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Supporting Information

Electrostatic vs Electronic interactions within oxidized multinuclear Pt(bipyridine)(dithiolene) complexes

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Fig. S1: Side view of 1,3-bis(dithiol-2-one) **3** with the central phenyl ring in the horizontal plane and the dithiole ring in the other one, the angle between the planes amounts to $14.2(2)^{\circ}$.



Fig. S2: Side view of compound 7 with the central phenyl ring in the horizontal plane showing the angles between the metalladithiolene planes and the phenyl ring plane rings in the range of $35.4(5)^{\circ}$ - $49.1(3)^{\circ}$. Butyl chains have been omitted for clarity



Fig. S3: Cyclic voltammogram of PtP in CH_2Cl_2 using 0.1 M of [NBu₄][PF₆] as supporting electrolytes. v=100 mV.s⁻¹.



Fig. S4: Cyclic voltammogram of Pt_2Fl in CH_2Cl_2 using 0.1 M of [NBu₄][PF₆] as supporting electrolytes. v=100 mV.s⁻¹.



Fig. S5: Cyclic voltammogram of $Pt_31,3,5-P$ in CH_2Cl_2 using 0.1 M of $[NBu_4][PF_6]$ as supporting electrolytes. v=100 mV.s⁻¹.



Fig. S6: Cyclic voltammogram of **Pt₃1,3,5-P** in CH₂Cl₂ using 0.005 M of [NBu₄][BArF] as supporting electrolytes. v=100 mV.s⁻¹.



Fig. S7: Cyclic voltammogram of **Pt₂1,3-P** (left) and **Pt₂1,4-P** (right)in CH₂Cl₂ using 0.005 M of [NBu₄][BArF] as supporting electrolytes. 20 mV/s<v<600 mV/s.



Fig. S8: Differential UV-vis-NIR spectra of **PtP** monitored upon gradual oxidation of the neutral complex with 0.2 M [Bu₄N][PF₆] as the supporting electrolyte.



Fig. S9: UV-vis-NIR spectrum of Oxidized Pt₂1,3-P and Pt₃1,3,5-P complexes.



Fig. S10: Differential UV-vis-NIR spectra of **Pt**₃**1**,3,5-P monitored upon gradual oxidation of the neutral complex with 0.005 M [Bu₄N][BArF] as the supporting electrolyte.



Fig. S11: Differential UV-vis-NIR spectra of $Pt_21,3-P$ (a), $Pt_21,4-P$ (b) and $Pt_31,3,5-P$ (c) monitored upon gradual oxidation with 0.005 M [Bu₄N][BArF] as the supporting electrolyte.



Fig. S12: Frontier molecular orbitals (HOMO, HOMO-1, LUMO and LUMO+1) and calculated energy levels for complex Pt21,3-P.







Fig. S14: ¹³C RMN of 3







Fig. S16: ¹³C RMN of 4







Fig. S18: ¹³C RMN of **6**







Fig. S20: ¹³C RMN of 7



Fig. S21: ¹H RMN of 8



Fig. S22: ¹H RMN of Pt₂1,3-P







Fig. S24: ¹H RMN of Pt₂1,4-P







Fig. S26: ¹H RMN of Pt₂Fl







Fig. S28: ¹H RMN of Pt₃1,3,5-P