Electronic Supplementary Information for Dalton Transactions

Synthesis and Properties of [Pt(4-CO_2CH_3-py)$_2$(mnt)]; comparison of pyridyl and bipyridyl-based dyes for Solar Cells.

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Supplementary Information

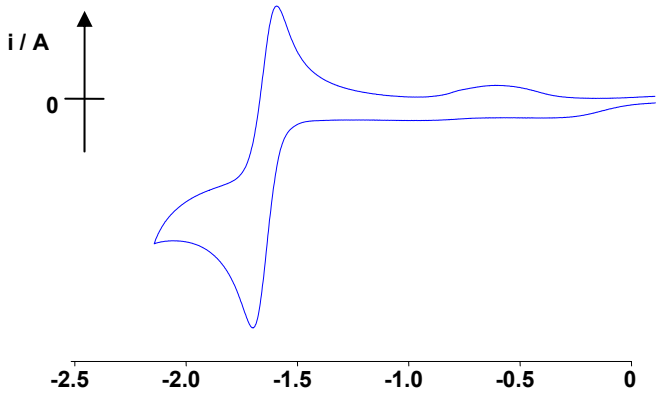


Figure S1 Cyclic Voltammetry of 4-CO_2CH_3-py in 0.1M $TBABF_4$ / DMF at 298 K. Scan rate 0.2 V s^{-1}. (All electrochemical measurements taken versus Ag/AgCl (saturated KCl) reference electrode against which the ferrocenium/ferrocene couple was measured to be +0.55 V)

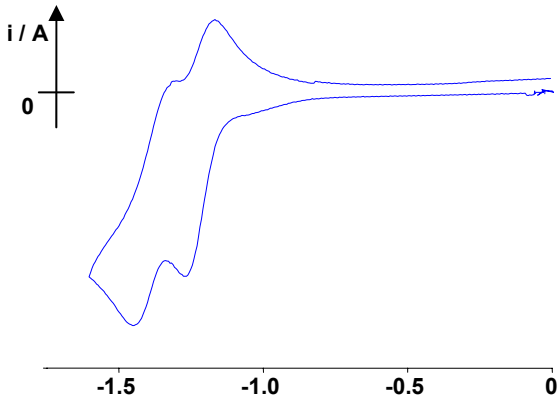
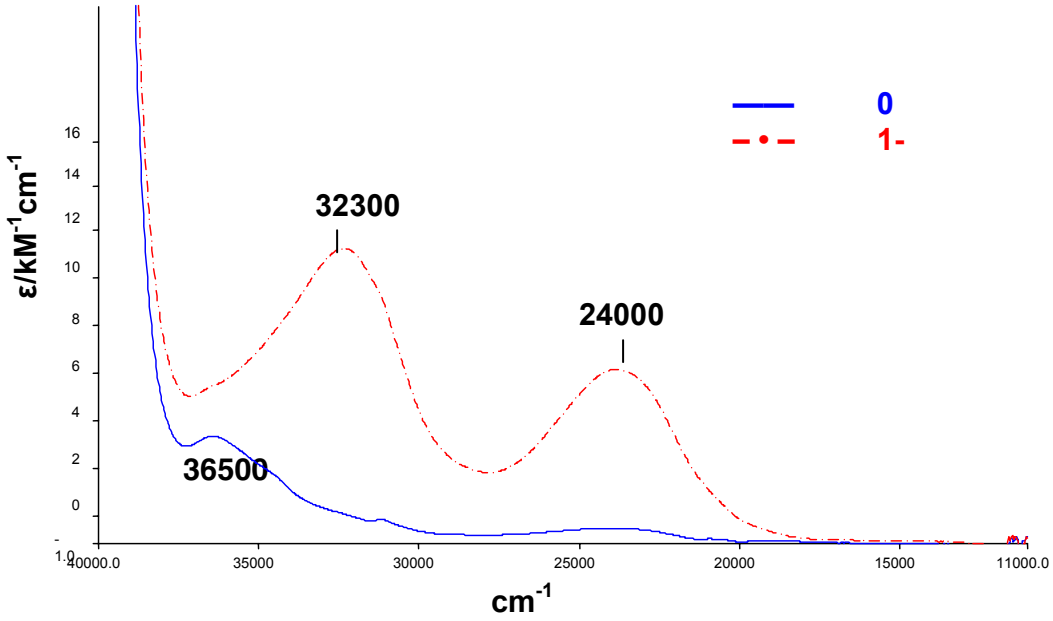
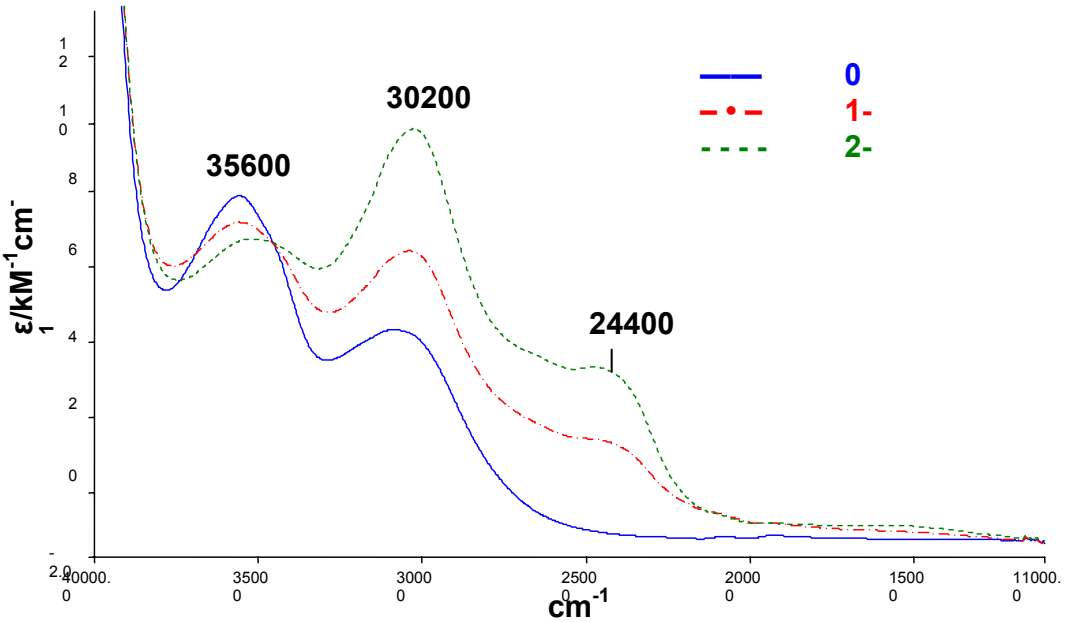


Figure S2 Cyclic Voltammetry of [$PtCl_2$(4-CO_2CH_3-py)$_2$] in 0.1M $TBABF_4$ / DMF at 298 K. Scan rate 0.8 V s^{-1}.



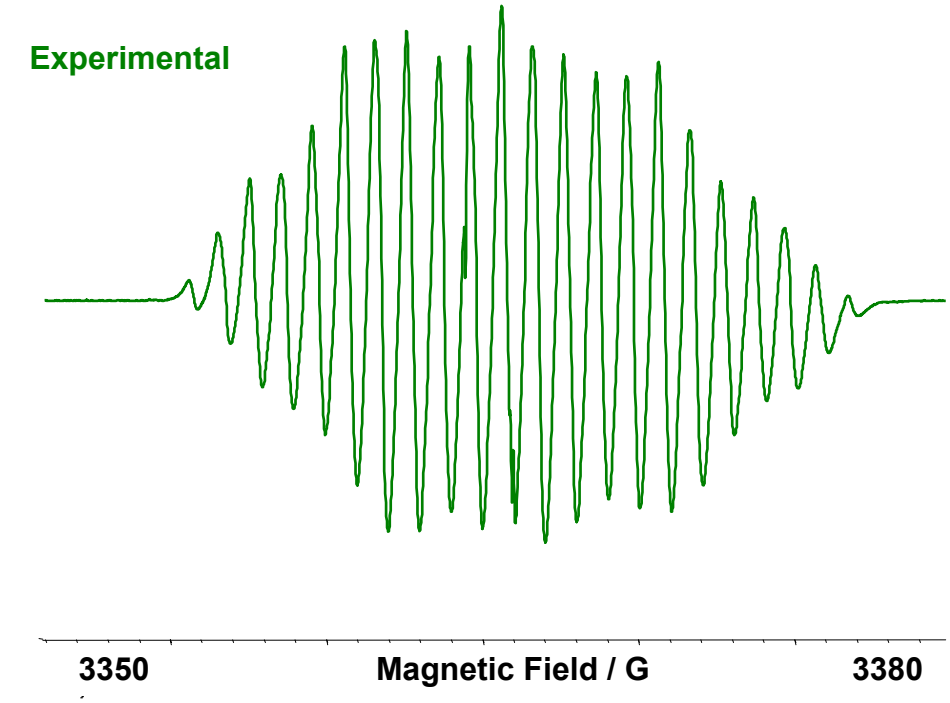
Oxidation State	0	-1
Peak Position / cm^{-1} (ε / $M^{-1}cm^{-1}$)	36,500 (2,700)	32,300 (11,500) 24,000 (6,000)

Figure S3 and Table S1 OTTLE of 4-CO_2CH_3-py in 0.1 M $TBABF_4$ / DMF at 233 K, E_{gen} = -2.28 V (1-)



Oxidation State	0	-1	-2
Peak Position / cm^{-1} (ε / $M^{-1}cm^{-1}$)	35,600 (7,800) 30,200 (4,800)	35, 600 (7,000) 30,200 (6,900) 24,400 (1,500)	35, 600 (6,500) 30,200 (10,400) 24,400 (3,200)

Figure S4 and Table S2 OTTLE of $[PtCl_2(4\text{-}CO_2CH_3\text{-}py)_2]$ in 0.1 M $TBABF_4$ / DMF at 233 K. E_{gen} = -1.3 V (1-) and -1.6 V (2-)



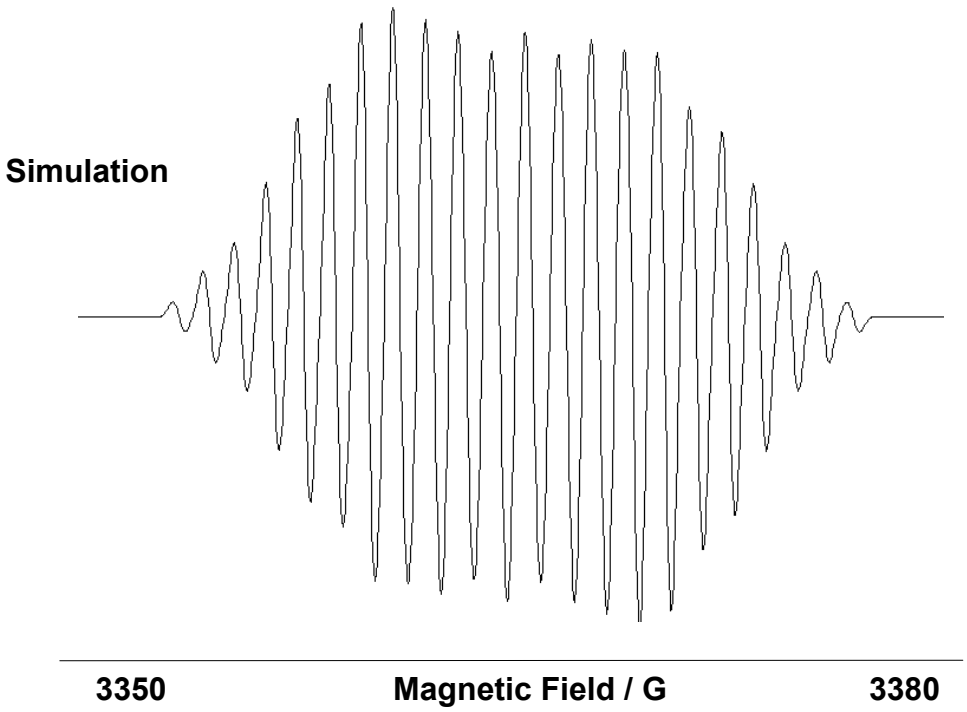
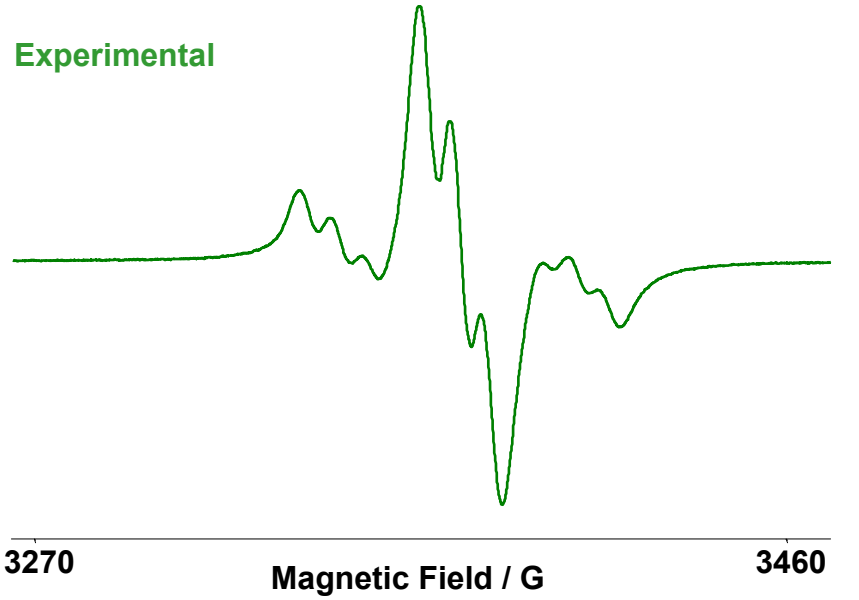


Figure S5 EPR Spectrum and Simulation of $[4\text{-}CO_2CH_3\text{-}py]^-$ in 0.1 M $TBABF_4$ / DMF at 233 K, E_{gen} = -1.8 V.

Parameter	$[4\text{-}CO_2CH_3\text{-}py]^-$
3H	1.050 G
2H	0.850 G
2H	2.985 G
1N	5.090 G
g	2.0028
Δ	0.35 G

Table S3 EPR Simulation Parameters for $[4\text{-}CO_2CH_3\text{-}py]^-$



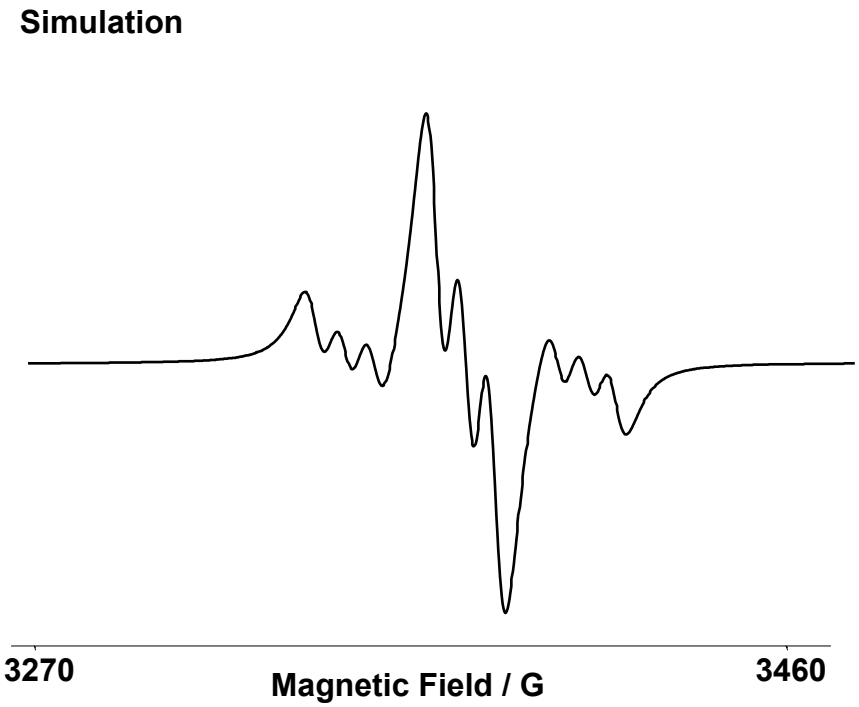
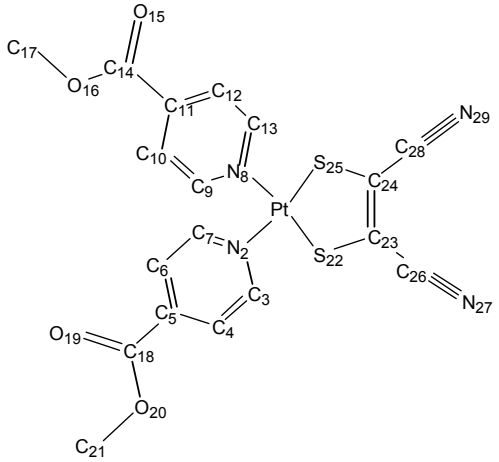


Figure S6 EPR Spectrum and Simulation of $[PtCl_2(4\text{-}CO_2CH_3\text{-}py)_2]^{2-}$ in 0.1 M $TBABF_4$ / DMF at 233 K, E_{gen} = -1.8 V.

Table S4 Energies and Percentage contributions for each atom (see atom numbering scheme below) in the HOMO, LUMO and LUMO+1 isosurfaces from DFT Calculations for $[Pt(4\text{-}CO_2CH_3\text{-}py)_2(mnt)]$.



Atom	HOMO / %	LUMO / %	LUMO+1 / %
Energy	-5.2525 eV	-3.2289 eV	-3.0136 eV
1 Pt	14.44	3.19	3.62
2 N	0.06	22.59	0.00
3 C	0.44	7.37	0.05
4 C	0.25	7.06	0.06
5 C	0.03	22.84	0.00
6 C	0.26	7.34	0.04
7 C	0.51	7.06	0.05
8 N	0.02	0.94	22.64
9 C	0.60	0.40	6.74
10 C	0.00	0.26	7.09
11 C	0.75	0.06	22.44
12 C	0.09	0.02	7.86
13 C	0.51	0.01	6.53
14 C	0.05	0.00	7.52
15 O	0.17	0.00	9.39
16 O	0.06	0.00	3.73
17 C	0.00	0.00	0.07
18 C	0.00	6.89	0.00
19 O	0.00	8.93	0.00
20 O	0.00	3.56	0.00
21 C	0.00	0.07	0.00
22 S	27.80	0.05	0.77
23 C	9.68	0.06	0.01
24 C	9.89	0.19	0.31
25 S	27.33	0.53	0.45
26 C	0.05	0.02	0.00
27 N	3.43	0.01	0.00
28 C	0.05	0.02	0.01

29	N	3.49	0.00	0.08
30	H	0.01	0.00	0.01
31	H	0.00	0.00	0.00
32	H	0.00	0.00	0.00
33	H	0.01	0.00	0.00
34	H	0.00	0.03	0.00
35	H	0.00	0.02	0.00
36	H	0.00	0.01	0.00
37	H	0.00	0.00	0.00
38	H	0.00	0.00	0.26
39	H	0.00	0.00	0.00
40	H	0.00	0.00	0.26
41	H	0.00	0.24	0.00
42	H	0.00	0.00	0.00
43	H	0.00	0.24	0.00

Table S5 TD-DFT Calculations for [Pt(4-CO_2CH_3-py)$_2$ (mnt)] **3b**. Selected transitions, with oscillator strength greater than 0.1, have been included.

Excited State	**Energy / cm^{-1} Calculated (nm)**	**Observed**	***f***	**Composition**
4	26311 (380)	25700	0.10	HOMO-LUMO+2 76%
14	33922 (295)	31600	0.27	HOMO-1 – LUMO+2 86%
18	36763 (272)	36300	0.17	HOMO-3 – LUMO 77%
22	39208 (255)		0.14	HOMO-3– LUMO+1 65%