Preparations

**Ru(pzt)Cl₃, 3.** To 125 mL of absolute ethanol in a 200 mL round-bottom flask was added RuCl₃·3H₂O (0.033 g, 0.124 mmol) and ligand pzt (0.070 g, 0.124 mmol). The mixture was heated at reflux for about 3 h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder which had appeared was filtered from the red-brown solution. The product was washed with 3 × 30 mL portions of diethyl ether and air-dried. Yield 0.0724 g, 75%.

**[Ru(pzt)₂](PF₆)₂, 4.** Ligand pzt (0.083 g, 0.147 mmol) and Ru(pzt)Cl₃ complex (0.072 g, 0.074 mmol) in dry MeOH (50 mL) in presence of N-methylmorpholine (12 drops) were heated at reflux for 4 h under Ar. The deep red solution was cooled to room temperature before it was filtered to remove any unreacted materials. The solution was taken to dryness under vacuum and the residue was purified by column chromatography (SiO₂ eluting with CH₃CN-saturated KNO₃ solution-H₂O, 10 : 2 : 1). An excess of NH₄PF₆ was added to the major red-brown fraction and the solution was reduced in volume under vacuum. The precipitate was collected by filtration over Celite, before it was dissolved in CH₃CN, and evaporated to dryness *in vacuo* to afford [Ru(pzt)₂](PF₆)₂ as a red-brown powder. Yield 0.095 g, 79%. ¹H NMR (500 MHz; solvent acetone-d₆, see Table 3). ¹³C NMR (75 MHz; solvent acetone-d₆) δ 158.8, 156.0, 152.8 (C₆, C₆'), 148.3, 141.0 (C₀₃, C₀₃', C₀₃''), 140.5, 138.5 (C₄, C₄'), 136.4, 131.2 (C₀₅, C₀₅', C₀₅''), 128.9 (C₃'', C₅''), 128.0 (C₂'', C₂'', C₅, C₅''), 125.0 (C₃, C₃''), 121.7 (C₃, C₅). 106.4 (C₀₅, C₀₅', C₀₅''), 73.4 (C₀₁), 73.06 (C₇). IR (KBr, cm⁻¹): 108.8, 106.4(C₀₄, C₀₄', C₀₄''), 73.4 (C₀₁), 73.0 (C₇). IR (KBr, cm⁻¹): 2960 w, 2920 w, 2850 w, 1609 msh, 1408 m, 1204 w, 849 ssh, 787 msh, 756 msh, 559 ssh. ES-MS:
m/z 1377.6 ([M-PF$_6$]$^+$), 616.3 ([M-2PF$_6$]$^{2+}$). UV-vis (CH$_3$CN): $\lambda_{\text{max}}$ ($\varepsilon$) = 284.9 (68100), 310.0 (62700), 490.1 (22000) nm (L mol$^{-1}$ cm$^{-1}$).

[(ttt)Ru(pzt)](PF$_6$)$_2$, 5. Ru(ttt)Cl$_3$ (0.265 g, 0.50 mmol) was added to pzt (0.283 g, 0.50 mmol) in MeOH (20 mL). 10 drops of N-methylmorpholine was added. The solution was heated to reflux with stirring for 1 hr. The resulting deep-red solution was filtered through Celite to remove any unreacted [Ru(ttt)Cl$_3$] and excess methanolic solution of ammonium hexafluorophosphate was added to the filtrate to precipitate the ligand complexes. Further purification was achieved by column chromatography over silica eluting with CH$_3$CN-saturated KNO$_3$ solution-H$_2$O (17: 0.5: 1). The major orange-red band was collected. The complex was isolated as its PF$_6$$^-$ salt as a red powder. Yield 0.6 g, 94%. $^1$H NMR (500 MHz; solvent acetone-$d_6$, see Table 3). $^{13}$C NMR (75 MHz; solvent acetone-$d_6$) $\delta$ 158.82, 158.74, 156.03, 155.93, 152.82 (C$_6$, C$_6^\prime$), 148.56, 148.19, 141.03 (C$_{03}$, C$_{03}^\prime$, C$_{03}^\prime\prime$), 140.43, 138.44 (C$_4$, C$_4^\prime$), 136.37, 133.95, 131.16 (C$_{05}$, C$_{05}^\prime$, C$_{05}^\prime\prime$), 130.43 (C$_3$-(ttt), C$_5$-(ttt)), 128.92 (C$_3$-(pzt), C$_5$-(pzt)), 128.00 (C$_2$-(pzt), C$_6$-(pzt), C$_5$(pzt), C$_5$-(pzt)), 127.96 (C$_2$-(ttt), C$_6$-(ttt), C$_5$(ttt), C$_5$-(ttt)), 125.00 (C$_3$, C$_3^\prime$), 121.68 (C$_3$(pzt), C$_5$(pzt)), 121.34 (C$_3$(ttt), C$_5$(ttt)), 106.37 (C$_{05}$, C$_{05}^\prime$, C$_{05}^\prime\prime$), 73.37 (C$_{01}$), 73.06 (C$_7$), 20.69 (CH$_3$(ttt)).

IR (KBr, cm$^{-1}$): 3080 w, 2950 w, 2852 w, 1605 ssh, 1520 m, 1408 msh, 1327 m, 1246 w, 1196 w, 1096 m, 1030 wsh, 949 w, 840 ssh, 787 ssh, 752 msh, 656 wsh, 617 w, 559 ssh, 509 w. ES-MS: $m/z$ 1135.5 ([M-PF$_6$]$^+$), 495.2 ([M-2PF$_6$]$^{2+}$). UV-vis (CH$_3$CN): $\lambda_{\text{max}}$ ($\varepsilon$) = 284.9 (60900), 310.0 (60400), 490.1 (21300) nm (L mol$^{-1}$ cm$^{-1}$).

[Cd(pzt)(NO$_3$)$_2$], 9. To the ligand pzt (0.011 g, 0.02 mmol) in CH$_2$Cl$_2$ (5 mL) was added Cd(NO$_3$)$_2$.4H$_2$O (0.006 g, 0.02 mmol) in CH$_3$CN (5 mL) dropwise under Ar atmosphere. The reaction mixture was stirred at r.t overnight. The clear solution was
filtered. Colourless crystals were obtained upon slow evaporation of the solution at r.t.
The crystals were separated by filtration, washed with diethyl ether, then dried under
vacuum. Yield 0.009 g, 56%. $^{1}$H NMR (500 MHz; solvent dmsø-d$_6$, see Table 3). $^{13}$C
NMR (75 MHz; solvent dmsø-d$_6$) $\delta$ 153.25, 149.76, 149.53, 148.66, 141.22, 141.10,
140.32, 135.29, 131.30, 128.42, 128.27, 127.46, 124.04, 121.06, 106.79, 89.51, 72.82,
72.39. IR (KBr, cm$^{-1}$): 3113 m, 3078 m, 2947 w, 2893 w, 1701 w, 1601 m, 1574 m,
1551 m, 1516 m, 1481 ssh, 1447 ssh, 1385 ssh, 1296 ssh, 1265 ssh, 1204 m, 1165 m,
111m, 1015 msh, 949 m, 918 m, 895 w, 818 m, 791 ssh, 752 m, 660 w, 640 w, 617 w,
513 w, 451 w. ES-MS: $m/z$ (intensity (%), fragment), 1305.3 (1, $[\text{Cd(pzt)}_2\text{-NO}_3]$)$^{\text{+}}$),
622.3 (100, $[\text{Cd(pzt)}_2\text{2NO}_3]^2$). Anal. Calc. for C$_{33}$H$_{27}$CdN$_{11}$O$_7$ (802.05): C 49.42, H
3.39, N 19.21%; found: C 49.43, H 3.40, N 18.83%.

{$\{[\text{Fe(pzt)}_2](\text{NO}_3)_2\}(\text{AgNO}_3)_2\}_\infty$, 10. To complex 6 (0.001 g, 0.0007 mmol) in acetone
(1 mL) was added a solution of AgNO$_3$ (0.0003 g, 0.0014 mmol) in acetonitrile (1 mL),
dropwise. The mixture was allowed to slowly evaporate in the air at r.t. The
microcrystalline solid which formed the reaction mixture was collected, washed with
diethyl ether, and air-dried. $^1$H NMR (500 MHz; solvent acetone-d$_6$, see Table 3). ES-
MS: $m/z$ 763.26 ($\{[\text{Fe(pzt)}_2\text{Ag}_{2}]\}(\text{NO}_3)_2)^{2+}$).

{$\{[\text{Fe(pzt)}_2](\text{BF}_4)_2\}(\text{AgBF}_4)_\infty$, 11. To complex 6 (0.001 g, 0.0007 mmol) in acetone
(1 mL) was added AgBF$_4$ (0.0003 g, 0.0014 mmol) in acetone (1 mL) dropwise. The
mixture was allowed to slowly evaporate in the air at r.t. The microcrystalline
compound which was crystallized from the reaction mixture was collected, washed
with small amount of cold acetone, and air-dried. ES-MS: $m/z$ 691.4
($\{[\text{Fe(pzt)}_2\text{Ag}]\}(\text{BF}_4)^{2+}$)
{{[Fe(pzt)₂](ClO₄)₂}(AgClO₄)₂}∞, 12. Same method was used as above except AgClO₄ (0.0003 g, 0.0014 mmol) in acetone (1 mL) was applied instead. ES-MS: m/z 801.23 ({{[Fe(pzt)₂Ag₂]}(ClO₄)₂}²⁺)
Fig. I. ES-MS of material obtained from the reaction of ligand pzt with AgBF$_4$ in acetone. (A) High resolution scans of the four major signals (a)-(d); (B) Calculated isotope distribution patterns for (a) [(pztH)$^+$], (b) [Ag$_2$(pzt)$_2$]$^{2+}$, (c) [Ag(pzt)$_2$]$^+$, (d) [Ag$_2$(pzt)$_2$+(BF$_4$)]$^{2+}$. 
Fig. II. ES-MS of [Ru(pzt)(ttp)](PF₆)₂ complex in CH₃CN. (A) High resolution scans of the two signals (a) and (b); (B) Calculated isotope distribution patterns for (a) [Ru(pzt)(ttp)]²⁺ and (b) [Ru(pzt)(ttp)+(PF₆)]⁺.
Fig. III. ES-MS of [Ru(pzt)₂](PF₆)₂ complex in CH₃CN. (A) High resolution scans of the two major signals (a) and (b); (B) Calculated isotope distribution patterns for (a) [Ru(pzt)₂]²⁺ and (b) [Ru(pzt)₂+(PF₆)]⁺.
Fig. IV. ES-MS of [Fe(pzt)_2](PF_6)_2 complex in CH_3CN. (A) High resolution scans of the two major signals (a) and (b); (B) Calculated isotope distribution patterns for (a) [Fe(pzt)_2]^{2+} and (b) [Fe(pzt)_2+(PF_6)]^+. 
Fig. V. ES-MS of the product obtained from the reaction of [Ru(pzt)(ttp)](PF6)2 complex with Ag NO3 in acetone. (A) High resolution scans of the three signals (a), (b), and (c); (B) Calculated isotope distribution patterns for (a) [Ru(pzt)(ttp)]^{2+}, (b) [Ru(pzt)(ttp)Ag(NO3)]^{2+}, and (c) [Ru(pzt)(ttp)Ag2(NO3)2]^{2+}. 
Fig. VI. Expanded region (m/z 1400 to 2400) of ES-MS data for the material formed in the reaction of [Fe(pzt)$_2$](PF$_6$)$_2$ with AgNO$_3$ in acetone.
Fig. VII. $^1$NMR titration of [Zn(pzt)Cl$_3$] in dmso-$d_6$ with AgBF$_4$ solution in dmso-$d_6$.

(A) [Zn(pzt)Cl$_3$] in dmso-$d_6$

(B) [Zn(pzt)Cl$_3$] + AgBF$_4$ in dmso-$d_6$ (1:3)

(C) [Zn(pzt)Cl$_3$] + AgBF$_4$ in dmso-$d_6$ (1:5)

(D) [Zn(pzt)Cl$_3$] + AgBF$_4$ in dmso-$d_6$ (1:7)

(E) [Zn(pzt)Cl$_3$] + AgBF$_4$ in dmso-$d_6$ (1:11)

(F) [Zn(pzt)Cl$_3$] + AgBF$_4$ in dmso-$d_6$ (1:20)
Fig. VIII $^1$NMR titration of pzt ligand in dmso-d$_6$ with ZnCl$_2$ solution in dmso-d$_6$.

A $^1$NMR of pzt ligand in dmso-d$_6$.

E $^1$NMR of pzt + ZnCl$_2$ in dmso-d$_6$ (L:M)(1:0.5).

I $^1$NMR of [Zn(pzt)Cl$_2$] complex in dmso-d$_6$ (L:M)(1:1)
Fig. IX $^1$NMR titration of pzt ligand in dmso-d$_6$ with ZnCl$_2$ solution in dmso-d$_6$.

A $^1$NMR of pzt ligand in dmso-d$_6$.

B $^1$NMR of pzt + ZnCl$_2$ in dmso-d$_6$ (L:M)(1:0.1).

C $^1$NMR of pzt + ZnCl$_2$ in dmso-d$_6$ (L:M)(1:0.5).
D $^1$NMR of [Zn(pzt)Cl$_2$] complex in dmso-d$_6$ (L:M)(1:1)