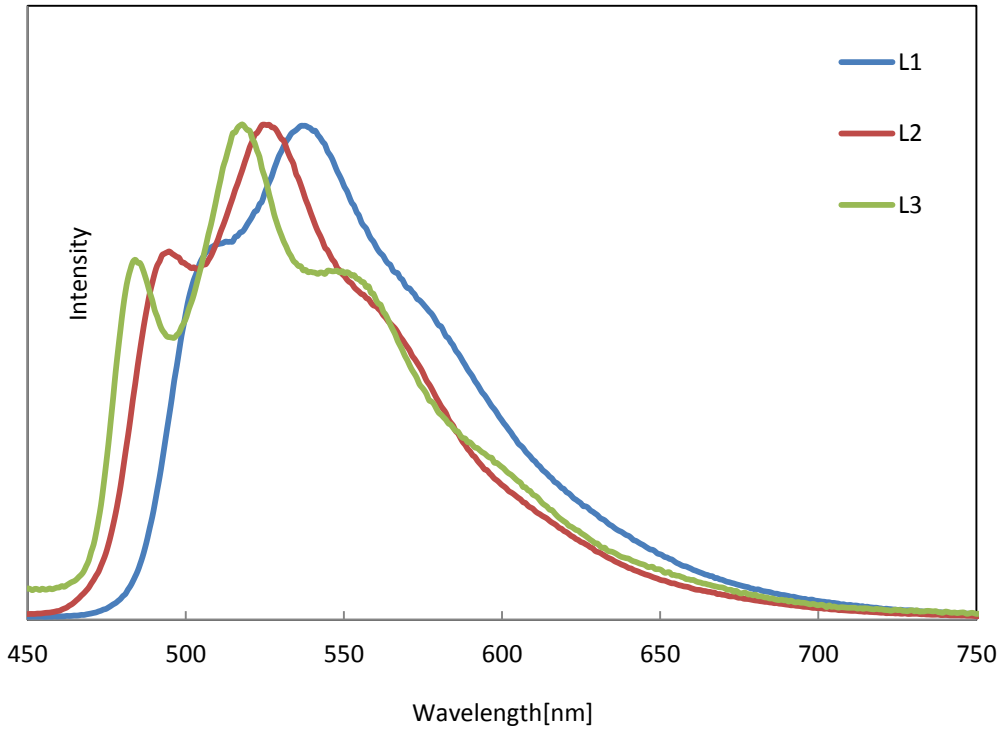
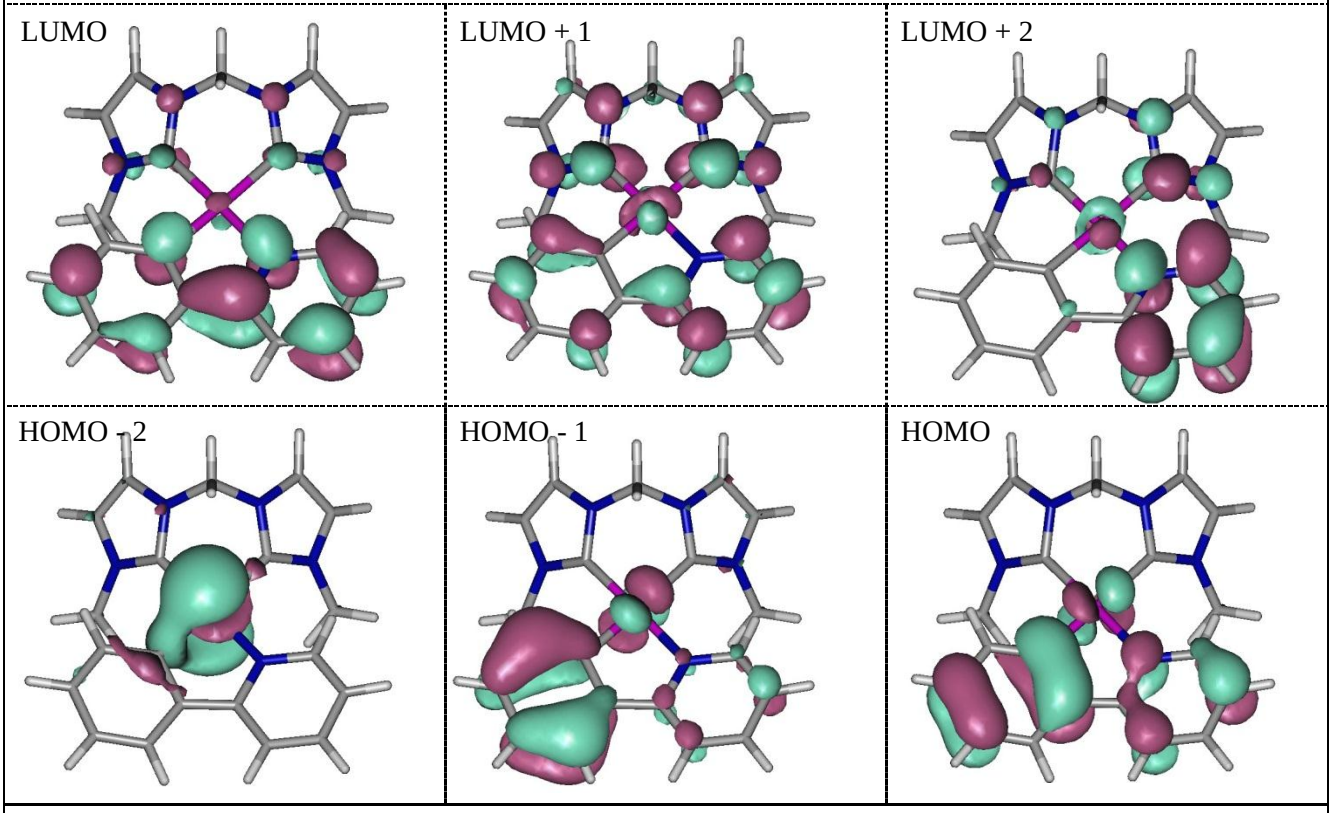



Fig. S1b. Emission spectra of [Pt(tol-ppy)(Ln)]$PF_6$ (**1b**$PF_6$, **2b**$PF_6$, and **3b**$PF_6$) in the solid state.

This journal is © The Royal Society of Chemistry 2013

**1a**$^+$ Orbitals calculated based on the optimized structure in the triplet excited state.




**3a**$^+$ Orbitals calculated based on the optimized structure in the triplet excited state.

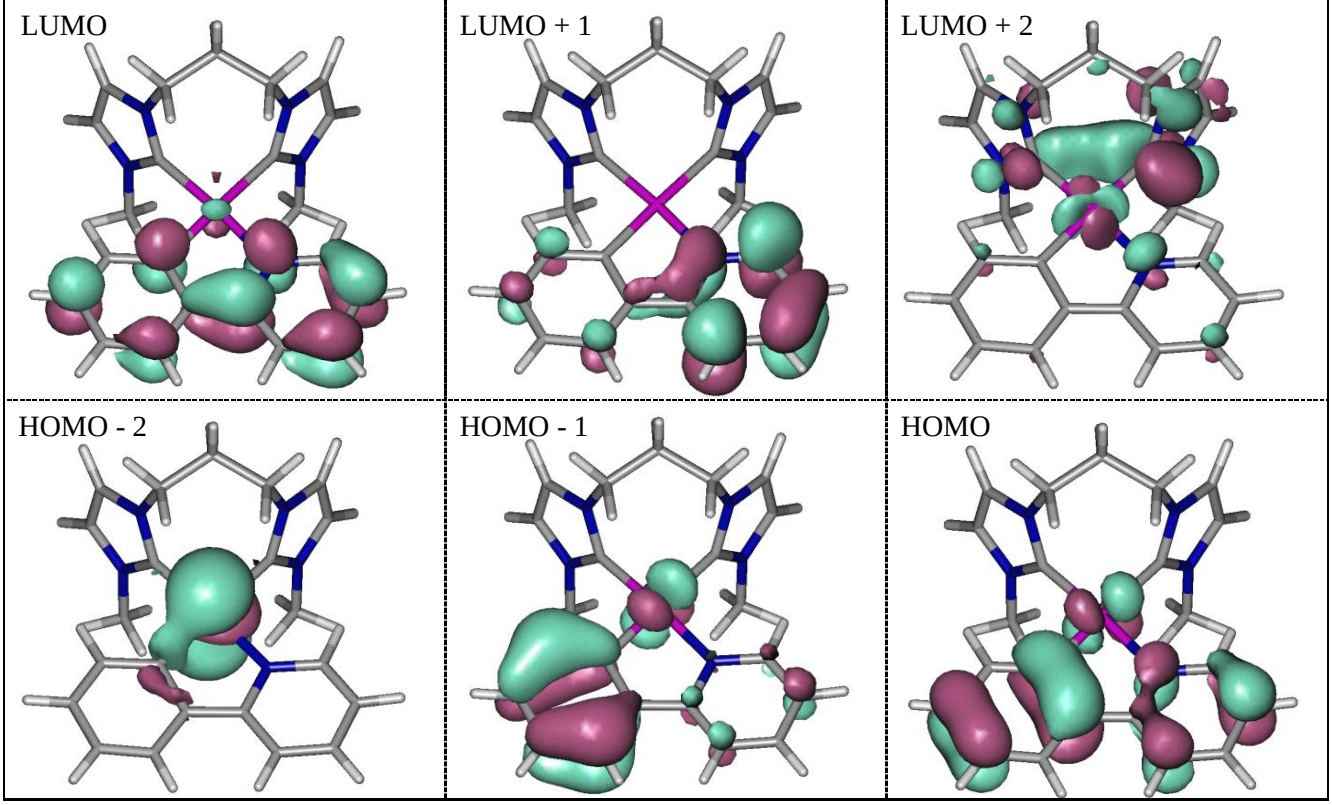



Fig. S2 Kohn-Sham orbitals of $[Pt(ppy)(L1)]^+$ (**1a**$^+$) and $[Pt(ppy)(L3)]^+$(**3a**$^+$). Orbitals calculated based on the optimized structure in the $T_1$ (triplet excited) states. (Contour value = 0.04)

This journal is © The Royal Society of Chemistry 2013

Table S1 Comparison of the important structural parameters of the platinum complexes.

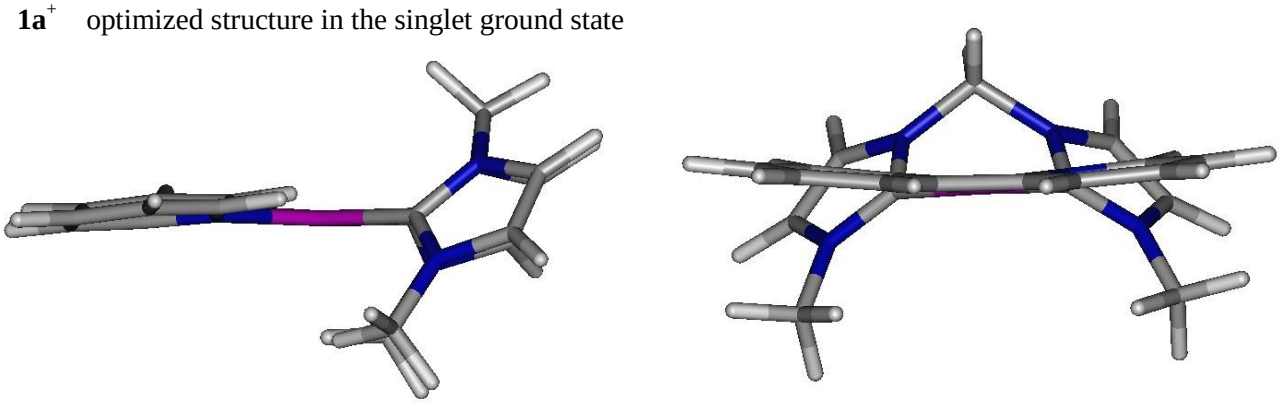
a) $[Pt(ppy)L1]^+$ (**1a**$^+$)

| | distances (Å) or angles (°) | | | | |
|---|---|---|---|---|---|
| atom - atom (- atom) | X-ray data | DFT optimized data (singlet) | differences X-ray and calculation | DFT optimized data (triplet) | differences X-ray and calculation |
| Pt1 - N5 | 2.091(12) | 2.13 | 0.04 | 2.09 | 0.00 |
| Pt1 - C1 | 2.068(10) | 2.06 | 0.01 | 2.02 | 0.05 |
| Pt1 - C13 | 2.009(13) | 2.00 | 0.01 | 2.01 | 0.00 |
| Pt1 - C17, | 2.065(9) | 2.12 | 0.06 | 2.02 | 0.04 |
| N5 - Pt1 - C1 | 80.1(5) | 79.4 | 0.7 | 80.2 | 0.1 |
| N5 - Pt1 - C13 | 175.7(5) | 176.1 | 0.4 | 176.7 | 0.6 |
| N5 - Pt1 - C17 | 99.4(4) | 100.2 | 0.8 | 99.1 | 0.9 |
| C1 - Pt1 - C13 | 97.2(5) | 97.2 | 0.0 | 97.1 | 0.1 |
| C1 - Pt1 - C17 | 174.8(5) | 176.5 | 1.7 | 176.1 | 0.4 |
| C13 - Pt1 - C17 | 82.9(4) | 83.1 | 0.2 | 83.4 | 0.3 |

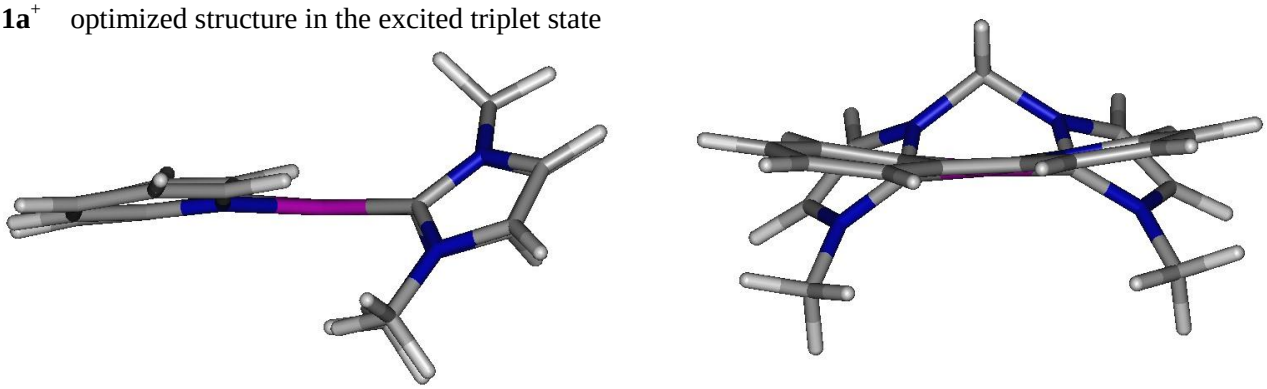
b) $[Pt(ppy)L3]^+$ (**3a**$^+$)

| | distances (Å) or angles (°) | | | | |
|---|---|---|---|---|---|
| atom - atom (- atom) | X-ray data | DFT optimized data (singlet) | differences X-ray and calculation | DFT optimized data (triplet) | differences X-ray and calculation |
| Pt1 - N5 | 2.059(4) | 2.13 | 0.07 | 2.09 | 0.03 |
| Pt1 - C1 | 2.049(5) | 2.06 | 0.01 | 2.03 | 0.02 |
| Pt1 - C12 | 1.991(5) | 2.00 | 0.01 | 2.02 | 0.03 |
| Pt1 - C22 | 2.019(5) | 2.11 | 0.09 | 2.12 | 0.10 |
| N5 - Pt1 - C1 | 81.2(2) | 79.2 | 1.0 | 80.8 | 0.4 |
| N5 - Pt1 - C12 | 175.3(2) | 174.4 | 0.9 | 175.6 | 0.3 |
| N5 - Pt1 - C22 | 96.2(2) | 98.0 | 1.8 | 97.1 | 0.9 |
| C1 - Pt1 - C12 | 94.7 (2) | 94.7 | 0.0 | 94.8 | 0.1 |
| C1 - Pt1 - C22 | 177.4(2) | 177.7 | 0.3 | 177.9 | 0.5 |
| C12 - Pt1 - C22 | 87.9(2) | 87.6 | 0.3 | 87.2 | 0.7 |

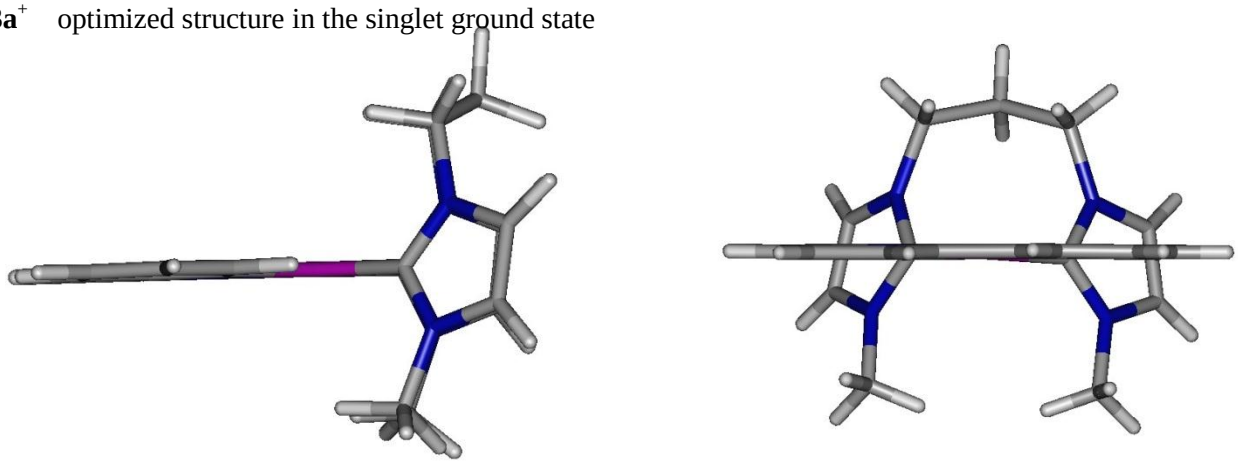
**1a**$^{+}$ optimized structure in the singlet ground state



**1a**$^{+}$ optimized structure in the excited triplet state



**3a**$^{+}$ optimized structure in the singlet ground state



**3a**$^{+}$ optimized structure in the excited triplet stat

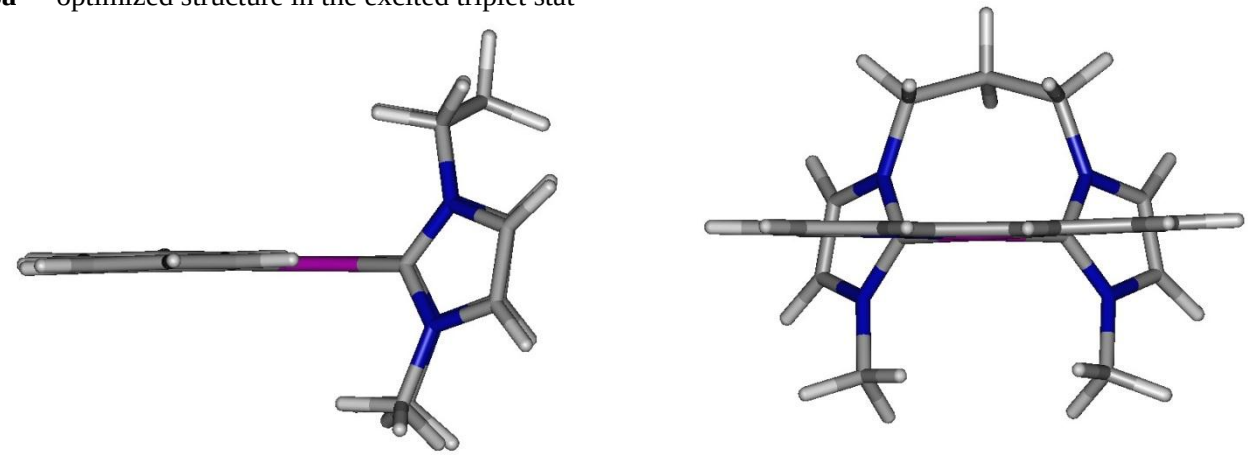


Figure S3 Comparison of the singlet-optimized structures and triplet optimized structures of $[Pt(ppy)(L1)]^{+}$ (**1a**$^{+}$) and $[Pt(ppy)(L3)]^{+}$ (**3a**$^{+}$).

This journal is © The Royal Society of Chemistry 2013

Table S2 TDDFT results. In addition to the values listed in Table 4 in the text, detailed data ate shown in this table. All components listed in Gaussian output are shown in this table.

| complexes | Singlets calculated using singlet-optimized structure | | | | Triplets calculated using triplet-optimized structure | | |
|---|---|---|---|---|---|---|---|
| | WL / nm | *f* | components and coefficients | | WL / nm | components and coefficients | |
| [Pt(ppy)(L1)]$^+$ (**1a**$^+$) | 378 | 0.036 | HOMO → LUMO | 0.68 | 614 | HOMO → LUMO | 0.74 |
| | | | | | | HOMO → LUMO+1 | -0.17 |
| | 324 | 0.066 | HOMO-1 → LUMO | 0.63 | | HOMO-1 → LUMO | 0.12 |
| | | | HOMO → LUMO+1 | -0.22 | | HOMO-1 → LUMO+1 | -0.11 |
| | | | HOMO → LUMO+2 | 0.10 | | HOMO-7 → LUMO+8 | 0.10 |
| | 317 | 0.012 | HOMO-2 → LUMO | 0.68 | 404 | HOMO-1 → LUMO | 0.67 |
| | | | | | | HOMO → LUMO+1 | -0.17 |
| | | | | | | HOMO-1 →LUMO+1 | -0.15 |
| | 298 | 0.014 | HOMO-3 → LUMO | 0.48 | | HOMO → LUMO | -0.13 |
| | | | HOMO → LUMO+1 | -0.39 | 358 | HOMO → LUMO+1 | 0.48 |
| | | | HOMO → LUMO+2 | -0.30 | | HOMO → LUMO+2 | 0.45 |
| | 293 | 0.12 | HOMO → LUMO+2 | 0.60 | | HOMO-1 → LUMO | -0.19 |
| | | | HOMO-3 → LUMO | 0.28 | | HOMO-7 → LUMO+2 | -0.14 |
| | | | | | | HOMO-1 → LUMO+2 | -0.13 |
| [Pt(ppy)(L3)]$^+$ (**3a**$^+$) | 361 | 0.041 | HOMO → LUMO | 0.67 | 597 | HOMO → LUMO | 0.75 |
| | | | | | | HOMO-1 → LUMO | -0.14 |
| | 312 | 0.039 | HOMO-2 → LUMO | 0.50 | | HOMO → LUMO+1 | -0.12 |
| | | | HOMO-1 → LUMO | 0.43 | | HOMO-1 → LUMO+1 | 0.14 |
| | | | HOMO → LUMO+1 | 0.18 | | HOMO-8 → LUMO+8 | 0.12 |
| | 311 | 0.040 | HOMO-2 → LUMO | 0.49 | 394 | HOMO-1 → LUMO | 0.69 |
| | | | HOMO-1 → LUMO | -0.42 | | HOMO-1 → LUMO+1 | -0.14 |
| | | | HOMO → LUMO+1 | -0.21 | | HOMO→LUMO | 0.13 |
| | 306 | 0.004 | HOMO-3 → LUMO | 0.64 | | HOMO→LUMO+1 | 0.12 |
| | | | HOMO → LUMO+1 | 0.24 | 365 | HOMO → LUMO+1 | 0.67 |
| | 290 | 0.058 | HOMO → LUMO+1 | 0.54 | | HOMO-8→LUMO+1 | -0.17 |
| | | | HOMO-3 → LUMO | -0.26 | | HOMO-1 → LUMO+1 | -0.16 |
| | | | HOMO-1 → LUMO | -0.22 | | HOMO-1 → LUMO | -0.16 |
| | | | HOMO-5→ LUMO | 0.17 | | | |