Electronic Supplementary Material (ESI) for RSC Advances.

Supramolecular complexes involving non-symmetric viologen cations and hexacyanoferrate(II) anions. A spectroscopic, crystallographic and computational study

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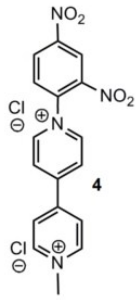
Supplementary data file

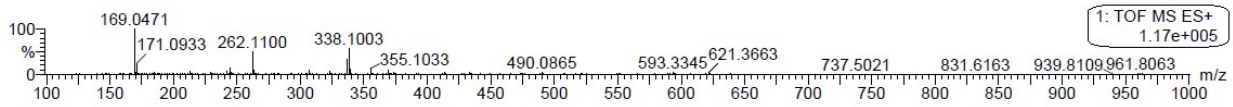
1. HRMS results for compounds **4** and **6a-e**.

Elemental Composition Report



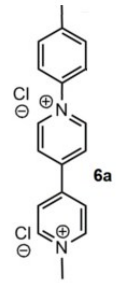
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
433 formula(e) evaluated with 14 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-10 O: 0-10



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
338.1003	338.1028	-2.5	-7.4	12.5	514.0	0.0	C19 H16 N O5
	338.1015	-1.2	-3.5	13.0	518.8	4.8	C17 H14 N4 O4
	338.1002	0.1	0.3	8.0	520.6	6.6	C16 H18 O8
	338.1028	-2.5	-7.4	18.0	522.5	8.4	C18 H10 N8
	338.1042	-3.9	-11.5	17.5	522.8	8.8	C20 H12 N5 O
	338.1002	0.1	0.3	13.5	522.8	8.8	C15 H12 N7 O3
	338.0988	1.5	4.4	8.5	523.3	9.2	C14 H16 N3 O7
	338.0988	1.5	4.4	14.0	526.4	12.4	C13 H10 N10 O2
	338.0975	2.8	8.3	9.0	526.7	12.7	C12 H14 N6 O6
	338.0970	3.3	9.8	21.5	527.0	13.0	C26 H12 N
	338.0961	4.2	12.4	4.0	527.8	13.7	C11 H18 N2 O10
	338.0961	4.2	12.4	9.5	529.4	15.3	C10 H12 N9 O5
	338.1047	-4.4	-13.0	5.0	531.7	17.7	C6 H14 N10 O7
	338.1020	-1.7	-5.0	0.5	533.4	19.4	C3 H16 N9 O10

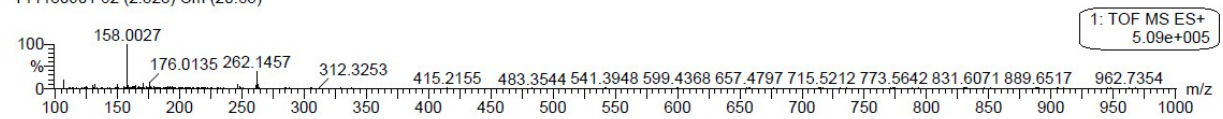
Elemental Composition Report



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-15

T11180901 62 (2.528) Cm (20:65)



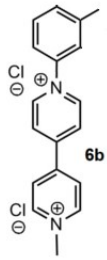
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
262.1461	262.1470	-0.9	-3.4	11.0	611.3	0.0	C18 H18 N2

Elemental Composition Report

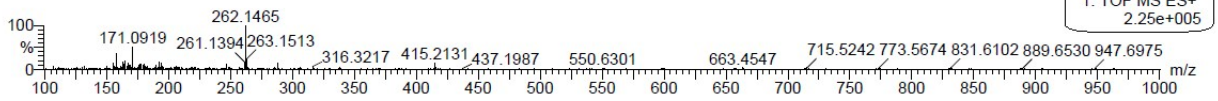
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-15



T11180904 26 (1.070) Cm (20:70)



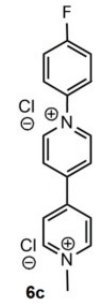
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
262.1463	262.1470	-0.7	-2.7	11.0	608.6	0.0	C18 H18 N2

Elemental Composition Report

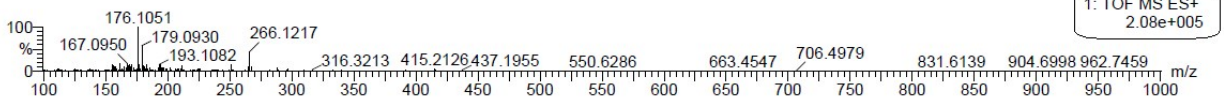
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
106 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-15 F: 0-1

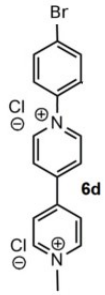


T11180907 58 (2.361) Cm (27:65)



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
266.1221	266.1219	0.2	0.8	11.0	597.1	0.0	C17 H15 N2 F
	266.1213	0.8	3.0	8.0	605.7	8.6	C5 H10 N14

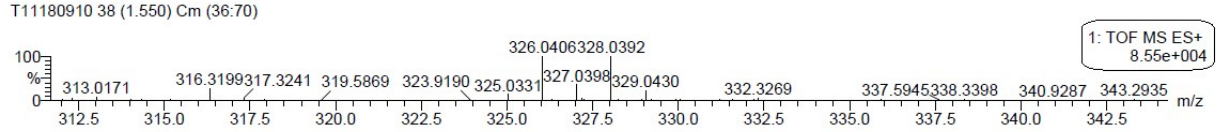
Elemental Composition Report



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

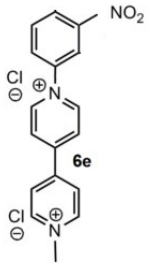
Monoisotopic Mass, Odd and Even Electron Ions
293 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-15 79Br: 0-8 81Br: 0-8

T11180910 38 (1.550) Cm (36:70)



Minimum:				-1.5						
Maximum:		5.0	5.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
326.0409	326.0400	0.9	2.8	19.5	510.3	0.5	C12	N13		
	326.0419	-1.0	-3.1	11.0	512.3	2.5	C17	H15	N2	79Br
	326.0426	-1.7	-5.2	8.0	511.1	1.4	C10	H13	N8	81Br
	326.0367	4.2	12.9	11.5	512.3	2.6	C18	H15	N	81Br

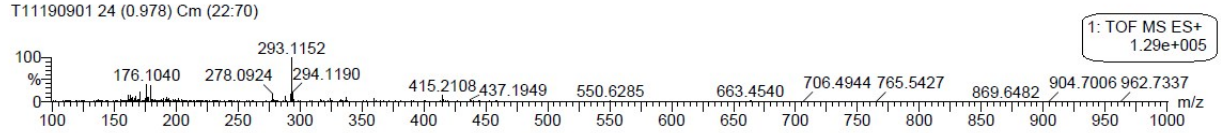
Elemental Composition Report



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
472 formula(e) evaluated with 15 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-200 N: 0-15 O: 0-10

T11190901 24 (0.978) Cm (22:70)

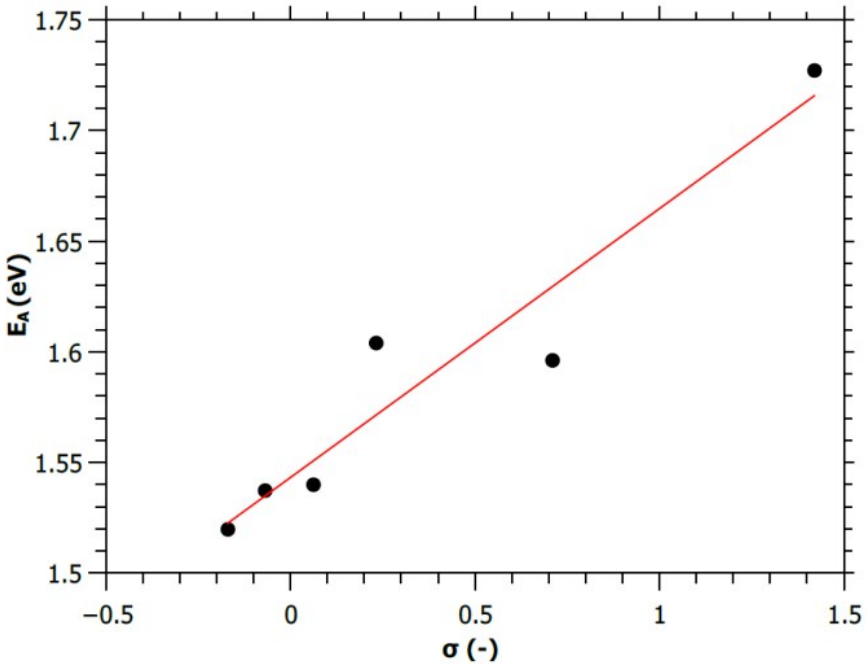


Minimum:				-1.5						
Maximum:		5.0	5.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
293.1154	293.1178	-2.4	-8.2	11.5	565.2	0.0	C19	H17	O3	
	293.1164	-1.0	-3.4	12.0	568.3	3.2	C17	H15	N3	O2
	293.1151	0.3	1.0	12.5	571.0	5.9	C15	H13	N6	O
	293.1137	1.7	5.8	7.5	571.6	6.5	C14	H17	N2	O5
	293.1137	1.7	5.8	13.0	573.4	8.2	C13	H11	N9	
	293.1124	3.0	10.2	8.0	573.5	8.4	C12	H15	N5	O4
	293.1111	4.3	14.7	3.0	574.5	9.4	C11	H19	N	O8
	293.1111	4.3	14.7	8.5	575.2	10.1	C10	H13	N8	O3
	293.1196	-4.2	-14.3	-1.5	576.5	11.4	C7	H21	N2	O10
	293.1196	-4.2	-14.3	4.0	577.1	12.0	C6	H15	N9	O5
	293.1183	-2.9	-9.9	-1.0	577.2	12.1	C5	H19	N5	O9
	293.1169	-1.5	-5.1	-0.5	578.2	13.1	C3	H17	N8	O8
	293.1183	-2.9	-9.9	4.5	578.3	13.2	C4	H13	N12	O4
	293.1156	-0.2	-0.7	0.0	579.6	14.5	C	H15	N11	O7
	293.1169	-1.5	-5.1	5.0	579.6	14.5	C2	H11	N15	O3

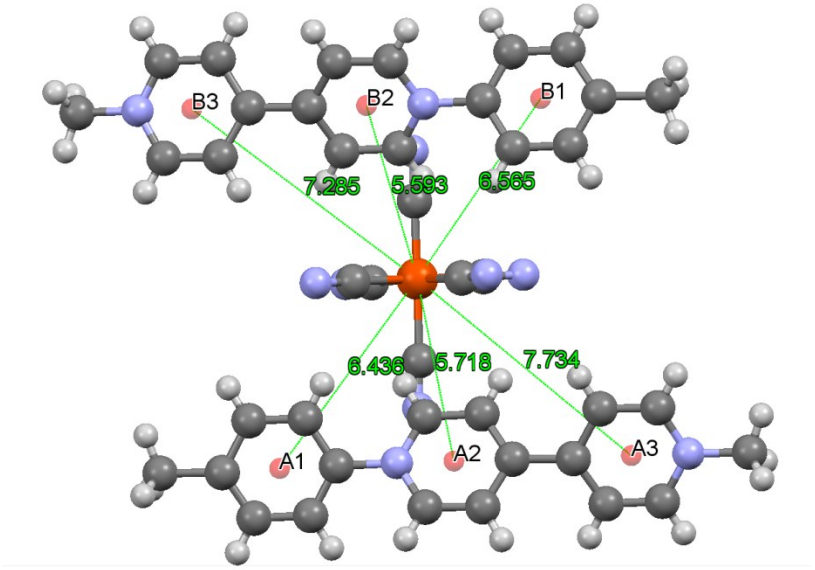
2. Hammett plots for $E_{A.}$

y = B + Ax
B (y-intercept) = 1.543174291807577e+00 +/- 1.207419073330252e-02
A (slope) = 1.214763657457835e-01 +/- 1.830042970633754e-02

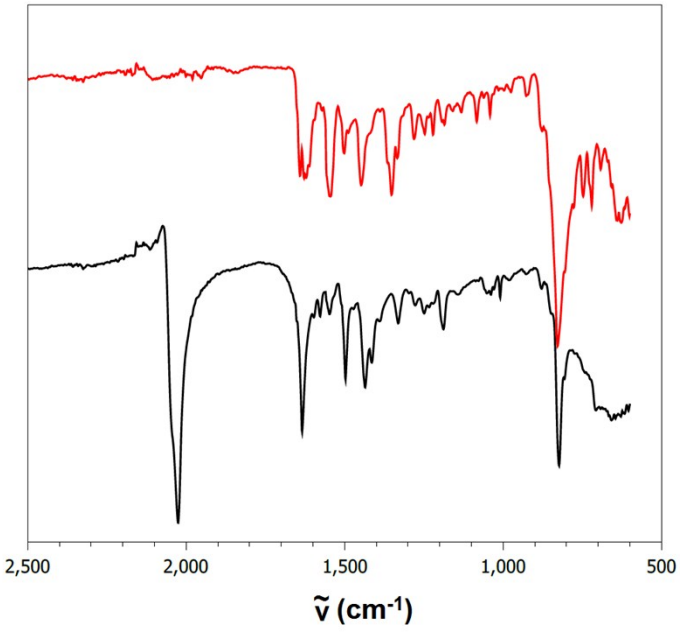
Chi^2/doF = 6.082306084231766e-04; R^2 = 0.916773604520418



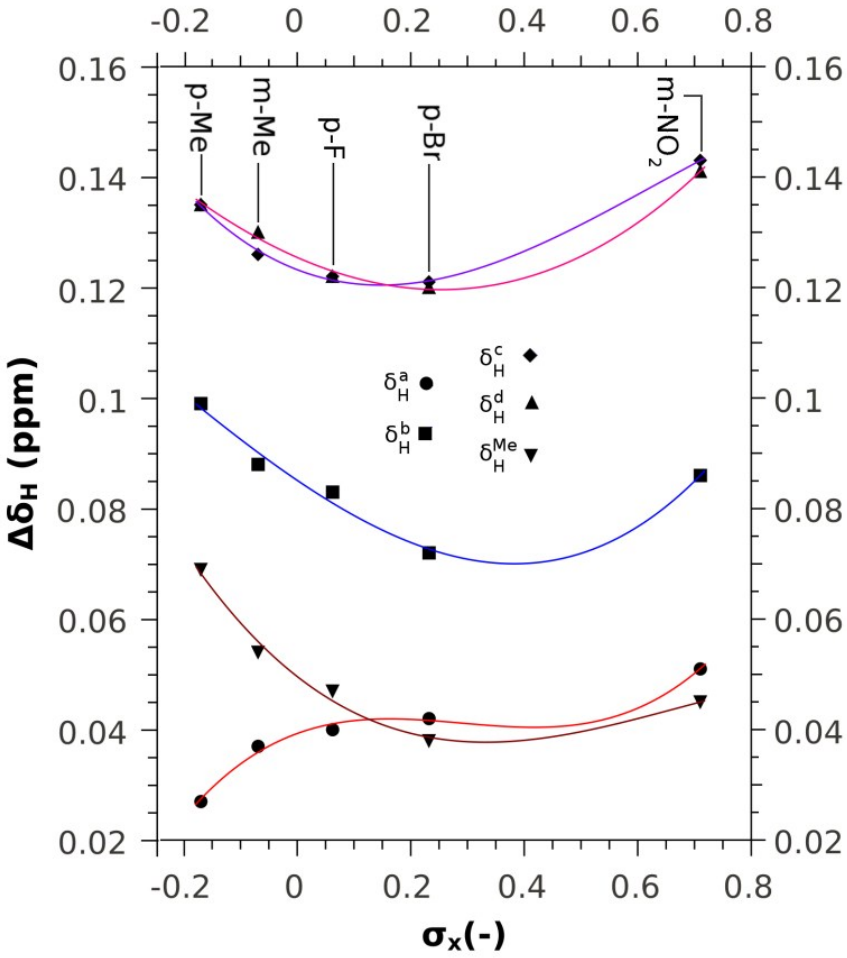
3. Distances between the centroids of the three rings of **6a**$^{2+}$ and Fe^{II} obtained through crystallographic analysis of CTC **7**.



4. FTIR (ATR) of CTC **7** (black) and **6a** as a chloride salt (red).



5. Correlations of Δδ (listed in Table 1) for compounds **4** and **6a-e** with the Hammett parameter.



6. HOMO, LUMO energies and HOMO-LUMO gaps of the dications of the viologens **4** and **6a-e** calculated at different levels of theory**.**

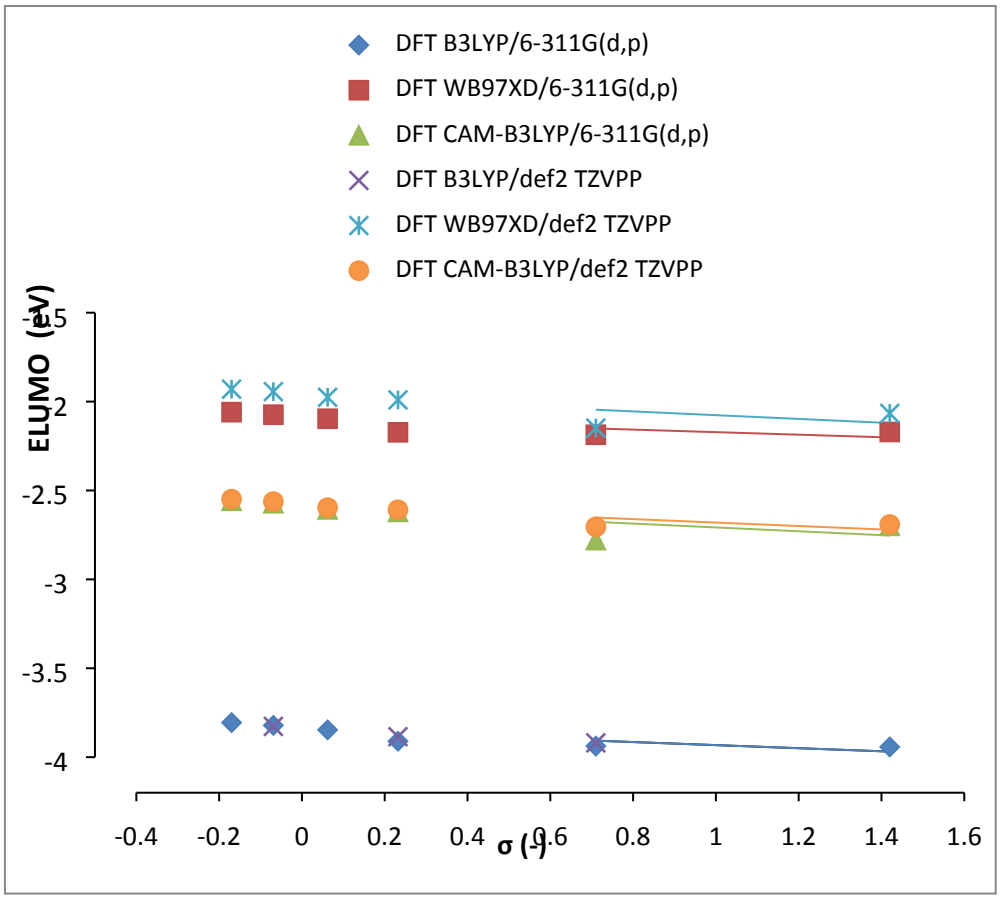
	$\mathbf{4^{2+}}$	$\mathbf{6a^{2+}}$	$\mathbf{6b^{2+}}$	$\mathbf{6c^{2+}}$	$\mathbf{6d^{2+}}$	$\mathbf{6e^{2+}}$
DFT B3LYP/6-311G(d,p)						
HOMO (H)	-0.32324	-0.27477	-0.27459	-0.28301	-0.27398	-0.30572
LUMO (H)	-0.14488	-0.13986	-0.14043	-0.14136	-0.14371	-0.14471
HOMO (eV)	-8.79580793	-7.47687212	-7.47197407	-7.70109393	-7.45537513	-8.31906447
LUMO (eV)	-3.94238539	-3.80578424	-3.82129473	-3.84660131	-3.91054807	-3.93775945
Gap HOMO-LUMO (eV)	4.85	3.67	3.65	3.85	3.54	4.38
DFT WB97XD/6-311G(d,p)						
HOMO (H)	-0.39904	-0.34695	-0.34767	-0.35626	-0.34637	-0.3795
LUMO (H)	-0.07978	-0.07568	-0.07621	-0.07704	-0.07985	-0.08035
HOMO (eV)	-10.8584309	-9.44098985	-9.46058205	-9.69432784	-9.42520725	-10.3267204
LUMO (eV)	-2.17092426	-2.05935758	-2.07377961	-2.09636506	-2.17282905	-2.18643474
Gap HOMO-LUMO (eV)	8.69	7.38	7.39	7.60	7.25	8.14
DFT CAM-B3LYP/6-311G(d,p)						
HOMO (H)	-0.37773	-0.32673	-0.32657	-0.33557	-0.32631	-0.35812
LUMO (H)	-0.09918	-0.09401	-0.09451	-0.09579	-0.0963	-0.10214
HOMO (eV)	-10.2785563	-8.89077566	-8.88642184	-9.1313243	-8.87934688	-9.74494102
LUMO (eV)	-2.69882511	-2.55814226	-2.57174795	-2.60657852	-2.62045633	-2.77937081
Gap HOMO-LUMO (eV)	7.58	6.33	6.31	6.52	6.26	6.97

DFT WB97XD/def2 TZVPP	**4^{2+}**	**4^{2+}**	**4^{2+}**	**4^{2+}**	**4^{2+}**	**4^{2+}**
HOMO (H)	-0.39792	-0.34665	-0.34694	-0.35558	-0.34588	-0.37801
LUMO (H)	-0.07593	-0.07093	-0.07144	-0.07261	-0.07315	-0.07898
HOMO (eV)	-10.8279541	-9.43282644	-9.44071774	-9.6758241	-9.41187367	-10.2861755
LUMO (eV)	-2.06616043	-1.9301035	-1.94398131	-1.97581863	-1.99051278	-2.14915515
Gap HOMO-LUMO (eV)	8.76	7.50	7.50	7.70	7.42	8.14

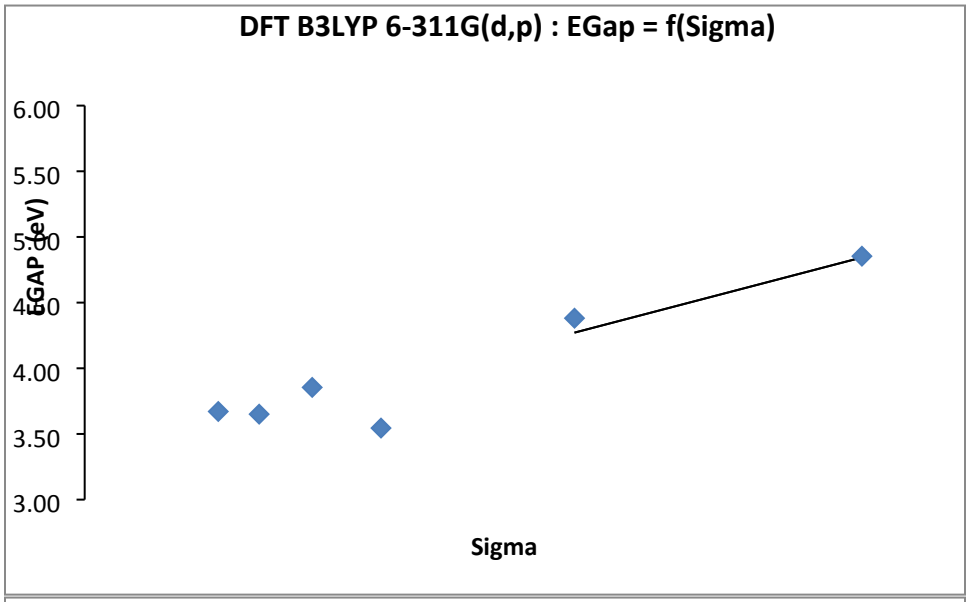
DFT CAM-B3LYP/def2 TZVPP						
HOMO (H)	-0.37798	-0.32621	-0.32626	-0.33583	-0.32257	-0.35856
LUMO (H)	-0.09891	-0.09366	-0.09417	-0.09542	-0.09586	-0.09939
HOMO (eV)	-10.2853591	-8.87662574	-8.87798631	-9.13839926	-8.7775763	-9.75691403
LUMO (eV)	-2.69147804	-2.54861827	-2.56249608	-2.59651031	-2.60848332	-2.70453951
Gap HOMO-LUMO (eV)	7.59	6.33	6.32	6.54	6.17	7.05

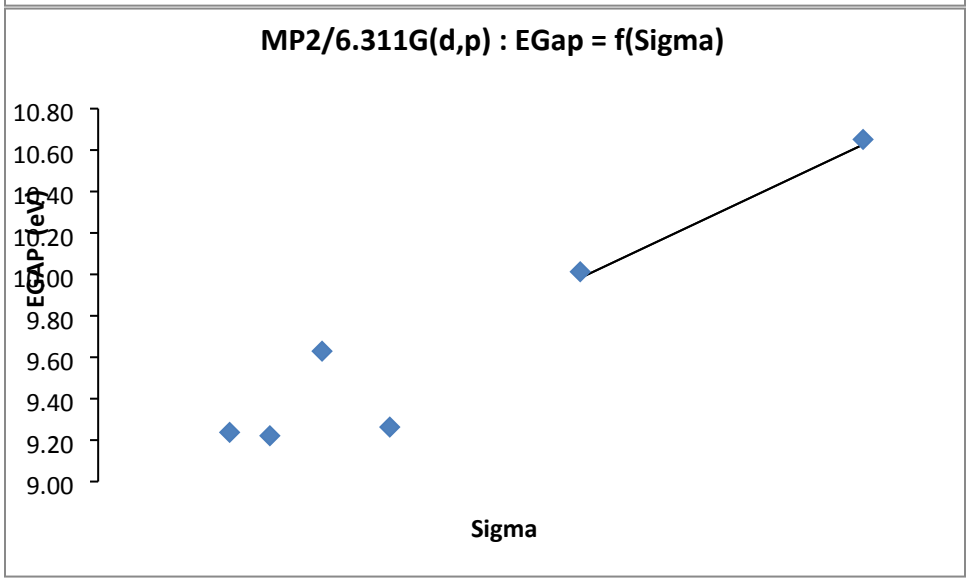
MP2/6,311g(d,p) single point calc.						
HOMO (H)	-0.40792	-0.35146	-0.35159	-0.36739	-0.35723	-0.38488
LUMO (H)	-0.01649	-0.01199	-0.01272	-0.01352	-0.01682	-0.01692
HOMO (eV)	-11.100068	-9.5637132	-9.56725068	-9.99719055	-9.72072288	-10.4731177
LUMO (eV)	-0.44871573	-0.3262645	-0.34612881	-0.36789792	-0.45769549	-0.46041663
Gap HOMO-LUMO (eV)	10.65	9.24	9.22	9.63	9.26	10.01

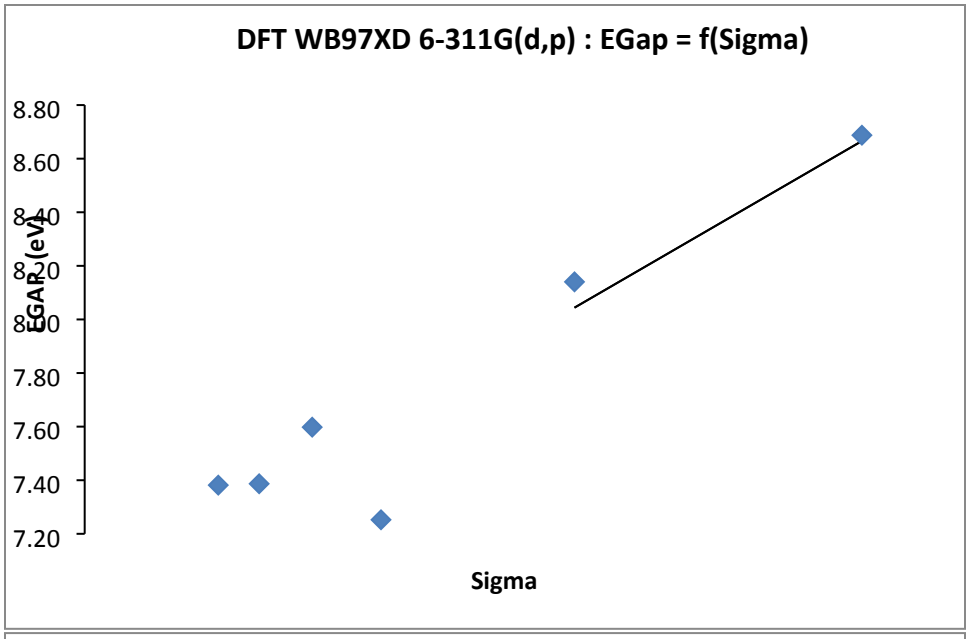
7. Correlations of calculated LUMO energies at different levels of theory for the dications **4** and **6a-e** with the Hammett parameter (σ).

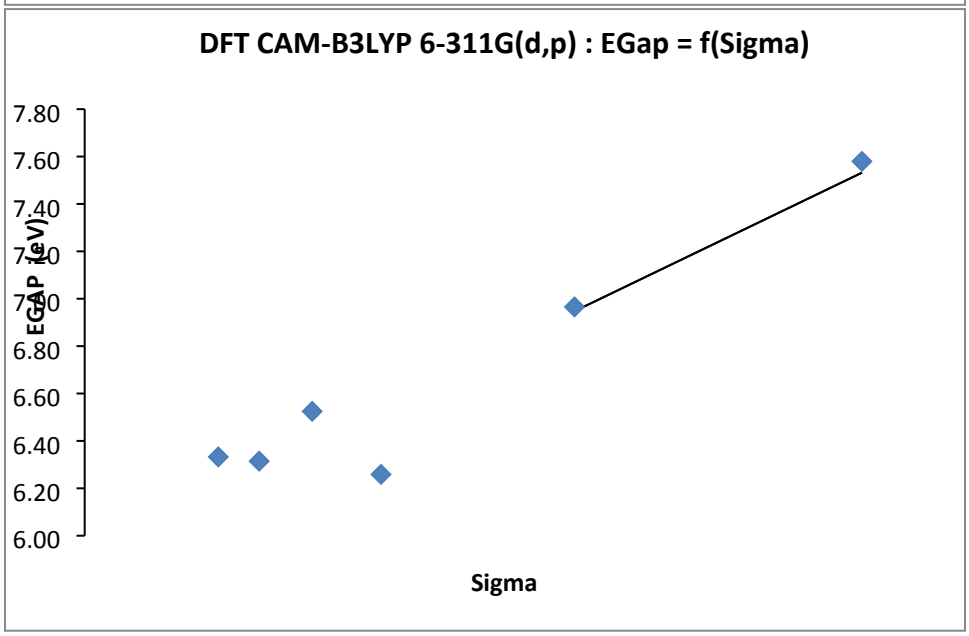


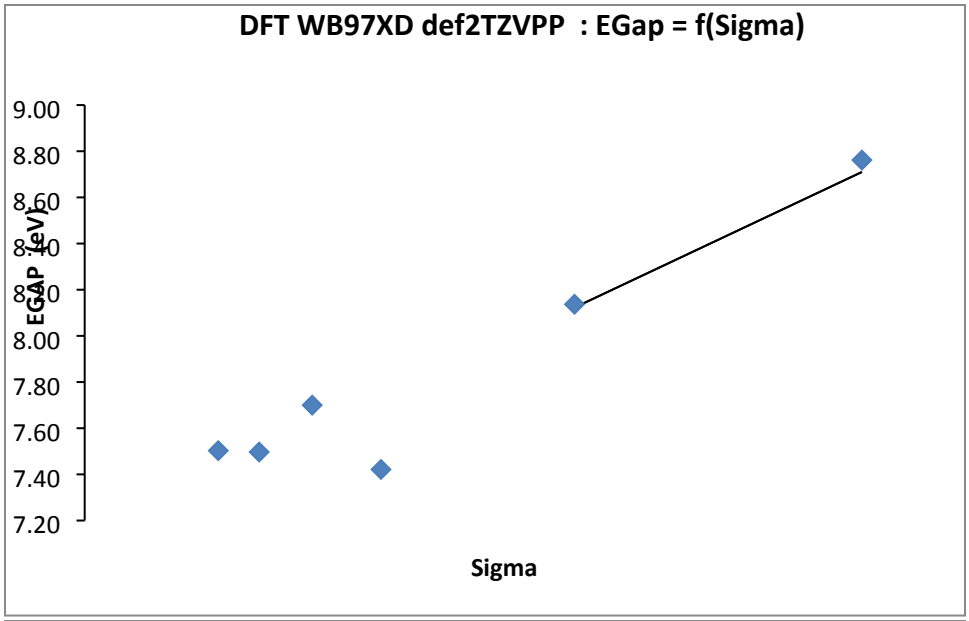
8. Correlations of E_{GAP} (calculated at various levels of theory) of dications of **4** and **6a-e** with the Hammett parameter (σ)

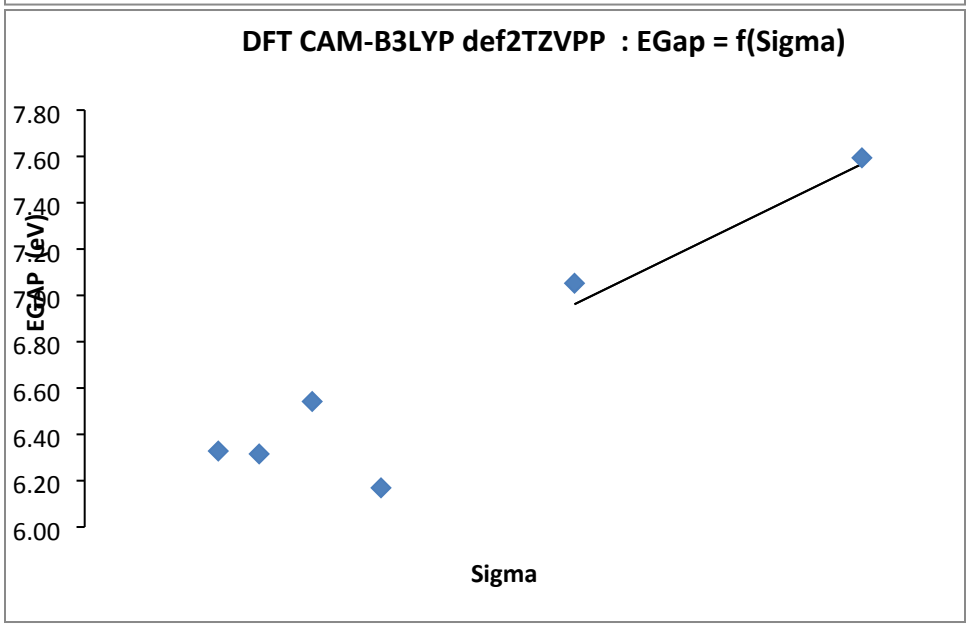





DFT WB97XD 6-311G(d,p) : EGap = f(Sigma)
8.80
8.60
8.40
8.20
8.00
7.80
7.60
7.40
7.20
EGAR (eV)
Sigma


DFT CAM-B3LYP 6-311G(d,p) : EGap = f(Sigma)
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
EGAP (eV)
Sigma


DFT WB97XD def2TZVPP : EGap = f(Sigma)
9.00
8.80
8.60
8.40
8.20
8.00
7.80
7.60
7.40
7.20
EGAP (eV)
Sigma


DFT CAM-B3LYP def2TZVPP : EGap = f(Sigma)
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
EGAP (eV)
Sigma