Electronic Supplementary Material (ESI) for Dalton Transactions

On the electronic structure of NO_2-substituted bipyridines and their platinum complexes: Electronic Supplementary Information

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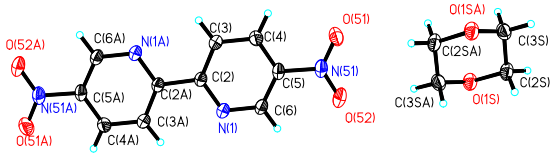

Figure S1. Crystal structure of 5,5'-$(NO_2)_2$-bpy with displacement ellipsoids at the 50% probability level. The additional "A" letters in the atom labels for the 5,5´-$(NO_2)_2$-bipy molecule indicate that these atoms are at (-x,-y,1-z), while the additional "A" letters in the atom labels for the dioxane molecule indicate that these atoms are at (1-x,2-y,2-z).

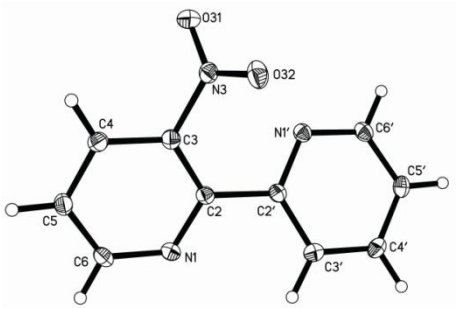

Figure S1 Crystal Structure of 3-NO_2-bpy with thermal ellipsoids at 30 % probability.

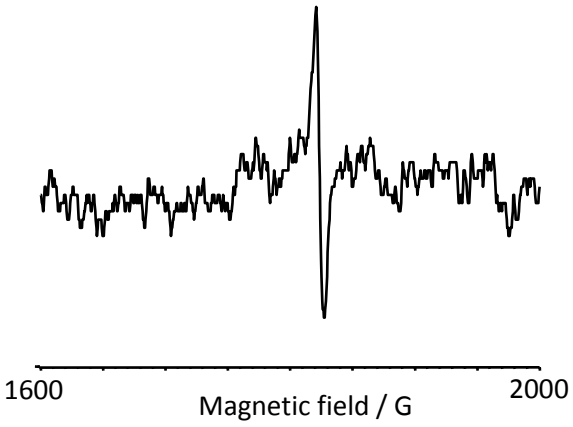

Figure S3. "Half-field" region of experimental frozen solution EPR spectrum of $[4,4'\text{-}(NO_2)_2\text{-bpy}]^{2-}$ in CH_2Cl_2/0.3 M $[^nBu_4]BF_4$/DMF.

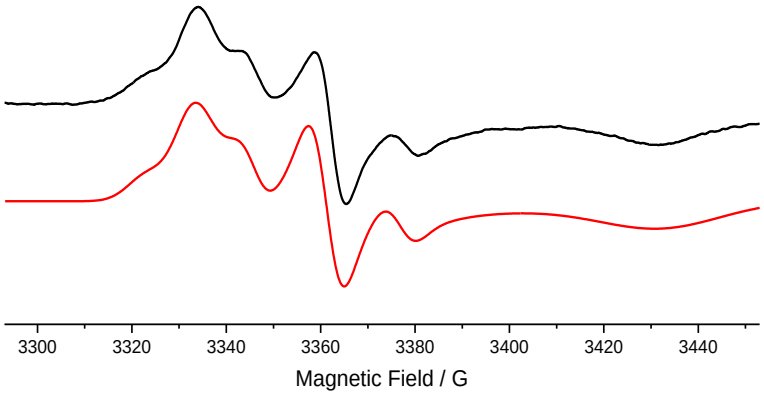

Figure S4. Experimental (black) and simulated (red) frozen solution EPR spectra of $[Pt\{5,5´\text{-}(NO_2)_2\text{-}bpy\}Cl_2]^-$ at 173 K, generated by in situ electrolysis at -0.68 V vs. Ag/AgCl at 233 K in 0.1 M $[^nBu_4][BF_4]$/DMF.

Table S1. $E_{½}$ values (vs. Ag/AgCl) as determined from differential pulse polarography on $5,5´\text{-}(NO_2)_2$-bpy in various solvents at 298 K (0.1 M $[^nBu_4N][BF_4]$ electrolyte)

Solvent	Acceptor Number	$E_{½,1}$ / V	$E_{½,2}$ / V	$\Delta E_{½}$ / V
Dichloromethane	20.4	-0.62	-	0
Dimethylsulphoxide	19.3	-0.57	-	0
Acetonitrile	18.9	-0.63	-	0
Dimethylformamide	16.0	-0.61	-0.70	0.10
Pyridine	14.2	-0.63	-0.70	0.06
Acetone	12.5	-0.64	-0.76	0.12
Ethyl Acetate	9.3	-0.64	-0.78	0.15
Tetrahydrofuran	8.0	-0.65	-0.81	0.16

Table S2. $E_{½}$ values (vs. Ag/AgCl) as determined from differential pulse voltammetry on $[Pt(5,5´\text{-}(NO_2)_2\text{-}bpy)Cl_2]$ in various solvents at 298 K (0.1 M $[^nBu_4N][BF_4]$ electrolyte).

Solvent	Acceptor Number	$E_{½,1}$ / V	$E_{½,2}$ / V	$\Delta E_{½}$ / V
Dimethylsulfoxide	19.3	-0.10	-0.24	0.14
Acetonitrile	18.9	-0.09	-0.28	0.19
Dimethylformamide	16.0	-0.17	-0.37	0.20
Acetone	12.5	-0.11	-0.31	0.20
Ethyl Acetate	9.3	-0.12	-0.35	0.23
Tetrahydrofuran	8.0	-0.08	-0.33	0.25

Table S3. UV/Vis/NIR peak positions (ν_{max} / 10^3 cm^{-1}) and molar extinction coefficients (ε_{max} / 10^3 $M^{-1}cm^{-1}$) for compounds studied, with applied potentials for *in situ* electrogeneration.

Compound	E_{gen} /V	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max}))	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})	ν_{max} (ε_{max})
2-NO_2-py	-	36.6 (5.4)	31.4sh (1.4)	-	-	-	-	-	-	-
[2-NO_2-py]$^{1-}$	-1.50	31.6 (15.7)	21.9 (4.5)	-	-	-	-	-	-	-
3-NO_2-py	-	36.6 (4.6)	31.4sh (1.4)	-	-	-	-	-	-	-
[3-NO_2-py]$^{1-}$	-1.50	31.8 (15.3)	21.4 (4.1)	-	-	-	-	-	-	-
4-NO_2-py	-	32.1 (7.1)	-	-	-	-	-	-	-	-
[4-NO_2-py]$^{1-}$	-1.30	31.5 (6.6)	21.8 (2.4)	-	-	-	-	-	-	-
bpy	-	35.3 (12.9)	-	-	-	-	-	-	-	-
[Na][bpy]	-	12.3	17.8	18.8	26.0	-	-	-	-	-
3-NO_2-bpy	-	36.5 (8.3)	-	-	-	-	-	-	-	-
[3-NO_2-bpy]$^{1-}$	-1.70	36.5 (5.1)	32.0 (6.0)	19.7 (2.4)	-	-	-	-	-	-
4-NO_2-bpy[13]	-	35.8 (13.1)	31.3 (5.2)	-	-	-	-	-	-	-
[4-NO_2-bpy]$^{1-}$	-1.50	34.9 (18.9)	30.3sh (8.7)	20.7 (6.2)	-	-	-	-	-	-
5-NO_2-bpy	-	31.7 (27.5)	-	-	-	-	-	-	-	-
[5-NO_2-bpy]$^{1-}$	-1.20	25.8 (34.7)	14.9 (8.6)	-	-	-	-	-	-	-
3,3´-$(NO_2)_2$-bpy	-	35.9 (6.1)	-	-	-	-	-	-	-	-
[3,3´-$(NO_2)_2$-bpy]$^{1-}$	-1.00	31.9 (9.6)	22.3 (2.5)	10.0 (1.0)	-	-	-	-	-	-
[3,3´-$(NO_2)_2$-bpy]$^{2-}$	-1.70	34.6 (18.8)	32.1 (17.7)	30.5 (14.4)	28.6 (12.2)	24.6 (5.5)	14.2 (7.6)	-	-	-
4,4´-$(NO_2)_2$-bpy	-	35.1 (6.6)	-	-	-	-	-	-	-	-
[4,4´-$(NO_2)_2$-bpy]$^{2-}$	-1.20	32.4 (15.8)	20.7 (8.0)	-	-	-	-	-	-	-
5,5´-$(NO_2)_2$-bpy	-	30.8 (34.8)	-	-	-	-	-	-	-	-
[5,5´-$(NO_2)_2$-bpy]$^{1-}$	-0.68	30.8 (18.0)	21.0 (15.0)	8.4 (13.0)	-	-	-	-	-	-
[5,5´-$(NO_2)_2$-bpy]$^{2-}$	-1.00	15.8 (72.0)	-	-	-	-	-	-	-	-
[Pt(4-NO_2-py)Cl_2]	-	33.8 (9.7)	30.9 (8.2)	27.9 (5.6)	-	-	-	-	-	-
[Pt(4-NO_2-py)Cl_2]$^{2-}$	-0.96	30.3 (15.1)	25.8 (17.8)	19.2 (11.1)	-	-	-	-	-	-
[Pt(bpy)Cl_2]	-	35.8 (33.8)	31.9 (14.6)	30.7 (17.4)	27.4 (5.1)	25.9 (6.3)	-	-	-	-
[Pt(bpy)Cl_2]$^{1-}$	-1.6	36.3 (28.3)	34.9sh (26.2)	27.9 (22.9)	23.9 (10.4)	21.6 (10.7)	20.1 (15.2)	11.0 (5.8)	-	-
[Pt(4-NO_2-bpy)Cl_2]	-	37.3 (18.4)	31.8 (14.0)	24.0 (6.1)	-	-	-	-	-	-
[Pt(4-NO_2-bpy)Cl_2]$^{1-}$	-0.75	36.5 (22.1)	32.9 (12.4)	30.0 (13.1)	28.2sh (9.2)	22.8 (12.0)	20.6sh (5.3)	17.7 (4.6)	16.8 (4.4)	10.6 (3.5)
[Pt(4-NO_2-bpy)Cl_2]$^{2-}$	-1.50	35.7 (21.6)	32.3 (21.8)	24.7 (8.7)	23.3 (7.1)	11.2 (5.9)	-	-	-	-
[Pt(5-NO_2-bpy)Cl_2]	-	36.5 (10.8)	32.8 (11.6)	30.5sh (8.2)	29.3sh (7.5)	24.3 (2.4)	-	-	-	-
[Pt(5-NO_2-bpy)Cl_2]$^{1-}$	-0.90	24.7 (2.4)	26.2 (7.3)	22.6 (6.6)	15.0 (3.5)	10.4 (2.4)	-	-	-	-
[Pt(5-NO_2-bpy)Cl_2]$^{2-}$	-1.60	19.3 (2.4)	-	-	-	-	-	-	-	-
[Pt(3,3´-$(NO_2)_2$-bpy)Cl_2]	0	34.0 (10.0)	21.4 (2.9)	-	-	-	-	-	-	-
[Pt(3,3´-$(NO_2)_2$-bpy)Cl_2]$^{1-}$	-0.31	32.0 (17.9)	26.9 (6.5)	21.0 (4.6)	11.0 (3.2)	-	-	-	-	-
[Pt(3,3´-$(NO_2)_2$-bpy)Cl_2]$^{2-}$	-1.00	31.3 (24.1)	25.8 (10.0)	12.0 (7.9)	-	-	-	-	-	-
[Pt(4,4´-$(NO_2)_2$-bpy)Cl_2]	-	32.4 (13.3)	29.9 (12.2)	23.0 (4.8)	-	-	-	-	-	-
[Pt(4,4´-$(NO_2)_2$-bpy)Cl_2]$^{1-}$	-0.43	36.4sh (11.6)	31.7 (11.3)	28.3 (9.7)	24.7 (6.5)	21.3 (5.3)	19.3 (3.7)	17.6 (3.0)	6.8 (2.1)	-
[Pt(4,4´-$(NO_2)_2$-bpy)Cl_2]$^{2-}$	-0.91	36.2 (14.4)	33.2 (11.1)	29.5 (9.3)	23.0 (14.9)	18.7 (5.9)	9.2 (3.5)	-	-	-
[Pt(5,5´-$(NO_2)_2$-bpy)Cl_2]	-	36.0 (15.6)	32.2 (20.1)	28.6 (11.0)	22.4 (1.5)	-	-	-	-	-
[Pt(5,5´-$(NO_2)_2$-bpy)Cl_2]$^{1-}$	-0.31	23.2 (11.0)	10.0 (17.0)	19.0 (5.0)	-	-	-	-	-	-
[Pt(5,5´-$(NO_2)_2$-bpy)Cl_2]$^{2-}$	-0.60	14.5 (40.0)	-	-	-	-	-	-	-	-