- Supporting Information -

Synthesis and Characterisation of Halide, Separated Ion Pair, and Hydride Cyclopentadienyl Iron *Bis*(Diphenylphosphino)ethane Derivatives

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Electrochemistry

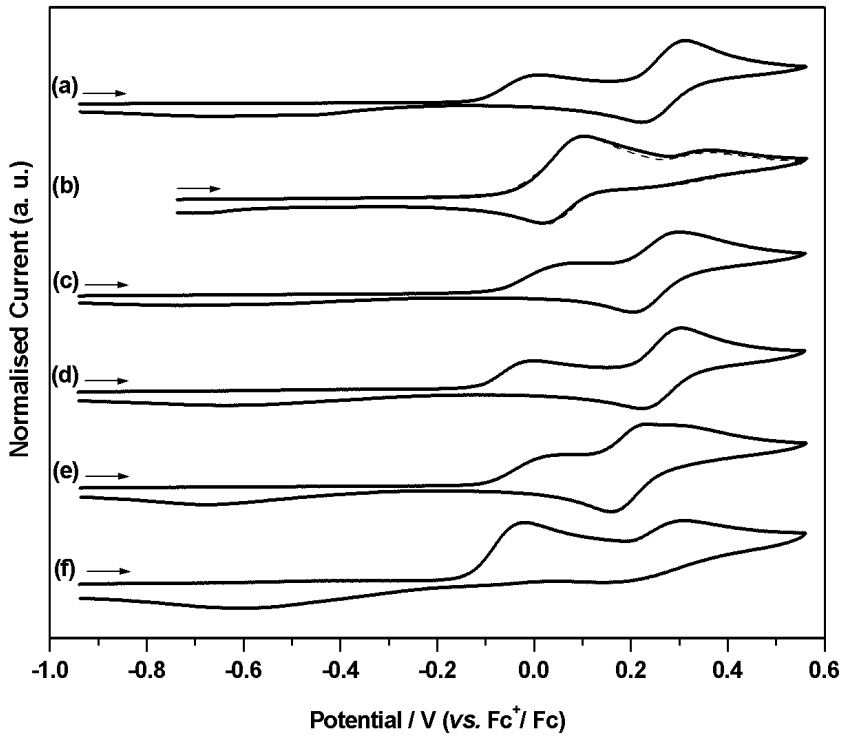


Figure S1*: Cyclic voltammograms for (a) [Fe(Cp)(l)(dppe)], (b) [Fe(Cp*)(I)(dppe)] (solid line) and* ***2SIP*** *(dashed line), (c) [Fe(Cp')(I)(dppe)], (d) [Fe(Cp'')(I)(dppe)], (e) [Fe(Cp^{tt})(I)(dppe)] and (f) [$^{n}Bu_4N$][I] in MeCN containing [NBu^{n}_4][BF_4] (0.1 M) as supporting electrolyte at 0.1 Vs^{-1}. Currents are normalised to I_p^a for clarity. Typical currents obtained from CV experiments for the separated ion pairs in MeCN are shown in Figure SI3 for* ***2SIP****, as are designations of OX, OX', OX'' and RED for* ***1SIP-5SIP*** *used in Table SI1.*

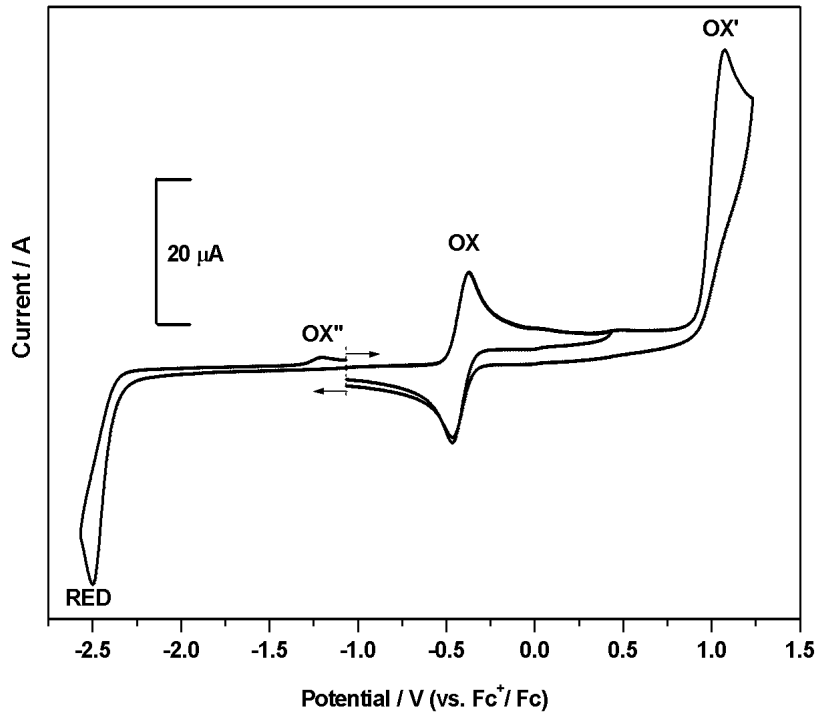


Figure S2a: *Cyclic voltammetry for [Fe(Cp*$^{+}$*)(Cl)(dppe)] in THF containing [NBu*$^{n}{}_{4}$*][BF*$_4$*] (0.5 M) as supporting electrolyte, at 0.1 Vs*$^{-1}$*, showing designations of OX, OX', OX'' and RED for* ***1Cl-5Cl****,* ***1Br-5Br****,* ***1I-5I*** *and* ***1H-5H*** *compounds used in Table SI1.*

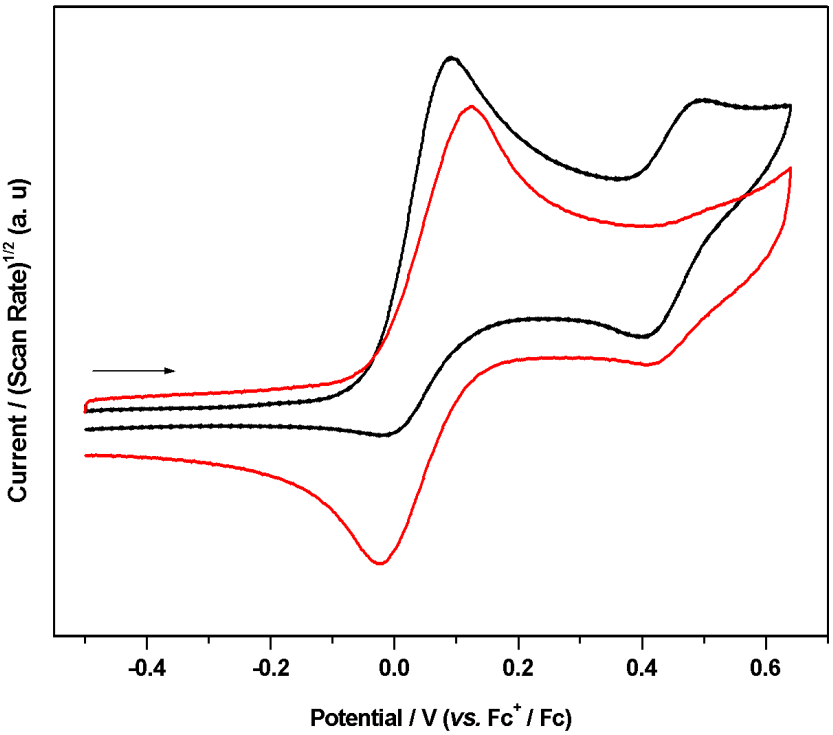


Figure S2b: *Cyclic voltammetry for compound* ***4H*** *in THF containing [NBu*$^{n}{}_{4}$*][BF*$_4$*] (0.5 M) as supporting electrolyte, at 0.1 Vs*$^{-1}$ *(black line) and 1.0 Vs*$^{-1}$ *(red line). Note that the oxidation process at* E_p^a *+ 0.49 V is scan rate dependent, and is diminished as OX becomes reversible at faster scan rate.*

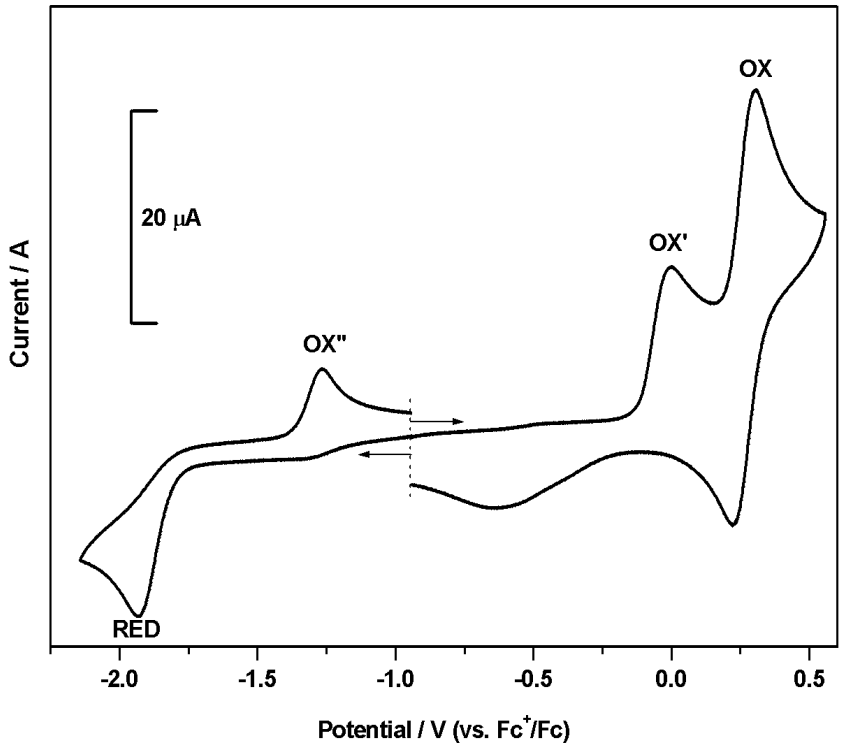


***Figure S3**: Cyclic voltammetry for [Fe(Cp†)(I)(dppe)] in MeCN containing [NBu$^n_4$][BF$_4$] (0.1 M) as supporting electrolyte, at 0.1 Vs^{-1}, showing designations of OX, OX', OX'' and RED for **1SIP-5SIP** compounds used in Table SI1.*

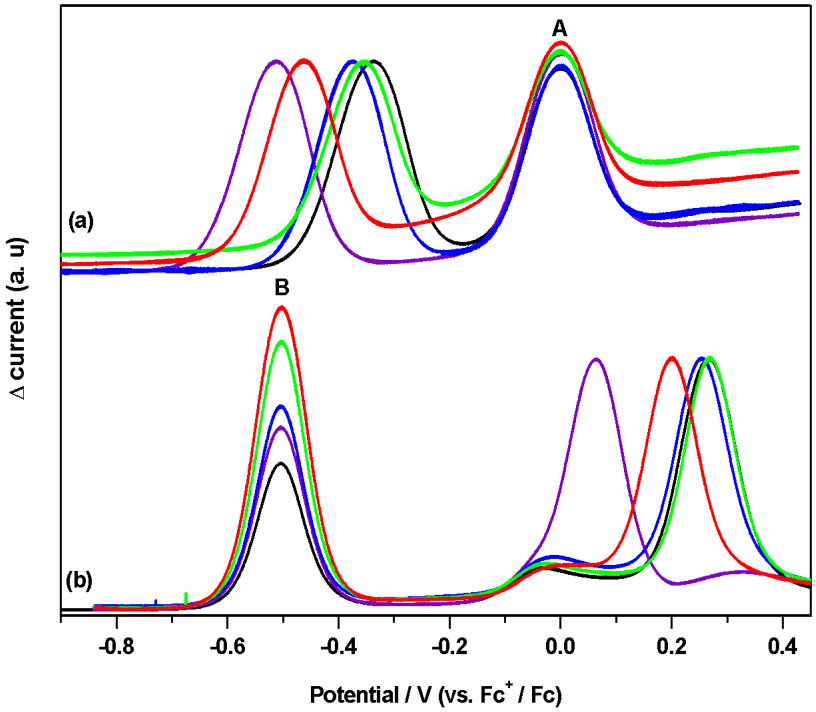


***Figure S4**: Square wave voltammetry showing OX for (a) [Fe(Cp†)(Cl)(dppe)] in THF containing [NBu$^n_4$][BF$_4$] (0.5 M) as supporting electrolyte and (b) [Fe(Cp†)(I)(dppe)] in MeCN containing [NBu$^n_4$][BF$_4$] (0.1 M) as supporting electrolyte (Cp† = Cp (black), Cp* (violet), Cp' (blue), Cp'' (green), Cp^{tt} (red)). The peaks labelled A and B are ferrocene and decamethylferrocene, respectively used is the internal standards.*

	OX $E_{1/2}$ / V[a]	ΔFc[b]	$-I_p^c/I_p^a$ [c]	I_p vs. (scan rate)$^{1/2}$ (R^2)[d]	Square wave / V	OX' (E_p^a) / V	RED (E_p^c) / V	OX'' (E_p^a) / V
1Cl	-0.42 (0.09)	(0.10)	1.03	1.000, 0.998	-0.42	+1.08	-2.50	-1.20
1Br	-0.38 (0.10)	(0.10)	1.05	1.000, 0.997	-0.38	+1.12	-2.49	-1.20
1I	-0.34 (0.09)	(0.10)	1.04	0.999, 0.997	-0.34	+1.09[g]	-2.32(sh), -2.48	-1.21
1H	-0.50 (0.09)	(0.09)	1.03	1.000, 0.994	-0.51	+0.73	-	-
1SIP[f]	+0.26 (0.09)	(0.07)			+0.27	-0.01	-2.10	-
2Cl	-0.59 (0.10)	(0.10)	0.99	0.999, 0.999	-0.59	+0.87[h]	-2.64	-1.29
2Br	-0.55 (0.09)	(0.09)	0.96	0.999, 0.999	-0.55	+0.95[g]	-2.55	-1.30
2I	-0.51 (0.09)	(0.10)	1.02	0.998, 0.998	-0.51	+0.81[i]	-2.42(sh), -2.57	-1.29
2H	-0.71 (0.09)	(0.10)	1.05	0.999, 0.991	-0.71	+0.57	-	-
2SIP[f]	+0.06 (0.09)	(0.07)			+0.06	-	-2.20	-
3Cl	-0.45 (0.09)	(0.10)	1.01	1.000, 0.997	-0.45	+0.51[p]	-2.49	-1.10
3Br	-0.41 (0.09)	(0.10)	1.04	0.999, 0.996	-0.41	+1.06	-2.49	-1.10
3I	-0.37 (0.09)	(0.09)	1.00	0.998, 0.998	-0.37	+0.99[j]	-2.51	-1.07
3H	-0.50 (0.09)	(0.09)	0.84	0.994, 0.985	-0.50	+0.56[g]	-	-
3SIP[f]	+0.25 (0.1)	(0.07			+0.25	+0.01	-2.05	-1.33
4Cl	-0.44 (0.09)	(0.10)	0.96	0.996, 0.998	-0.44	+0.51[k]	-2.47	-1.01
4Br	-0.40 (0.09)	(0.10)	0.91	0.996, 0.999	-0.39	-	-2.50[l]	-1.01
4I	-0.36 (0.10)	(0.10)	1.06	0.996, 0.999	-0.35	+0.38	-2.26, -2.47[m]	-1.03
4H	-0.53 (0.15)[e]	(0.16)	-	0.955, -	-0.50	-	-	-
4SIP[f]	+0.26 (0.08)	(0.07			+0.27	0.00	-1.93	-1.27
5Cl	-0.54 (0.08)	(0.09)	0.77	0.992, 0.974	-0.54	-0.10[p]	-[n]	-1.07[p]
5Br	-0.50 (0.09)	(0.09)	0.76	0.998, 0.983	-0.51	+0.54	-1.85[p]	-1.10[p]
5I	-0.46 (0.09)	(0.09)	0.89	0.999, 0.996	-0.46	-	-[o]	-
5H	-0.62 (0.09)	(0.09)	1.05	0.998, 0.999	-0.62	+0.77	-	-
5SIP[f]	+0.20 (0.08)[q]	(0.07			+0.20	+0.06	-2.05	-1.31

Table S1: *[a] In THF containing $[NBu^n_4][BF_4]$ (0.5 M) as supporting electrolyte. At ambient temperature. Potentials quoted against $E_{1/2}$ Fc^+/Fc at 0.10 Vs^{-1} used as the internal standard unless stated otherwise. Values in brackets are ΔE (= E_p^a - E_p^c); $E_{1/2}$ = (E_p^a + E_p^c)/2; E_p^a = peak anodic (oxidation) potential; E_p^c = peak cathodic (reduction) potential. [b] ΔFc = E_p^a - E_p^c for the Fc^+/Fc couple at 0.10 Vs^{-1}. [c] at 0.1 Vs^{-1}. [d] from data recorded at 0.1, 0.2, 0.3, 0.05 and 0.02 Vs^{-1}, R^2 values for I_p^a and I_p^c, respectively. [e] at 1.00 Vs^{-1} and $[CoCp_2][PF_6]$ used as the internal standard to avoid overlap of couples. Potential quoted against the Fc^+/Fc couple using an independent calibration where $E_{1/2}$ $[CoCp_2]^+/[CoCp_2]$ = -1.359 V vs. Fc^+/Fc under identical conditions. [f] In MeCN containing $[NBu^n_4][BF_4]$ (0.1 M) as supporting electrolyte and $[Fe(\eta^5$-*

$C_5Me_5)_2$] used as the internal standard to avoid overlap of couples. Potentials quoted against the Fc^+/Fc couple using an independent calibration where $E_{1/2}$ [Fe(η^5-$C_5Me_5)_2$]$^+$/ [Fe(η^5-$C_5Me_5)_2$] = -0.505 V vs. Fc^+/Fc under identical conditions. Current analysis not performed due to the presence of overlapping iodide electrochemistry. [g] increase in current but not resolved as a well-defined peak. [h] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.81 V (0.13) (ΔFc 0.12) at 0.3 Vs^{-1}. [i] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.76 V (0.13) (ΔFc 0.13) at 0.3 Vs^{-1}. [j] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.94 V (0.11) at 0.1 Vs^{-1} ($E_{1/2}$ +0.94 V (0.12) (ΔFc 0.12) at 0.3 Vs^{-1}). [k] small couple noted at $E_{1/2}$ +0.09 V (0.08). [l] a small return wave was associated with this reduction at E_p^a -2.37 V. [m] return wave noted for this reduction process in oxidation half-cycle: $E_{1/2}$ +2.42 V (0.10) at 0.1 Vs^{-1}. [n] no defined peak but small current noted at potentials more cathodic than ca. -1.15 V. [o] asymmetric couple noted E_p^c -1.22 V (broad) E_p^a -1.11 V (sharp) at 0.1 Vs^{-1}. [p] small feature. [q] overlaps with an additional feature at E_p^a +0.36 V.

DFT Experimental and Supplementary Information

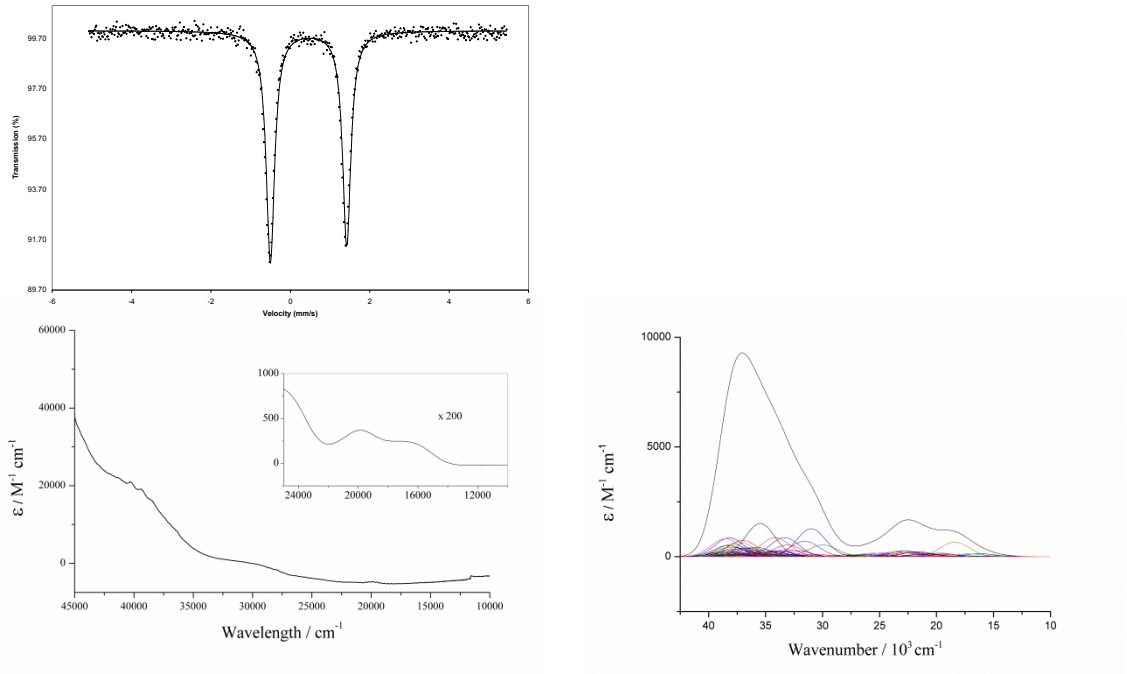
Compound	Fe1-Ct	Fe1-Cl1	Fe1-P1	Fe1-P2	Ct-Fe1-Cl1	Cl1-Fe1-P1	Cl1-Fe1-P2
1Cl	1.699(3) 1.711	2.3317(9) 2.343	2.1963(10) 2.191	2.1846(10) 2.181	123.9(9) 121.64	87.90(3) 88.73	89.11(3) 89.26
2Cl	1.732 1.744	2.346(1) 2.358	2.197(1) 2.202	2.210(1) 2.216	119.06 118.6	87.23(5) 87.47	86.03(4) 85.83
3Cl	1.716(5) 1.72	2.3298(16) 2.343	2.198(16) 2.202	2.1881(15) 2.186	123.8(19) 123.19	90.18(6) 88.96	86.15(6) 86.08
4Cl	1.704(7) 1.742	2.294(2) 2.348	2.184(2) 2.201	2.194(2) 2.213	121.24(2) 120.47	89.09(9) 89.57	87.64(8) 87.62
5Cl	1.739(4) 1.759	2.3423(10) 2.351	2.2358(10) 2.235	2.2107(11) 2.221	122.8(11) 121.48	89.18(4) 89.94	84.18(4) 85.08

***Table S2**: Representative comparison of experimental and theoretical bond lengths (Å) and angles (°) of **1Cl-5Cl** where Ct = centroid.*

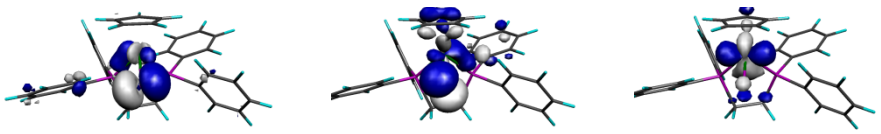
Compound	HOMO (eV)	Total Fe (%)	Fe s (%)	Fe p (%)	Fe d (%)	Total X (%)	X s (%)	X p (%)	X d (%)	Total Cp (%)	Cp s (%)	Cp p (%)	Cp d (%)	Total dppe (%)	dppe s (%)	dppe p (%)	dppe d (%)
1Cl	-3.73	70.23	0	0.95	69.28	14.35	0	13.95	0.40	9.38	0.04	8.93	0.41	6.04	1.05	3.96	1.02
2Cl	-3.53	72.68	0	0.80	71.88	11.11	0	10.70	0.41	10.13	1.60	7.98	0.53	6.09	0.82	4.18	1.09
3Cl	-3.69	70.06	0.04	0.84	69.18	13.22	0	12.82	0.41	10.45	0.19	9.64	0.62	6.27	0.92	4.34	1.01
4Cl	-3.74	69.14	0	0.73	68.41	12.02	0	11.63	0.39	12.42	0.41	11.18	0.83	6.44	0.88	4.51	1.04
5Cl	-3.54	73.07	0	0.83	72.24	12.29	0	11.88	0.41	9.15	0.42	8.30	0.43	5.48	0.74	3.79	0.95
1Br	-3.78	67.96	0	0.94	67.02	17.27	0	16.72	0.55	8.94	0.02	8.53	0.39	5.83	1.04	3.78	1.00
2Br	-3.56	72.00	0	0.83	71.19	13.44	0	12.88	0.57	9.46	1.43	7.53	0.50	5.10	0.69	3.42	1.00
3Br	-3.74	68.84	0.02	0.85	67.96	13.93	0	13.33	0.60	10.80	0.20	9.96	0.64	6.42	0.81	4.57	1.04
4Br	-3.78	67.29	0	0.75	66.55	13.69	0	13.13	0.56	12.58	0.46	11.29	0.84	6.43	0.82	4.58	1.04
5Br	-3.66	68.14	0	0.91	67.23	11.96	0	11.37	0.59	12.97	0.69	11.73	0.56	6.91	1.01	4.87	1.02
1I	-3.83	61.91	0	0.86	61.05	25.05	0	24.92	0.12	7.96	0.08	7.52	0.35	5.09	0.88	3.31	0.91
2I	-3.62	68.26	0	0.88	67.39	17.80	0	17.68	0.12	8.87	1.2	7.21	0.47	5.05	0.53	3.55	0.98
3I	-3.78	61.96	0.01	0.71	61.24	22.86	0	22.74	0.12	9.70	0.15	8.93	0.62	5.47	0.60	3.94	0.92
4I	-3.86	63.87	0.01	0.76	63.10	18.08	0	17.96	0.12	11.93	0.41	10.72	0.80	6.12	0.56	4.58	0.98
5I	-3.74	66.17	0	0.98	65.21	14.24	0	14.12	0.13	12.47	0.58	11.35	0.54	7.11	1.01	5.09	1.01
1H	-3.84	73.36	0.61	3.45	69.30	0.76	0.35	0.42	0	10.01	0.45	9.12	0.44	15.87	0.79	10.99	4.09
2H	-3.56	70.71	0.54	3.79	66.38	0.86	0.50	0.36	0	11.92	1.98	9.32	0.62	16.58	0.25	12.18	4.09
3H	-3.79	73.96	0.82	3.76	69.38	0.09	0.08	0.01	0	9.63	0.28	8.93	0.42	16.32	0.70	11.57	4.05
4H	-3.70	72.50	1.25	3.64	67.60	0.58	0.20	0.38	0	11.47	0.22	10.55	0.70	15.46	0.28	11.39	3.80
5H	-3.64	68.13	0.75	4.68	62.71	0.57	0.37	0.21	0	13.96	0.80	12.53	0.62	17.34	0.35	12.82	4.18

***Table S3**: Energies and compositions of the HOMO in **1Cl-5Cl**, **1Br-5Br**, **1I-5I** and **1H-5H**. Calculated using AOMix*

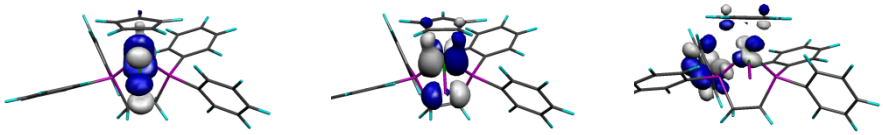
Analytical Data
[Fe(Cp)(Cl)(dppe)], 1Cl



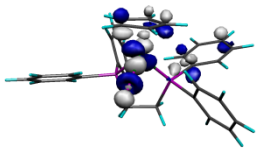
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.782 eV –5.687 eV –4.528 eV



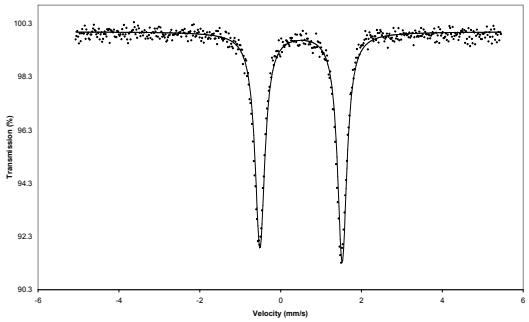
–4.174 eV –3.732 eV –2.015 eV

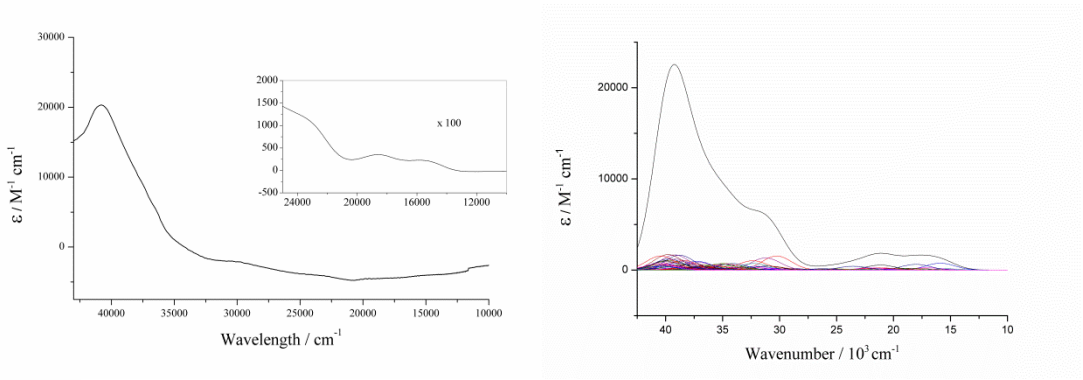


–1.9 eV

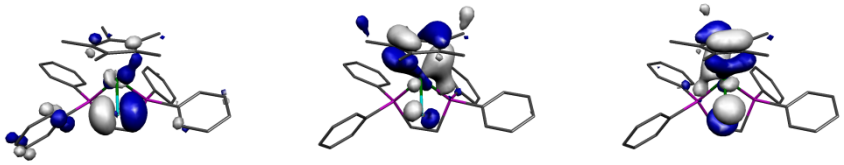
Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

[Fe(Cp*)(Cl)(dppe)], 2Cl

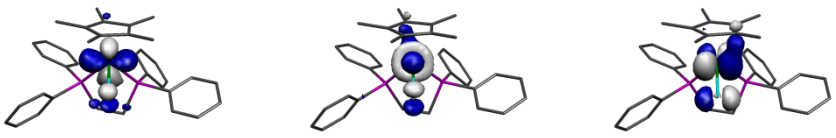




Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.654 eV –5.546 eV –5.364 eV



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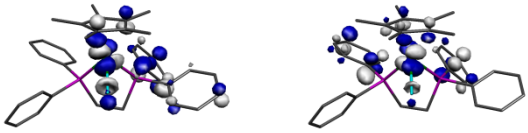
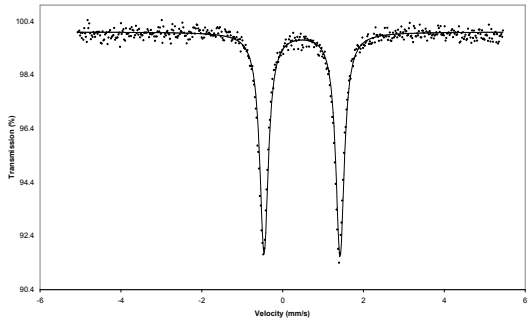
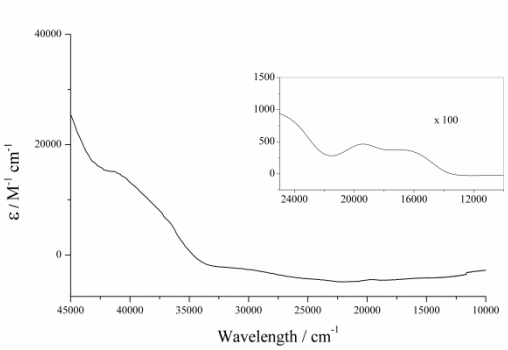


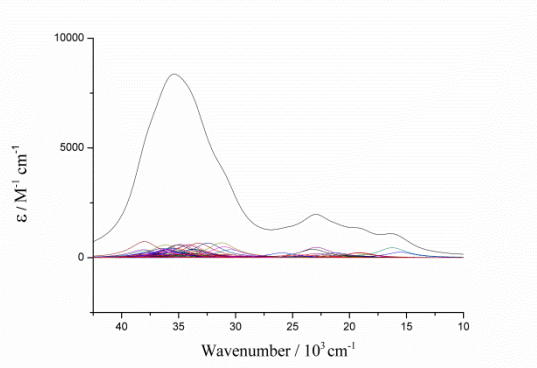
–1.796 eV –1.769 eV

Kohn-Sham MO plots from HOMO-5 (top left) to LUMO+1 (bottom left)

[Fe(Cp')(Cl)(dppe)], 3Cl







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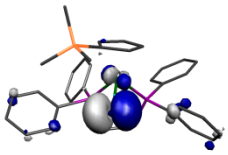

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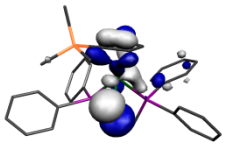
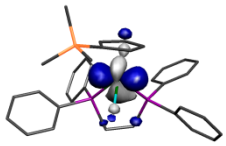
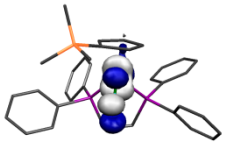


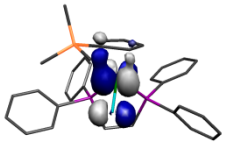
–5.657 eV



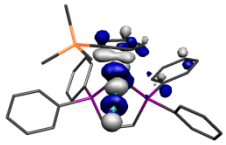
–4.473 eV



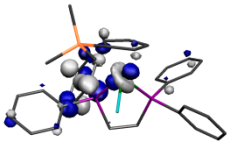
–4.161 eV



–3.693 eV



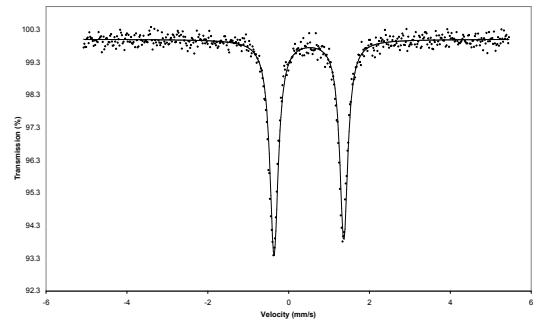
–1.963 eV

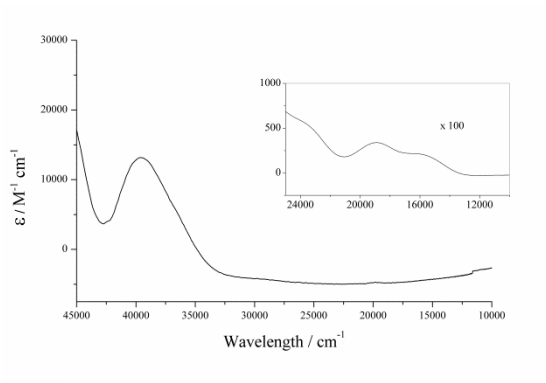


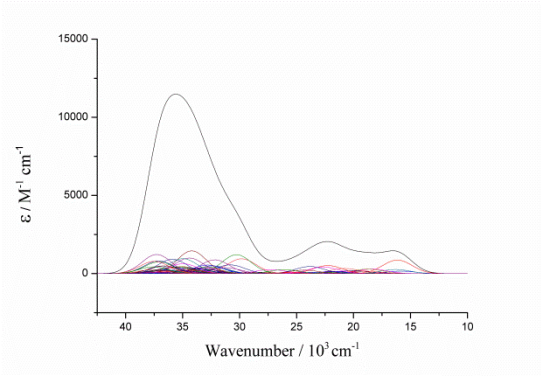
–1.893 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

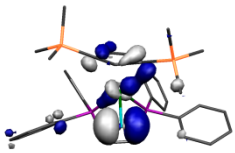
[Fe(Cp'')(Cl)(dppe)], 4Cl



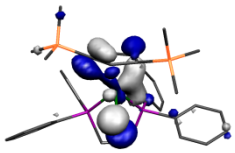




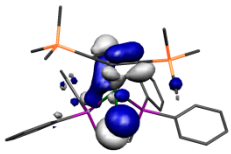
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



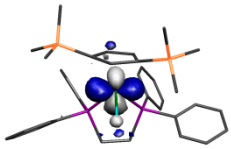
–5.902 eV



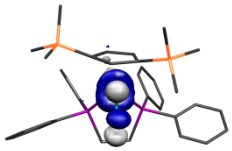
–5.825 eV



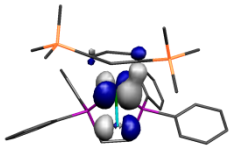
–5.579 eV



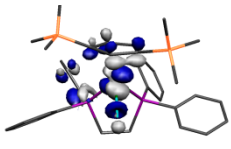
–4.441 eV



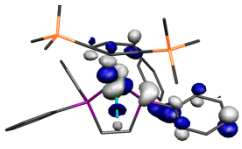
–4.072 eV



–3.747 eV



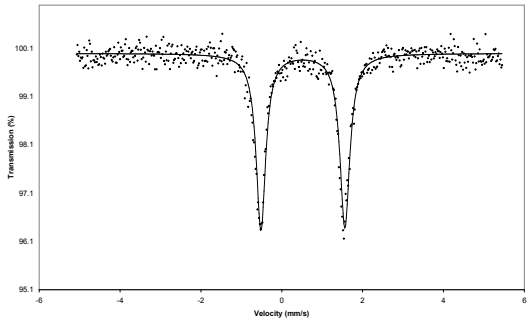
–1.995 eV

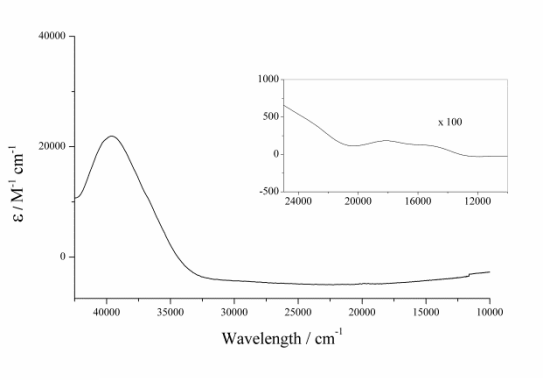


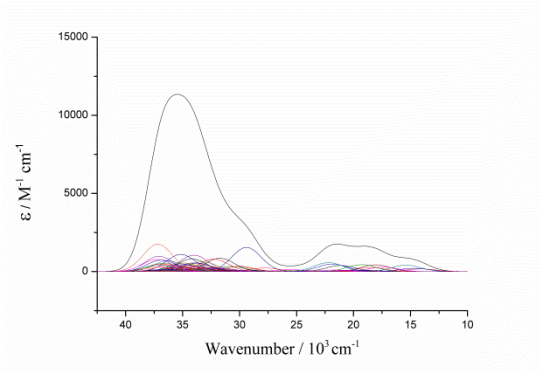
–1.935 eV

Kohn-Sham MO plots from HOMO-5 (top left) to LUMO+1 (bottom left)

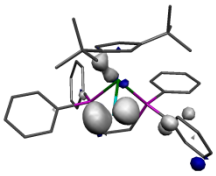
[Fe(Cp^{tt})(Cl)(dppe)], 5Cl



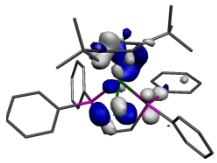




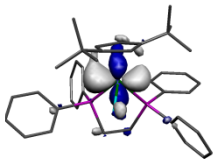
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



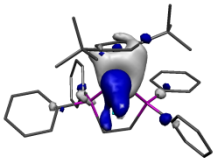
–5.661 eV



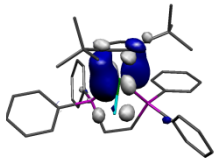
–5.415 eV



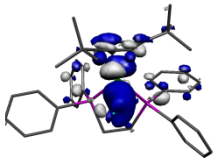
–4.309 eV



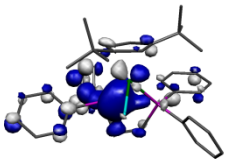
–3.948 eV



–3.545 eV



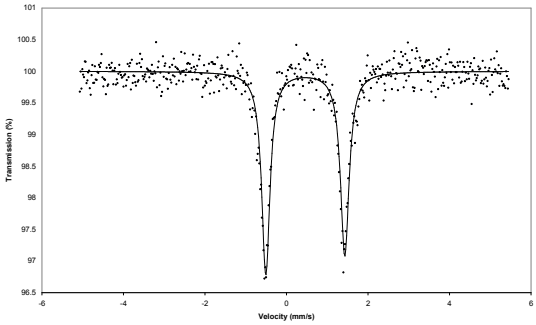
–1.922 eV

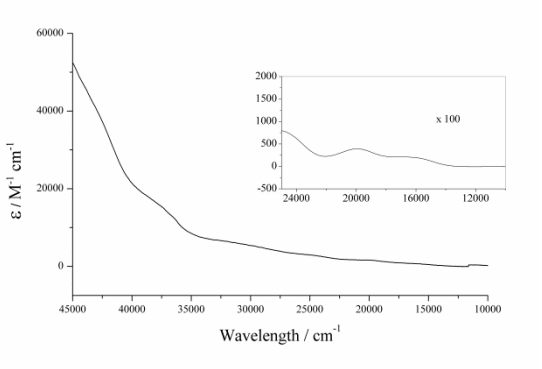


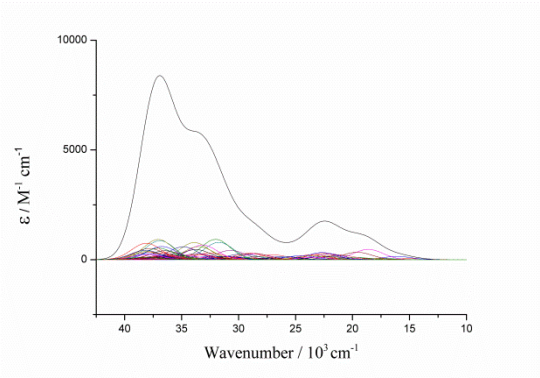
–1.876 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

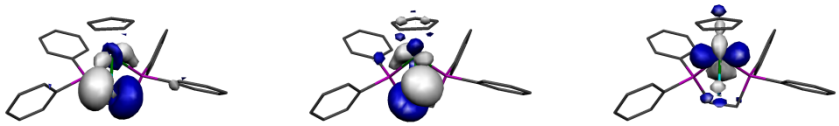
[Fe(Cp)(Br)(dppe)], 1Br



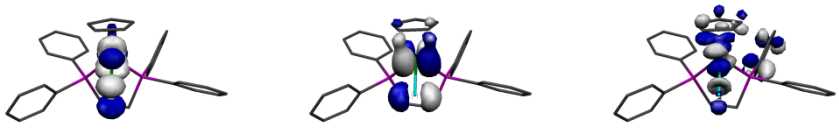




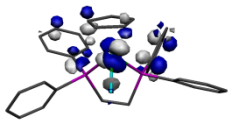
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.537 eV –5.488 eV –4.555 eV



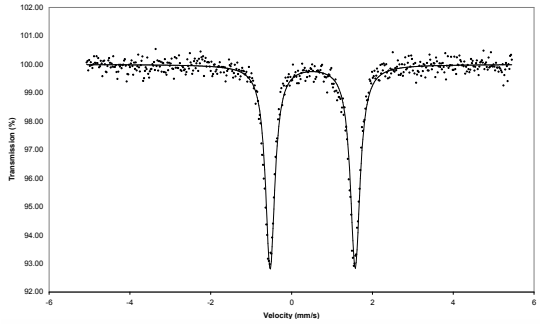
–4.223 eV –3.788 eV –2.051 eV

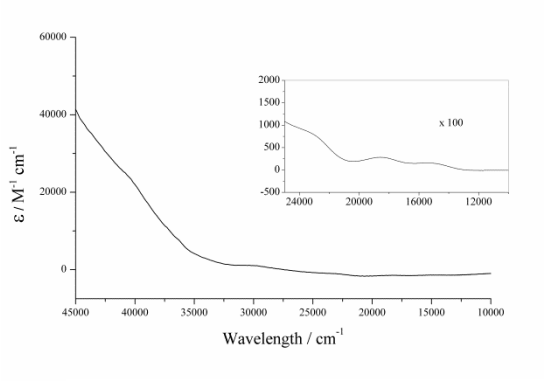


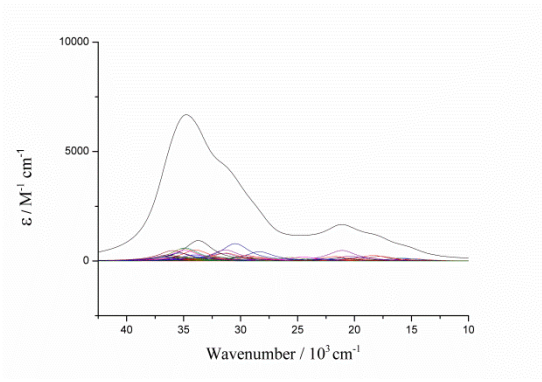
–1.970 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

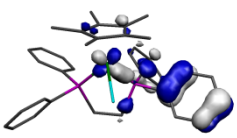
[Fe(Cp*)(Br)(dppe)], 2Br



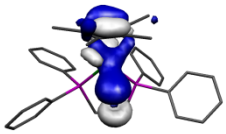




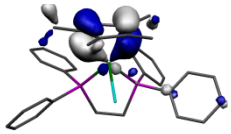
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



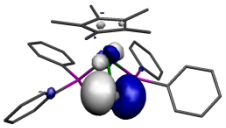
–5.927 eV



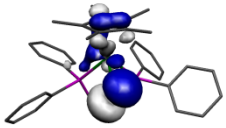
–5.751 eV



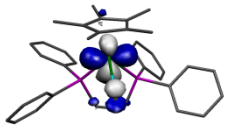
–5.581 eV



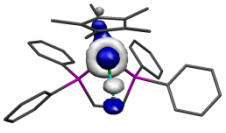
–5.349 eV



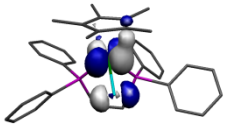
–5.285 eV



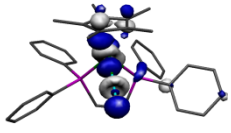
–4.277 eV



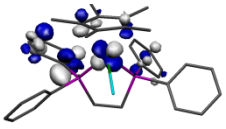
–3.880 eV



–3.561 eV



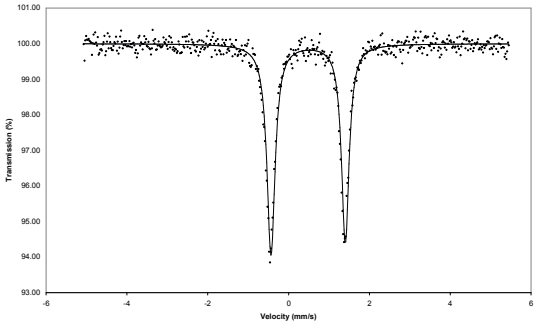
–1.880 eV

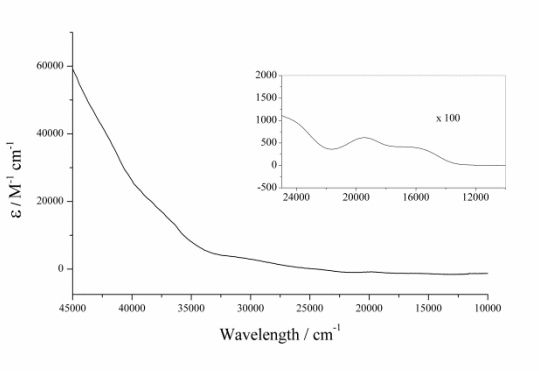


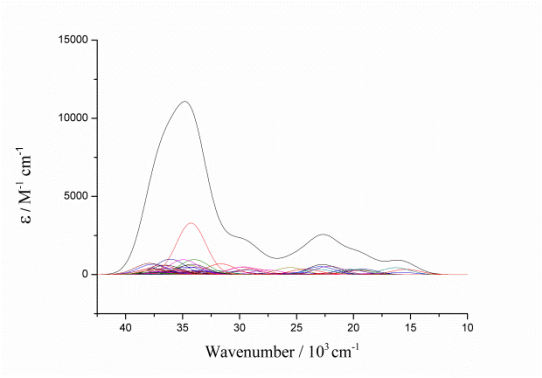
–1.796 eV

Kohn-Sham MO plots from HOMO-7 (top left) to LUMO+1 (bottom left)

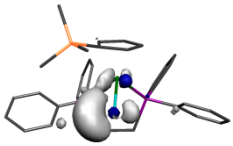
[Fe(Cp')(Br)(dppe)], 3Br



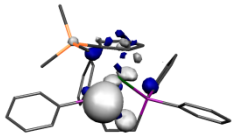




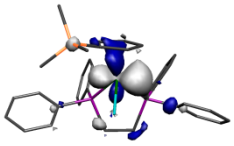
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



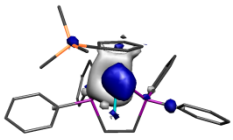
–5.653 eV



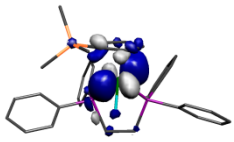
–5.519 eV



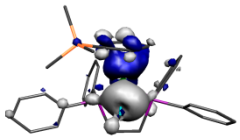
–4.515 eV



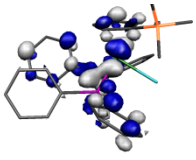
–4.190 eV



–3.741 eV



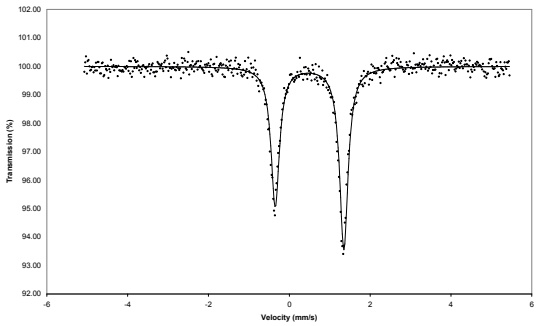
–2.074 eV

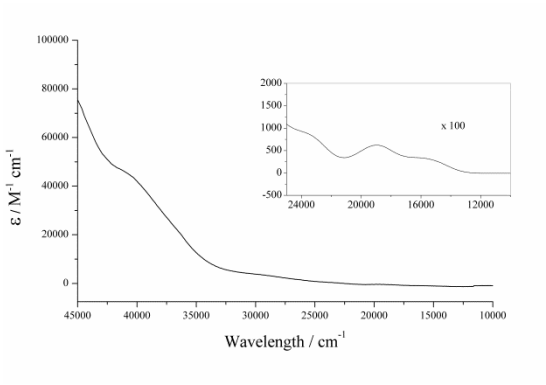


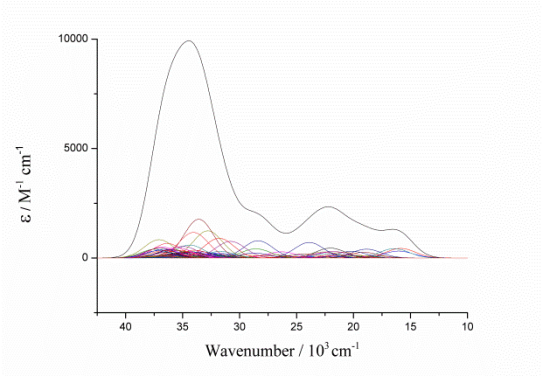
–1.891 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

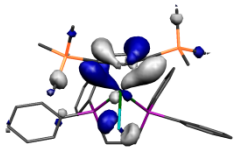
[Fe(Cp'')(Br)(dppe)], 4Br



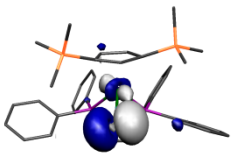




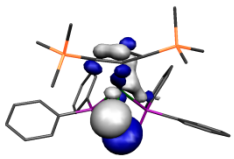
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



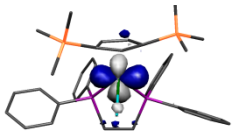
–5.786 eV



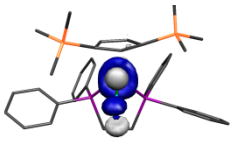
–5.646 eV



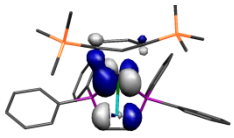
–5.437 eV



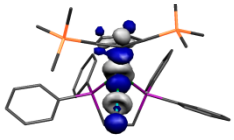
–4.463 eV



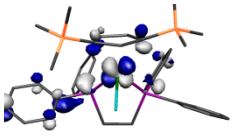
–4.110 eV



–3.787 eV



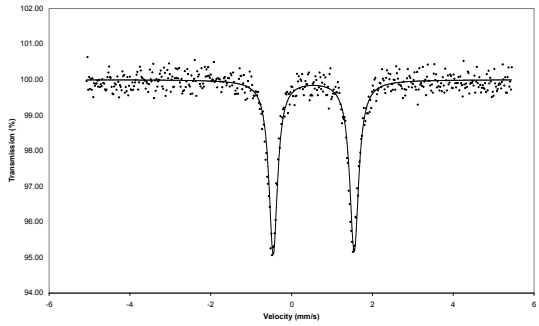
–2.031 eV

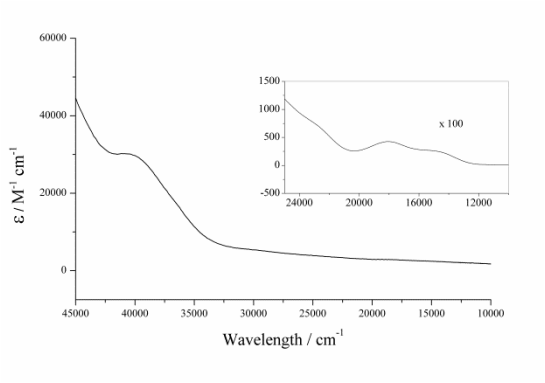


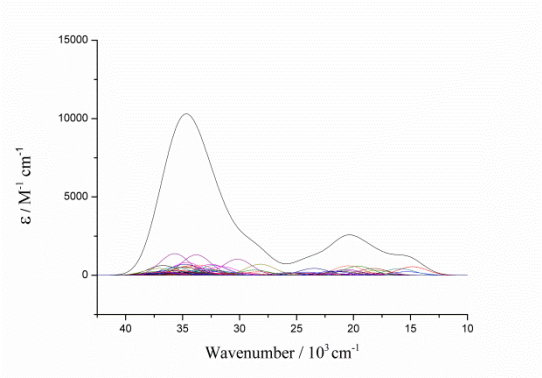
–1.957 eV

Kohn-Sham MO plots from HOMO-5 (top left) to LUMO+1 (bottom left)

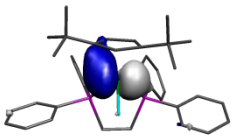
[Fe(Cp^{tt})(Br)(dppe)], 5Br



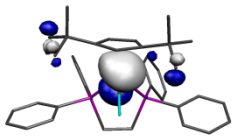




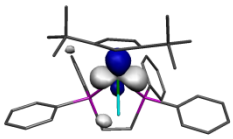
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



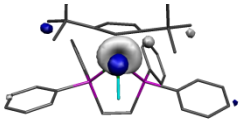
–5.595 eV



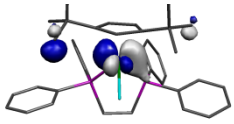
–5.398 eV



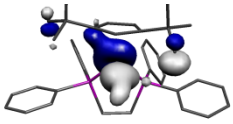
–4.363 eV



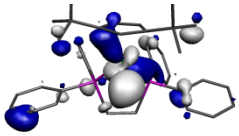
–3.968 eV



–3.665 eV



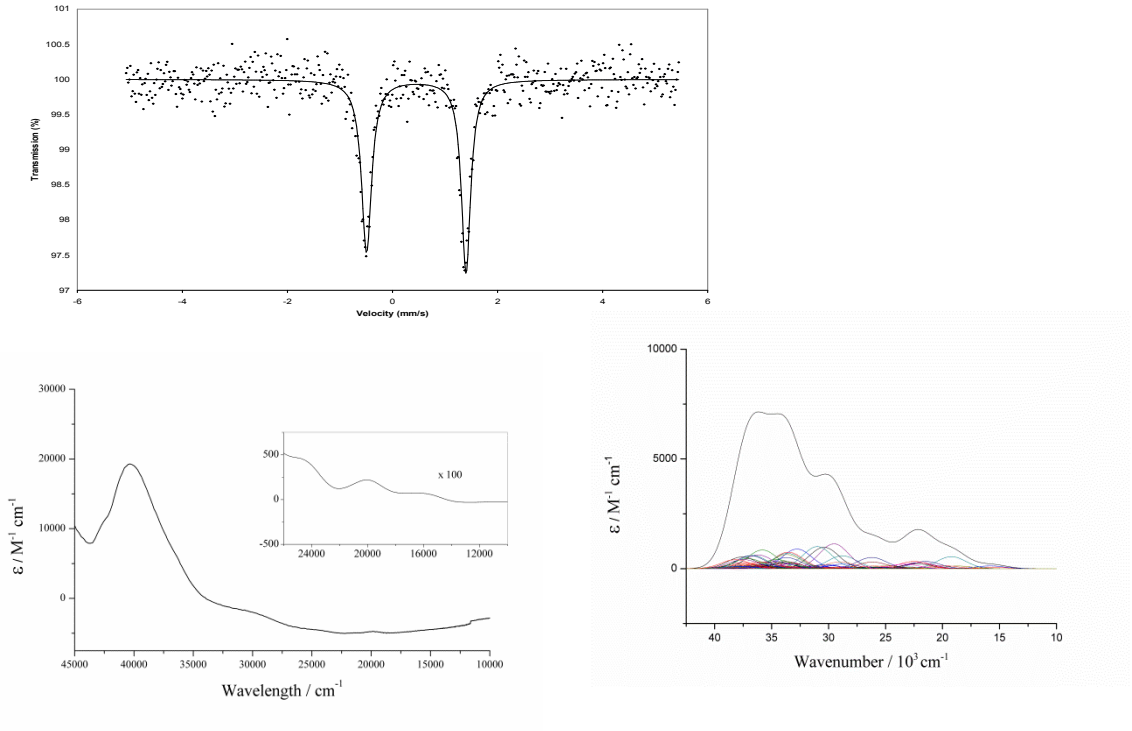
–2.035 eV



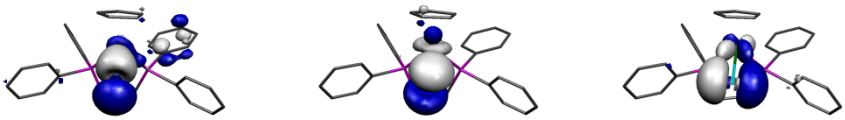
–1.906 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

[Fe(Cp)(I)(dppe)], 1I



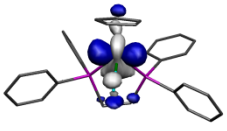
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



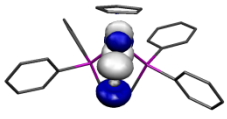
–6.019 eV

–5.249 eV

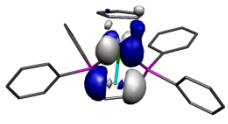
–5.183 eV



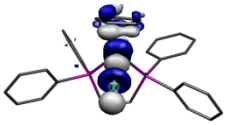
–4.598 eV



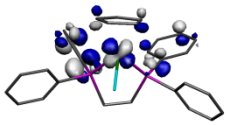
–4.256 eV



–3.836 eV



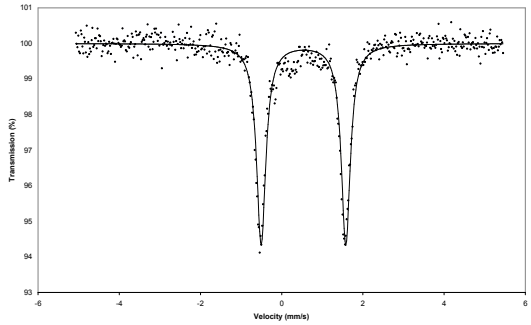
–2.096 eV

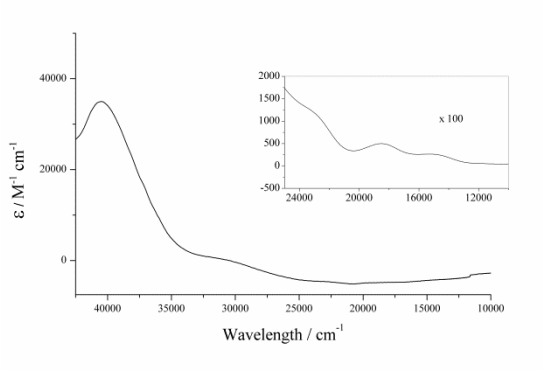


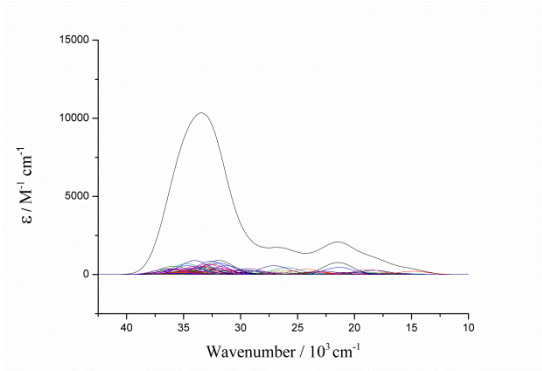
–1.998 eV

Kohn-Sham MO plots from HOMO-5 (top left) to LUMO+1 (bottom left)

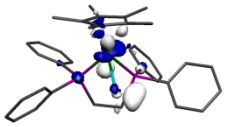
[Fe(Cp*)(I)(dppe)], 2I



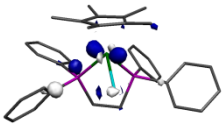




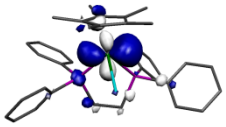
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



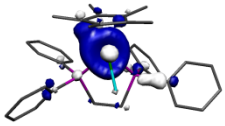
–5.074 eV



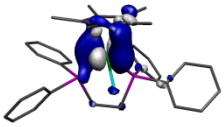
–4.991 eV



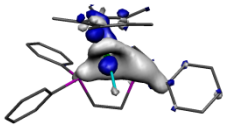
–4.311 eV



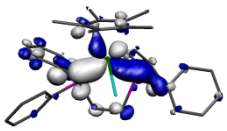
–3.958 eV



–3.625 eV



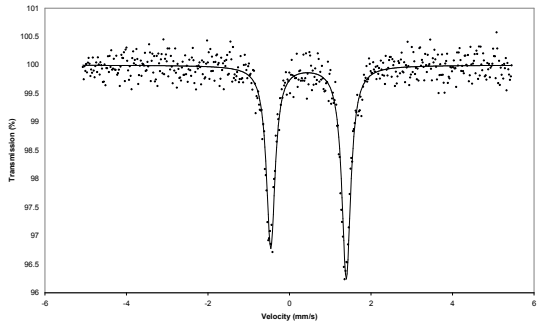
–1.996 eV

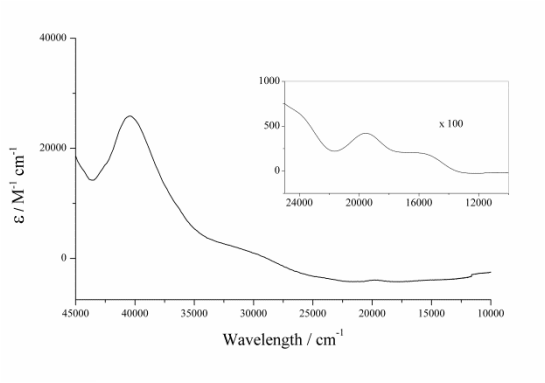


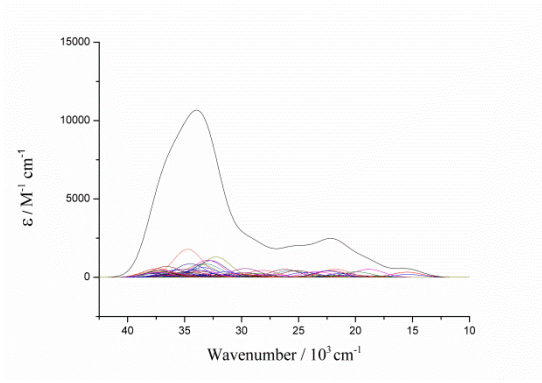
–1.819 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

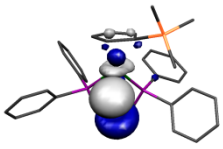
[Fe(Cp')(I)(dppe)], 3I



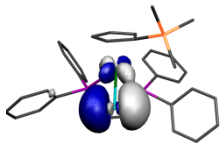




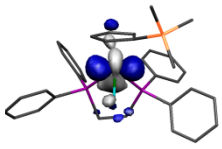
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



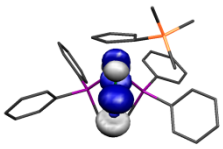
–5.218 eV



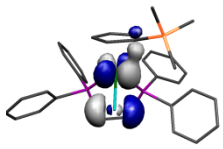
–5.092 eV



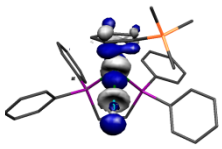
–4.533 eV



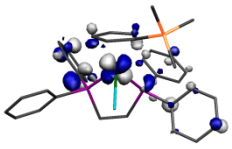
–4.214 eV



–3.781 eV



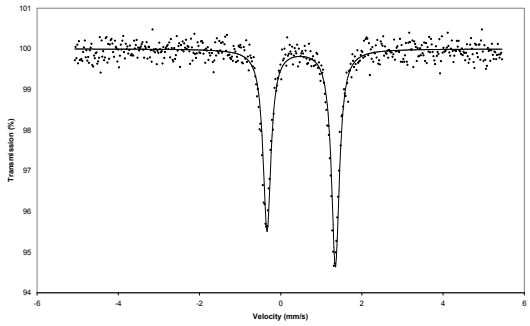
–2.090 eV

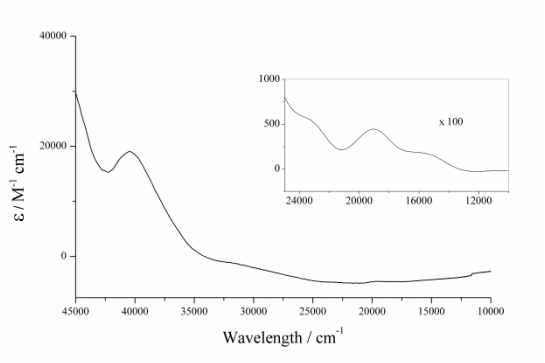


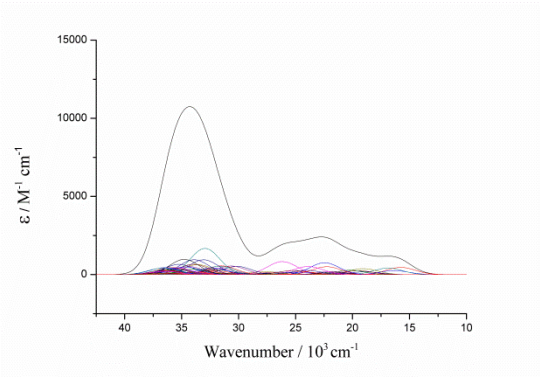
–1.993 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

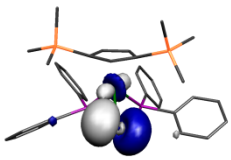
[Fe(Cp'')(I)(dppe)], 4I

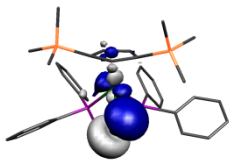


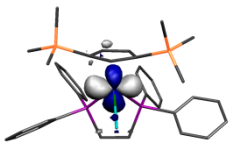


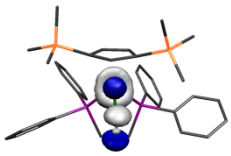


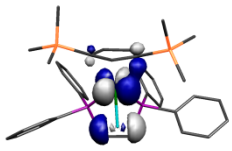
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right Calculated UV-vis

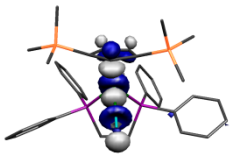

–5.342 eV

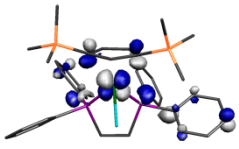

–5.206 eV


–4.502 eV


–4.175 eV

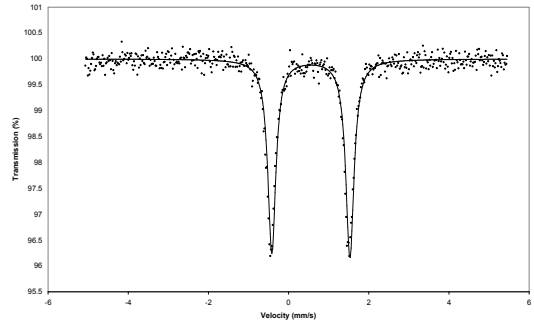

–3.868 eV

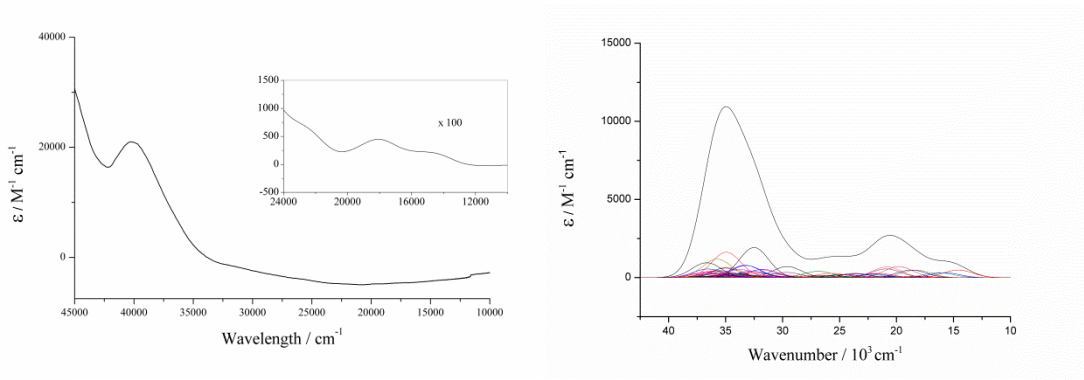

–2.123 eV


–2.000 eV

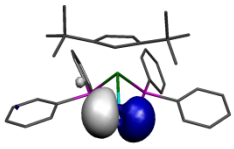
Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

[Fe(Cp^{tt})(I)(dppe)], 5I

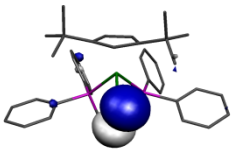




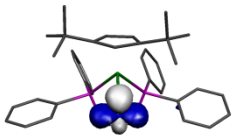
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



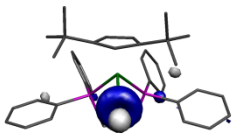
–5.300 eV



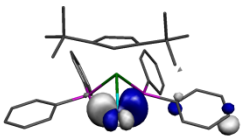
–5.165 eV



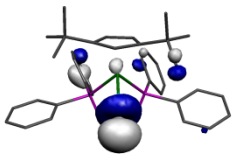
–4.404 eV



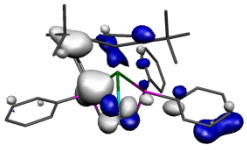
–4.035 eV



–3.741 eV



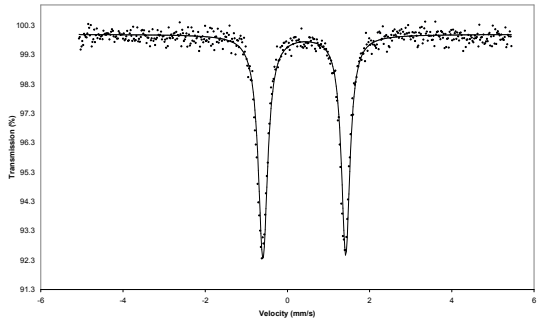
–2.142 eV

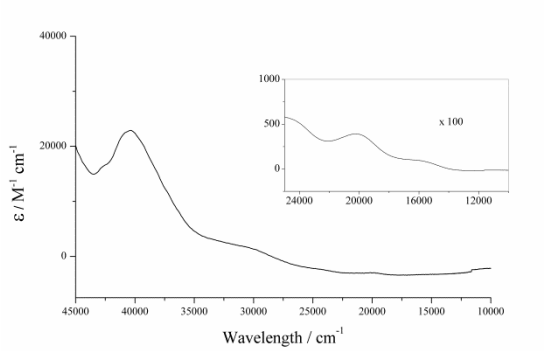


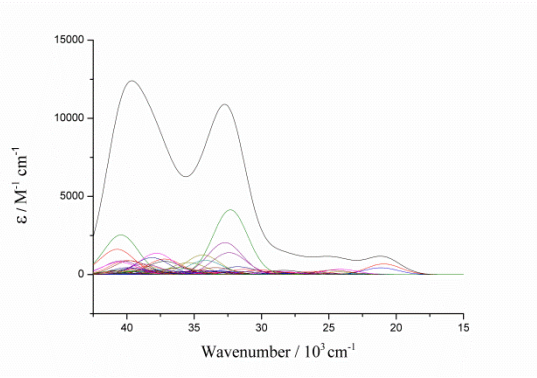
–1.945 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

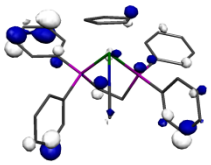
[Fe(Cp)(NCMe)(dppe)][I], 1SIP



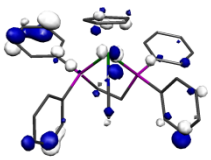




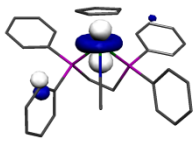
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



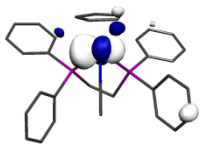
–8.765 eV



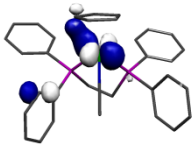
–8.645 eV



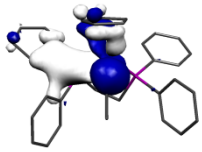
–7.744 eV



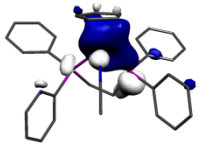
–7.504 eV



–7.218 eV



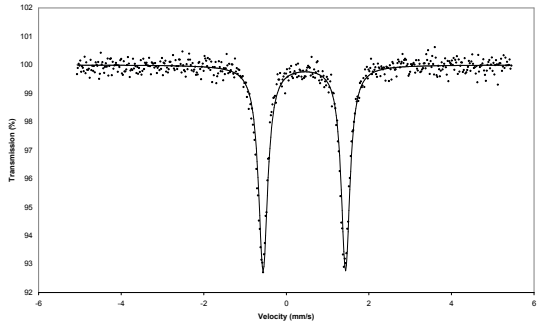
–4.850 eV

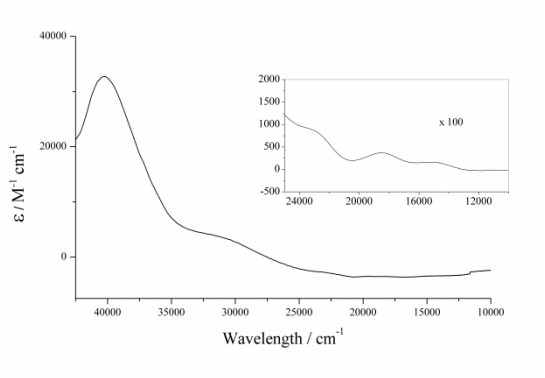


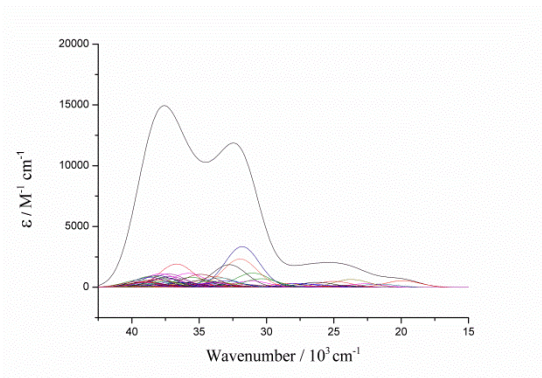
–4.784 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

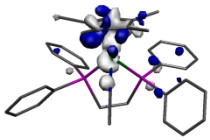
[Fe(Cp*)(NCMe)(dppe)][I], 2SIP



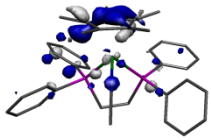




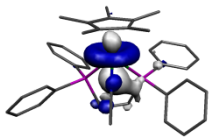
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



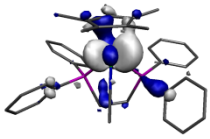
–8.439 eV



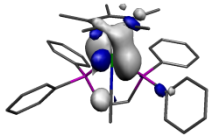
–8.362 eV



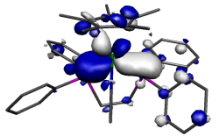
–7.458 eV



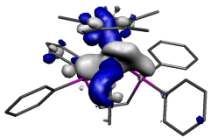
–7.077 eV



–6.958 eV



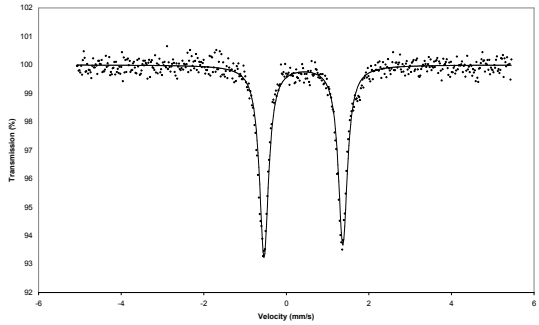
–4.699 eV

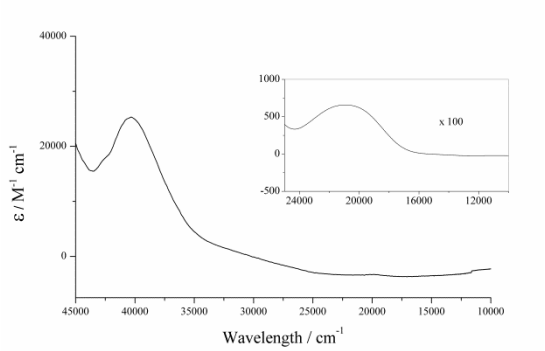


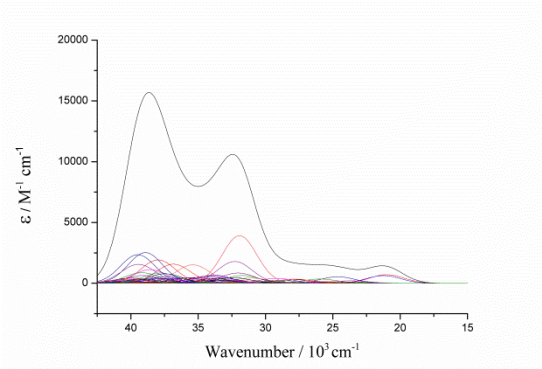
–4.502 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

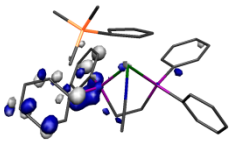
[Fe(Cp')(NCMe))(dppe)][I], 3SIP



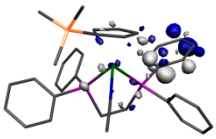




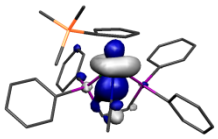
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



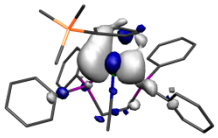
–8.614 eV



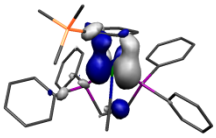
–8.540 eV



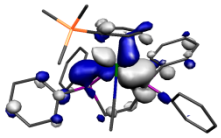
–7.629 eV



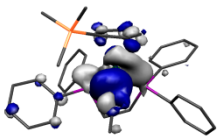
–7.438 eV



–7.125 eV



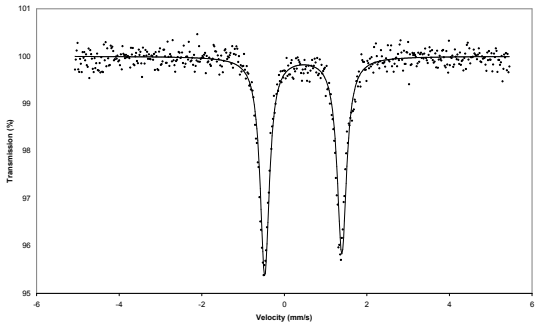
–4.757 eV

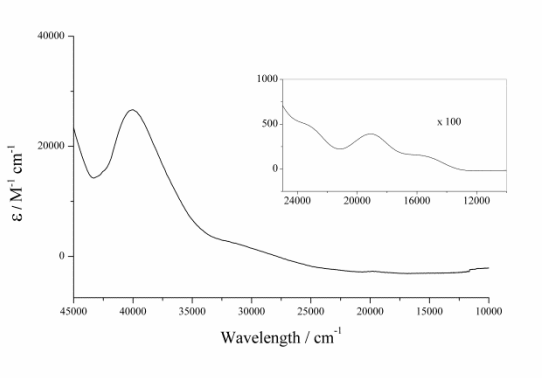


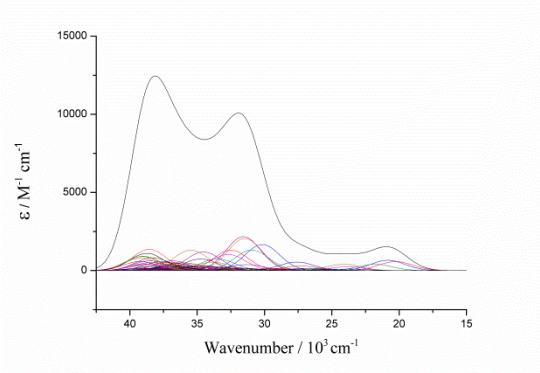
–4.696 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

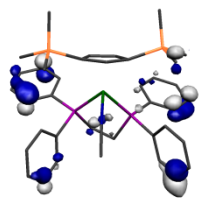
[Fe(Cp'')(NCMe)(dppe)][I], 4SIP



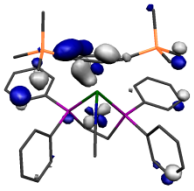




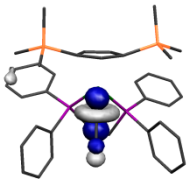
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



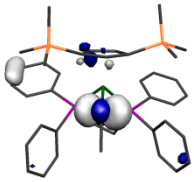
–8.608 eV



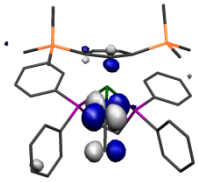
–8.403 eV



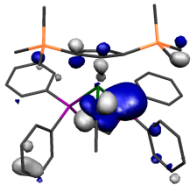
–7.504 eV



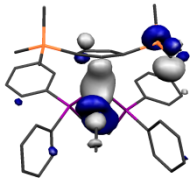
–7.210 eV



–7.073 eV



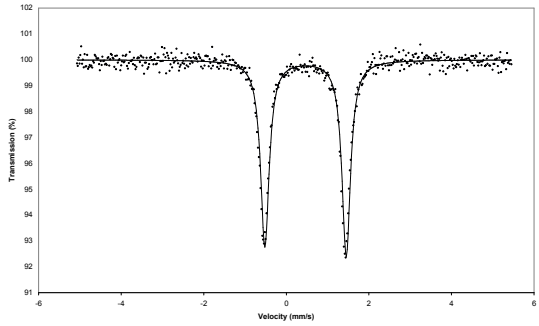
–4.780 eV

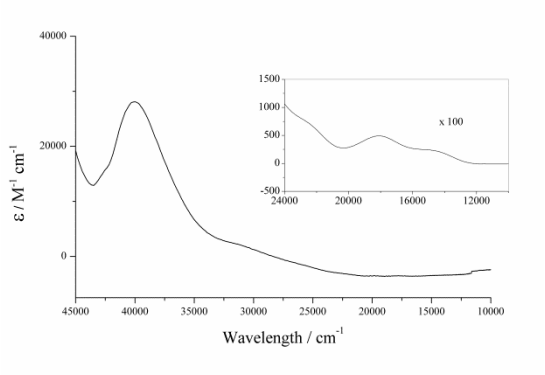


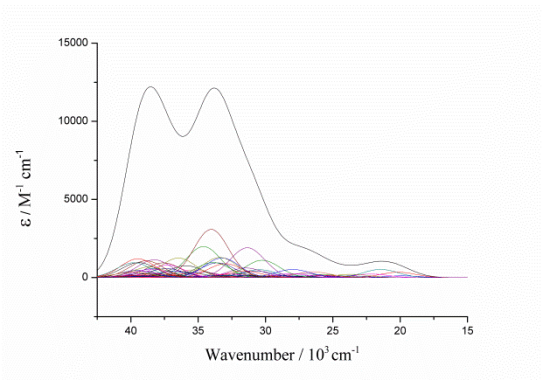
–4.630 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

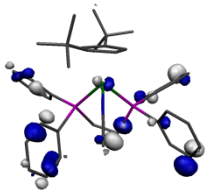
[Fe(Cp^{tt})(NCMe)(dppe)][I], 5SIP

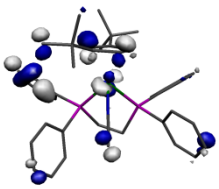


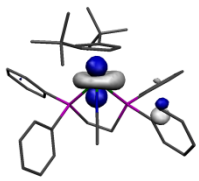


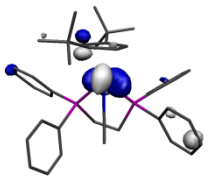


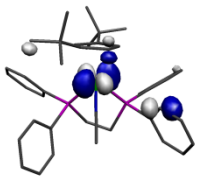
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis

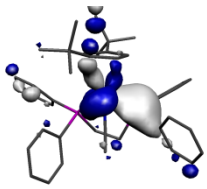

–8.470 eV

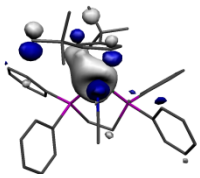

–8.414 eV


–7.505 eV


–7.119 eV

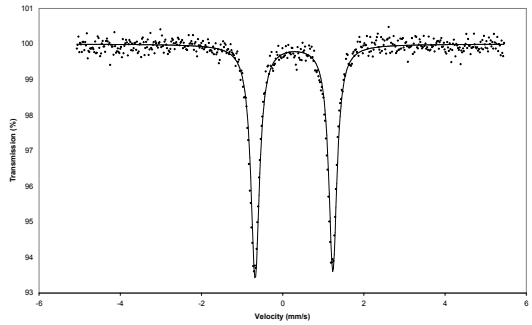

–6.997 eV

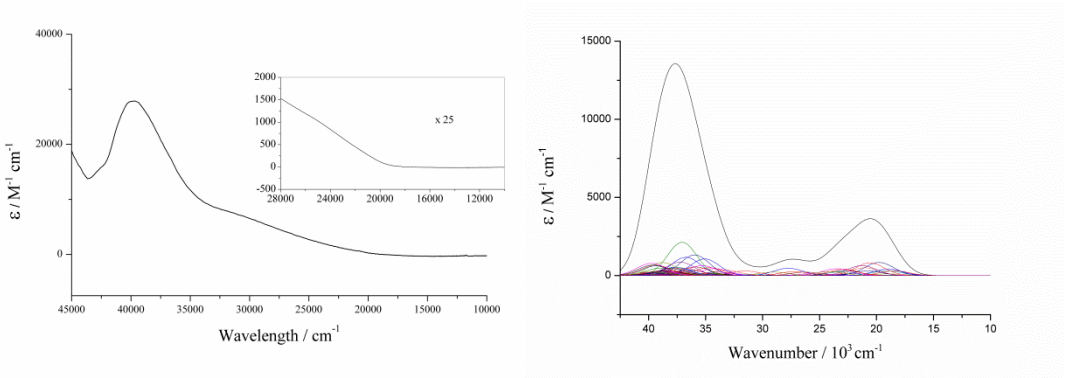

–4.739 eV


–4.626 eV

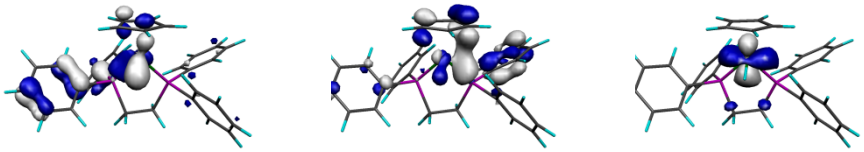
Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

[Fe(Cp)(H)(dppe)], 1H

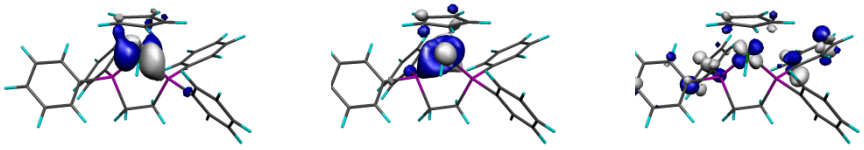




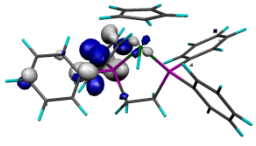
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.886 eV –5.697 eV –4.383 eV



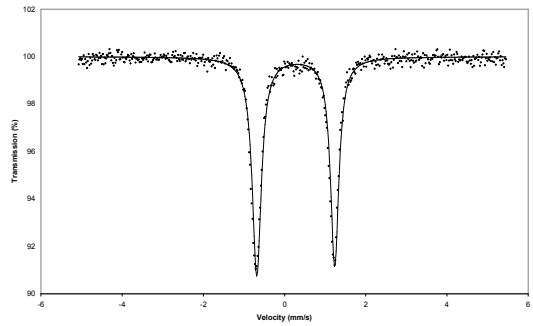
–3.847 eV –3.838 eV –1.616 eV

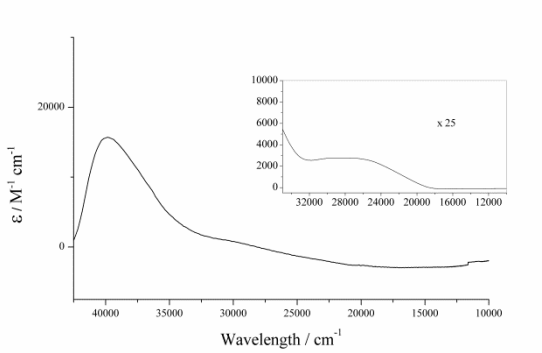


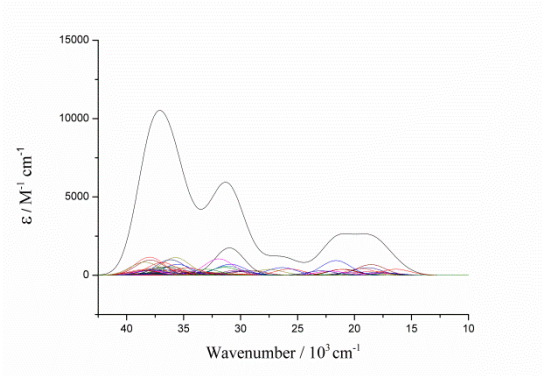
–1.575 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

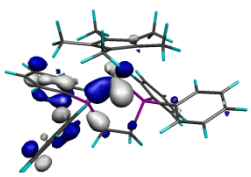
[Fe(Cp*)(H)(dppe)], 2H



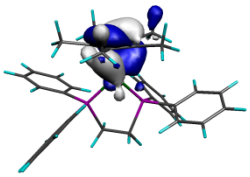




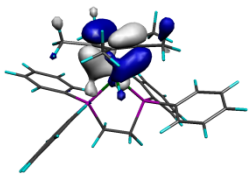
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



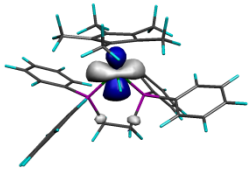
–5.797 eV



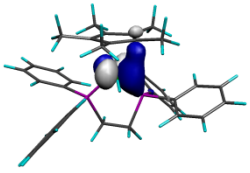
–5.291 eV



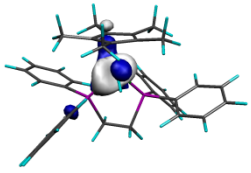
–5.173 eV



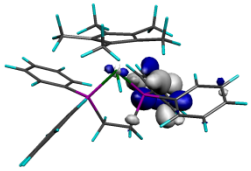
–4.157 eV



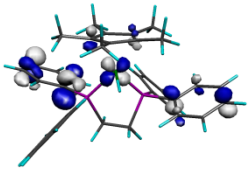
–3.616 eV



–3.562 eV



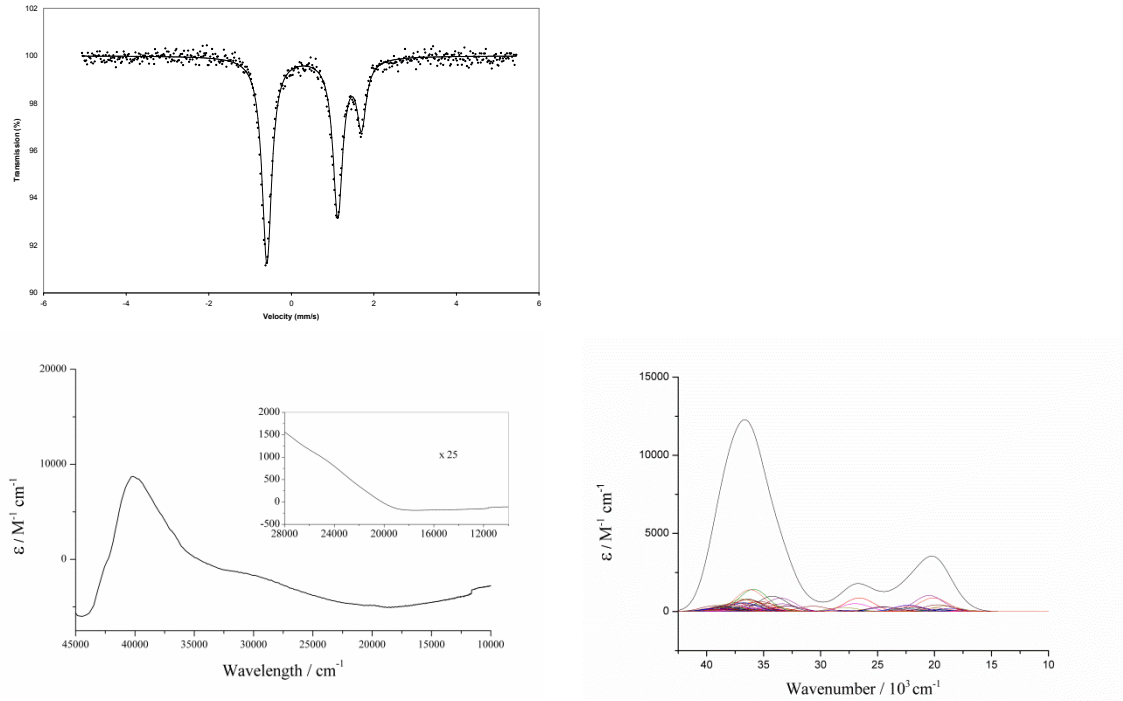
–1.561 eV



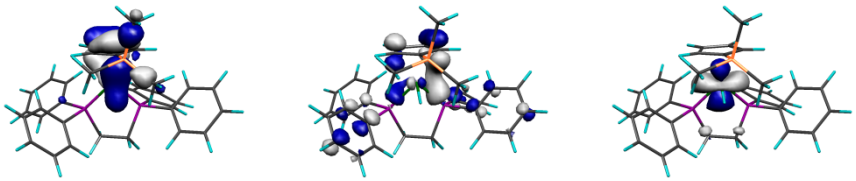
–1.535 eV

Kohn-Sham MO plots from HOMO-5 (top left) to LUMO+1 (bottom left)

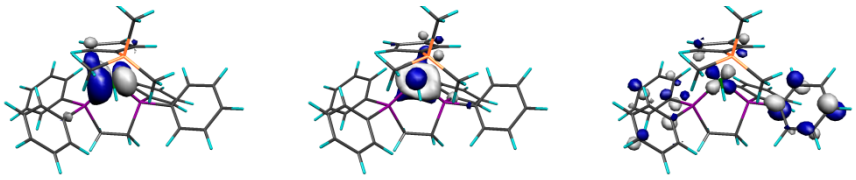
[Fe(Cp')(H)(dppe)], 3H



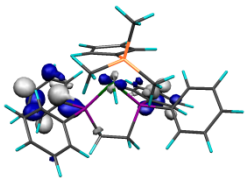
Top – Mossbauer. The Mössbauer spectrum of this compound showed two species, the major component is **3H** and the minor component is most likely a product of decomposition.
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.804 eV –5.658 eV –4.353 eV



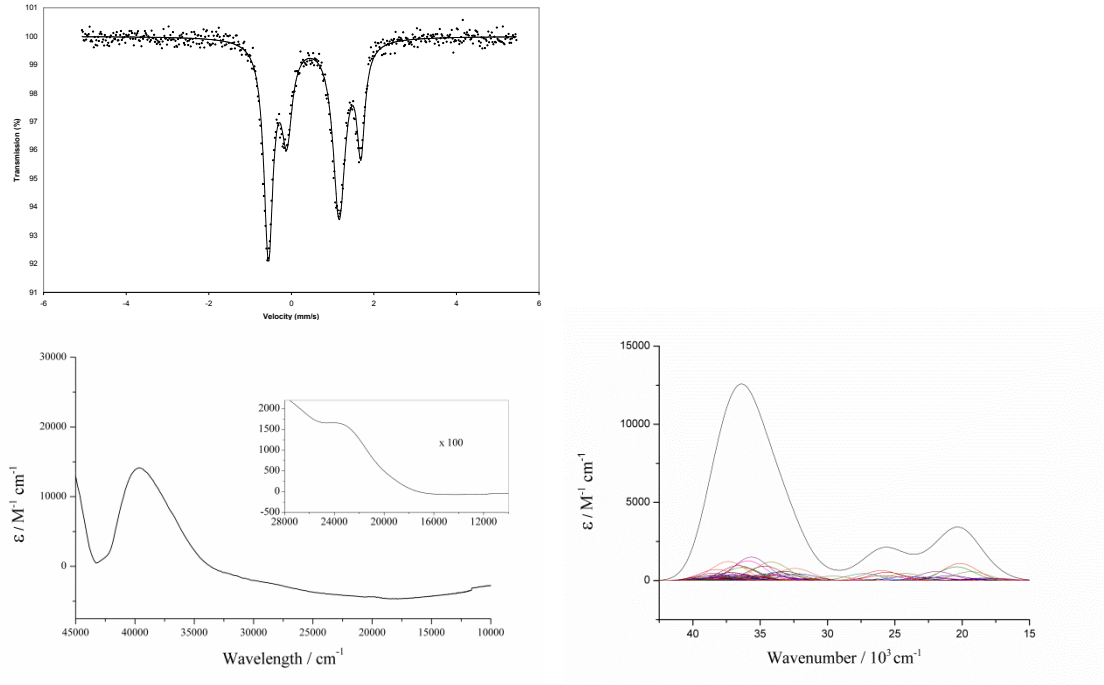
–3.820 eV –3.789 eV –1.652 eV



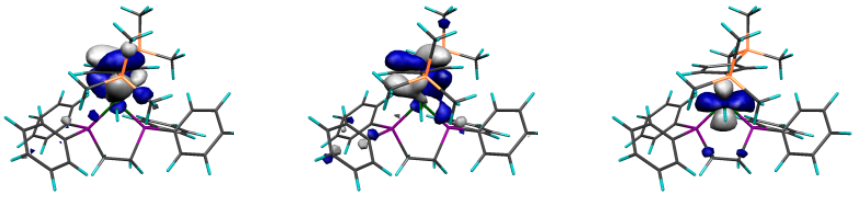
–1.597 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

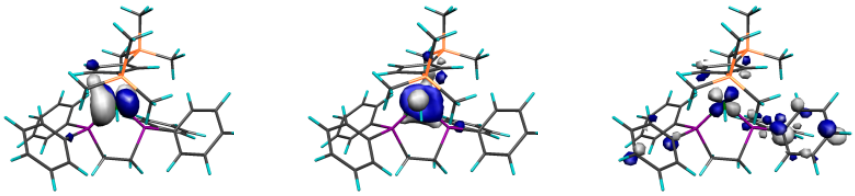
[Fe(Cp'')(H)(dppe)], 4H



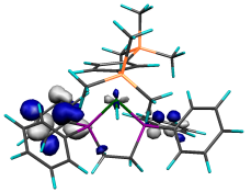
Top – Mossbauer. The Mössbauer spectrum of this compound showed two species, the major component is **4H** and the minor component is most likely a product of decomposition'
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis



–5.726 eV –5.564 eV –4.321 eV



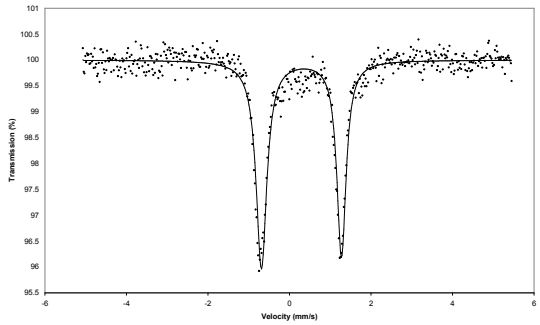
–3.831 eV –3.706 eV –1.662 eV

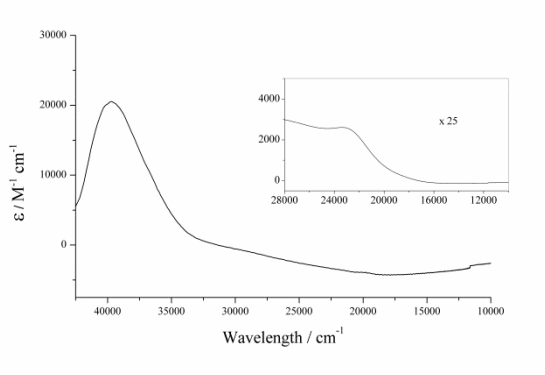


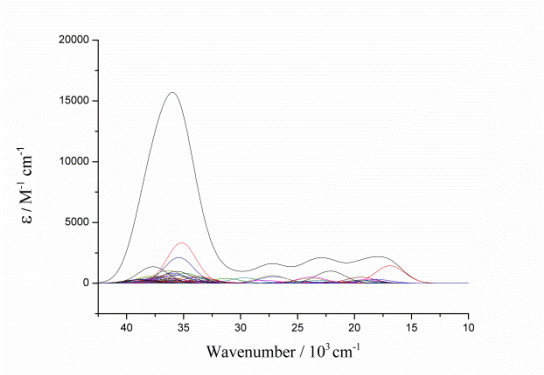
–1.573 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)

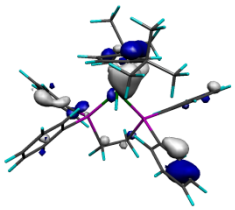
[Fe(Cp^{tt})(H)(dppe)], 5H

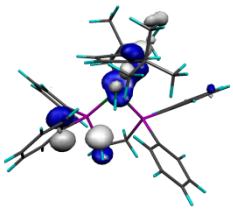


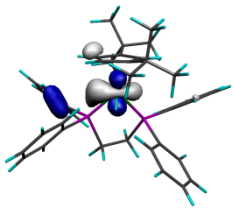


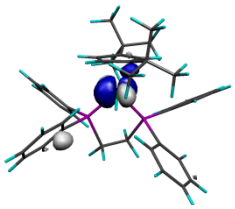


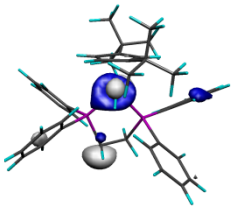
Top – Mossbauer
Bottom Left – Experimental UV-vis, Bottom Right – Calculated UV-vis

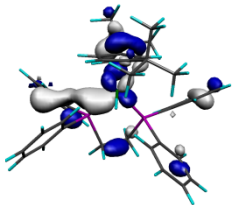

–5.659 eV

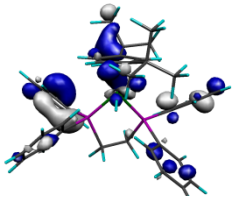

–5.475 eV


–4.317 eV


–3.810 eV


–3.638 eV


–1.639 eV


–1.465 eV

Kohn-Sham MO plots from HOMO-4 (top left) to LUMO+1 (bottom left)