Supporting Information for the manuscript

Platinum(II) imidazo[4,5-*f*]-1,10-phenanthroline chlorides and thiolates: synthesis and crystal structures

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SI.1. General information

In-house facilities were used for CHN and EI MS analysis. The following instruments were used: absorption spectra, a Cary 50 Bio UV-Visible spectrophotometer; luminescence spectra, a Perkin Elmer LS 50B spectrofluorimeter; ^{1}H NMR spectra (recorded in DMSO-d_6 and presented as δ in ppm and J in Hz), a Bruker 250 MHz spectrometer.

SI.2. Synthesis of 1,10-phenanthroline-5,6-dione

The synthesis was carried out under air. 1,10-Phenanthroline (4 g, 22.2 mmol) and KBr (4 g, 33.6 mmol) were thoroughly mixed as a solids and slowly (5 min) added to a mixture of H_2SO_4 (98%, 40 ml) and HNO_3 (69%, 20 ml) cooled to 0^0C. The temperature during the addition was kept at 0-5^0C. The resulting solution was refluxed (bath temperature - 100^0C) for 4 hr (CAUTION: the reaction is accompanied by formation of Br_2 fumes). The reaction mixture was cooled to r.t., poured onto crushed ice and cautiously neutralized (CAUTION: exothermic reaction) with concentrated aqueous NaOH (70-80 g of NaOH) to pH 4-5 in an ice bath to give a yellow suspension. At higher pH the mixture turns dark green, but addition of acid to pH 4-5 restores the yellow colour. The solution was extracted with $CHCl_3$ (2x250 ml). Organic phase was washed with water, briefly dried if necessary ($MgSO_4$) and evaporated. The crude product was dissolved in 100 ml of boiling ethanol. Cooling to r.t. provided 2.3-2.8 g of pure product as yellow needles ($C_{12}H_6N_2O_2$, M.W. 210.19). The compound could not be purified by column chromatography (SiO_2 or Al_2O_3, CH_2Cl_2:CH_3OH). The compound should not be kept for a long time in $CHCl_3$ and especially CH_2Cl_2 because it seems to decompose to give colourless suspension.

*SI.3. Analytical results for the **imP** ligands*

imP-^{t}Bu. 1,10-Phenathroline-5,6-dione (0.5 g, 2.38 mmol), trimethylacetaldehyde (0.25 g, 2.90 mmol) and ammonium acetate (3g, 39 mmol) gave 0.504 g (1.71 mmol, 72%) of beige product. Calc. for $C_{17}H_{16}N_4 \cdot H_2O$ (M.W. 294.35): C, 69.37; H, 6.16; N, 19.03. Found: C, 68.73; H, 5.81; N, 18.92. EI MS *m/z*: 276 (65%, M^+), 261 (100%, $\{M - CH_3\}^+$). ^{1}H NMR: 1.53 (s, 9H), 7.70-7.85 (m, 2H), 8.81 (d, J 8.3, 1H), 8.91 (d, J 8.2, 1H), 8.95-8.92 (m, 2H), 12.94 (s, 1H).

L-H. 1,10-Phenathroline-5,6-dione (0.45 g, 2.14 mmol), benzaldehyde (0.3 g, 2.83 mmol) and ammonium acetate (3g, 39 mmol) gave 0.604 g (1.77 mmol, 83%) of beige product. Calc. for $C_{19}H_{12}N_4 \cdot (H_2O)_{2.5}$ (M.W. 341.37): C, 66.85; H, 5.02; N,

16.41. Found: C, 66.42; H, 4.48; N, 16.23. EI MS *m/z*: 296 (100%, M^+). ^{1}H NMR (DMSO-d_6): 7.47-7.69 (m, 3H), 7.78-7.91 (br, 2H), 8.29 (d, *J* 7.3, 2H), 8.93 (d, *J* 7.6, 2H), 9.04 (d, *J* 3.1, 2H), 13.77 (s, 1H).

L-^{t}Bu. 1,10-Phenathroline-5,6-dione (0.5 g, 2.38 mmol), 4-tert-butylbenzaldehyde (0.5 g, 3.08 mmol) and ammonium acetate (3g, 39 mmol) gave 0.813 g (2.00 mmol, 84%) of beige product. Calc. for $C_{23}H_{20}N_4 \cdot (H_2O)_3$ (M.W. 406.48): C, 67.96; H, 6.45; N, 13.78. Found: C, 68.27; H, 5.98; N, 13.82. EI MS *m/z*: 352 (100%, M^+). ^{1}H NMR: 1.36 (s, 9H), 7.64 (d, *J* 8.6, 2H), 7.84 (m, 2H), 8.22 (d, *J* 8.6, 2H), 8.94 (m, 2H), 9.03 (m, 2H), 13.70 (s, 1H).

L-OMe. 1,10-Phenathroline-5,6-dione (0.5 g, 2.38 mmol), 4-methoxybenzaldehyde (0.4 g, 2.94 mmol) and ammonium acetate (3g, 39 mmol) gave 0.734 g (1.96 mmol, 82%) of pale yellow product. Calc. for $C_{20}H_{14}N_4O \cdot (CH_3CO_2H)_{0.2} \cdot (H_2O)_2$ (M.W. 374.39): C, 65.44; H, 5.06; N, 14.96. Found: C, 65.66; H, 4.87; N, 15.73. EI MS *m/z*: 326 (100%, M^+). ^{1}H NMR (DMSO-d_6): 3.68 (s, 3H), 7.18 (d, *J* 8.9, 2H), 7.83 (dd, *J* 8.3, *J* 4.3, 2H), 8.23 (d, *J* 8.9, 2H), 8.91 (dd, *J* 8.3, *J* 1.8, 2H), 9.02 (dd, *J* 4.3, *J* 1.9, 2H), N*H* proton was not observed.

L-NMe$_2$. 1,10-Phenathroline-5,6-dione (0.5 g, 2.38 mmol), 4-dimethylaminobenzaldehyde (0.36 g, 2.41 mmol) and ammonium acetate (3g, 39 mmol) gave 0.557 g (1.52 mmol, 64%) of yellow product. Calc. for $C_{21}H_{17}N_5 \cdot (H_2O)_{1.5}$ (M.W. 366.42): C, 68.84; H, 5.50; N, 19.11. Found: C, 68.20; H, 4.95; N, 18.94. EI MS *m/z*: 339 (100%, M^+). ^{1}H NMR (DMSO-d_6): 3.02 (s, 6H), 6.90 (d, *J* 9.2, 2H), 7.82 (br, 2H), 8.11 (d, *J* 8.9, 2H), 8.90 (d, *J* 8.3, 2H), 9.00 (d, *J* 4.9, 2H), 13.39 (s, br, 1H).

L-NO$_2$. 1,10-Phenathroline-5,6-dione (0.5 g, 2.38 mmol), 4-nitrobenzaldehyde (0.4 g, 2.65 mmol) and ammonium acetate (3g, 39 mmol) gave 0.792 g (2.06 mmol, 86%) of orange product. Calc. for $C_{19}H_{11}N_5O_2 \cdot (CH_3CO_2H)_{0.3} \cdot (H_2O)_{1.3}$ (M.W. 385.36): C, 61.30; H, 3.92; N, 18.17. Found: C, 60.83; H, 3.59; N, 18.21. EI MS *m/z*: 341 (100%, M^+). ^{1}H NMR (DMSO-d_6): 7.85 (br, 2H), 8.45-8.56 (m, 4H), 8.92 (dd, *J* 8.3, *J* 1.9, 2H), 9.06 (dd, *J* 4.3, *J* 1.2, 2H), 14.13 (s, 1H).

L-Ph. 1,10-Phenathroline-5,6-dione (0.28 g, 1.33 mmol), biphenyl-4-carboxaldehyde (0.26 g, 1.43 mmol) and ammonium acetate (2g, 26 mmol) gave 0.458 g (1.12 mmol, 84%) of pale yellow product. Calc. for $C_{25}H_{16}N_4 \cdot (H_2O)_2$ (M.W. 408.45): C, 73.51; H, 4.94; N, 13.72. Found: C, 72.84; H, 5.29; N, 13.67. EI MS *m/z*: 372 (100%, M^+). ^{1}H NMR: 7.38-7.46 (m, 1H), 7.48-7.57 (m, 2H), 7.77-7.92 (m, 4H), 7.95 (d, *J* 8.6, 2H), 8.39 (d, *J* 8.6, 2H), 8.92-8.99 (m, br, 2H), 9.02-9.07 (m, br, 2H), 13.83 (s, 1H).

L-Nap. 1,10-Phenathroline-5,6-dione (0.33 g, 1.57 mmol), 2-naphthaldehyde (0.26 g, 1.66 mmol) and ammonium acetate (2g, 26 mmol) gave 0.376 g (1.03 mmol, 66%) of pale yellow product. Calc. for $C_{23}H_{14}N_4 \cdot H_2O$ (M.W. 364.40): C, 75.81; H, 4.43; N, 15.38. Found: C, 74.70; H, 4.54; N, 15.19. EI MS *m/z*: 346 (100%, M^+). ^{1}H NMR: 7.57-7.68 (m, 2H), 7.80-7.93 (m, 2H), 7.99-8.16 (m, 2H), 8.16 (d, *J* 9.2, 1H), 8.44 (dd, *J* 8.6, 2.3, 1H), 8.82 (s, 1H), 8.94-9.02 (m, 2H), 9.03-9.08 (m, 2H), 13.95 (s, 1H).

*SI.4. Analytical results for the complexes Pt(**imP**)Cl$_2$*

Pt(imP-^{t}Bu)Cl$_2$. Calc. for $C_{17}H_{16}Cl_2N_4Pt \cdot H_2O$ (M.W. 560.33): C, 36.44; H, 3.24; N, 10.00. Found: C, 36.67; H, 3.36; N, 9.53.

Pt(L-H)Cl$_2$. Calc. for $C_{19}H_{12}Cl_2N_4Pt \cdot H_2O$ (M.W. 580.32): C, 39.32; H, 2.43; N, 9.65. Found: C, 38.78; H, 2.09; N, 9.38. ^{1}H NMR: 7.52-7.72 (m, 3H), 8.03-8.23

(m, 2H), 8.25 (d, *J* 7.0, 2H), 9.17 (d, *J* 7.6, 1H), 9.22 (d, *J* 8.6, 1H), 9.55 (d, *J* 5.8, 1H), 9.57 (d, *J* 5.5, 1H), 14.25 (s, 1H).

Pt(L-^{t}Bu)Cl$_2$. Calc. for $C_{23}H_{20}Cl_2N_4Pt\cdot H_2O$ (M.W. 636.43): C, 43.41; H, 3.48; N, 8.80. Found: C, 43.68; H, 3.23; N, 8.73. ^{1}H NMR: 1.39 (s, 9H), 7.65 (d, *J* 8.6, 2H), 7.90-8.15 (m, 2H), 8.10 (d, *J* 8.3, 2H), 9.06 (d, *J* 7.9, 1H), 9.12 (d, *J* 8.3, 1H), 9.47 (d, *J* 5.2, 1H), 9.53 (d, *J* 5.8, 1H), 14.01 (s, 1H).

Pt(L-OMe)Cl$_2$. Calc. for $C_{20}H_{14}Cl_2N_4OPt\cdot H_2O$ (M.W. 610.35): C, 39.36; H, 2.64; N, 9.18. Found: C, 39.59; H, 2.65; N, 9.19.

Pt(L-NMe$_2$)Cl$_2$. Calc. for $C_{21}H_{17}Cl_2N_5Pt$ (M.W. 605.38): C, 41.66; H, 2.83; N, 11.57. Found: C, 41.14; H, 2.97; N, 11.06. ^{1}H NMR: 3.05 (s, 6H), 6.87 (d, *J* 8.9, 2H), 8.02 (d, *J* 9.2, 2H), 8.0-8.25 (br, 2H), 9.22 (d, *J* 7.6, 2H), 9.61 (d, *J* 5.2, 2H), 13.83 (s, 1H).

Pt(L-NO$_2$)Cl$_2$. Calc. for $C_{19}H_{11}Cl_2N_5O_2Pt\cdot(H_2O)_2$ (M.W. 643.34): C, 35.47; H, 2.35; N, 10.89. Found: C, 35.31; H, 2.26; N, 10.63.

Pt(L-Ph)Cl$_2$. Calc. for $C_{25}H_{16}Cl_2N_4Pt\cdot(H_2O)_{1.5}$ (M.W. 665.43): C, 45.12; H, 2.88; N, 8.42. Found: C, 44.90; H, 2.42; N, 8.23.

Pt(L-Nap)Cl$_2$. The synthesis was carried out in 2-methoxyethanol. Calc. for $C_{23}H_{14}Cl_2N_4Pt\cdot(H_2O)_{0.5}$ (M.W. 621.38): C, 44.46; H, 2.43; N, 9.02. Found: C, 44.44; H, 2.11; N, 9.09.

*SI.5. Analytical results for the complexes Pt(**imP**)(thiolate)$_2$*

Pt(imP-^{t}Bu)(S-CO$_2$Me)$_2$. Calc. for $C_{33}H_{30}N_4O_4PtS_2$ (M.W. 805.83): C, 49.19; H, 3.75; N, 6.95. Found: C, 48.89; H, 3.83; N, 6.63. ^{1}H NMR: 1.55 (s, 9H), 3.79 (s, 6H), 6.86 (t, *J* 7.0, 2H), 6.98 (t, *J* 7.3, 2H), 7.43 (d, *J* 7.6, 2H), 8.08-8.26 (br, 2H), 8.21 (d, *J* 8.0, 2H), 9.15-9.35 (br, 2H), 9.76 (d, *J* 5.2, 2H), 13.49 (s, 1H).

Pt(imP-^{t}Bu)(S-^{t}Bu)$_2$. Calc. for $C_{37}H_{42}N_4PtS_2\cdot H_2O$ (M.W. 819.98): C, 54.20; H, 5.41; N, 6.83. Found: C, 54.41; H, 4.92; N, 6.70. ^{1}H NMR: 1.17 (s, 18H), 1.55 (s, 9H), 6.93 (d, *J* 8.6, 4H), 7.43 (d, *J* 8.6, 4H), 8.08-8.23 (m, 2H), 9.20 (d, *J* 8.3, 1H), 9.30 (d, *J* 7.9, 1H), 9.89 (m, 2H), 13.47 (s, 1H).

Pt(L-H)(S-Me^{t}Bu)$_2$. Calc. for $C_{41}H_{42}N_4PtS_2\cdot H_2O$ (M.W. 868.02): C, 56.73; H, 5.11; N, 6.45. Found: C, 56.85; H, 4.72; N, 6.45. ^{1}H NMR: 0.87 (s, 18H), 2.31 (s, 6H), 6.74 (dd, *J* 8.0, 2.2, 2H), 6.86 (d, *J* 8.0, 2H), 7.53-7.71 (m, 3H), 7.87 (d, *J* 2.1, 2H), 8.01-8.15 (br, 2H), 8.30 (d, *J* 7.0, 2H), 9.27 (dd, *J* 8.6, 1.2, 2H), 9.60 (dd, *J* 5.2, 1.2, 2H), 14.29 (s, 1H).

Pt(L-^{t}Bu)(S-^{t}Bu)$_2$. Calc. for $C_{43}H_{46}N_4PtS_2$ (M.W. 878.06): C, 58.82; H, 5.28; N, 6.38. Found: C, 58.64; H, 5.42; N, 6.26. ^{1}H NMR: 1.17 (s, 18H), 1.36 (s, 9H), 6.95 (d, *J* 8.6, 4H), 7.46 (d, *J* 8.6, 4H), 7.65 (d, *J* 8.6, 2H), 8.05-8.22 (br, 2H), 8.17 (d, *J* 8.6, 2H), 9.20 (d, *J* 8.3, 2H), 9.88 (dd, *J* 5.5, 1.2, 2H), 14.06 (s, 1H).

Pt(L-^{t}Bu)(S-CO$_2$Me)$_2$. Calc. for $C_{39}H_{34}N_4O_4PtS_2\cdot H_2O$ (M.W. 899.94): C, 52.05; H, 4.03; N, 6.23. Found: C, 51.83; H, 3.77; N, 6.19. ^{1}H NMR: 1.36 (s, 9H), 3.80 (s, 6H), 6.87 (td, *J* 7.3, 1.2, 2H), 7.00 (td, *J* 7.6, 1.8, 2H), 7.44 (dd, *J* 7.7, 1.5, 2H), 7.64 (d, *J* 8.9, 2H), 8.05-8.20 (br, 2H), 8.16 (d, *J* 8.6, 2H), 8.26 (dd, *J* 7.9, 0.9, 2H), 9.20 (d, *J* 7.9, 2H), 9.75 (dd, *J* 5.5, 1.5, 2H), 14.06 (s, 1H).

Pt(L-OMe)(S-Me^{t}Bu)$_2$. Calc. for $C_{42}H_{44}N_4OPtS_2\cdot H_2O$ (M.W. 898.05): C, 56.17; H, 5.16; N, 6.24. Found: C, 55.58; H, 4.95; N, 6.10. ^{1}H NMR: 0.87 (s, 18H), 2.31 (s, 6H), 3.88 (s, 3H), 6.74 (dd, *J* 8.0, 1.9, 2H), 6.86 (d, *J* 7.7, 2H), 7.22 (d, *J* 8.9, 2H), 7.87 (d, *J* 1.5, 2H), 7.97-8.17 (br, 2H), 8.24 (d, *J* 9.2, 2H), 9.25 (dd, *J* 8.3, 1.2, 2H), 9.57-9.63 (dd, br, 2H), 14.12 (s, 1H).

Pt(L-NMe$_2$)(S-^{t}Bu)$_2$. Calc. for $C_{41}H_{43}N_5PtS_2 \cdot H_2O$ (M.W. 883.04): C, 55.77; H, 5.14; N, 7.93. Found: C, 55.28; H, 4.95; N, 7.92. ^{1}H NMR: 1.18 (s, 18H), 3.03 (s, 6H), 6.89 (d, *J* 9.5, 2H), 6.94 (d, *J* 8.6, 4H), 7.45 (d, *J* 8.3, 4H), 8.07 (d, *J* 8.6, 2H), 8.00-8.20 (br, 2H), 9.21 (d, *J* 8.3, 2H), 9.80-9.92 (br, 2H), 13.77 (s, 1H).

Pt(L-NMe$_2$)(S-CO$_2$Me)$_2$. Calc. for $C_{37}H_{31}N_5O_4PtS_2 \cdot (H_2O)_2$ (M.W. 904.91): C, 49.11; H, 3.90; N, 7.74. Found: C, 49.36; H, 3.67; N, 7.72. ^{1}H NMR: 3.03 (s, 6H), 3.80 (s, 6H), 6.81-6.93 (m, 4H), 7.00 (td, *J* 7.3, 1.8, 2H), 7.44 (dd, *J* 7.7, 1.6, 2H), 8.07 (d, *J* 8.9, 2H), 8.14 (dd, *J* 8.3, 5.5, 2H), 8.25 (dd, *J* 7.9, 1.2, 2H), 9.22 (dd, *J* 8.3, 1.2, 2H), 9.74 (d, *J* 5.2, 2H), 13.79 (s, 1H).

Pt(L-NO$_2$)(S-Me^{t}Bu)$_2$. Calc. for $C_{41}H_{41}N_5O_2PtS_2$ (M.W. 895.01): C, 55.02; H, 4.62; N, 7.82. Found: C, 54.80; H, 4.63; N, 7.56. ^{1}H NMR: 0.86 (s, 18H), 2.31 (s, 6H), 6.73 (dd, *J* 8.0, 2.2, 2H), 6.85 (d, *J* 8.0, 2H), 7.84 (d, *J* 1.9, 2H), 7.97-8.15 (br, 2H), 8.51 (m, 4H), 9.20 (dd, br, *J* 8.3, 1.2, 2H), 9.57 (d, br, *J* 4.9, 2H), 14.57 (s, 1H).

Pt(L-Ph)(S-^{t}Bu)$_2$. Calc. for $C_{45}H_{42}N_4PtS_2 \cdot (H_2O)_{0.5}$ (M.W. 907.06): C, 59.59; H, 4.78; N, 6.18. Found: C, 59.41; H, 4.61; N, 6.24. ^{1}H NMR: 1.17 (s, 18H), 6.95 (d, *J* 8.6, 4H), 7.39 -7.47 (t, 1H), 7.46 (d, *J* 8.6, 4H), 7.53 (t, *J* 7.0, 2H), 7.81 (d, *J* 7.0, 2H), 7.96 (d, *J* 8.6, 2H), 8.11-8.22 (t, br, 2H), 8.35 (d, *J* 8.6, 2H), 9.24 (dd, *J* 8.6, 1.5, 2H), 9.90 (dd, *J* 5.5, 1.2, 2H), 14.22 (s, 1H).

Pt(L-Nap)(S-^{t}Bu)$_2$. Calc. for $C_{43}H_{40}N_4PtS_2$ (M.W. 872.01): C, 59.23; H, 4.62; N, 6.43. Found: C, 59.18; H, 4.56; N, 6.33. ^{1}H NMR: 1.18 (s, 18H), 6.96 (d, *J* 8.5, 4H), 7.47 (d, *J* 8.3, 4H), 7.57-7.69 (m, 2H), 7.95-8.24 (m, 5H), 8.38 (d, *J* 8.6, 1H), 8.78 (s, 1H), 9.27 (d, *J* 8.3, 2H), 9.55 (d, *J* 5.5, 2H), 14.34 (s, 1H).