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1.1 Materials and methods

All the reactions involving sensitive compounds were carried out under dry Ar, in flame-dried glassware. If not noted otherwise, reactants and reagents were commercially available and used as received from Fluorochem, TCI-Chemicals, Sigma-Aldrich and Acros Organics. TLC analyses were carried out with Merk 60 F_{254} plates (0.2mm). ^{1}H NMR spectra were recorded in methylene chloride-d_2, on a Bruker 400MHz NMR spectrometer. The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, dt=double triplet, dtt=double triple triplet, m=multiplet. ^{13}C NMR spectra were recorded at 101 MHz. ^{1}H and ^{13}C NMR chemical shifts (ppm) are referred to TMS as external standard. Elemental analyses were obtained using an Elementar Vario MICRO cube equipment.

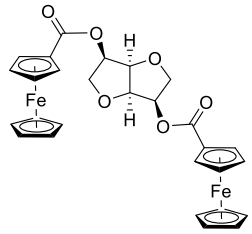
UV-Vis NIR absorption spectra were recorded on J&M TIDAS spectrophotometer. IR spectra were obtained using a Nicolet 6700 FT-IR instrument. Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) were carried out in 0.1 M $Bu_4NB(Ar^F)_4/CH_2Cl_2$ (BAr^F= tetrakis[3,5-bis(trifluoromethyl)phenyl]boron) solutions using a three-electrode configuration (glassy carbon working electrode, Pt wire counter electrode, and Ag quasi reference electrode) and were performed using a Metrohm Autolab potentiostat. The ferrocene/ferrocenium ($FcH^{0/+}$) couple served as internal reference to all potentials reported. Spectroelectrochemistry was performed using an Optically Transparent Thin Layer Electrochemical (OTTLE) cell.

The geometry for the neutral species was optimized from the X-ray crystal structure data when available, using the ORCA 4.0 program package. Computational analysis was performed using restricted Kohn-Sham density functional theory (DFT) at the B3LYP level of theory with Becke-Johnson damping (D3BJ) using the def2-TZVP [40] basis set and Weigend J as an auxiliary basis set on a m5 grid and TightSCF (ΔE 1.0 x 10^{-8} au). The geometry of the different oxidation states, was obtained by removing one or two electrons, respectively, using unrestricted Kohn-Sham DFT along with the same parameters for the neutral species. TD-DFT calculations were performed with a maximum dimension of 5, and the conductor-like polarizable continuum mode (CPCM) for CH_2Cl_2 was used for solvent modelling. The Kohn-Sham orbitals of the complexes were analyzed.

1.2 General Procedure for the Synthesis of the bis-ferrocene carboxylates 3 and 4.

Under an Ar atmosphere, N-ethyl-N′-(3-dimethylaminopropyl)carbodiimide, EDC (2.3mmol) and N,N-4-dimethylaminopyridine, DMAP (0.5mmol) were added to a brown heterogeneous mixture of the isohexide (1.0mmol) and ferrocene carboxylic acid (2.3mmol) in CH_2Cl_2 (2.5mL) at 0°C. The mixture was stirred at room temperature and the reaction was monitored by TLC analysis (hexane:ethyl acetate 1:1). After 24h the solvent was removed under reduced pressure and the crude was purified through flash chromatography on silica gel (hexane:ethyl acetate 1:1) and recrystallized from hexane:ethyl acetate, giving the pure product as orange crystals.

*1.2.1 (3R,3R,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-yl-di-ferrocenecarboxylate, **3***



Orange crystals. 485mg (85%). **M.p.** 162-166°C; **$[\alpha]_D^{25}$** = +102 (c 0.7, CH_2Cl_2)

^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ:5.21 (dtt, *J* = 10.3, 5.4, 2.7 Hz, 2H), 4.86–4.82 (m, 6H), 4.45 (dt, *J* = 4.0, 2.2 Hz, 4H), 4.28 (s, 10H), 4.13 (dd, *J* = 9.2, 6.5 Hz, 2H), 3.96 (dd, *J* = 9.2, 7.0 Hz, 2H).

^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ:171.4, 81.1, 74.1, 72.1, 72.1, 71.3, 71.2, 70.9, 70.6, 70.6.

Elemental Analysis: Anal. Calc. for $C_{28}H_{26}Fe_2O_6$: C, 58.98; H, 4.60; Found C, 58.81; H, 4.65.

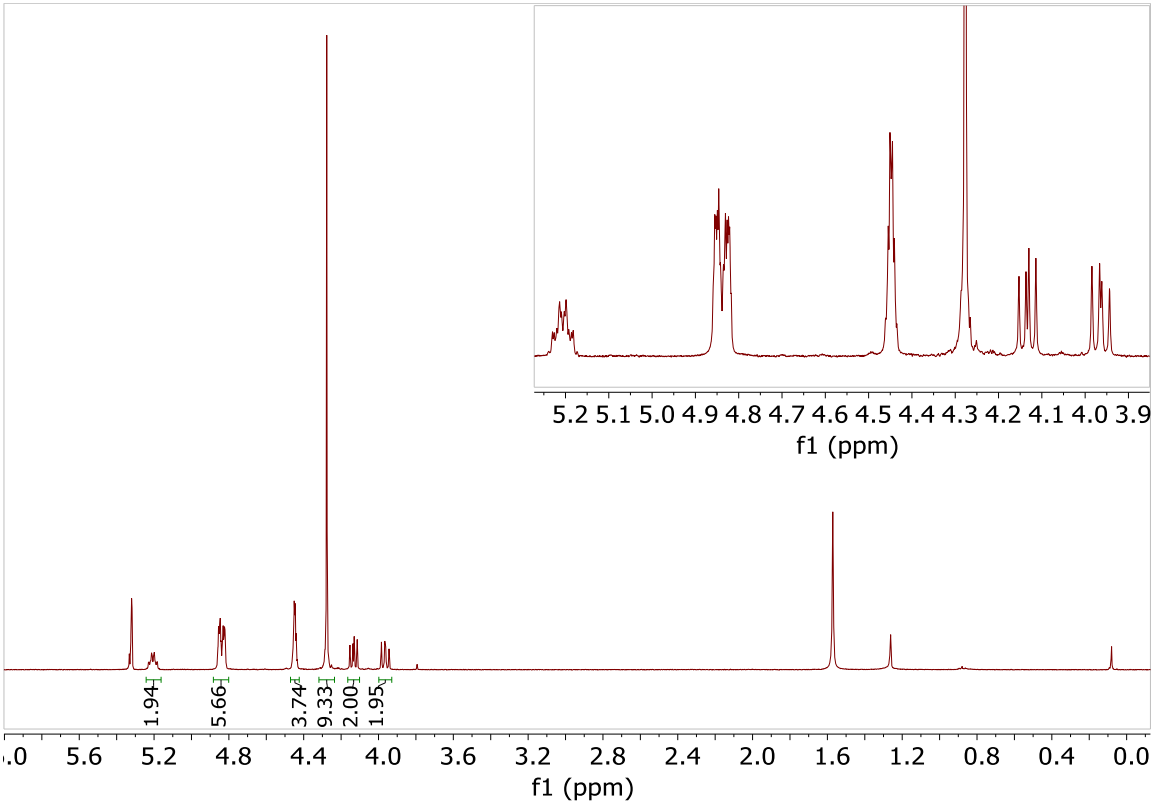


Figure S1. ^{1}H NMR(400 MHz, Methylene Chloride-d_2) spectrum of compound 3.

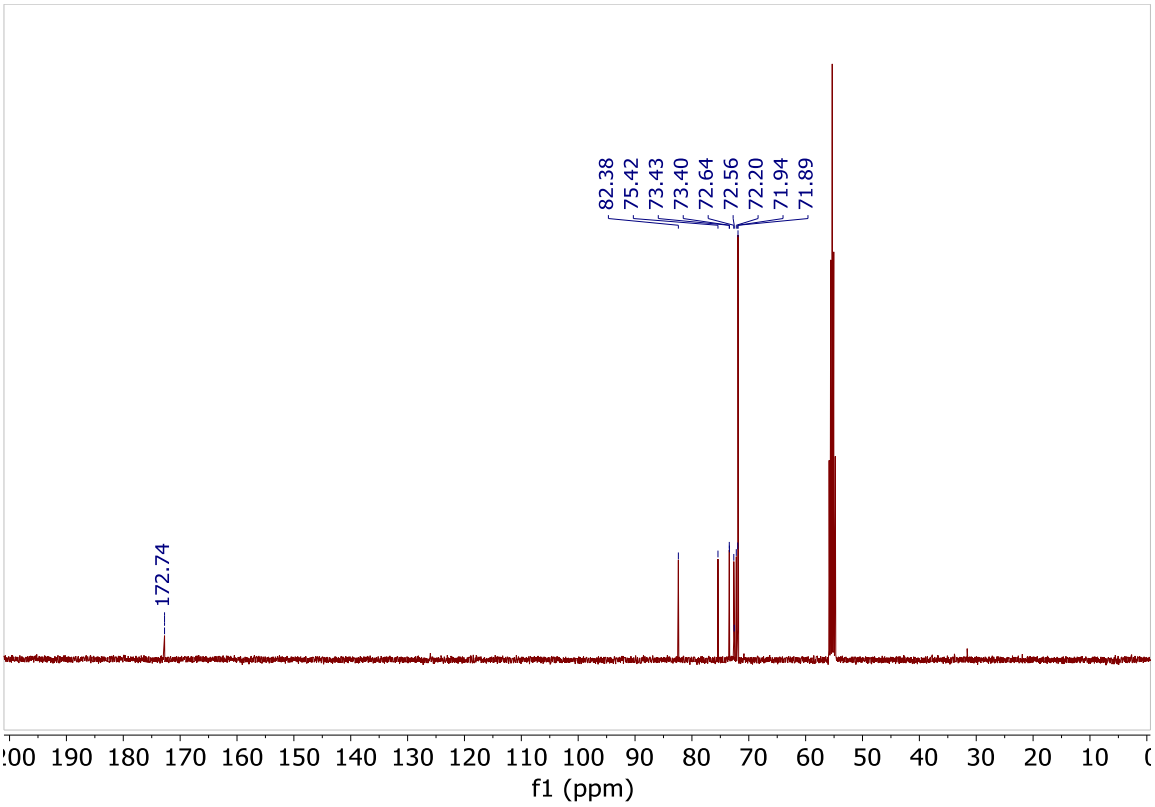
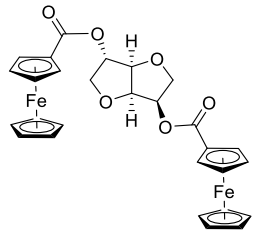


Figure S2. ^{13}C NMR (101 MHz, Methylene Chloride-d_2) spectrum of compound 3.

1.2.2 (3R,3R,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-yl-di-ferrocenecarboxylate, ***4***



Orange crystals. 492mg. (86%). **M.p.** 169°C; **$[\alpha]_D^{26}$** = +3 (c 0.2, CH_2Cl_2)

^{1}H NMR (401 MHz, Methylene Chloride-d_2) δ:5.36–5.28 (m, 2H), 5.01 (t, *J* = 5.2 Hz, 1H), 4.85–4.78 (m, 4H), 4.61 (d, *J* = 4.9 Hz, 1H), 4.47–4.41 (m, 4H), 4.27 (s, 5H), 4.21 (s, 5H), 4.14– 4.10 (m, 2H), 4.03–3.91 (m, 2H). **^{13}C NMR** (101 MHz, Methylene Chloride-d_2) δ:171.4, 171.3, 86.9, 81.6, 78.5, 74.3, 74.0, 72.3, 72.1, 72.1, 71.5, 71.3, 71.0, 70.9, 70.8, 70.7, 70.7, 70.5, 70.5, 70.4.

Elemental Analysis: Anal. Calc. for $C_{28}H_{26}Fe_2O_6$: C, 58.98; H, 4.60; Found C, 58.83; H, 4.67.

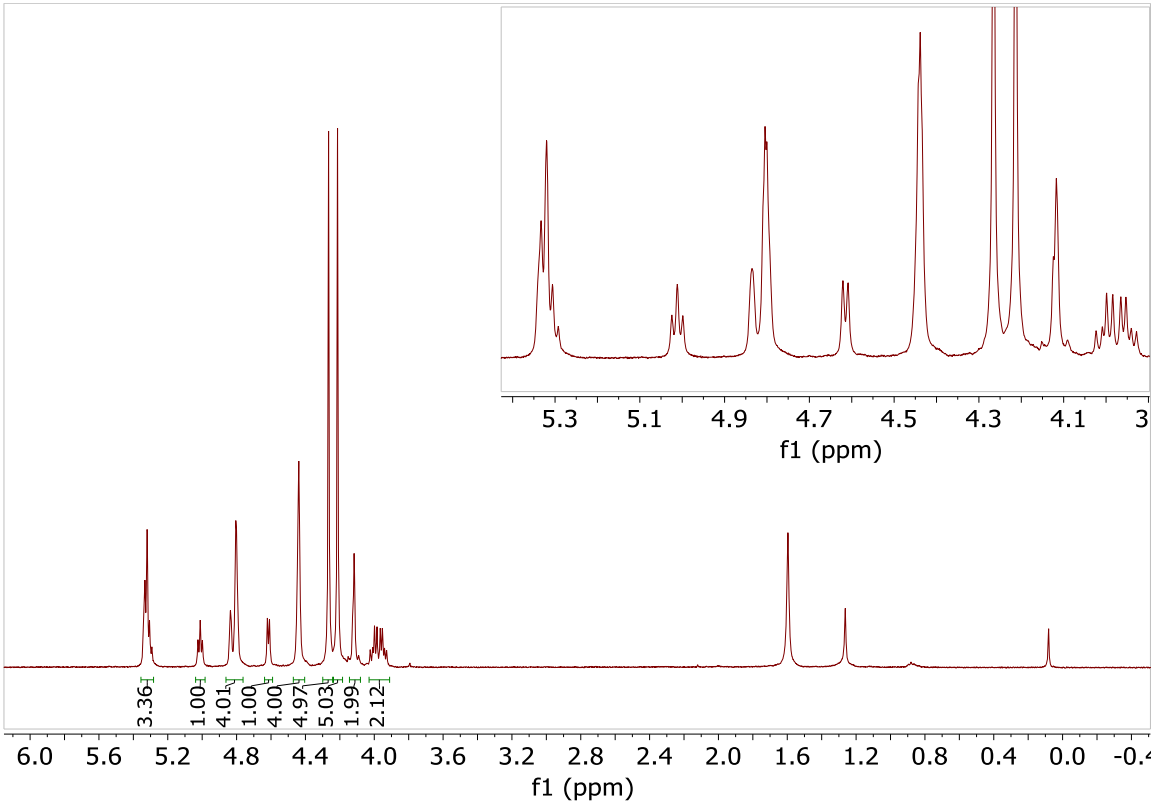


Figure S3. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) spectrum of compound 4.

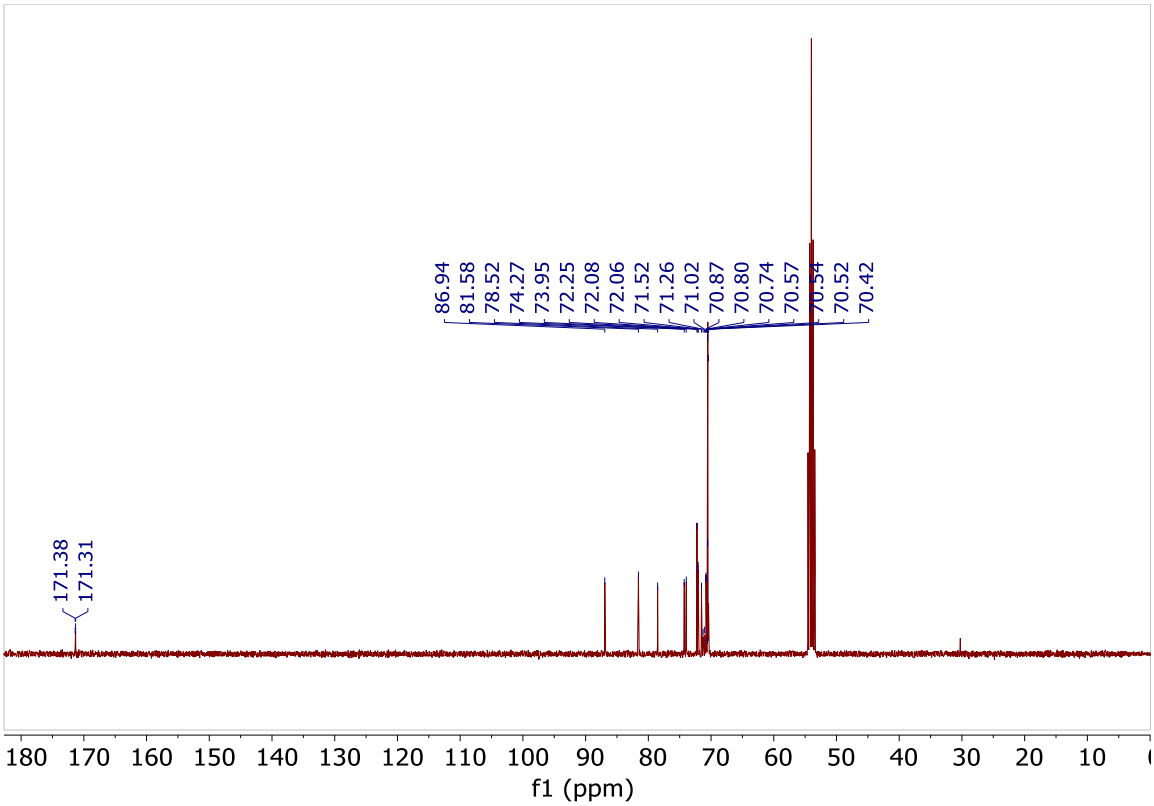


Figure S4. ^{13}C NMR (400 MHz, Methylene Chloride-d_2) spectrum of compound 4.

1.3 Pertinent Metric Parameters for Complexes 3 and 4 Characterized by Single-crystal X-ray Diffraction (XRD).

Identification code	[3]	[4]
Empirical formula	$C_{28}H_{26}Fe_2O_6$	$C_{28}H_{26}Fe_2O_6$
Formula weight	569.95	570.205
Temperature/K	135.03	134.98
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12$	$P2_12_12_1$
a/Å	10.6299(6)	7.6065(5)
b/Å	21.1093(13)	10.1524(6)
c/Å	10.3411(5)	29.6525(18)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	2320.4(2)	2289.9(3)
Z	4	4
ρcalcg/cm^3	1.6313	1.654
μ/mm-1	1.295	1.312
F(000)	1177.2	1179.5
Crystal size/mm3	0.243×0.186×0.18	0.244×0.151×0.021
Radiation	MoKα(λ = 0.71073)	MoKα(λ = 0.71073)
2Θ range for data/°	3.86 to 61.00	2.74 to 56.68
Index ranges	-15 ≤ h ≤ 15	-10 ≤ h ≤ 10
	-30 ≤ k ≤ 30	-13 ≤ k ≤ 9
	-14 ≤ l ≤ 7	-39 ≤ l ≤ 39
Reflections collected	32993	23417
Independent reflections	7081	5690
	[Rint = 0.0338, Rσ = 0.0341]	[Rint = 0.0748, Rσ = 0.0766]
Data/restraints/parameters	7081/24/345	5690/0/325
Goodness-of-fit on F2	0.914	1.041
Final R indexes [I>=2σ (I)]	R1=0.0306,wR2 0.0730	R1 = 0.0498, wR2 = 0.0841
Final R indexes [all data]	R1 = 0.0399, wR2 = 0.0781	R1 = 0.0734, wR2 = 0.0929
Largest diff. peak/hole / e Å-3	0.47/-0.40	0.80/-0.69
Flack parameter	0.019(11)	-0.01(2)

1.4 Time-dependent DFT (TD-DFT) Analysis of Compounds 3 and 4.

*1.4.1 Spin Density Plot of **3**⁺*

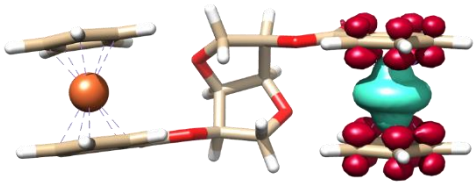
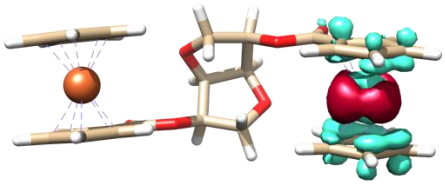


Figure S5. Spin density plot of 3⁺. Light-blue color denotes spin up, red denotes spin down.

*1.4.2 Electron Density Difference Maps of **3**⁺*

Electron density difference maps of **3**⁺ determined from TD-DFT calculations:

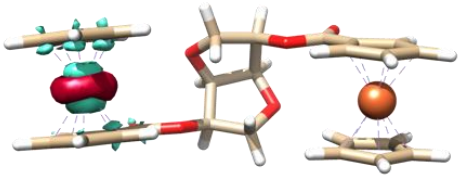


STATE 6:

E= 0.055239 au 1.503 eV 12123.5 cm**-1

139b -> 148b : 0.200627 (c= -0.44791412)

140b -> 147b : 0.489178 (c= 0.69941294)



STATE 18:

E= 0.081802 au 2.226 eV 17953.6 cm**-1

145a -> 150a : 0.084788 (c= 0.29118452)

145a -> 151a : 0.112472 (c= 0.33536823)

146a -> 150a : 0.112370 (c= -0.33521563)

146a -> 151a : 0.084187 (c= 0.29015063)

146a -> 152a : 0.055607 (c= 0.23581137)

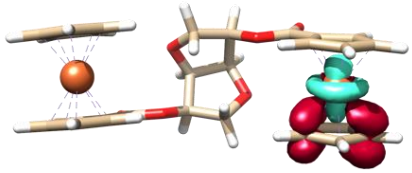
144b -> 150b : 0.084137 (c= -0.29006416)

144b -> 151b : 0.113122 (c= -0.33633617)

145b -> 150b : 0.113008 (c= 0.33616709)

145b -> 151b : 0.083557 (c= -0.28906285)

145b -> 152b : 0.055915 (c= -0.23646393)



STATE 27:

E= 0.088071 au 2.397 eV 19329.4 cm**-1

126b -> 146b : 0.190140 (c= 0.43605027)

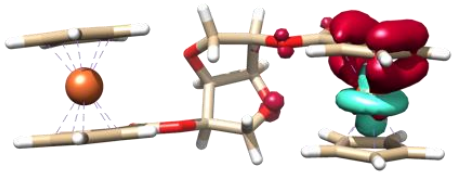
127b -> 146b : 0.017435 (c= 0.13204332)

128b -> 146b : 0.138282 (c= -0.37186233)

132b -> 146b : 0.490975 (c= -0.70069586)

133b -> 146b : 0.062375 (c= 0.24975082)

135b -> 146b : 0.039483 (c= -0.19870431)



STATE 31:

E= 0.092885 au 2.528 eV 20385.9 cm**-1

136a -> 148a : 0.011586 (c= 0.10763838)

126b -> 146b : 0.187217 (c= 0.43268598)

127b -> 146b : 0.282341 (c= 0.53135784)

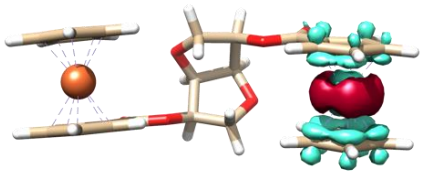
128b -> 146b : 0.037976 (c= -0.19487502)

131b -> 146b : 0.034190 (c= -0.18490530)

132b -> 146b : 0.080925 (c= 0.28447282)

133b -> 146b : 0.151792 (c= -0.38960453)

135b -> 146b : 0.129810 (c= 0.36029146)

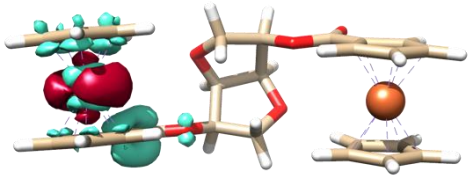


STATE 41:

E= 0.058704 au 1.597 eV 12884.0 cm**-1

135b -> 146b : 0.012376 (c= 0.11124735)

137b -> 146b : 0.978691 (c= 0.98928831)



STATE 45:

E= 0.124334 au 3.383 eV 27288.1 cm**-1

144a -> 150a : 0.132823 (c= 0.36444882)

145a -> 151a : 0.112609 (c= -0.33557330)

146a -> 150a : 0.085098 (c= -0.29171518)

146a -> 151a : 0.062738 (c= -0.25047572)

143b -> 150b : 0.132639 (c= -0.36419661)

144b -> 151b : 0.113159 (c= 0.33639083)

145b -> 150b : 0.085902 (c= 0.29308964)

145b -> 151b : 0.062165 (c= 0.24932927)

*1.4.3 Spin Density Plot of **4**⁺*

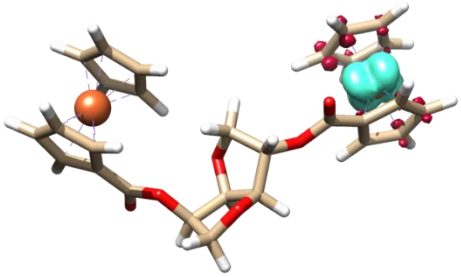
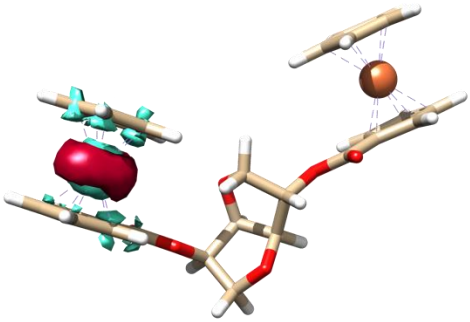


Figure S 6. Spin density plot of 4⁺. Light-blue color denotes spin up, red denotes spin down.

*1.4.4 Electron Density Difference Maps of **4**⁺*

Electron density difference maps of **4**⁺ determined from TDDFT calculations:



STATE 12:

E= 0.081796 au 2.226 eV 17952.2 cm**-1

145a -> 150a : 0.187285 (c= -0.43276419)

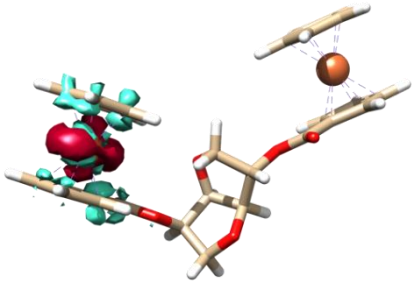
145a -> 152a : 0.084772 (c= -0.29115714)

146a -> 151a : 0.185383 (c= -0.43056124)

144b -> 150b : 0.187297 (c= -0.43277772)

144b -> 152b : 0.084804 (c= -0.29121201)

145b -> 151b : 0.185370 (c= -0.43054620)



STATE 22:

E= 0.092767 au 2.524 eV 20360.1 cm**-1

144a -> 150a : 0.213355 (c= -0.46190393)

144a -> 152a : 0.098885 (c= -0.31445940)

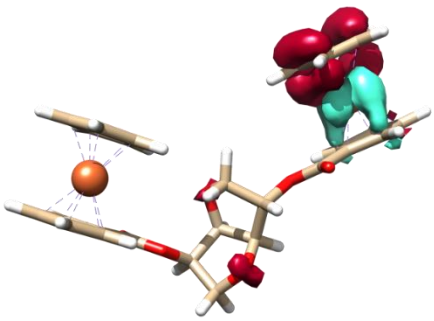
145a -> 150a : 0.041687 (c= 0.20417441)

146a -> 151a : 0.112359 (c= -0.33520029)

143b -> 150b : 0.213327 (c= -0.46187287)

143b -> 152b : 0.098891 (c= -0.31446903)

145b -> 151b : 0.112356 (c= -0.33519552)



STATE 28:

E= 0.099028 au 2.695 eV 21734.2 cm**-1

131a -> 148a : 0.041108 (c= 0.20275194)

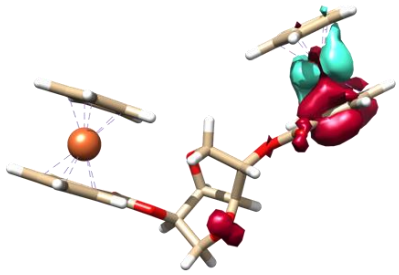
127b -> 146b : 0.058569 (c= 0.24200997)

128b -> 146b : 0.053211 (c= -0.23067454)

133b -> 146b : 0.535447 (c= 0.73174267)

134b -> 146b : 0.087308 (c= -0.29547921)

140b -> 146b : 0.086766 (c= -0.29456145)



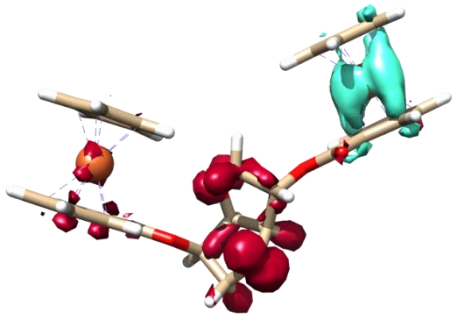
STATE 30:

E= 0.103965 au 2.829 eV 22817.8 cm**-1

128b -> 146b : 0.557368 (c= 0.74657054)

134b -> 146b : 0.079449 (c= -0.28186715)

137b -> 146b : 0.101572 (c= 0.31870381)



STATE 37:

E= 0.082484 au 2.244 eV 18103.1 cm**-1

127b -> 146b : 0.041859 (c= 0.20459564)

133b -> 146b : 0.073186 (c= -0.27052990)

137b -> 146b : 0.727857 (c= 0.85314518)

139b -> 146b : 0.083318 (c= -0.28864854)