**Supporting Information**

**Highly Emissive Cycloplatinated(II) Complexes Obtained by the Chloride Abstraction from the Complex [Pt(ppy)(PPh3)(Cl)]: Employing Various Silver Salts**

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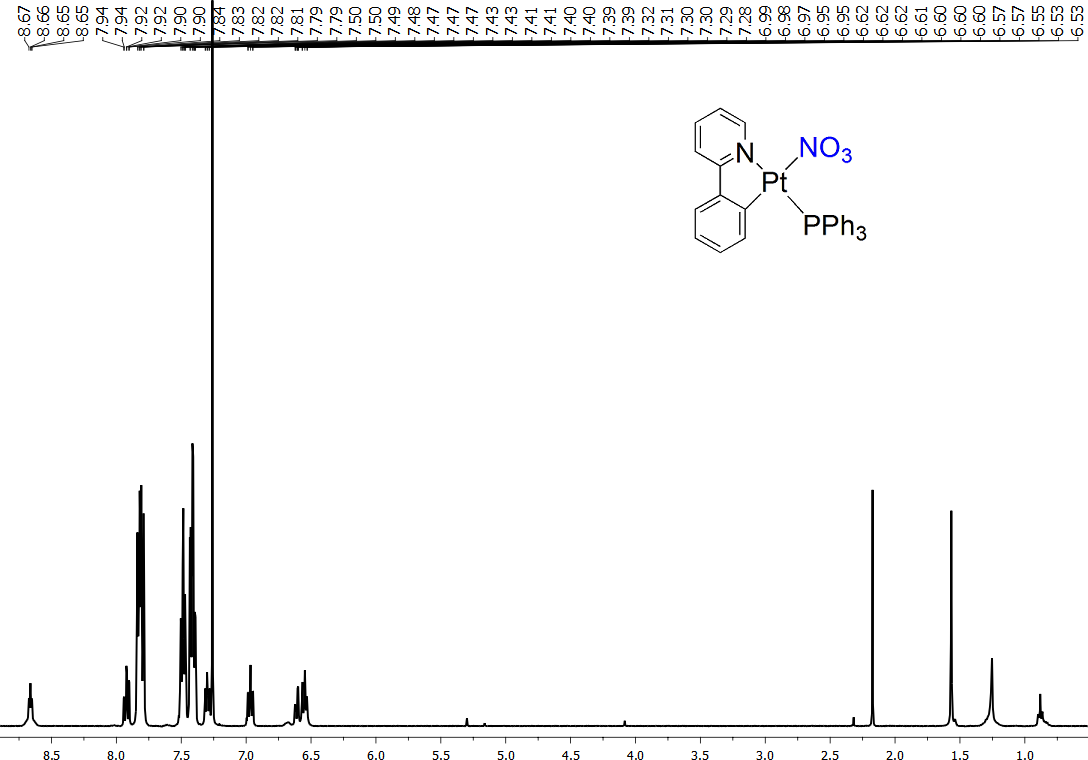
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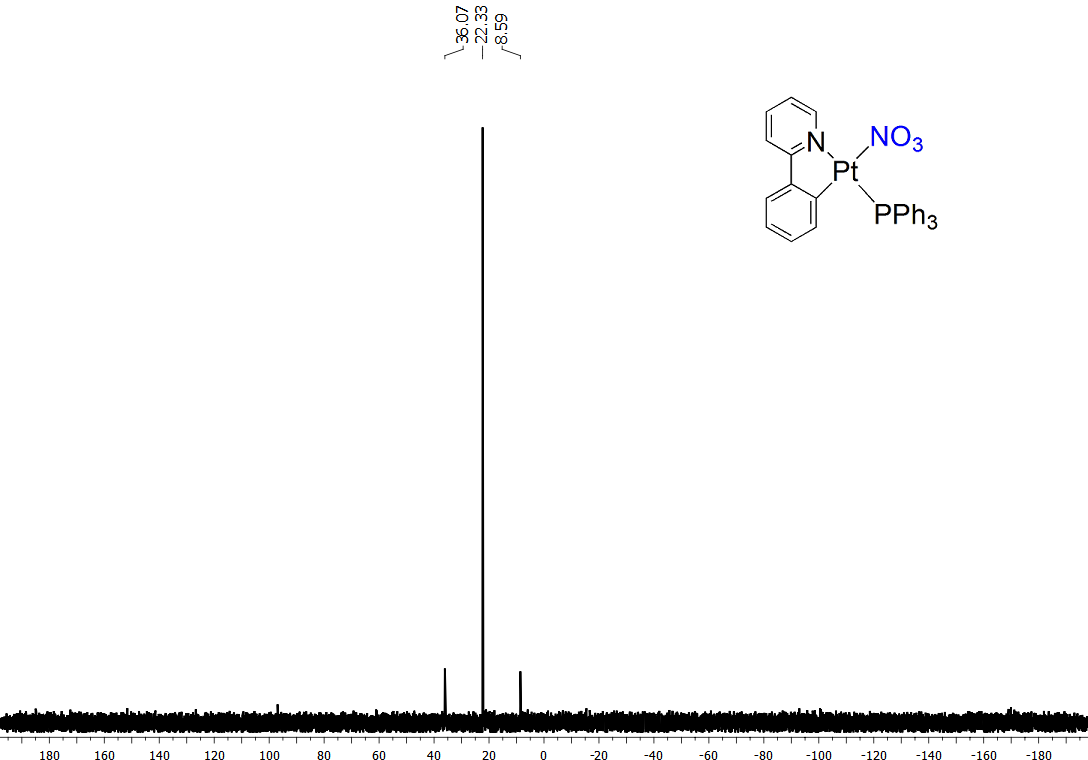
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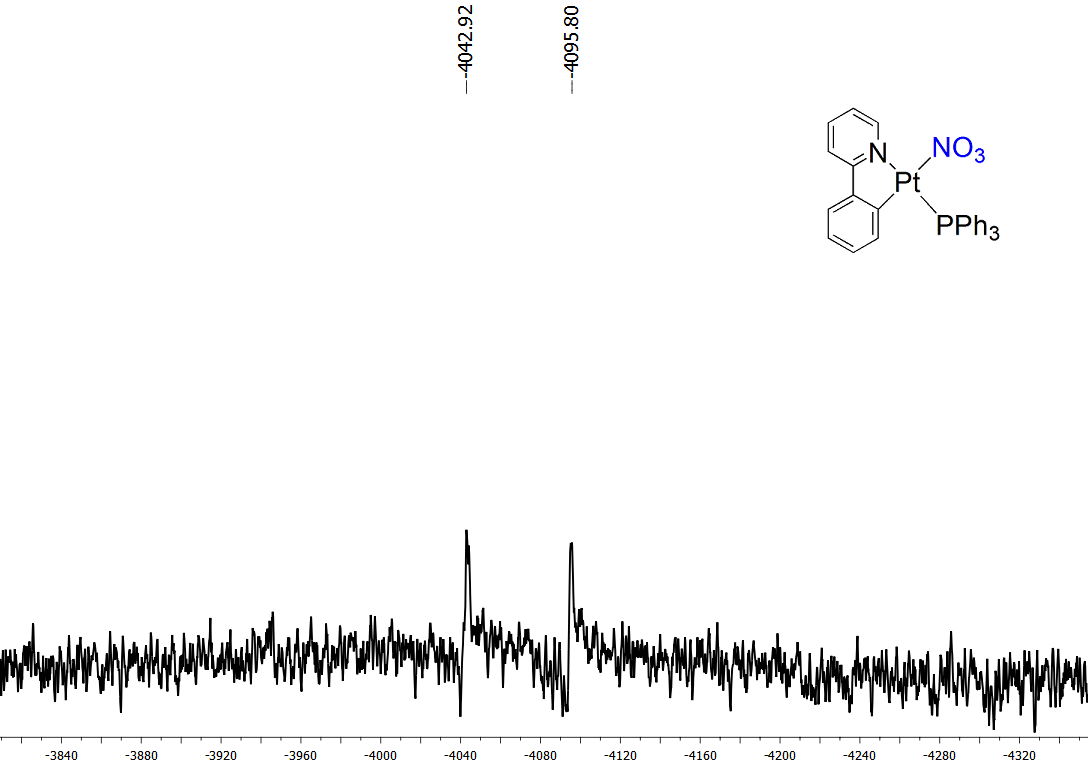
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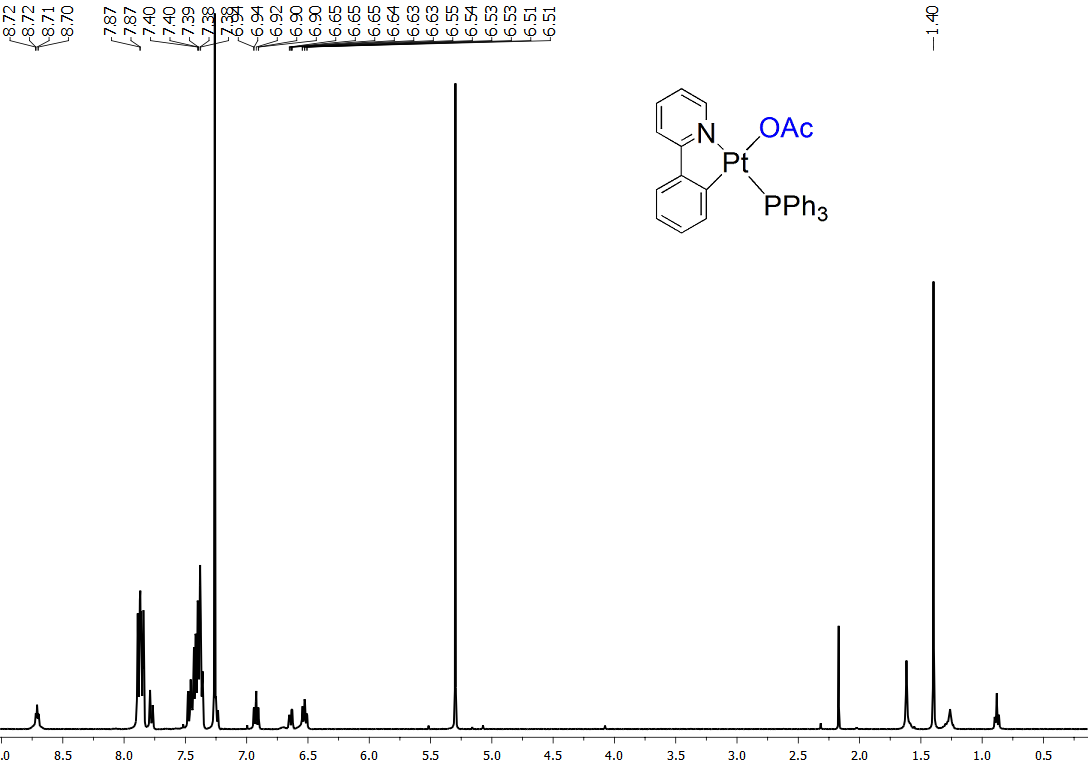
**Figure S1.** 1HNMR spectrum of the complex **4a** in CDCl3.



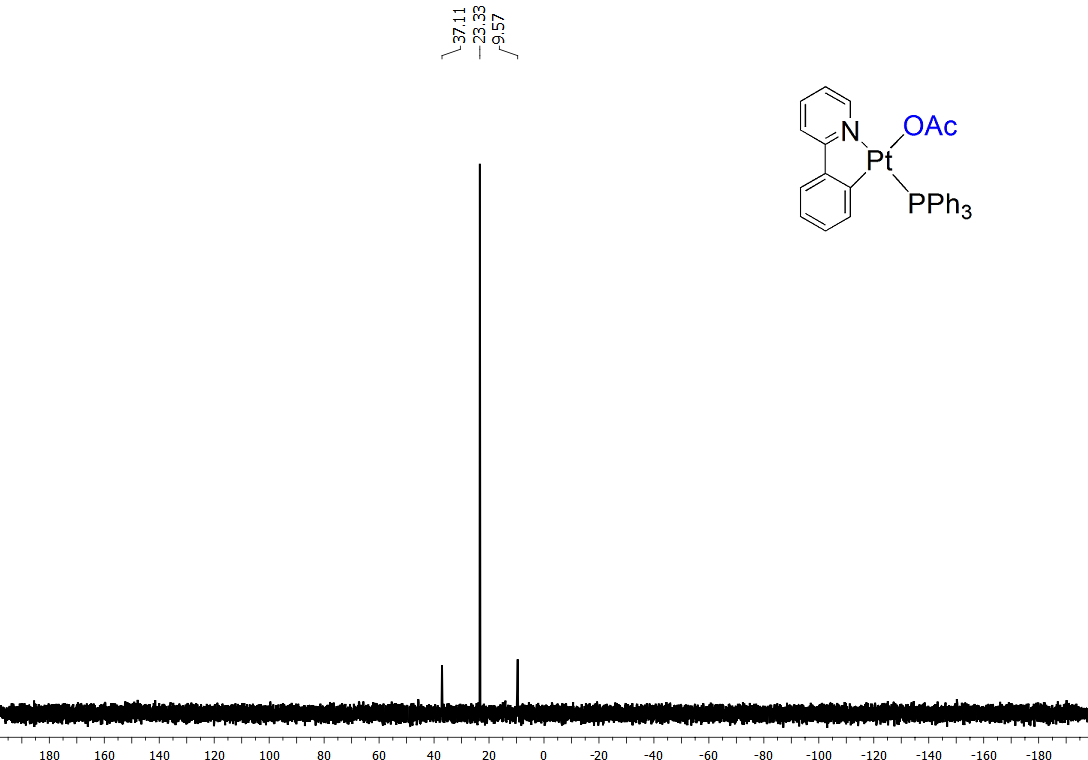
**Figure S2.** 31P{H}NMR spectrum of the complex **4a** in CDCl3.



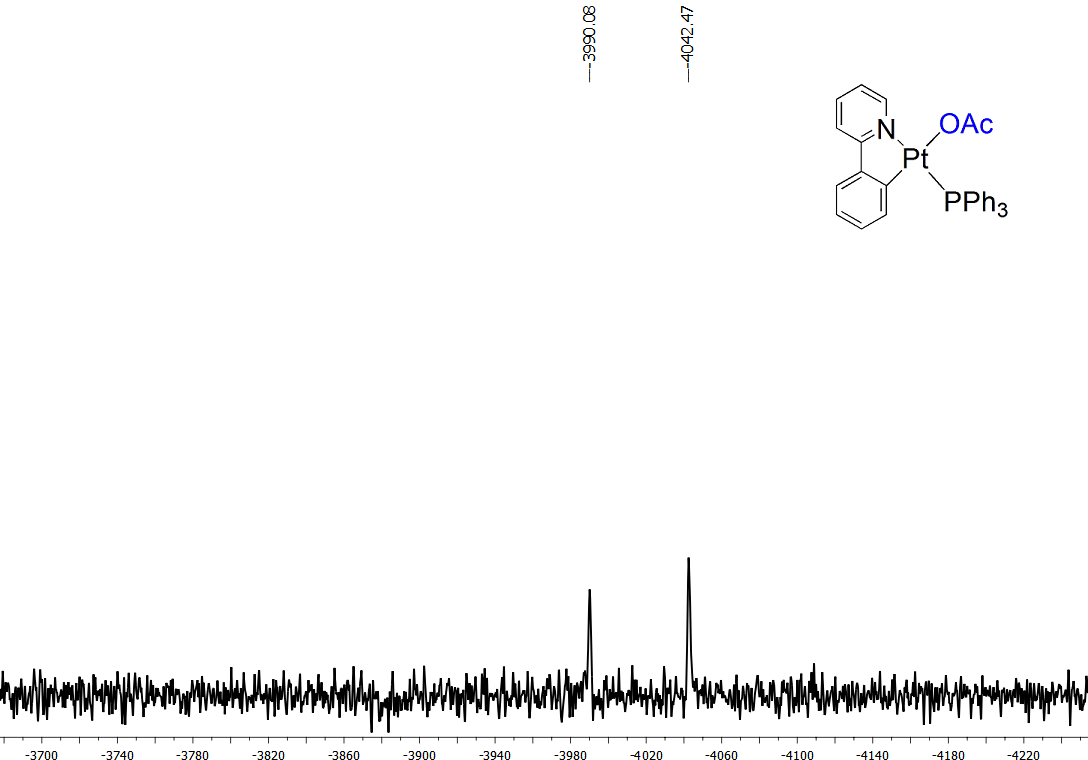
**Figure S3.** 195PtNMR spectrum of the complex **4a** in CDCl3.



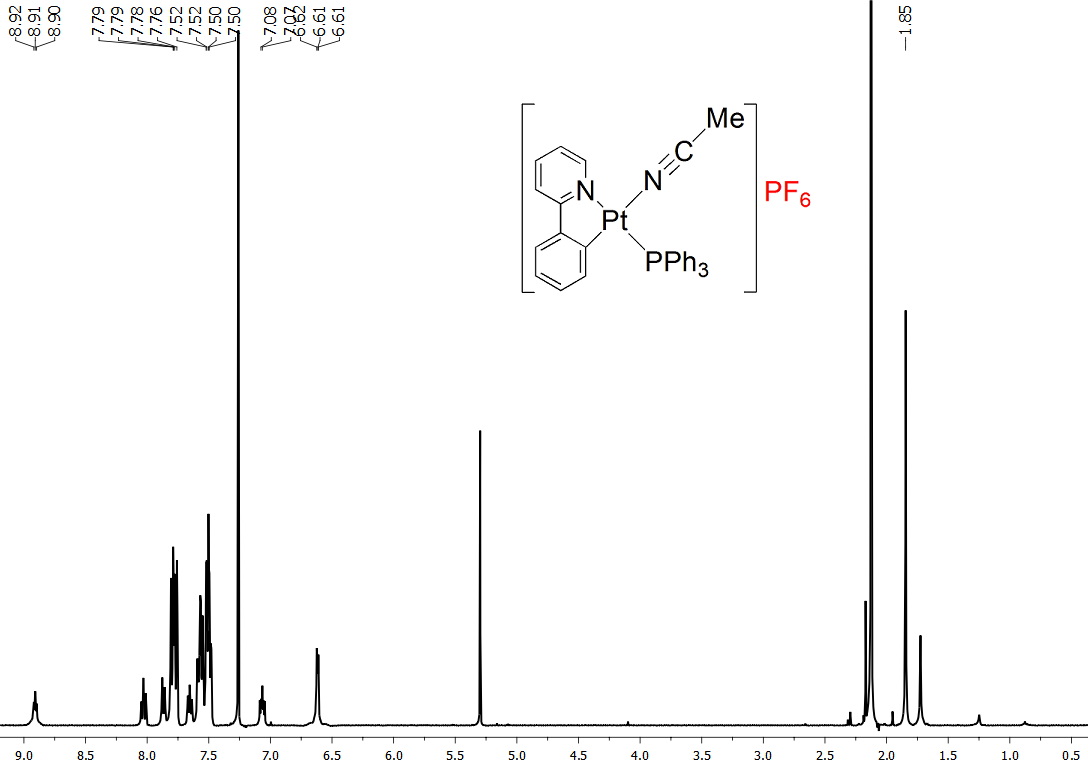
**Figure S4.** 1HNMR spectrum of the complex **4b** in CDCl3.



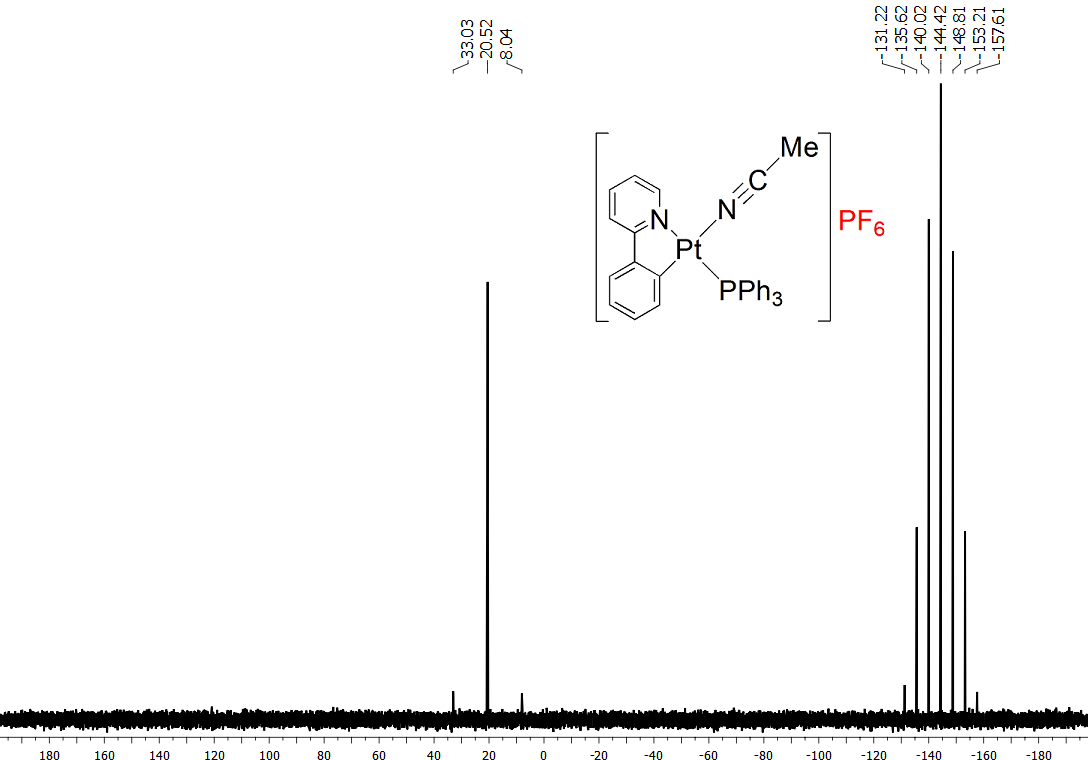
**Figure S5.** 31P{H}NMR spectrum of the complex **4b** in CDCl3.



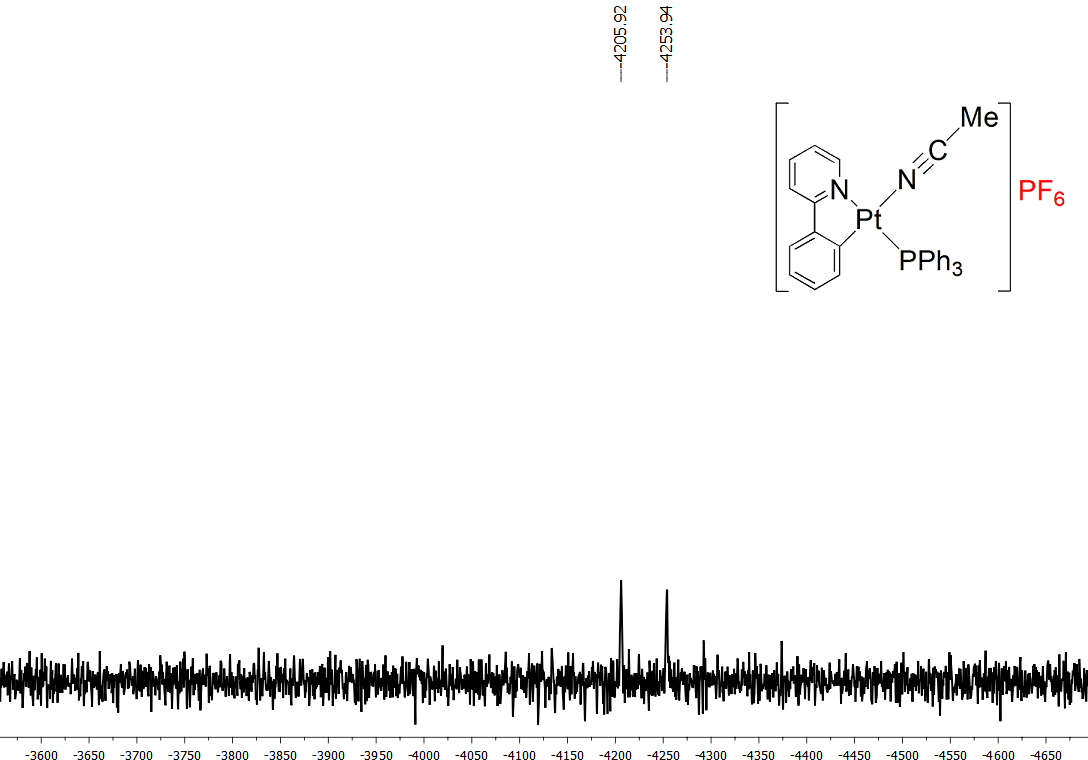
**Figure S6.** 195PtNMR spectrum of the complex **4b** in CDCl3.



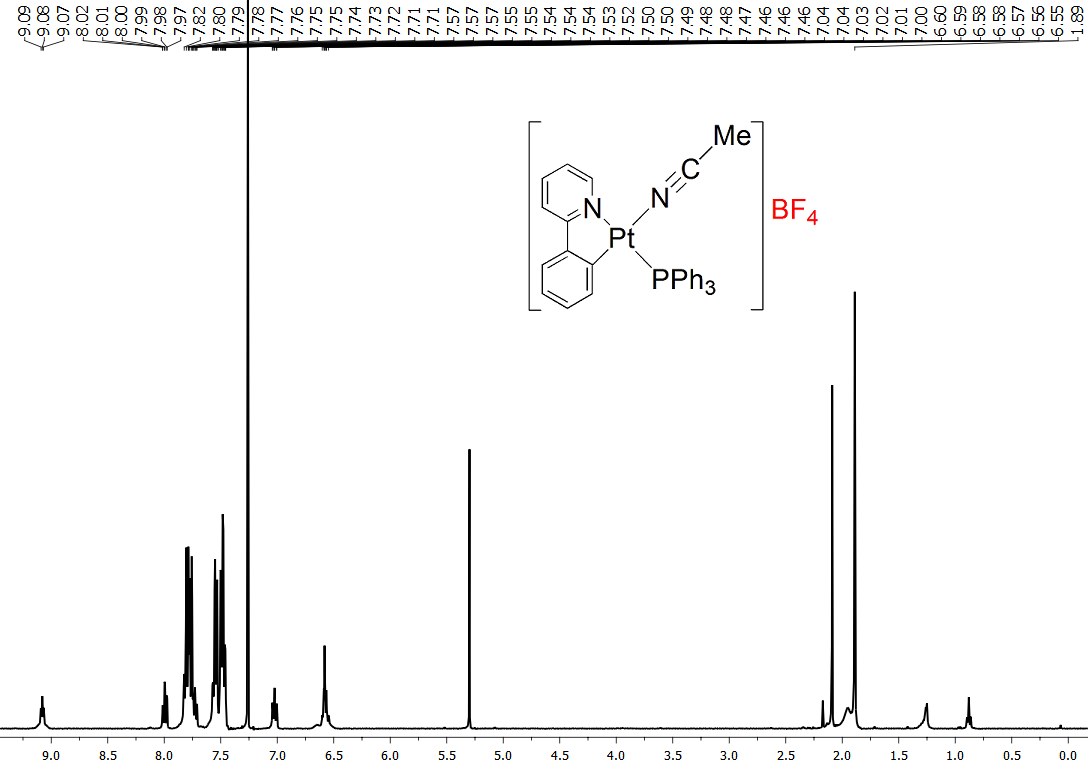
**Figure S7.** 1HNMR spectrum of the complex **5a** in CDCl3.



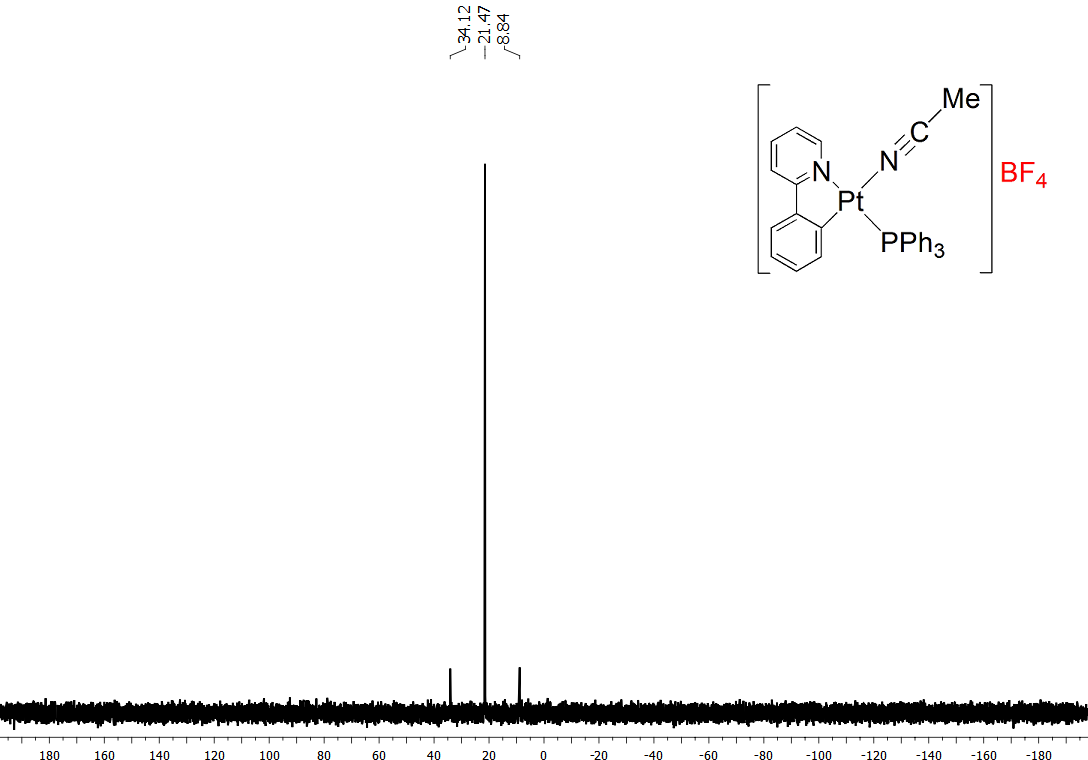
**Figure S8.** 31P{H}NMR spectrum of the complex **5a** in CDCl3.



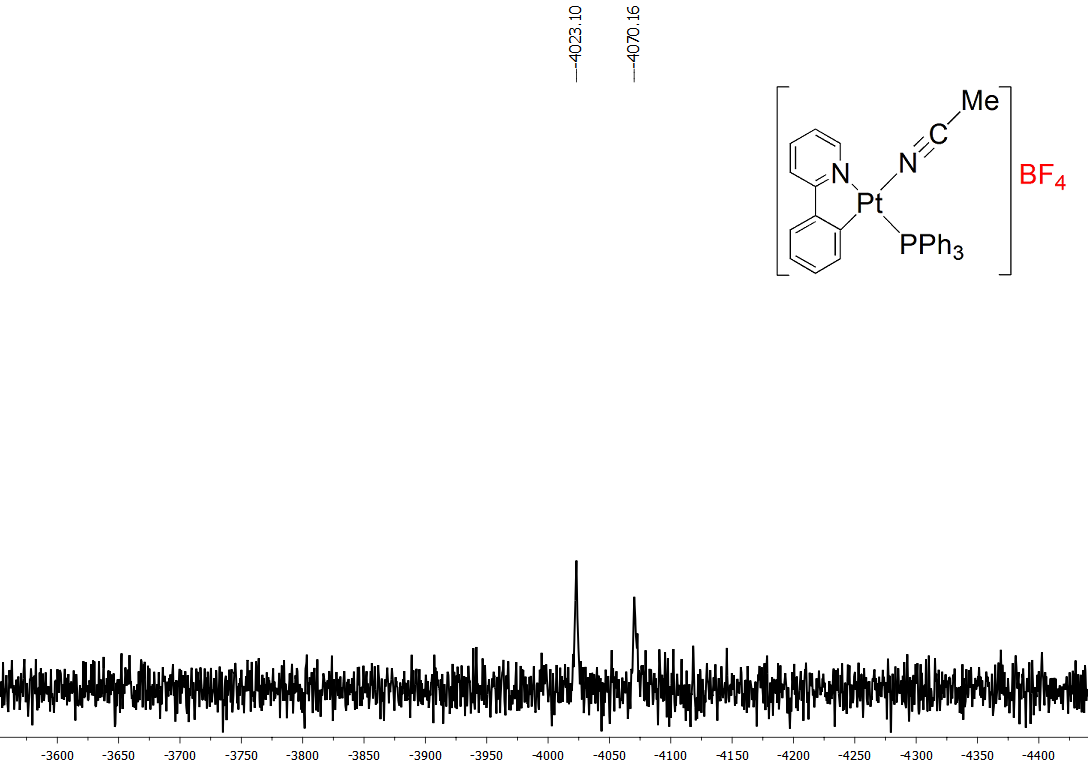
**Figure S9.** 195PtNMR spectrum of the complex **5a** in CDCl3.



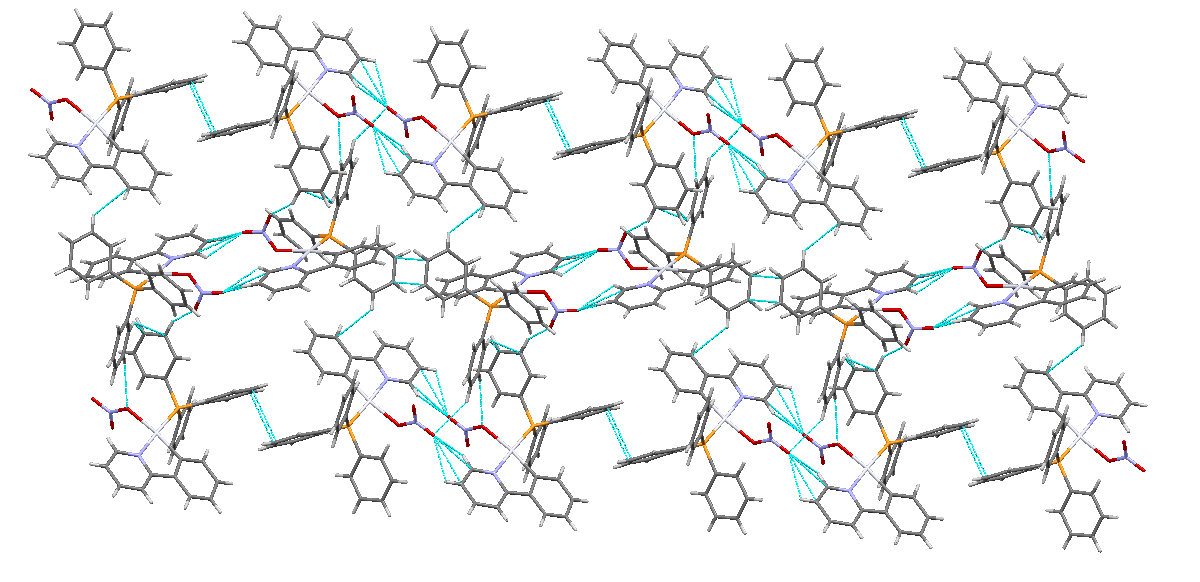
**Figure S10.** 1HNMR spectrum of the complex **5b** in CDCl3.



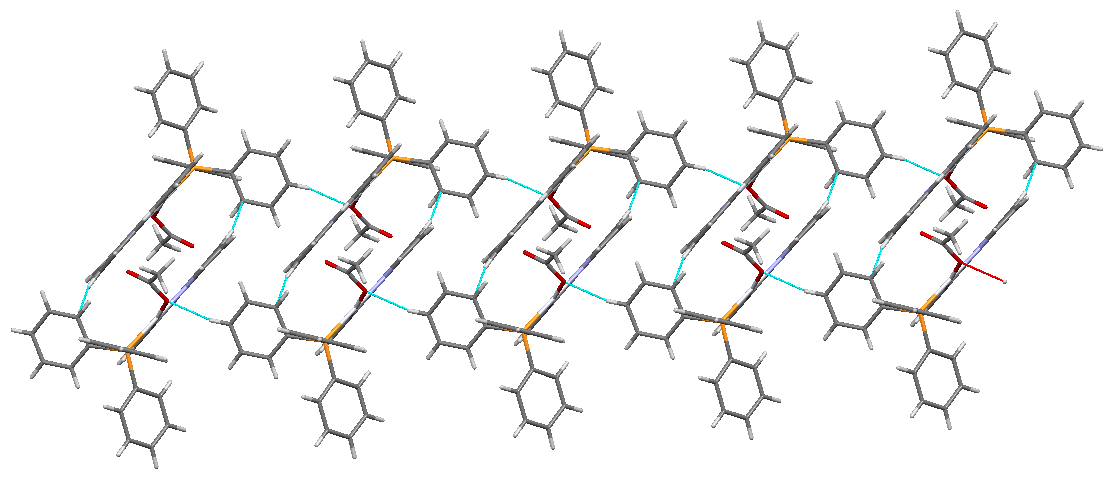
**Figure S11.** 31P{H}NMR spectrum of the complex **5b** in CDCl3.



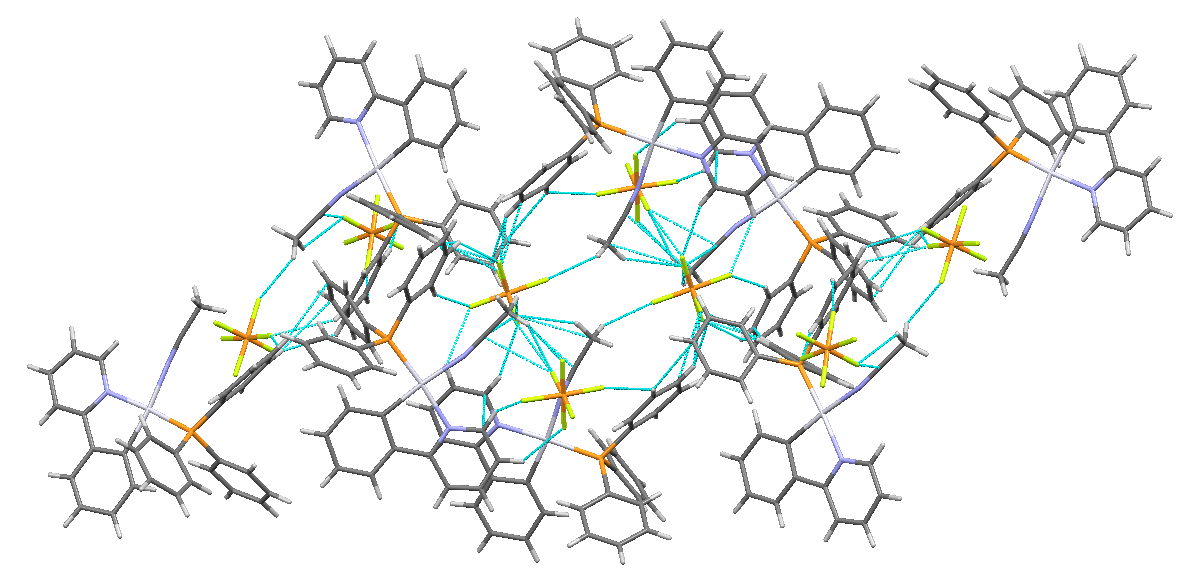
**Figure S12.** 195PtNMR spectrum of the complex **5b** in CDCl3.



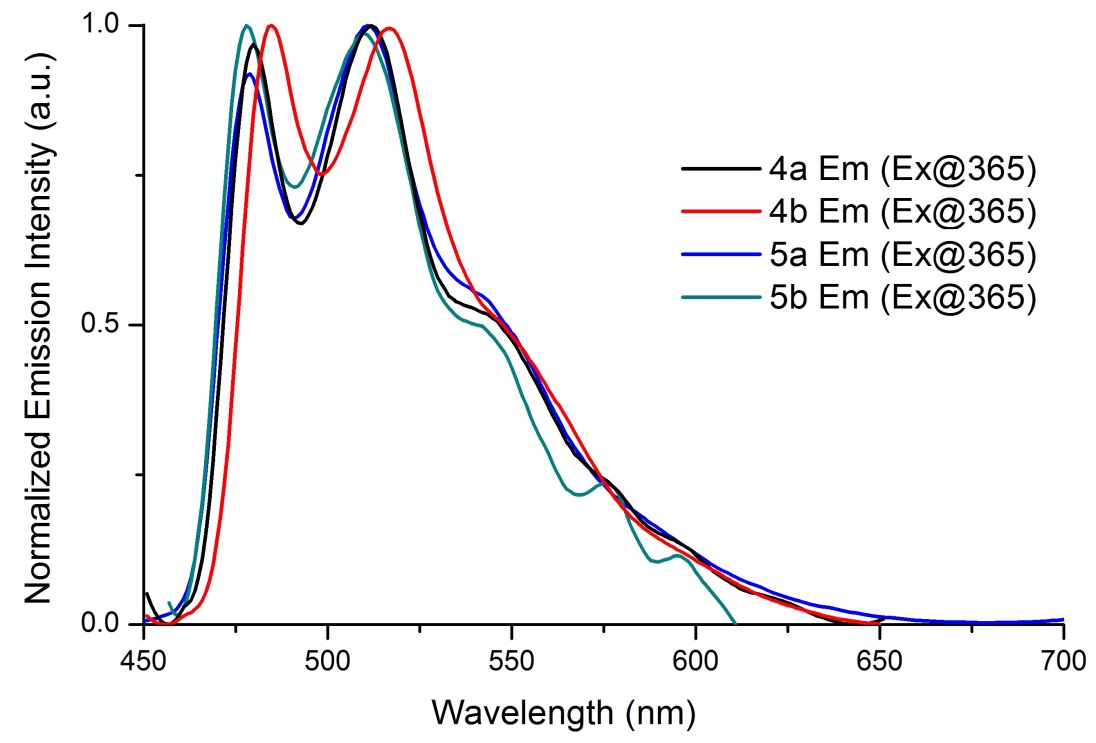
**Figure S13.** Crystal packing of the complex **4a**.



**Figure S14.** Crystal packing of the complex **4b**.



**Figure S15.** Crystal packing of the complex **5a**.



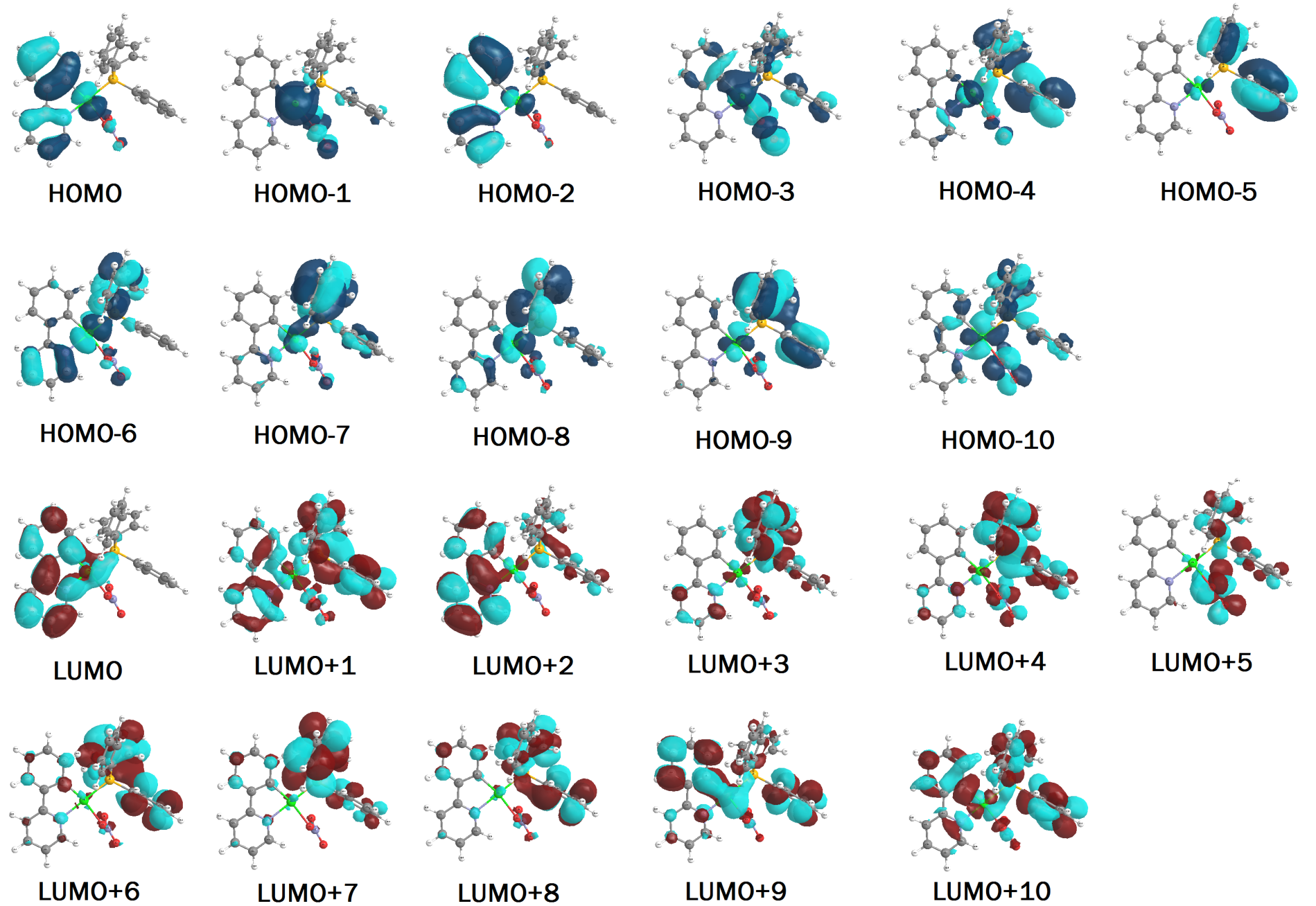
**Figure S16.** Normalized emission spectra for the complexes **4a**, **4b**, **5a** and **5b** in PMMA films at 298 K.

**Table S1.** Selected geometrical parameters (Å, °) for the complexes **4a** and **5a** in gas phase and CH2Cl2 solution.

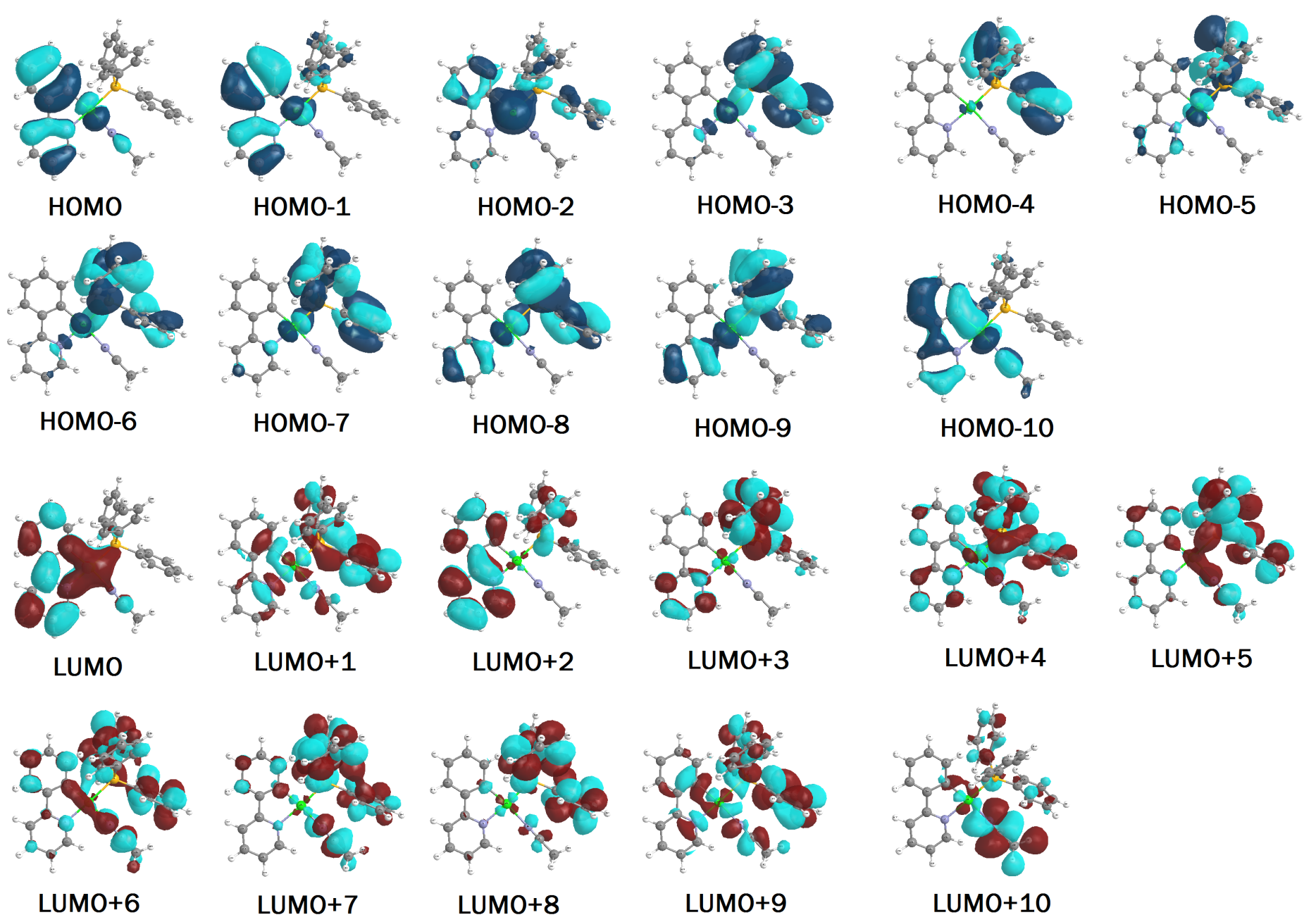
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex 4a | | | Complex 5a | | |
| Bond distances and angles | Gas phase | CH2Cl2 | Bond distances and angles | Gas phase | CH2Cl2 |
| Pt1-P1 | 2.31070 | 2.31891 | Pt1-P1 | 2.34392 | 2.34235 |
| Pt1-C1 | 2.01854 | 2.01484 | Pt1-C1 | 2.02047 | 2.02165 |
| Pt1-N1 | 2.10089 | 2.10913 | Pt1-N1 | 2.11820 | 2.11873 |
| Pt1-O1 | 2.17076 | 2.20380 | Pt1-N2 | 2.16009 | 2.15186 |
| P1-C12 | 1.84517 | 1.84599 | P1-C12 | 1.84665 | 1.84486 |
| P1-C18 | 1.84616 | 1.84389 | P1-C18 | 1.83545 | 1.83702 |
| P1-C24 | 1.83783 | 1.83773 | P1-C24 | 1.83791 | 1.84013 |
| N2-O1 | 1.32290 | 1.30908 | N2-C30 | 1.15702 | 1.15698 |
| N2-O2 | 1.24321 | 1.24294 | C30-C31 | 1.45690 | 1.45493 |
| N2-O3 | 1.22780 | 1.23565 | P1-Pt1-C1 | 96.59953 | 96.88339 |
| P1-Pt1-C1 | 99.50941 | 98.87025 | C1-Pt1-N1 | 80.43856 | 80.38248 |
| C1-Pt1-N1 | 80.53301 | 80.49588 | N1-Pt1-N2 | 92.48777 | 92.39304 |
| N1-Pt1-O1 | 87.73111 | 88.92951 | N2-Pt1-P1 | 90.48867 | 90.34251 |
| O1-Pt1-P1 | 92.22709 | 91.63043 | P1-Pt1-N1 | 176.98078 | 177.26112 |
| P1-Pt1-N1 | 176.47798 | 176.30621 | N2-Pt1-C1 | 172.75787 | 172.75439 |
| O1-Pt1-C1 | 168.25822 | 169.39360 | Pt1-N2-C30 | 176.42784 | 179.23936 |
| Pt1-O1-N2 | 115.78547 | 117.57872 | N2-C30-C31 | 178.94206 | 179.48706 |
| O1-N2-O2 | 118.71986 | 119.47292 |  |  |  |
| O2-N2-O3 | 124.36731 | 123.35855 |  |  |  |
| O1-N2-O3 | 116.91236 | 117.16831 |  |  |  |

**Table S2**. The energies of the selected molecular orbitals of complexes **4a** and **5a** together with their compositions in CH2Cl2.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Complex 4a | | | | | Complex 5a | | | | |
|  |  | Energy  (eV) | Components(%) | | | | Energy  (eV) | Components(%) | | | |
|  | MO | Pt | ppy | PPh3 | NO3 | Pt | ppy | PPh3 | CH3CN |
|  | LUMO+10 | +0.037 | 20 | 26 | 50 | 3 | -0.306 | 5 | 8 | 13 | 74 |
|  | LUMO+9 | -0.098 | 11 | 47 | 40 | 2 | -0.424 | 16 | 19 | 55 | 10 |
|  | LUMO+8 | -0.168 | 3 | 7 | 89 | 1 | -0.541 | 2 | 4 | 89 | 5 |
|  | LUMO+7 | -0.357 | 3 | 8 | 88 | 1 | -0.619 | 4 | 7 | 74 | 15 |
|  | LUMO+6 | -0.540 | 4 | 7 | 88 | 1 | -0.760 | 5 | 12 | 71 | 12 |
|  | LUMO+5 | -0.696 | 8 | 4 | 21 | 67 | -0.982 | 6 | 10 | 75 | 8 |
|  | LUMO+4 | -0.718 | 4 | 6 | 80 | 10 | -1.099 | 6 | 15 | 73 | 6 |
|  | LUMO+3 | -1.063 | 3 | 6 | 90 | 1 | -1.403 | 3 | 11 | 85 | 1 |
|  | LUMO+2 | -1.091 | 6 | 77 | 16 | 1 | -1.454 | 2 | 79 | 19 | 0 |
|  | LUMO+1 | -1.180 | 29 | 19 | 49 | 3 | -1.639 | 32 | 16 | 48 | 4 |
|  | LUMO | -1.817 | 5 | 88 | 6 | 1 | -2.234 | 6 | 84 | 8 | 3 |
|  | HOMO | -6.000 | 43 | 54 | 1 | 3 | -6.468 | 32 | 65 | 1 | 2 |
|  | HOMO-1 | -6.255 | 72 | 2 | 7 | 18 | -6.900 | 17 | 75 | 7 | 1 |
|  | HOMO-2 | -6.558 | 11 | 84 | 4 | 1 | -6.966 | 77 | 11 | 12 | 0 |
|  | HOMO-3 | -6.845 | 13 | 14 | 13 | 60 | -7.285 | 13 | 5 | 81 | 1 |
|  | HOMO-4 | -6.899 | 16 | 7 | 71 | 6 | -7.390 | 2 | 1 | 97 | 0 |
|  | HOMO-5 | -7.003 | 3 | 1 | 95 | 1 | -7.444 | 16 | 5 | 79 | 0 |
|  | HOMO-6 | -7.065 | 58 | 11 | 27 | 3 | -7.464 | 10 | 6 | 83 | 1 |
|  | HOMO-7 | -7.132 | 8 | 5 | 84 | 3 | -7.534 | 18 | 4 | 78 | 0 |
|  | HOMO-8 | -7.156 | 27 | 5 | 64 | 4 | -7.657 | 33 | 7 | 60 | 0 |
|  | HOMO-9 | -7.231 | 13 | 3 | 81 | 3 | -7.748 | 41 | 11 | 48 | 0 |
|  | HOMO-10 | -7.317 | 44 | 7 | 17 | 32 | -8.268 | 63 | 29 | 3 | 5 |



**Figure S17.** Selected molecular orbital plots of the complex **4a**.



**Figure S18.** Selected molecular orbital plots of the complex **5a**.

**Table S3.** Wavelengths and nature of transitions for the complex **4a** where M = Pt, L = ppy, Lʹ = PPh3 and Lʹʹ = NO3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Excited state | Oscillator strength | Calculated λ (nm) | Transitions  (Major Contribution) | Assignment |
| S0→S1 | 0.0620 | 362 | HOMO→LUMO (96%) | ILCT/MLCT |
| S0→S5 | 0.0696 | 302 | H-2→LUMO (57%)  HOMO→L+2 (30%) | ILCT/MLCT  ILCT/MLCT/MLʹCT |
| S0→S7 | 0.0943 | 290 | H-2→LUMO (27%)  HOMO→L+2 (46%) | ILCT/MLCT  ILCT/MLCT/MLʹCT |
| S0→S11 | 0.0431 | 275 | H-1→L+3 (73%) H-6→LUMO (8%) H-6→LUMO (8%) | MLCT/LʹʹLʹCT |
| S0→S12 | 0.1923 | 274 | H-6→LUMO (38%)  H-1→L+3 (18%) | MLCT/LʹLCT/ILCT  MLCT/LʹʹLʹCT |
| S0→S17 | 0.0232 | 264 | HOMO→L+4 (72%)  HOMO→L+5 (19%) | MLCT/LLʹCT/MLʹʹCT  LMCT/MLʹʹCT/MLʹCT |
| S0→S25 | 0.0663 | 253 | HOMO→L+6 (51%)  H-2→L+2 (20%) | MLʹCT/LLʹCT  ILCT/MLʹCT |
| S0→S26 | 0.1253 | 251 | H-2→L+2(48%)  HOMO→L+6 (33%) | ILCT/MLʹCT  MLʹCT/LLʹCT |

**Table S4.** Wavelengths and nature of transitions for the complex **5a** where M = Pt, L = ppy, Lʹ = PPh3 and Lʹʹ = CH3CN.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Excited state | Oscillator strength | Calculated λ (nm) | Transitions  (Major Contribution) | Assignment |
| S0→S1 | 0.067 | 354 | HOMO→LUMO (96%) | ILCT/MLCT |
| S0→S4 | 0.074 | 306 | H-1→LUMO (60%)  HOMO→L+2 (7%) | ILCT/MLCT  ILCT/MLCT/MLʹCT |
| S0→S5 | 0.052 | 303 | H-2→L+1 (58%)  H-1→LUMO (14%) | MLʹCT/ILCT  ILCT/MLCT |
| S0→S6 | 0.074 | 282 | HOMO→L+2 (66%) | ILCT/MLCT/MLʹCT |
| S0→S10 | 0.274 | 269 | H-5→LUMO (39%)  H-8→LUMO (12%)  H-7→LUMO (11%)  H-9→LUMO (11%) | LʹLCT/MLCT  LʹLCT/MLCT  LʹLCT/MLCT  MLCT/LʹLCT |
| S0→S13 | 0.095 | 261 | HOMO→L+4 (52%)  H-6→LUMO (17%)  H-5→LUMO (11%) | LLʹCT/MLʹCT  LʹLCT/MLCT  LʹLCT/MLCT |
| S0→S15 | 0.066 | 260 | H-2→L+2 (36%)  HOMO→L+4 (19%)  H-5→LUMO (15%)  H-7→LUMO (10%) | MLCT/MLʹCT  LLʹCT/MLʹCT  LʹLCT/MLCT  LʹLCT/MLCT |
| S0→S19 | 0.058 | 252 | HOMO→L+5 (38%)  H-8→LUMO (18%)  H-7→LUMO (15%)  H-1→L+2 (10%) | LLʹCT/MLʹCT  LʹLCT/MLCT  LʹLCT/MLCT  ILCT/MLʹCT/MLCT |
| S0→S21 | 0.149 | 250 | H-1→L+3 (31%)  HOMO→L+5 (27%)  H-1→L+2 (16%)  H-8→LUMO (10%) | LLʹCT/MLʹCT  LLʹCT/MLʹCT  ILCT/MLʹCT/MLCT  LʹLCT/MLCT |

**Table S5.** Crystallographic and structure refinement data for the complexes **4a**, **4b** and **5a**.

|  |  |  |  |
| --- | --- | --- | --- |
|  | 4a | 4b | 5a |
| Empirical formula | C29H23N2O3PPt | C33H30Cl4NO2PPt | C63H53Cl3F12N4P4Pt2 |
| Formula weight | 673.54 | 840.43 | 1714.50 |
| Temperature | 298(2) K | 298(2) K | 120(2) K |
| Wavelength | 0.71073 A | 0.71073 A | 0.71073 A |
| Crystal system, space group | Monoclinic, P 21/c | Triclinic, P -1 | Monoclinic, P 21/c |
| Unit cell dimensions | a = 9.5709(19) A  alpha = 90 deg.  b = 15.243(3) A  beta = 90.86(3) deg.  c = 17.427(4) A  gamma = 90 deg. | a = 9.839(2) A  alpha = 99.84(3) deg.  b = 12.558(3) A  beta = 94.66(3) deg.  c = 14.419(3) A  gamma = 109.04(3) deg. | a = 16.538(3) A  alpha = 90 deg.  b = 15.168(3) A  beta = 122.59(2) deg.  c = 30.380(9) A  gamma = 90 deg. |
| Volume | 2542.0(9) A3 | 1641.3(6) A3 | 6421(3) A3 |
| Z, Calculated density | 4, 1.760 Mg/m3 | 2, 1.701 Mg/m3 | 4, 1.774 Mg/m3 |
| Absorption coefficient | 5.617 mm-1 | 4.680 mm-1 | 4.655 mm-1 |
| F(000) | 1312 | 824 | 3336 |
| Crystal size | 0.30 x 0.20 x 0.18 | 0.45 x 0.30 x 0.20 mm | 0.20 x 0.12 x 0.10 mm |
| Theta range for data collection | 2.13 to 25.00 deg. | 2.21 to 25.00 deg. | 2.41 to 25.00 deg. |
| Limiting indices | -11<= h <=11  -17<= k <=18  -18<= l <=20 | -11<= h <=11  -14<= k <=12  -17<= l <=17 | -19<= h <=19  -18<= k <=15  -32<= l <=36 |
| Reflections collected / unique | 18213 / 4477 [R(int) = 0.1309] | 11934 / 5749 [R(int) = 0.0986] | 26614 /11299 [R(int) = 0.1796] |
| Completeness to theta = 25.00 | 99.8 % | 99.4 % | 99.9 % |
| Absorption correction | Numerical | Numerical | Numerical |
| Max. and min. transmission | 0.4313 and 0.2836 | 0.4546 and 0.2272 | 0.6532 and 0.4562 |
| Refinement method | Full-matrix least-squares on F2 | Full-matrix least-squares on F2 | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 4477 / 0 / 325 | 5749 / 0 / 380 | 11299 / 0 / 471 |
| Goodness-of-fit on F2 | 0.927 | 0.989 | 0.998 |
| Final R indices [I>2sigma(I)] | R1 = 0.0499, wR2 = 0.0983 | R1 = 0.0588, wR2 = 0.1383 | R1 = 0.1047, wR2 = 0.1915 |
| R indices (all data) | R1 = 0.0886, wR2 = 0.1075 | R1 = 0.0797, wR2 = 0.1497 | R1 = 0.1923, wR2 = 0.2218 |
| Largest diff. peak and hole | 2.074 and -1.221 e.A-3 | 2.269 and -2.961 e.A-3 | 2.574 and -2.621 e.A-3 |