Electronic Supporting Information

Intervalence of Two Planar Chiral 2-Methylferrocenyl Groups Over a Diaurum Bridge

Mark R. Ringenberg[†]*, Julia Holz[‡], and René Peters[‡]

[†] Insitut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany

[‡] Insitut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany

Contents

1 DFT Calculations **3**

2 Cyclic Voltammetry **5**

3 Infrared Spectroelectrochemistry **6**

4 Absorption Spectroscopy and TD-DFT **7**

4.1 UV-vis-NIR Spectra Fitting 7

5 DFT Coordinates **31**

List of Figures

1 MOs of 2X 3
2 MOs of 2OAc 4
3 CV of **2**X 5
4 CV of **2**Cl 5
5 IR SEC of [**2**Cl]$^+$ in 0.1 MBu_4NBAr^F/ CH_2Cl_2 6
6 UV-vis-NIR Curve Fit of $\mathbf{1}^{iPr}$ 7
7 UV-vis-NIR Curve Fit of **2**Cl 8
8 UV-vis-NIR Curve Fit of **2**Br 9
9 UV-vis-NIR Curve Fit of **2**OAc 10
10 UV-vis-NIR Curve Fit of $\mathbf{1}^{iPr}$ 11
11 UV-vis-NIR Curve Fit of **2**Cl 12
12 UV-vis-NIR Curve Fit of **2**Br 13
13 UV-vis-NIR Curve Fit of **2**OAc 14
14 EDDM of $\mathbf{1}^{iPr}$ 15
15 EDDM of $\mathbf{1}^{iPr}$+ 16
16 EDDM of $\mathbf{1}^{iPr2+}$ 18
17 EDDM of $\mathbf{1}^{iPr2+}$ 19
18 EDDM of **2**Cl 20
19 EDDM of **2**Cl$^+$ 22
20 EDDM of **2**Cl^{2+} S1 24
21 EDDM of **2**Cl^{2+} S1 26
22 EDDM of **2**I 28
23 EDDM of **2**Br 28
24 EDDM of **2**OAc 29

List of Tables

1 Transitions Determined by TD-DFT of [**1**^{iPr}]* 15
2 Transitions Determined by TD-DFT of [**1**^{iPr}]$^{+}$* 17
3 Transitions Determined by TD-DFT of [**1**^{iPr}]$^{2+}$* 18
4 Transitions Determined by TD-DFT of S3 [**1**^{iPr}]$^{2+}$* 20
5 Transitions Determined by TD-DFT of [**2**Cl]* 21
6 Transitions Determined by TD-DFT of [**2**Cl]$^{+}$* 23
7 Transitions Determined by TD-DFT of [**2**Cl]$^{2+}$ S1* 25
8 Transitions Determined by TD-DFT of [**2**Cl]$^{2+}$ S1* 27
9 Transitions Determined by TD-DFT of [**2**I]* 28
10 Transitions Determined by TD-DFT of [**2**Br]* 29
11 Transitions Determined by TD-DFT of [**2**OAc]* 30
12 XYZ coordinates for Optimized structure B3LYP **1**$^{\mathrm{iPr}}$ 31
13 XYZ coordinates for Optimized structure B3LYP [**1**^{iPr}]$^{+}$ 32
14 XYZ coordinates for Optimized structure B3LYP [**1**^{iPr}]$^{2+}$ S1 33
15 XYZ coordinates for Optimized structure B3LYP **2**Cl 34
16 XYZ coordinates for Optimized structure B3LYP [**2**Cl]$^{+}$ 35
17 XYZ coordinates for Optimized structure B3LYP [**2**Cl]$^{2+}$ S1 36
18 XYZ coordinates for Optimized structure B3LYP **2**Br 37
19 XYZ coordinates for Optimized structure B3LYP **2**I 38
20 XYZ coordinates for Optimized structure B3LYP **2**OAc 39

1 DFT Calculations

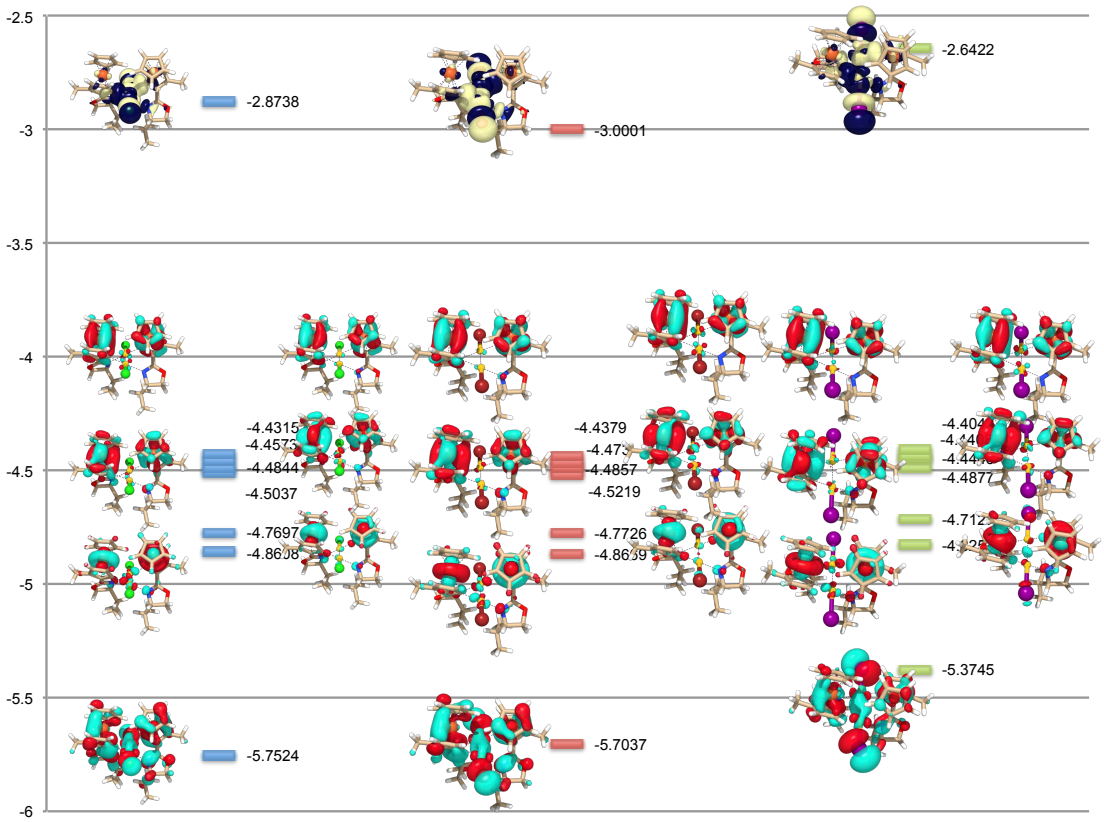


Figure 1: Frontier Kohn-Sham Orbitals and Energy (eV) of **2**Cl, **2**Br, **2**I at B3LYP level of theory.

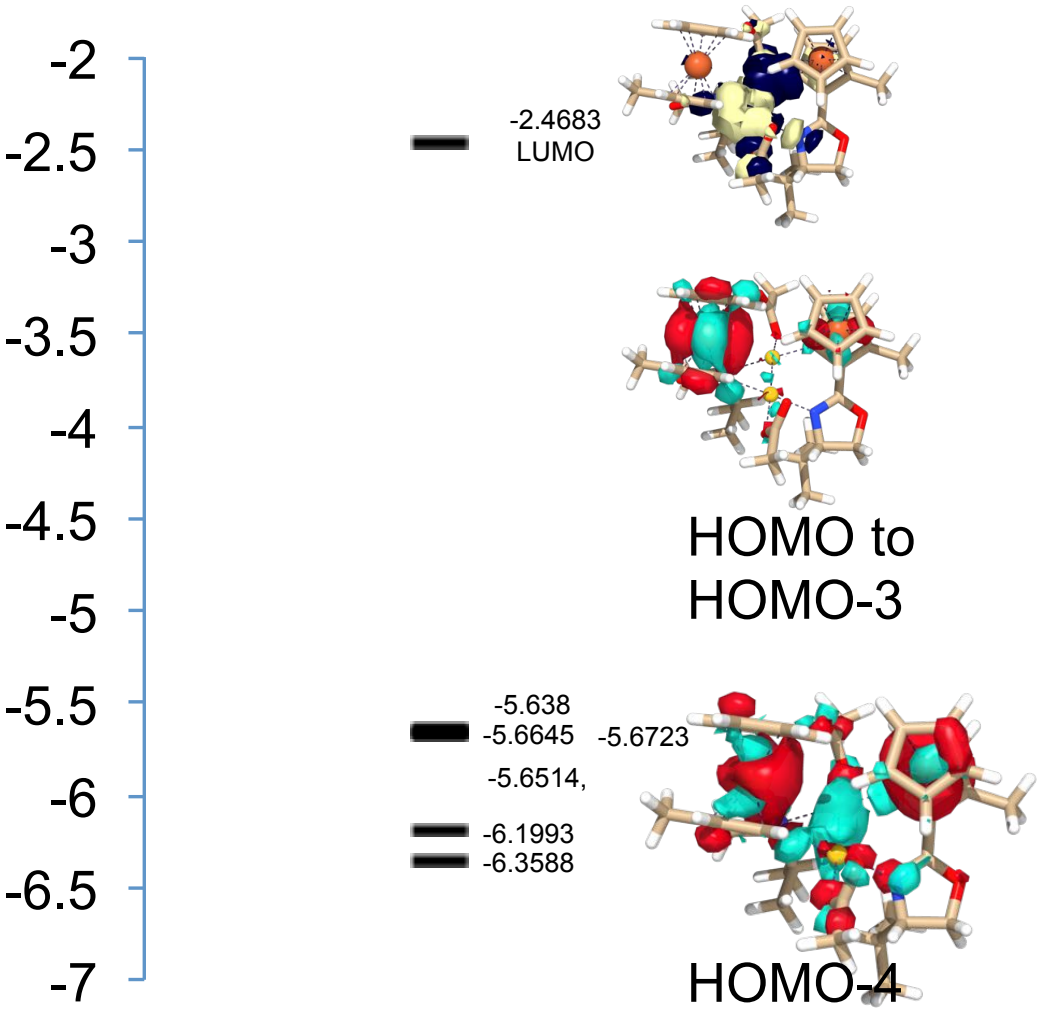


Figure 2: Frontier Kohn-Sham Orbitals and Energy (eV) of **2**OAc at B3LYP level of theory. HOMO-1 to HOMO-3 are not pictured but can be represent by different symmetry aligned orbitals based on HOMO shown on both iron atoms

2 Cyclic Voltammetry

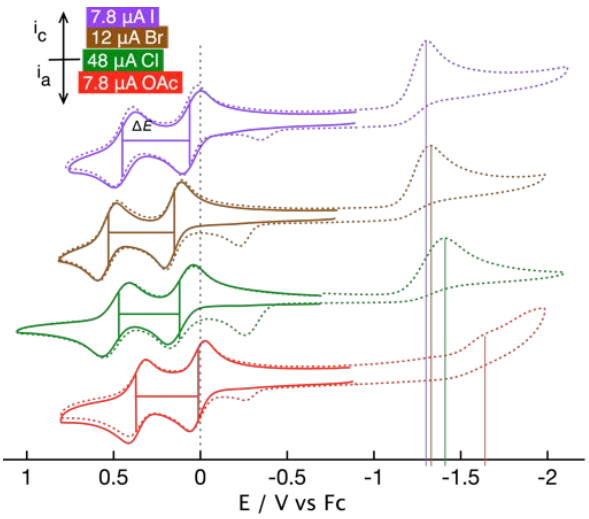


Figure 3: Cyclicvoltammogram of **2**X in 0.1 M $Bu_4NB(Ar^F)/CH_2Cl_2$

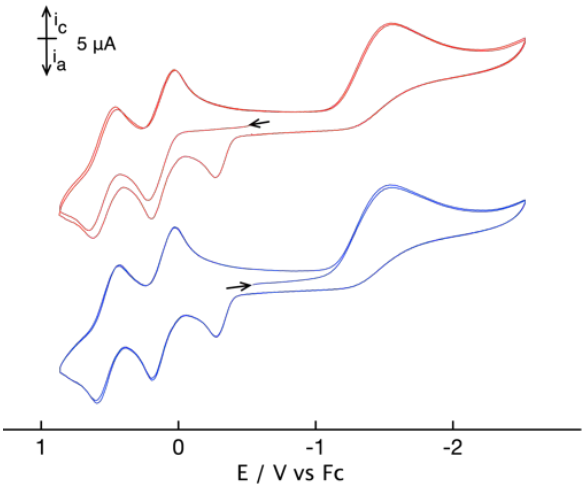


Figure 4: Cyclicvoltammogram of **2**Cl in 0.1 M $Bu_4NB(Ar^F)/CH_2Cl_2$

3 Infrared Spectroelectrochemistry

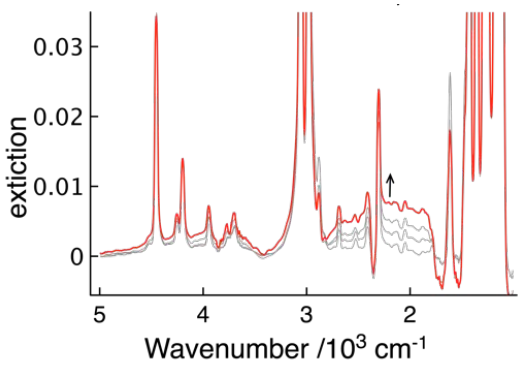
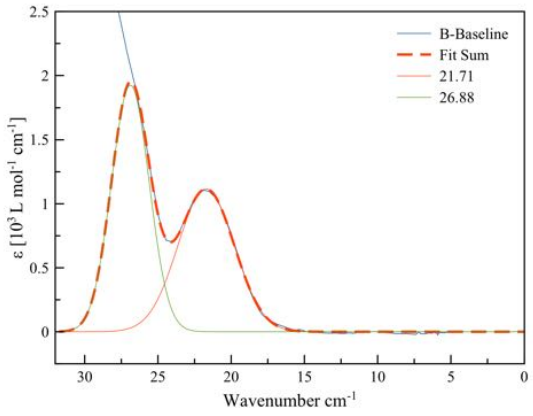


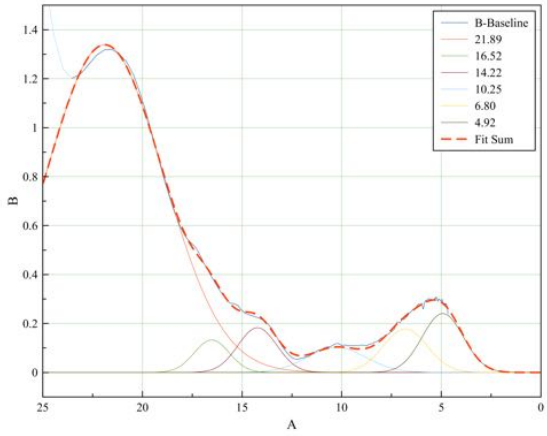
Figure 5: IR SEC of $[\mathbf{2}Cl]^+$ in 0.1 MBu_4NBAr^F/ CH_2Cl_2

4 Absorption Spectroscopy and TD-DFT

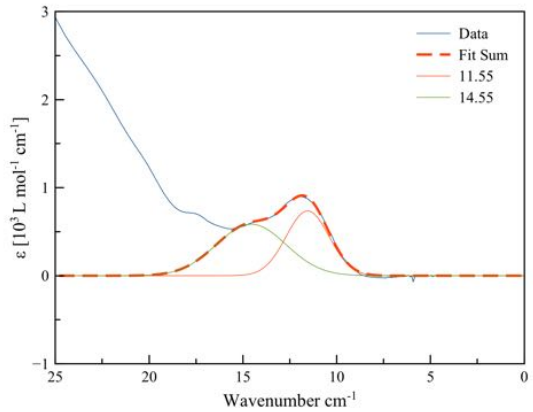
4.1 UV-vis-NIR Spectra Fitting



(a) $\mathbf{1}^{iPr}$

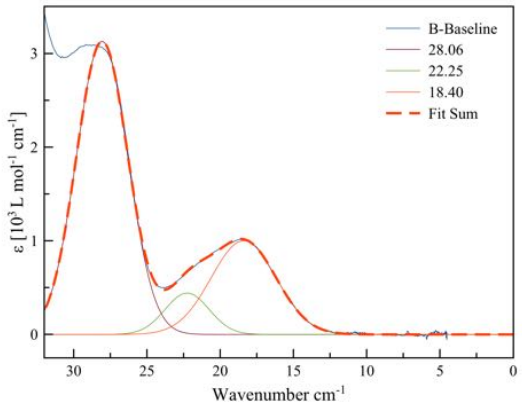


(b) $[\mathbf{1}^{iPr}]^{+}$

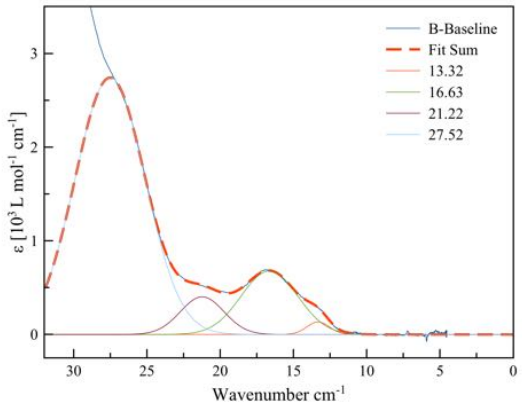


(c) $[\mathbf{1}^{iPr}]^{2+}$

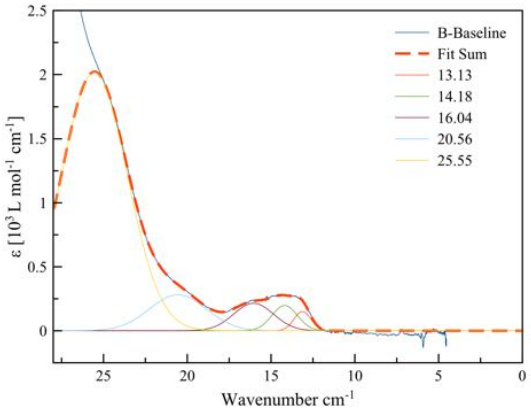
Figure 6: UV-vis-NIR Spectra for $\mathbf{1}^{iPr}$ were fitted using Gaussian Curves



(a) **2**Cl

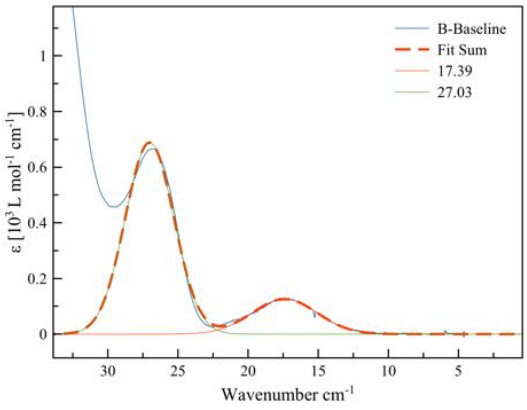


(b) $[\mathbf{2}\mathrm{Cl}]^{+}$

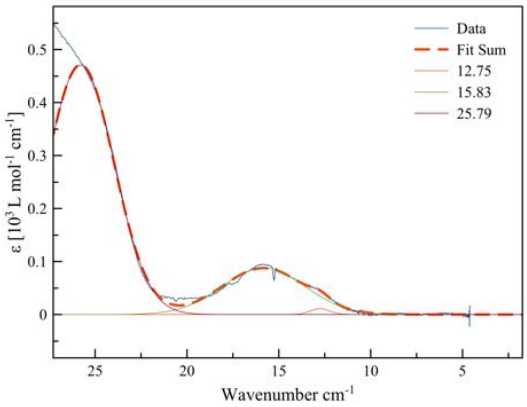


(c) $[\mathbf{2}\mathrm{Cl}]^{2+}$

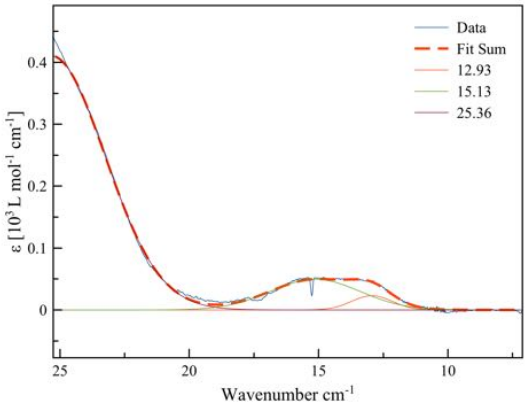
Figure 7: UV-vis-NIR Spectra of **2**Cl were fitted using Gaussian Curves



(a) **2**Br

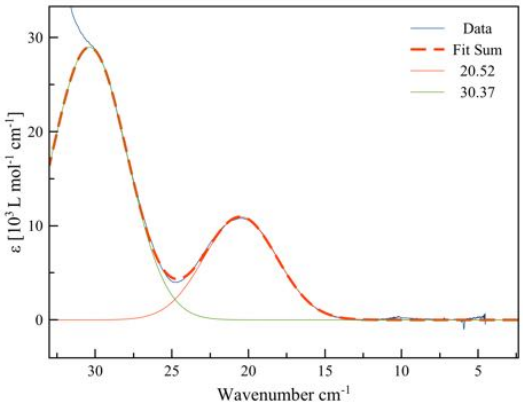


(b) [**2**Br]$^{+}$

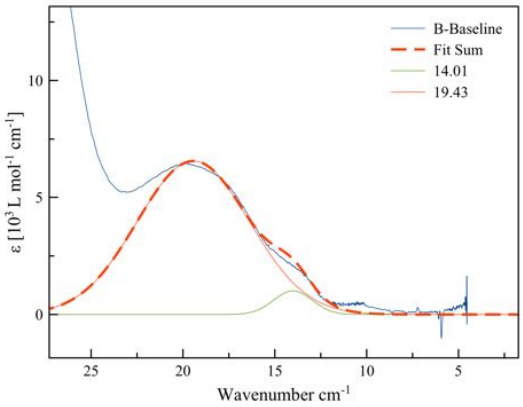


(c) [**2**Br]$^{2+}$

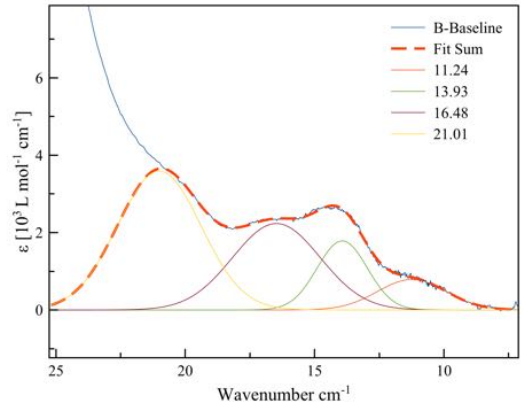
Figure 8: UV-vis-NIR Spectra of **2**Br were fitted using Gaussian Curves



(a) **2**OAc

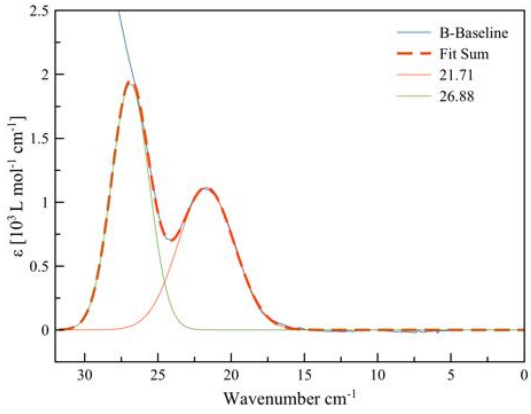


(b) [**2**OAc]$^{+}$

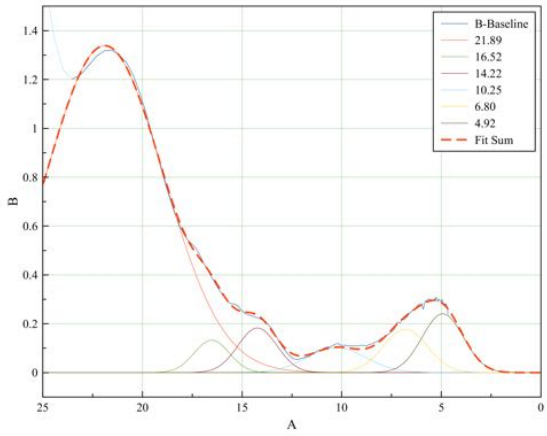


(c) [**2**OAc]$^{2+}$

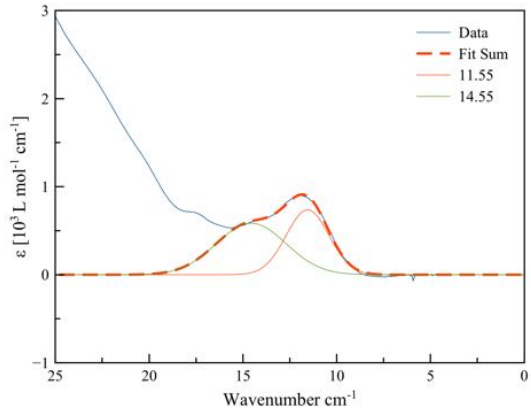
Figure 9: UV-vis-NIR Spectra of **2**OAc were fitted using Gaussian Curves



(a) $\mathbf{1}^{iPr}$

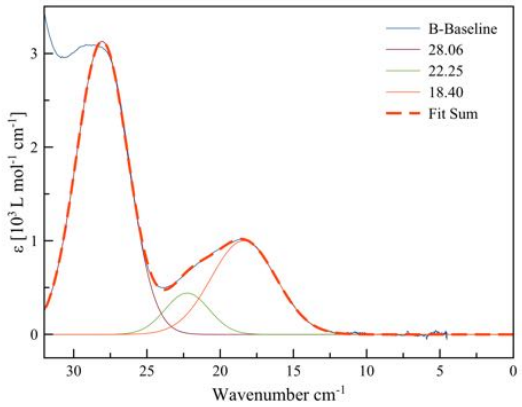


(b) $[\mathbf{1}^{iPr}]^{+}$

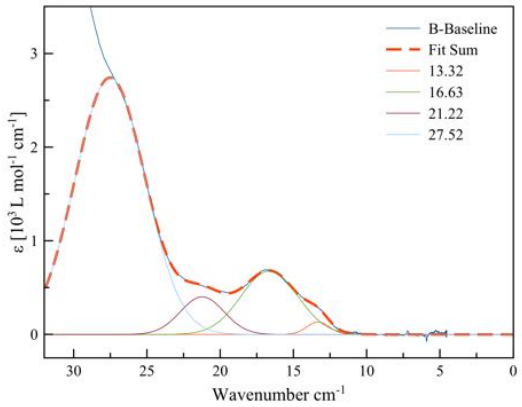


(c) $[\mathbf{1}^{iPr}]^{2+}$

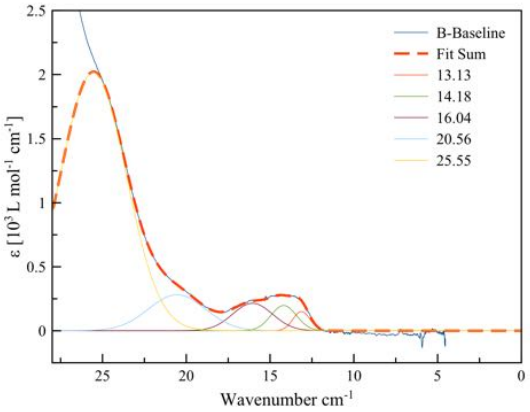
Figure 10: UV-vis-NIR Spectra for $\mathbf{1}^{iPr}$ were fitted using Gaussian Curves



(a) **2**Cl

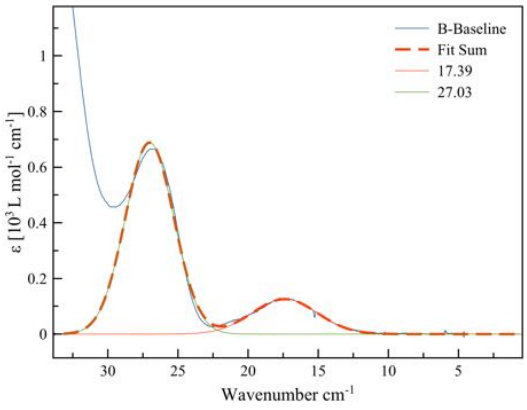


(b) [**2**Cl]$^{+}$

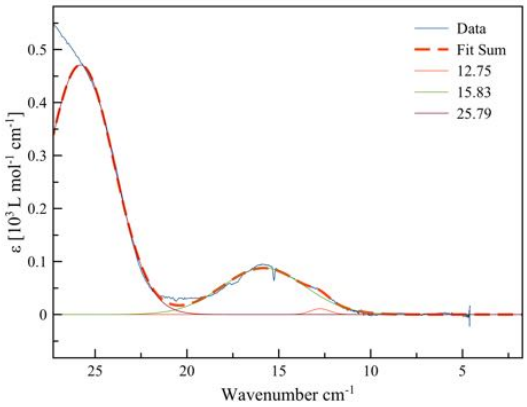


(c) [**2**Cl]$^{2+}$

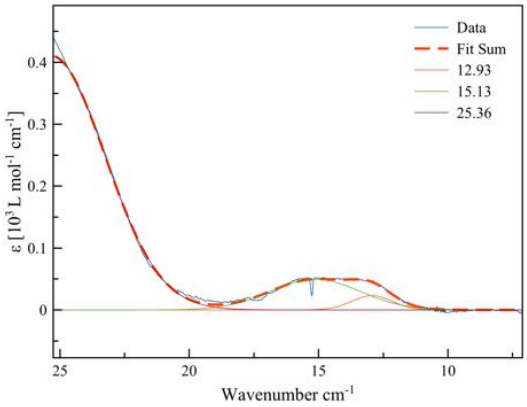
Figure 11: UV-vis-NIR Spectra of **2**Cl were fitted using Gaussian Curves



(a) **2**Br

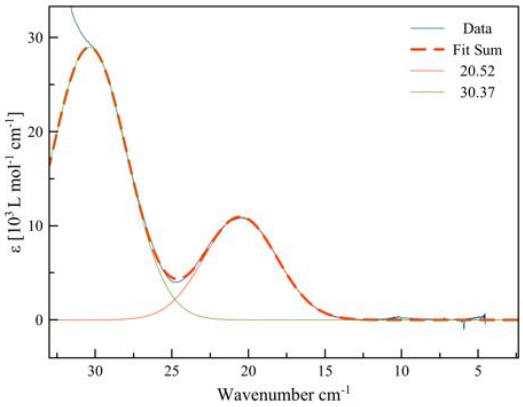


(b) [**2**Br]$^{+}$

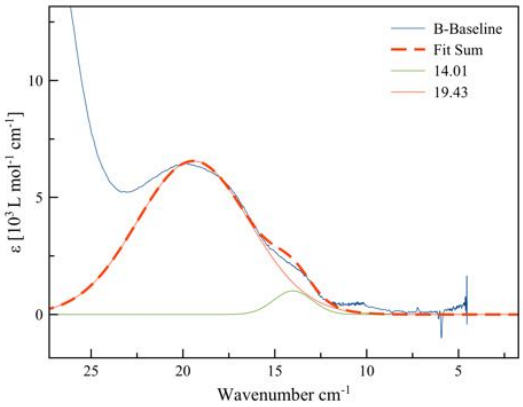


(c) [**2**Br]$^{2+}$

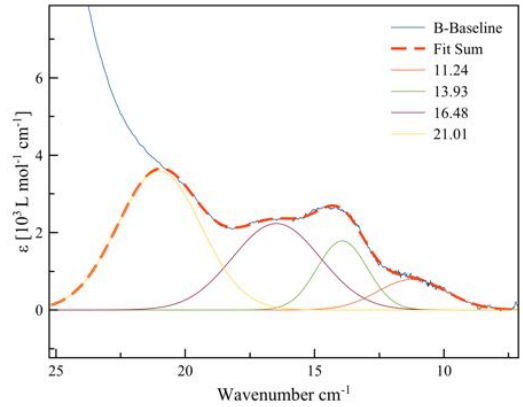
Figure 12: UV-vis-NIR Spectra of **2**Br were fitted using Gaussian Curves



(a) **2**OAc

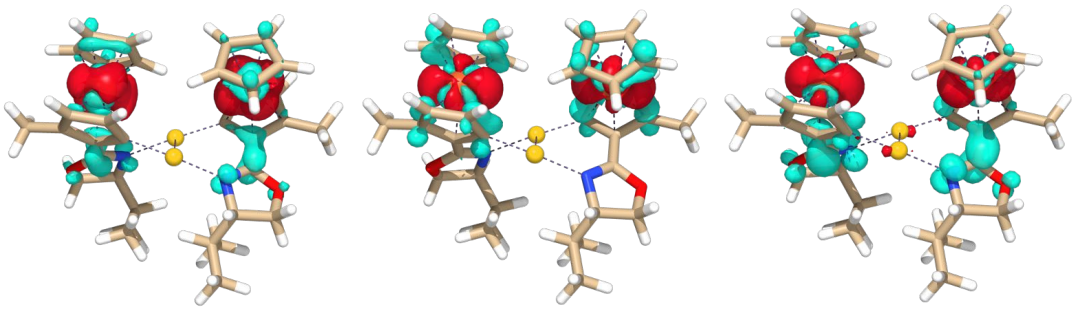


(b) [**2**OAc]$^{+}$



(c) [**2**OAc]$^{2+}$

Figure 13: UV-vis-NIR Spectra of **2**OAc were fitted using Gaussian Curves



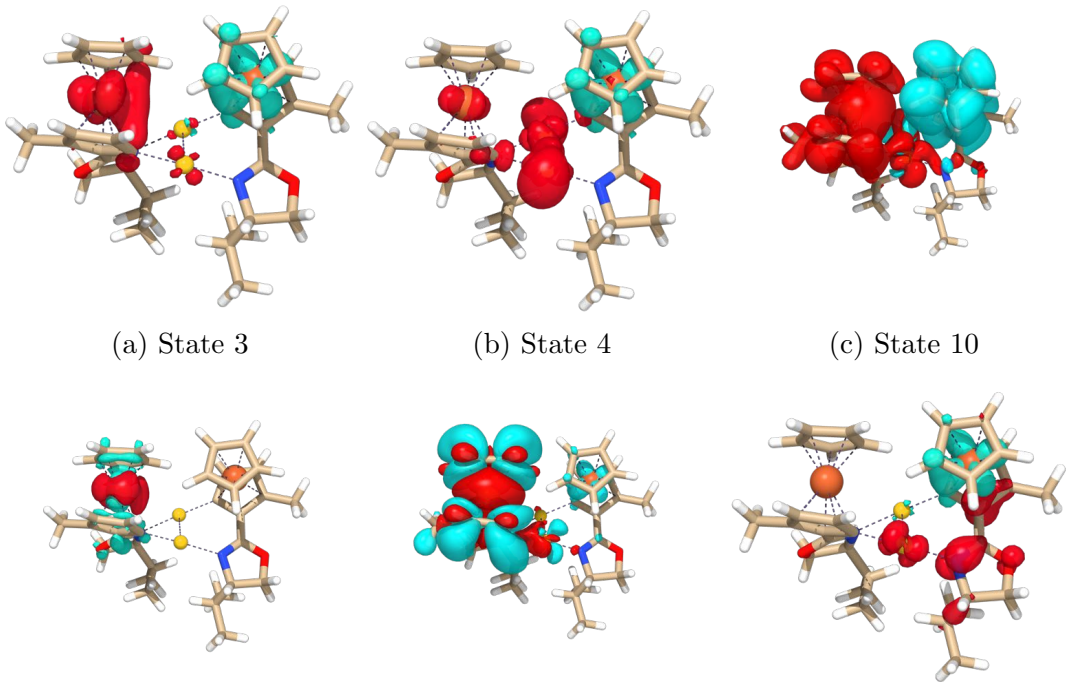
(a) State 1 (b) State 8 (c) State 10

Figure 14: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $\mathbf{1}^{iPr}$. Green denotes gain in electron density and red loss of electron density

Table 1: Transitions Determined by TD-DFT of $[\mathbf{1}^{iPr}]$*

181	HOMO
182	LUMO
STATE 1:	E= 0.086609 au 2.357 eV 19008.6 cm^{-1}
	177a $\longrightarrow$ 184a : 0.102595 (c= -0.32030418)
	178a $\longrightarrow$ 183a : 0.053070 (c= -0.23037021)
	178a $\longrightarrow$ 185a : 0.113285 (c= 0.33657905)
	179a $\longrightarrow$ 183a : 0.162235 (c= 0.40278378)
	179a $\longrightarrow$ 188a : 0.104830 (c= -0.32377401)
	180a $\longrightarrow$ 182a : 0.201649 (c= -0.44905325)
	180a $\longrightarrow$ 186a : 0.112630 (c= -0.33560405)
STATE 8:	E= 0.099757 au 2.715 eV 21894.2 cm^{-1}
	173a $\longrightarrow$ 185a : 0.059423 (c= -0.24376881)
	175a $\longrightarrow$ 185a : 0.120935 (c= 0.34775728)
	176a $\longrightarrow$ 184a : 0.107417 (c= -0.32774484)
	176a $\longrightarrow$ 187a : 0.056026 (c= 0.23669715)
	177a $\longrightarrow$ 185a : 0.107946 (c= 0.32855181)
	179a $\longrightarrow$ 184a : 0.091531 (c= -0.30254081)
	180a $\longrightarrow$ 185a : 0.089635 (c= -0.29939089)
STATE 10:	E= 0.124423 au 3.386 eV 27307.6 cm^{-1}
	176a $\longrightarrow$ 182a : 0.080167 (c= -0.28313801)
	177a $\longrightarrow$ 185a : 0.131109 (c= 0.36209039)
	178a $\longrightarrow$ 184a : 0.144748 (c= -0.38045759)
	179a $\longrightarrow$ 182a : 0.227015 (c= -0.47646133)
	180a $\longrightarrow$ 183a : 0.095498 (c= 0.30902781)

*transitions below 5% were omitted



(a) State 3 (b) State 4 (c) State 10

(d) State 12 (e) State 14 (f) State 27

Figure 15: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $[\mathbf{1}^{iPr}]^+$. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
177	1.0000	-0.247182	-6.7262	177	1.0000	-0.235780	-6.4159
178	1.0000	-0.235812	-6.4168	178	1.0000	-0.217424	-5.9164
179	1.0000	-0.217563	-5.9202	179	1.0000	-0.211715	-5.7610
180	1.0000	-0.211738	-5.7617	180	1.0000	-0.207383	-5.6432
181	1.0000	-0.207525	-5.6471	181	0.0000	-0.142015	-3.8644
182	0.0000	-0.100977	-2.7477	182	0.0000	-0.078684	-2.1411
183	0.0000	-0.096996	-2.6394	183	0.0000	-0.070943	-1.9305
184	0.0000	-0.052231	-1.4213	184	0.0000	-0.046787	-1.2731

Table 2: Transitions Determined by TD-DFT of $[\mathbf{1}^{iPr}]^{+*}$

STATE 3: E= 0.021256 au 0.578 eV 4665.1 cm^{-1}
180b $\longrightarrow$ 181b : 0.966068 (c= -0.98288744)

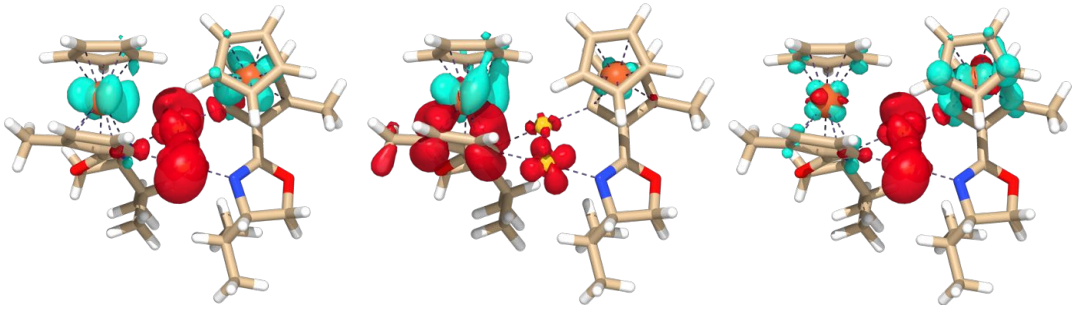
STATE 4: E= 0.032902 au 0.895 eV 7221.2 cm^{-1}
178b $\longrightarrow$ 181b : 0.767704 (c= 0.87618719)
179b $\longrightarrow$ 181b : 0.153105 (c= 0.39128605)

STATE 10: E= 0.049701 au 1.352 eV 10908.1 cm^{-1}
177b $\longrightarrow$ 181b : 0.975202 (c= -0.98752292)

STATE 12: E= 0.080804 au 2.199 eV 17734.5 cm^{-1}
180a $\longrightarrow$ 186a : 0.106427 (c= -0.32623204)
181a $\longrightarrow$ 185a : 0.151866 (c= 0.38969975)
181a $\longrightarrow$ 188a : 0.106381 (c= 0.32616133)
179b $\longrightarrow$ 186b : 0.112412 (c= 0.33527872)
180b $\longrightarrow$ 184b : 0.138240 (c= -0.37180652)
180b $\longrightarrow$ 185b : 0.059374 (c= 0.24366773)
180b $\longrightarrow$ 188b : 0.104954 (c= -0.32396623)

STATE 14: E= 0.083096 au 2.261 eV 18237.4 cm^{-1}
177a $\longrightarrow$ 186a : 0.051176 (c= -0.22622200)
178a $\longrightarrow$ 186a : 0.227087 (c= 0.47653673)
178a $\longrightarrow$ 187a : 0.060023 (c= 0.24499641)
176b $\longrightarrow$ 186b : 0.056480 (c= -0.23765444)
177b $\longrightarrow$ 186b : 0.247146 (c= -0.49713771)
177b $\longrightarrow$ 188b : 0.045335 (c= -0.21292116)

STATE 27: E= 0.089533 au 2.436 eV 19650.3 cm^{-1}
165b $\longrightarrow$ 181b : 0.063693 (c= 0.25237432)
172b $\longrightarrow$ 181b : 0.123781 (c= -0.35182537)
174b $\longrightarrow$ 181b : 0.600514 (c= 0.77492863)



(a) State 6 (b) State 12 (c) State 18

Figure 16: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $[\mathbf{1}^{iPr}]^{2+}$ antiferromagnetic S1 state. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
177	1.0000	-0.287907	-7.8344	177	1.0000	-0.287913	-7.8345
178	1.0000	-0.287716	-7.8292	178	1.0000	-0.287704	-7.8288
179	1.0000	-0.282694	-7.6925	179	1.0000	-0.282690	-7.6924
180	1.0000	-0.242764	-6.6060	180	1.0000	-0.242762	-6.6059
181	0.0000	-0.150618	-4.0985	181	0.0000	-0.150592	-4.0978
182	0.0000	-0.117773	-3.2048	182	0.0000	-0.117823	-3.2061
183	0.0000	-0.115346	-3.1387	183	0.0000	-0.115444	-3.1414
184	0.0000	-0.093389	-2.5413	184	0.0000	-0.093360	-2.5405

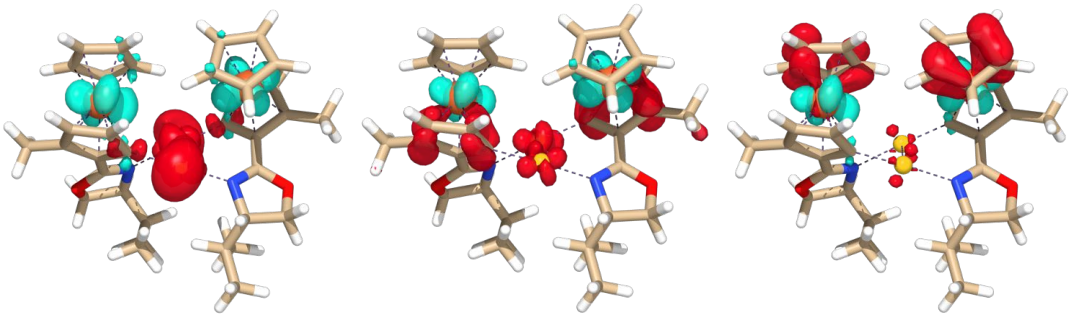
Table 3: Transitions Determined by TD-DFT of $[\mathbf{1}^{iPr}]^{2+}$*

STATE 6: E= 0.053913 au 1.467 eV 11832.6 $^{-1}$
180a $\longrightarrow$ 181a : 0.446706 (c= -0.66836084)
180b $\longrightarrow$ 181b : 0.500272 (c= -0.70729887)

STATE 12: E= 0.087012 au 2.368 eV 19096.9 $^{-1}$
175a $\longrightarrow$ 181a : 0.242541 (c= -0.49248412)
176a $\longrightarrow$ 181a : 0.085068 (c= -0.29166420)
177a $\longrightarrow$ 181a : 0.296163 (c= 0.54420903)
179a $\longrightarrow$ 181a : 0.088709 (c= -0.29783974)

STATE 18: E= 0.092880 au 2.527 eV 20384.8 $^{-1}$
180a $\longrightarrow$ 183a : 0.456848 (c= 0.67590510)
180b $\longrightarrow$ 183b : 0.236755 (c= 0.48657475)

*transitions below 5% were omitted S3



(a) State 5 (b) State 11 (c) State 28

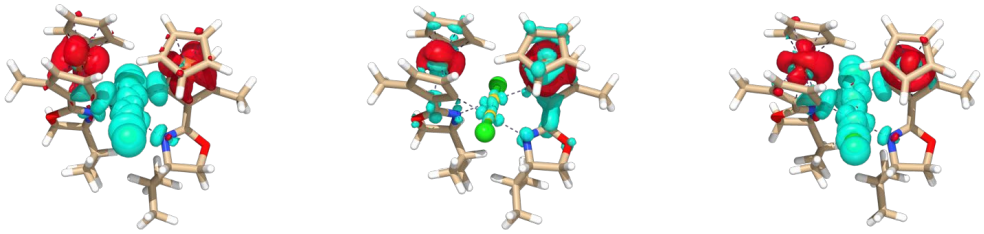
Figure 17: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $[\mathbf{1}^{iPr}]^{2+}$ antiferromagnetic S3 state. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
177	1.0000	-0.290651	-7.9090	177	1.0000	-0.287485	-7.8229
178	1.0000	-0.288371	-7.8470	178	1.0000	-0.282439	-7.6856
179	1.0000	-0.287527	-7.8240	179	1.0000	-0.242580	-6.6009
180	1.0000	-0.282982	-7.7003	180	0.0000	-0.152514	-4.1501
181	1.0000	-0.242878	-6.6091	181	0.0000	-0.148517	-4.0413
182	0.0000	-0.118888	-3.2351	182	0.0000	-0.095160	-2.5894
183	0.0000	-0.117216	-3.1896	183	0.0000	-0.091964	-2.5025
184	0.0000	-0.116065	-3.1583	184	0.0000	-0.088199	-2.4000

Table 4: Transitions Determined by TD-DFT of S3 $[\mathbf{1}^{iPr}]^{2+}$*

STATE 5:	E= 0.051931 au	1.413 eV	11397.6 cm^{-1}
	179b $\longrightarrow$ 180b : 0.950009 (c= 0.97468429)		
STATE 11:	E= 0.087896 au	2.392 eV	19290.9 cm^{-1}
	173b $\longrightarrow$ 180b : 0.103834 (c= -0.32223252)		
	174b $\longrightarrow$ 181b : 0.160675 (c= -0.40084305)		
	175b $\longrightarrow$ 181b : 0.129609 (c= 0.36001211)		
	176b $\longrightarrow$ 180b : 0.086054 (c= 0.29335043)		
	177b $\longrightarrow$ 180b : 0.248180 (c= -0.49817655)		
	178b $\longrightarrow$ 181b : 0.072309 (c= 0.26890389)		
STATE 28:	E= 0.109536 au	2.981 eV	24040.5 cm^{-1}
	162b $\longrightarrow$ 181b : 0.056730 (c= -0.23818117)		
	163b $\longrightarrow$ 181b : 0.099099 (c= -0.31479959)		
	164b $\longrightarrow$ 180b : 0.269451 (c= -0.51908717)		
	169b $\longrightarrow$ 181b : 0.096421 (c= -0.31051752)		
	172b $\longrightarrow$ 181b : 0.064787 (c= 0.25453379)		

*transitions below 5% were omitted



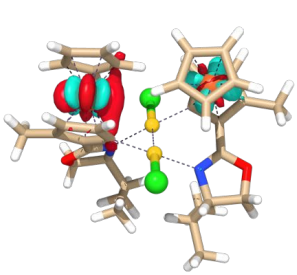
(a) State 4 (b) State 7 (c) State 13

Figure 18: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of **2**Cl. Green denotes gain in electron density and red loss of electron density

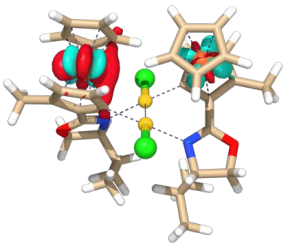
Table 5: Transitions Determined by TD-DFT of [**2**Cl]*

198	HOMO
199	LUMO
STATE 4:	E= 0.077590 au 2.111 eV 17029.1 cm^{-1}
	195a $\longrightarrow$ 199a : 0.906230 (c= 0.95196139)
STATE 7:	E= 0.090973 au 2.475 eV 19966.2 cm^{-1}
	195a $\longrightarrow$ 201a : 0.136718 (c= -0.36975449)
	195a $\longrightarrow$ 205a : 0.102150 (c= -0.31960846)
	196a $\longrightarrow$ 202a : 0.057151 (c= -0.23906205)
	196a $\longrightarrow$ 204a : 0.051122 (c= 0.22610163)
	197a $\longrightarrow$ 201a : 0.050725 (c= 0.22522101)
	197a $\longrightarrow$ 203a : 0.115087 (c= -0.33924534)
	198a $\longrightarrow$ 200a : 0.141502 (c= 0.37616814)
	198a $\longrightarrow$ 202a : 0.068468 (c= 0.26166466)
	198a $\longrightarrow$ 204a : 0.063336 (c= 0.25166629)
STATE 13:	E= 0.104478 au 2.843 eV 22930.4 cm^{-1}
	194a $\longrightarrow$ 199a : 0.634328 (c= 0.79644730)
	198a $\longrightarrow$ 203a : 0.073719 (c= -0.27151295)

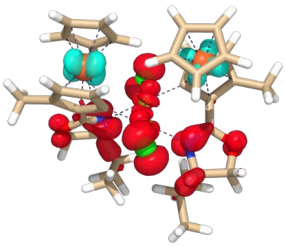
*transitions below 5% were omitted



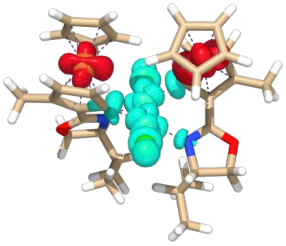
(a) State 2



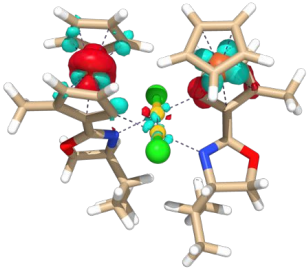
(b) State 4



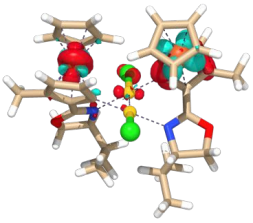
(c) State 9



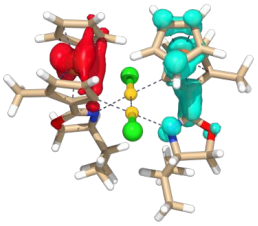
(d) State 12



(e) State 18



(f) State 19



(g) State 21

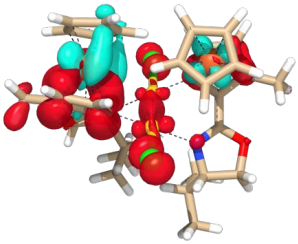
Figure 19: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of [**2**Cl]$^+$. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
195	1.0000	-0.257591	-7.0094	195	1.0000	-0.247599	-6.7375
196	1.0000	-0.247679	-6.7397	196	1.0000	-0.223838	-6.0909
197	1.0000	-0.223861	-6.0916	197	1.0000	-0.222279	-6.0485
198	1.0000	-0.222290	-6.0488	198	0.0000	-0.155772	-4.2388
199	0.0000	-0.123363	-3.3569	199	0.0000	-0.122924	-3.3449

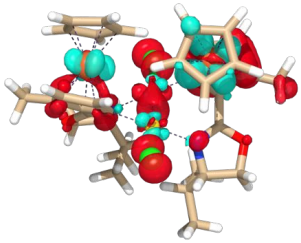
Table 6: Transitions Determined by TD-DFT of [**2**Cl]$^{+}$*

STATE 2:	E= 0.012531 au	0.341 eV 2750.2 cm^{-1}
	193b $\longrightarrow$ 198b : 0.556681 (c= -0.74611082)	
	194b $\longrightarrow$ 198b : 0.337635 (c= 0.58106336)	
	196b $\longrightarrow$ 198b : 0.066158 (c= -0.25721107)	
STATE 4:	E= 0.021778 au	0.593 eV 5046.3 cm^{-1}
	195b $\longrightarrow$ 198b : 0.979251 (c= 0.98957114)	
STATE 9:	E= 0.059529 au	1.620 eV 13065.2 cm^{-1}
	198a $\longrightarrow$ 199a : 0.713914 (c= -0.84493405)	
	197b $\longrightarrow$ 199b : 0.185042 (c= -0.43016540)	
STATE 12:	E= 0.061998 au	1.687 eV 13607.0 cm^{-1}
	197a $\longrightarrow$ 199a : 0.704757 (c= 0.83949794)	
	196b $\longrightarrow$ 199b : 0.194227 (c= 0.44071206)	
STATE 18:	E= 0.083110 au	2.262 eV 18240.5 cm^{-1}
	196a $\longrightarrow$ 204a : 0.160972 (c= -0.40121275)	
	184b $\longrightarrow$ 198b : 0.062651 (c= -0.25030224)	
	192b $\longrightarrow$ 198b : 0.106547 (c= 0.32641580)	
	193b $\longrightarrow$ 198b : 0.071601 (c= 0.26758445)	
	194b $\longrightarrow$ 198b : 0.050867 (c= -0.22553790)	
	195b $\longrightarrow$ 204b : 0.163884 (c= -0.40482631)	
STATE 19:	E= 0.082202 au	2.237 eV 18041.2 cm^{-1}
	196a $\longrightarrow$ 204a : 0.092920 (c= 0.30482798)	
	184b $\longrightarrow$ 198b : 0.111146 (c= -0.33338523)	
	192b $\longrightarrow$ 198b : 0.207481 (c= 0.45550068)	
	193b $\longrightarrow$ 198b : 0.144571 (c= 0.38022500)	
	195b $\longrightarrow$ 204b : 0.086119 (c= 0.29346026)	
STATE 21:	E= 0.066434 au	1.808 eV 14580.6 cm^{-1}
	198a $\longrightarrow$ 200a : 0.930314 (c= -0.96452795)	

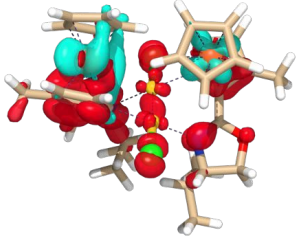
*transitions below 5% were omitted



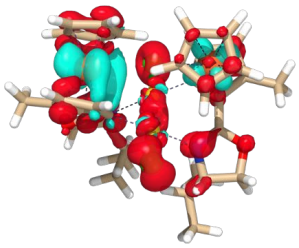
(a) State 9



(b) State 10



(c) State 14



(d) State 20

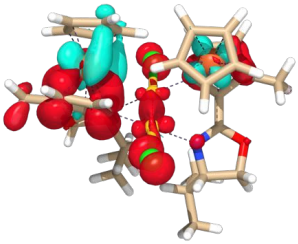
Figure 20: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $[\mathbf{2}\mathrm{Cl}]^{2+}$ S1. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
192	1.0000	-0.308819	-8.4034	192	1.0000	-0.308807	-8.4031
193	1.0000	-0.306423	-8.3382	193	1.0000	-0.306427	-8.3383
194	1.0000	-0.303952	-8.2709	194	1.0000	-0.303950	-8.2709
195	1.0000	-0.302650	-8.2355	195	1.0000	-0.302607	-8.2344
196	1.0000	-0.298514	-8.1230	196	1.0000	-0.298519	-8.1231
197	1.0000	-0.284621	-7.7449	197	1.0000	-0.284621	-7.7449
198	0.0000	-0.164302	-4.4709	198	0.0000	-0.164400	-4.4735
199	0.0000	-0.147394	-4.0108	199	0.0000	-0.147348	-4.0095

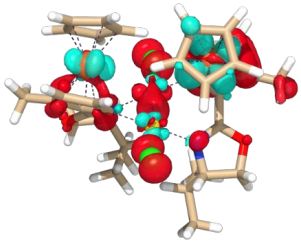
Table 7: Transitions Determined by TD-DFT of $[\mathbf{2}\mathrm{Cl}]^{2+}$ S1*

STATE 9:	E= 0.086950 au	2.366 eV 19083.3 cm^{-1}
	197a $\longrightarrow$ 198a :	0.076423 (c= -0.27644730)
	188b $\longrightarrow$ 198b :	0.053792 (c= -0.23193140)
	189b $\longrightarrow$ 198b :	0.077280 (c= 0.27799221)
	191b $\longrightarrow$ 198b :	0.053099 (c= -0.23043240)
	195b $\longrightarrow$ 198b :	0.129461 (c= -0.35980726)
	197b $\longrightarrow$ 198b :	0.302097 (c= -0.54963319)
STATE 10:	E= 0.087478 au	2.380 eV 19199.2 cm^{-1}
	189a $\longrightarrow$ 198a :	0.074912 (c= -0.27370093)
	191a $\longrightarrow$ 198a :	0.050080 (c= -0.22378469)
	195a $\longrightarrow$ 198a :	0.116349 (c= 0.34109993)
	197a $\longrightarrow$ 198a :	0.306890 (c= 0.55397674)
	197b $\longrightarrow$ 198b :	0.086595 (c= -0.29427068)
STATE 14:	E= 0.095937 au	2.611 eV 21055.7 cm^{-1}
	194a $\longrightarrow$ 198a :	0.053196 (c= -0.23064283)
	195a $\longrightarrow$ 198a :	0.052198 (c= -0.22846936)
	197a $\longrightarrow$ 198a :	0.091736 (c= 0.30287937)
	194b $\longrightarrow$ 198b :	0.088017 (c= 0.29667664)
	195b $\longrightarrow$ 198b :	0.090428 (c= -0.30071279)
	196b $\longrightarrow$ 198b :	0.089426 (c= 0.29904207)
	197b $\longrightarrow$ 198b :	0.154588 (c= 0.39317686)
STATE 20:	E= 0.105268 au	2.864 eV 23103.7 cm^{-1}
	196a $\longrightarrow$ 198a :	0.101935 (c= -0.31927320)
	184b $\longrightarrow$ 198b :	0.056941 (c= -0.23862367)
	196b $\longrightarrow$ 198b :	0.216154 (c= 0.46492344)
	197b $\longrightarrow$ 198b :	0.102547 (c= -0.32022973)

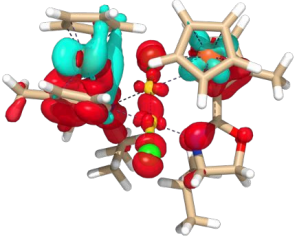
*transitions below 5% were omitted



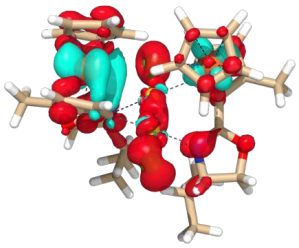
(a) State 9



(b) State 10



(c) State 14



(d) State 20

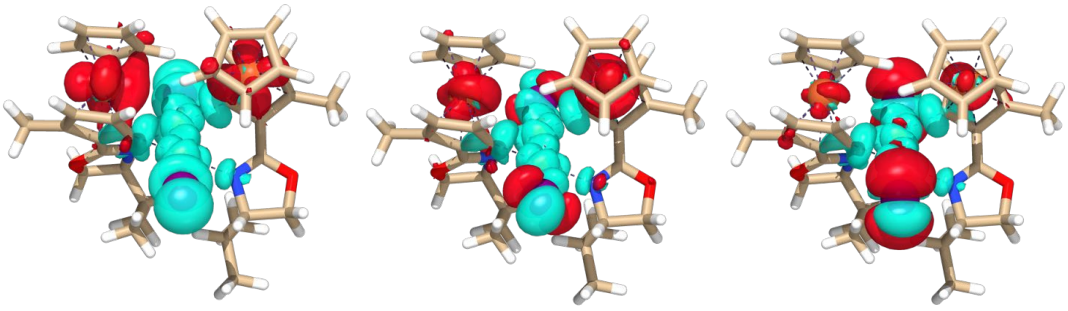
Figure 21: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of $[\mathbf{2}\mathrm{Cl}]^{2+}$ S1. Green denotes gain in electron density and red loss of electron density

α				β			
No.	Occ.	E(Eh)	E(eV)	No.	Occ.	E(Eh)	E(eV)
192	1.0000	-0.308819	-8.4034	192	1.0000	-0.308807	-8.4031
193	1.0000	-0.306423	-8.3382	193	1.0000	-0.306427	-8.3383
194	1.0000	-0.303952	-8.2709	194	1.0000	-0.303950	-8.2709
195	1.0000	-0.302650	-8.2355	195	1.0000	-0.302607	-8.2344
196	1.0000	-0.298514	-8.1230	196	1.0000	-0.298519	-8.1231
197	1.0000	-0.284621	-7.7449	197	1.0000	-0.284621	-7.7449
198	0.0000	-0.164302	-4.4709	198	0.0000	-0.164400	-4.4735
199	0.0000	-0.147394	-4.0108	199	0.0000	-0.147348	-4.0095

Table 8: Transitions Determined by TD-DFT of $[\mathbf{2}\mathrm{Cl}]^{2+}$ S1*

STATE 9:	E= 0.086950 au	2.366 eV 19083.3 cm^{-1}
	197a $\longrightarrow$ 198a : 0.076423 (c= -0.27644730)	
	188b $\longrightarrow$ 198b : 0.053792 (c= -0.23193140)	
	189b $\longrightarrow$ 198b : 0.077280 (c= 0.27799221)	
	191b $\longrightarrow$ 198b : 0.053099 (c= -0.23043240)	
	195b $\longrightarrow$ 198b : 0.129461 (c= -0.35980726)	
	197b $\longrightarrow$ 198b : 0.302097 (c= -0.54963319)	
STATE 10:	E= 0.087478 au	2.380 eV 19199.2 cm^{-1}
	189a $\longrightarrow$ 198a : 0.074912 (c= -0.27370093)	
	191a $\longrightarrow$ 198a : 0.050080 (c= -0.22378469)	
	195a $\longrightarrow$ 198a : 0.116349 (c= 0.34109993)	
	197a $\longrightarrow$ 198a : 0.306890 (c= 0.55397674)	
	197b $\longrightarrow$ 198b : 0.086595 (c= -0.29427068)	
STATE 14:	E= 0.095937 au	2.611 eV 21055.7 cm^{-1}
	194a $\longrightarrow$ 198a : 0.053196 (c= -0.23064283)	
	195a $\longrightarrow$ 198a : 0.052198 (c= -0.22846936)	
	197a $\longrightarrow$ 198a : 0.091736 (c= 0.30287937)	
	194b $\longrightarrow$ 198b : 0.088017 (c= 0.29667664)	
	195b $\longrightarrow$ 198b : 0.090428 (c= -0.30071279)	
	196b $\longrightarrow$ 198b : 0.089426 (c= 0.29904207)	
	197b $\longrightarrow$ 198b : 0.154588 (c= 0.39317686)	
STATE 20:	E= 0.105268 au	2.864 eV 23103.7 cm^{-1}
	196a $\longrightarrow$ 198a : 0.101935 (c= -0.31927320)	
	184b $\longrightarrow$ 198b : 0.056941 (c= -0.23862367)	
	196b $\longrightarrow$ 198b : 0.216154 (c= 0.46492344)	
	197b $\longrightarrow$ 198b : 0.102547 (c= -0.32022973)	

*transitions below 5% were omitted



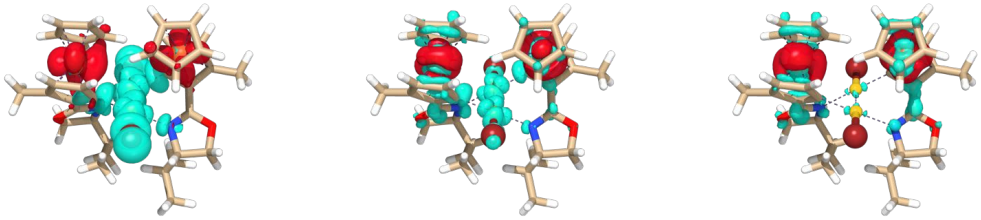
(a) State 2 (b) State 9 (c) State 17

Figure 22: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of **2**I. Green denotes gain in electron density and red loss of electron density

Table 9: Transitions Determined by TD-DFT of [**2**I]*

206	HOMO
207	LUMO
STATE 2:	E= 0.069168 au 1.882 eV 15180.5 cm^{-1}
	202a $\longrightarrow$ 207a : 0.087052 (c= -0.29504605)
	206a $\longrightarrow$ 207a : 0.859977 (c= 0.92734947)
STATE 9:	E= 0.093528 au 2.545 eV 20527.0 cm^{-1}
	198a $\longrightarrow$ 207a : 0.236785 (c= 0.48660549)
	202a $\longrightarrow$ 207a : 0.554557 (c= 0.74468598)
STATE 17:	E= 0.105166 au 2.862 eV 23081.2 cm^{-1}
	196a $\longrightarrow$ 207a : 0.676916 (c= 0.82274884)
	198a $\longrightarrow$ 207a : 0.163746 (c= -0.40465513)

*transitions below 5% were omitted



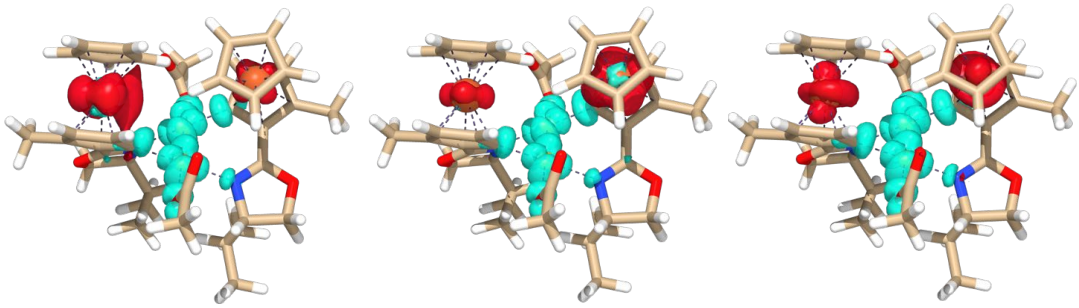
(a) State 2 (b) State 9 (c) State 17

Figure 23: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of **2**Br. Green denotes gain in electron density and red loss of electron density

Table 10: Transitions Determined by TD-DFT of [**2**Br]*

216	HOMO		
217	LUMO		
STATE 2:	E= 0.072363 au	1.969 eV	15881.8 cm^{-1}
	216a $\longrightarrow$ 217a : 0.932768 (c= -0.96579900)		
STATE 7:	E= 0.091099 au	2.479 eV	19994.0 cm^{-1}
	213a $\longrightarrow$ 219a : 0.142822 (c= 0.37791821)		
	213a $\longrightarrow$ 223a : 0.106708 (c= 0.32666128)		
	214a $\longrightarrow$ 218a : 0.052266 (c= -0.22861730)		
	214a $\longrightarrow$ 222a : 0.062173 (c= -0.24934525)		
	215a $\longrightarrow$ 221a : 0.123557 (c= -0.35150650)		
	216a $\longrightarrow$ 218a : 0.138514 (c= 0.37217467)		
	216a $\longrightarrow$ 220a : 0.081773 (c= -0.28595937)		
	216a $\longrightarrow$ 222a : 0.056923 (c= 0.23858588)		
STATE 9:	E= 0.098512 au	2.681 eV	21620.8 cm^{-1}
	210a $\longrightarrow$ 219a : 0.050910 (c= -0.22563333)		
	210a $\longrightarrow$ 223a : 0.040854 (c= -0.20212303)		
	211a $\longrightarrow$ 218a : 0.133535 (c= 0.36542481)		
	211a $\longrightarrow$ 222a : 0.096895 (c= 0.31127969)		
	212a $\longrightarrow$ 217a : 0.187481 (c= 0.43299118)		
	212a $\longrightarrow$ 219a : 0.093875 (c= 0.30638991)		
	212a $\longrightarrow$ 223a : 0.058372 (c= 0.24160222)		
	213a $\longrightarrow$ 220a : 0.070797 (c= 0.26607710)		
	214a $\longrightarrow$ 221a : 0.096247 (c= 0.31023734)		

*transitions below 5% were omitted



(a) State 1 (b) State 2 (c) State 13

Figure 24: Electron density difference map shown at isosurface = 0.001, of the major transitions found in the UV-Vis NIR spectrum of **2**OAc. Green denotes gain in electron density and red loss of electron density

Table 11: Transitions Determined by TD-DFT of [**2**OAc]*

212	HOMO
213	LUMO
STATE 1:	E= 0.083112 au 2.262 eV 18241.0 cm^{-1}
	211a $\longrightarrow$ 213a : 0.423300 (c= 0.65061488)
	212a $\longrightarrow$ 213a : 0.259343 (c= 0.50925736)
	212a $\longrightarrow$ 216a : 0.041156 (c= -0.20286932)
STATE 2:	E= 0.084359 au 2.296 eV 18514.6 cm^{-1}
	209a $\longrightarrow$ 214a : 0.067354 (c= 0.25952677)
	211a $\longrightarrow$ 213a : 0.233385 (c= 0.48309963)
	212a $\longrightarrow$ 213a : 0.351301 (c= -0.59270612)
STATE 13:	E= 0.108397 au 2.950 eV 23790.3 cm^{-1}
	208a $\longrightarrow$ 213a : 0.864549 (c= 0.92981148)

*transitions below 5% were omitted

5 DFT Coordinates

Table 12: XYZ coordinates for Optimized structure B3LYP $\mathbf{1}^{\mathrm{iPr}}$

Au	17.840983	13.359789	4.623573
Fe	15.160862	15.650237	3.336520
O	14.200781	12.057936	1.779951
N	16.373644	12.566951	1.563693
C	15.967874	14.030862	4.389515
C	15.002926	13.636250	3.361682
C	13.712108	14.257464	3.635962
C	13.890284	15.047682	4.815726
H	13.120018	15.669616	5.268096
C	15.246164	14.919530	5.256437
H	15.675975	15.427178	6.117004
C	16.642314	16.536908	2.233743
H	17.647554	16.136187	2.129117
C	15.525381	16.196866	1.401884
H	15.548151	15.503921	0.563932
C	14.369104	16.877492	1.903998
H	13.358456	16.796414	1.511115
C	14.769100	17.638698	3.052141
H	14.116017	18.242965	3.676989
C	16.173935	17.427566	3.256824
H	16.770637	17.852165	4.059853
C	12.421300	14.110201	2.892196
H	11.909514	13.176209	3.175076
H	12.570002	14.082800	1.805430
H	11.752450	14.948667	3.130707
C	15.263976	12.776395	2.219078
C	14.627316	11.363125	0.568080
H	14.194267	11.895071	-0.290382
H	14.227954	10.343270	0.612711
C	16.157091	11.451468	0.612506
H	16.561426	11.738898	-0.368298
C	16.880828	10.172886	1.083458
H	17.942614	10.459904	1.185535
C	16.390217	9.682590	2.446593
H	16.519489	10.452991	3.220466
H	16.960954	8.796732	2.758112
H	15.327802	9.394536	2.416155
C	16.776494	9.082798	0.014896
H	17.357057	8.197698	0.311488
H	17.159245	9.434577	-0.954851
H	15.732916	8.760512	-0.128102

Au	18.295158	13.360977	1.814890
Fe	20.974564	15.650922	3.104179
O	21.935678	12.057741	4.657182
N	19.762789	12.566382	4.874277
C	20.167998	14.032502	2.049313
C	21.133067	13.636992	3.076670
C	22.423702	14.258922	2.803094
C	22.245250	15.050450	1.624240
H	23.015313	15.673136	1.172561
C	20.889390	14.922405	1.183411
H	20.459411	15.430903	0.323433
C	19.492919	16.535890	4.208010
H	18.487822	16.134681	4.312153
C	20.609989	16.195277	5.039457
H	20.587481	15.501344	5.876596
C	21.766017	16.876838	4.538046
H	22.776712	16.795640	4.930788
C	21.365737	17.639192	3.390760
H	22.018608	18.244358	2.766562
C	19.960956	17.427862	3.185924
H	19.364080	17.853167	2.383407
C	23.714553	14.111216	3.546698
H	24.226589	13.177655	3.262850
H	23.565848	14.082659	4.633433
H	24.383183	14.950105	3.309060
C	20.872206	12.776200	4.218661
C	21.509897	11.362386	5.868864
H	21.944390	11.893097	6.727334
H	21.908781	10.342361	5.822418
C	19.980008	11.451803	5.826344
H	19.577400	11.740690	6.807451
C	19.254430	10.173288	5.358185
H	18.193155	10.461985	5.255609
C	19.744045	9.679444	3.995982
H	19.615728	10.448306	3.220434
H	19.171995	8.793762	3.686351
H	20.806035	9.389854	4.026805
C	19.356465	9.085376	6.429175
H	18.773999	8.200866	6.134605
H	18.974410	9.440136	7.398098
H	20.399141	8.760530	6.573122

Table 13: XYZ coordinates for Optimized structure B3LYP $[\mathbf{1}^{iPr}]^+$

Au	17.885047	13.340214	4.618734
Fe	15.276604	15.672941	3.233804
O	14.184340	12.028512	1.893984
N	16.346449	12.526857	1.593451
C	16.020181	14.041721	4.401373
C	15.042274	13.667148	3.384715
C	13.781829	14.349314	3.636101
C	14.007767	15.189523	4.769437
H	13.279970	15.871154	5.191037
C	15.353476	15.010142	5.213737
H	15.811100	15.541535	6.037808
C	16.777228	16.574503	2.084424
H	17.795160	16.211988	2.032109
C	15.701309	16.117641	1.265571
H	15.776769	15.375193	0.482601
C	14.505260	16.774639	1.695984
H	13.515458	16.627892	1.285942
C	14.845734	17.629349	2.794141
H	14.159082	18.243245	3.360733
C	16.251070	17.502032	3.032365
H	16.803023	18.004374	3.814356
C	12.478676	14.211917	2.907345
H	11.944158	13.322829	3.261676
H	12.620895	14.104596	1.830262
H	11.851722	15.087162	3.097444
C	15.259465	12.750436	2.270634
C	14.571783	11.285480	0.683711
H	14.105495	11.789956	-0.165075
H	14.177832	10.275288	0.790189
C	16.103358	11.379091	0.675491
H	16.477210	11.642464	-0.316438
C	16.840827	10.121785	1.179790
H	17.899511	10.406730	1.249449
C	16.365854	9.686220	2.570351
H	16.517422	10.480445	3.308891
H	16.927332	8.807753	2.900298
H	15.303833	9.415179	2.563764
C	16.709561	8.990528	0.152638
H	17.291744	8.120655	0.472399
H	17.073085	9.306258	-0.831313
H	15.665777	8.671526	0.045679

Au	18.250784	13.339898	1.822678
Fe	20.858839	15.673231	3.206708
O	21.951230	12.028314	4.546752
N	19.789358	12.527248	4.848206
C	20.115423	14.041471	2.039737
C	21.093305	13.667373	3.056601
C	22.353739	14.349503	2.805044
C	22.127826	15.189256	1.671381
H	22.855614	15.870746	1.249544
C	20.782177	15.009547	1.227056
H	20.324691	15.540469	0.402614
C	19.358011	16.575037	4.355679
H	18.340121	16.212383	4.408156
C	20.433820	16.118427	5.174782
H	20.358290	15.376207	5.957956
C	21.629898	16.775375	4.744411
H	22.619628	16.628805	5.154696
C	21.289522	17.629814	3.646003
H	21.976240	18.243673	3.079445
C	19.884215	17.502376	3.407504
H	19.332304	18.004355	2.625139
C	23.656813	14.212468	3.534026
H	24.191536	13.323399	3.179965
H	23.514449	14.105330	4.611113
H	24.283652	15.087780	3.343895
C	20.876194	12.750683	4.170725
C	21.563947	11.284878	5.756841
H	22.030594	11.788933	6.605673
H	21.957572	10.274625	5.649865
C	20.032387	11.378991	5.765566
H	19.659220	11.641834	6.757903
C	19.294378	10.122236	5.260849
H	18.235768	10.407571	5.191632
C	19.768783	9.687451	3.869862
H	19.617380	10.482204	3.131866
H	19.206890	8.809379	3.539562
H	20.830695	9.415956	3.876007
C	19.425530	8.990388	6.287340
H	18.843060	8.120824	5.967232
H	19.062287	9.305644	7.271545
H	20.469241	8.671010	6.393899

Table 14: XYZ coordinates for Optimized structure B3LYP $[\mathbf{1}^{iPr}]^{2+}$ S1

Au	17.884138	13.324285	4.625188
Fe	15.275680	15.679908	3.232777
O	14.191875	12.013199	1.900807
N	16.349685	12.519366	1.590987
C	16.014518	14.005701	4.421295
C	15.048374	13.651689	3.389293
C	13.786565	14.330557	3.639391
C	14.012143	15.168269	4.777314
H	13.285158	15.848904	5.201418
C	15.351744	14.975858	5.230880
H	15.807264	15.502379	6.059069
C	16.745390	16.656516	2.024840
H	17.770078	16.320486	1.937245
C	15.662862	16.173390	1.236148
H	15.736876	15.442520	0.442321
C	14.462410	16.792463	1.707499
H	13.466844	16.626394	1.319960
C	14.811893	17.645317	2.805110
H	14.128246	18.238290	3.396604
C	16.227294	17.555052	2.997459
H	16.787278	18.066468	3.768073
C	12.484289	14.189622	2.914130
H	11.964439	13.296188	3.278115
H	12.621788	14.076818	1.837521
H	11.851604	15.058674	3.109324
C	15.263830	12.730187	2.270598
C	14.575208	11.271448	0.682679
H	14.095478	11.776011	-0.157636
H	14.188909	10.259399	0.794427
C	16.106465	11.375476	0.662597
H	16.471029	11.653238	-0.328460
C	16.855582	10.119965	1.153338
H	17.913556	10.409230	1.219496
C	16.387541	9.667028	2.540646
H	16.536882	10.451141	3.290673
H	16.953993	8.787459	2.857848
H	15.327314	9.389806	2.534916
C	16.725347	8.999264	0.114381
H	17.312181	8.129265	0.424267
H	17.084713	9.326767	-0.867010
H	15.682679	8.677059	0.008167

Au	18.253472	13.323814	1.817575
Fe	20.859828	15.679160	3.207541
O	21.944690	12.011116	4.541538
N	19.787267	12.518266	4.852576
C	20.123667	14.003494	2.021000
C	21.088803	13.650855	3.054417
C	22.350544	14.329964	2.805225
C	22.126275	15.165912	1.665735
H	22.853544	15.846335	1.241773
C	20.787385	14.972368	1.210593
H	20.332634	15.497883	0.381352
C	19.386082	16.657210	4.408782
H	18.361461	16.320042	4.492635
C	20.466297	16.176162	5.201959
H	20.390361	15.446722	5.996920
C	21.667934	16.795014	4.733294
H	22.662310	16.630230	5.124433
C	21.321534	17.645554	3.632931
H	22.006780	18.237672	3.042431
C	19.906856	17.554049	3.436057
H	19.349623	18.062640	2.661611
C	23.651544	14.190801	3.533135
H	24.173012	13.297612	3.170893
H	23.511776	14.078705	4.609541
H	24.283812	15.060307	3.338649
C	20.873065	12.729127	4.172847
C	21.561234	11.267951	5.758715
H	22.041339	11.771118	6.599650
H	21.946941	10.255835	5.645540
C	20.030032	11.372768	5.779180
H	19.666174	11.648791	6.770987
C	19.280261	10.118409	5.286500
H	18.222485	10.408407	5.220427
C	19.748375	9.667162	3.898673
H	19.600179	10.452519	3.149729
H	19.181100	8.788670	3.579955
H	20.808298	9.388773	3.904449
C	19.409550	8.996170	6.323911
H	18.822366	8.126940	6.012547
H	19.050031	9.322435	7.305657
H	20.452021	8.673289	6.429989

Table 15: XYZ coordinates for Optimized structure B3LYP **2**Cl

Au	9.582459	17.008351	2.618134
Cl	11.621207	17.695235	3.757048
Fe	7.104220	19.832177	2.956305
Au	7.440216	16.323553	1.428339
Cl	5.394989	15.694134	0.266760
Fe	9.825527	17.673566	-1.164854
O	5.578913	16.890111	5.228161
N	6.415418	16.220786	3.266294
C	8.501836	18.454792	3.528135
O	11.494123	14.216337	0.015182
N	10.644340	15.455002	1.670527
C	7.250299	18.302325	4.255635
C	6.961421	19.531994	4.969123
C	8.035590	20.428423	4.674072
H	8.100663	21.450422	5.025666
C	8.964485	19.780302	3.802551
H	9.873482	20.214691	3.411083
C	6.792064	19.688663	0.932602
H	7.309137	19.004055	0.274068
C	5.585215	19.413394	1.648011
H	5.036264	18.481118	1.618980
C	5.268079	20.560401	2.444038
H	4.430061	20.651797	3.122027
C	6.282980	21.546538	2.220866
H	6.346831	22.514043	2.700576
C	7.228430	21.005819	1.289836
H	8.123526	21.500579	0.938352
C	5.801019	19.831697	5.869823
H	5.656181	20.913155	5.945123
H	5.989205	19.441383	6.877806
H	4.877045	19.377333	5.506111
C	6.419036	17.122941	4.201569
C	4.794553	15.692857	4.868825
H	3.791807	16.036275	4.607772
H	4.762061	15.058112	5.754031
C	5.552999	15.088936	3.675699
H	4.873129	14.860708	2.851826
C	6.407140	13.843887	3.985821
H	6.974901	13.641435	3.068415
C	7.402012	14.084462	5.126066
H	8.032718	13.201700	5.269776
H	6.884402	14.277804	6.072963
H	8.056190	14.935891	4.910927
C	5.500617	12.639341	4.265373
H	4.903948	12.795845	5.172293
H	6.102128	11.736959	4.415012
H	4.813823	12.461001	3.430714
C	8.486709	16.394038	-0.299889
C	9.755357	15.744509	-0.596044
C	10.013552	15.831456	-2.021083
C	8.903838	16.532964	-2.587457
H	8.809164	16.796375	-3.633407
C	7.983190	16.875267	-1.549400
H	7.053052	17.410023	-1.680026
C	10.107032	19.293357	0.063595
H	9.603353	19.447892	1.008124
C	11.335377	18.586783	-0.125638
H	11.916775	18.116432	0.656743
C	11.625047	18.564973	-1.527634
H	12.470970	18.078703	-1.994800
C	10.571544	19.258870	-2.206571
H	10.481642	19.389216	-3.276714
C	9.630015	19.705364	-1.223120
H	8.711869	20.240336	-1.423935
C	11.178093	15.282108	-2.789006
H	11.285398	15.816520	-3.737277
H	11.021552	14.219173	-3.011792
H	12.111254	15.368961	-2.228421
C	10.626505	15.170975	0.402502
C	12.314231	13.886387	1.196740
H	13.298266	14.330272	1.034948
H	12.388205	12.799972	1.237742
C	11.553841	14.520663	2.372438
H	12.224673	15.105664	3.005489
C	10.749810	13.544991	3.254102
H	10.170815	14.177636	3.939301
C	9.770819	12.690979	2.441650
H	9.083547	13.315787	1.861713
H	9.173693	12.062224	3.109216
H	10.300446	12.026468	1.749031
C	11.703003	12.680569	4.087810
H	12.311431	12.031805	3.446022
H	11.136164	12.037300	4.768476
H	12.379034	13.302638	4.684514

Table 16: XYZ coordinates for Optimized structure B3LYP [**2**Cl]$^+$

Au	9.598324	16.998374	2.612305
Cl	11.631610	17.709955	3.714934
Fe	7.098253	19.826502	2.942132
Au	7.446973	16.322837	1.430480
Cl	5.405143	15.757412	0.266703
Fe	9.826432	17.687789	-1.155639
O	5.607712	16.883899	5.231024
N	6.424095	16.222981	3.260055
C	8.526892	18.443825	3.531936
O	11.472253	14.184328	0.018087
N	10.653741	15.451248	1.665373
C	7.268116	18.299796	4.248464
C	6.994858	19.520227	4.982243
C	8.070547	20.409526	4.687040
H	8.140428	21.431598	5.036660
C	8.992066	19.763168	3.815000
H	9.895299	20.204094	3.417412
C	6.728534	19.700906	0.916759
H	7.222675	19.019860	0.238648
C	5.543683	19.419250	1.670806
H	4.993396	18.487810	1.659317
C	5.237636	20.577256	2.453963
H	4.421953	20.670814	3.157928
C	6.232440	21.565519	2.188717
H	6.309277	22.533418	2.665276
C	7.153454	21.026494	1.242085
H	8.035661	21.528305	0.868934
C	5.841574	19.817746	5.889992
H	5.710227	20.898273	5.987542
H	6.041068	19.404437	6.885755
H	4.912494	19.374573	5.527196
C	6.434042	17.113993	4.203652
C	4.812944	15.686609	4.873476
H	3.809892	16.039305	4.629848
H	4.793163	15.048218	5.755616
C	5.555707	15.089299	3.666749
H	4.867266	14.876915	2.846398
C	6.406439	13.838264	3.958252
H	6.969688	13.641956	3.036563
C	7.403390	14.060833	5.100237
H	8.028692	13.173101	5.232687
H	6.887716	14.244603	6.049728
H	8.063966	14.910660	4.897536
C	5.492325	12.636605	4.226059
H	4.897994	12.787431	5.135205
H	6.090491	11.730858	4.366081
H	4.804682	12.470639	3.389926
C	8.486953	16.379126	-0.299491
C	9.752098	15.728861	-0.597248
C	9.999195	15.788040	-2.019849
C	8.903159	16.498701	-2.587151
H	8.813496	16.760143	-3.633721
C	7.988429	16.861303	-1.552638
H	7.062863	17.401168	-1.692728
C	10.090669	19.325171	0.056374
H	9.574145	19.482980	0.992864
C	11.338622	18.646809	-0.105589
H	11.915592	18.187718	0.686599
C	11.657247	18.632521	-1.495584
H	12.514972	18.149541	-1.944001
C	10.609024	19.296353	-2.198994
H	10.537964	19.410324	-3.272121
C	9.634656	19.725851	-1.242851
H	8.714975	20.246543	-1.470918
C	11.168434	15.243242	-2.779922
H	11.260848	15.752705	-3.742064
H	11.016278	14.174017	-2.969307
H	12.101825	15.351206	-2.224398
C	10.625687	15.146354	0.403702
C	12.302646	13.854352	1.199041
H	13.288632	14.283855	1.016979
H	12.358412	12.767953	1.249794
C	11.561413	14.513314	2.373657
H	12.243876	15.100581	2.991052
C	10.750342	13.558681	3.271354
H	10.179175	14.204864	3.950813
C	9.764926	12.698720	2.472978
H	9.076862	13.315630	1.885146
H	9.167941	12.082165	3.151215
H	10.289564	12.021825	1.789053
C	11.701920	12.700171	4.113335
H	12.303825	12.039414	3.478061
H	11.131480	12.070084	4.802772
H	12.382597	13.326184	4.700048

Table 17: XYZ coordinates for Optimized structure B3LYP [**2**Cl]$^{2+}$ S1

Au	9.602193	16.974531	2.629732
Cl	11.633372	17.707011	3.683425
Fe	7.074899	19.819701	2.903501
Au	7.437707	16.290122	1.455158
Cl	5.399195	15.748717	0.307616
Fe	9.853619	17.711531	-1.127176
O	5.632460	16.875809	5.254608
N	6.432968	16.199854	3.284284
C	8.555510	18.413810	3.575596
O	11.455263	14.184723	0.017742
N	10.645054	15.434444	1.679595
C	7.275022	18.290526	4.245197
C	6.977831	19.526684	4.944006
C	8.055009	20.417278	4.635032
H	8.124147	21.446919	4.961018
C	9.003189	19.739941	3.814418
H	9.912945	20.173440	3.422861
C	6.646277	19.758664	0.827561
H	7.134873	19.103779	0.119805
C	5.504329	19.425201	1.621409
H	4.963708	18.488368	1.593640
C	5.210726	20.555194	2.454290
H	4.410020	20.622143	3.177622
C	6.182363	21.567704	2.176683
H	6.264393	22.525941	2.671163
C	7.064288	21.071509	1.172713
H	7.929369	21.593596	0.786929
C	5.824422	19.828943	5.846356
H	5.674991	20.908630	5.917520
H	6.048181	19.445825	6.848672
H	4.902443	19.354707	5.506999
C	6.445473	17.093128	4.223749
C	4.836897	15.667247	4.917819
H	3.829278	16.016608	4.691701
H	4.839917	15.036413	5.805012
C	5.562980	15.066239	3.701354
H	4.864600	14.860046	2.888188
C	6.413855	13.813764	3.983202
H	6.966742	13.614742	3.055711
C	7.420032	14.033025	5.117592
H	8.044650	13.144162	5.243145
H	6.911945	14.214374	6.071193
H	8.081453	14.882389	4.914633
C	5.495580	12.616738	4.258332
H	4.908373	12.771756	5.171047
H	6.091432	11.709511	4.396395
H	4.802674	12.452049	3.426629
C	8.447484	16.324041	-0.288805
C	9.746758	15.747306	-0.578733
C	10.009442	15.848283	-2.002046
C	8.890038	16.547121	-2.556058
H	8.787632	16.833797	-3.594629
C	7.951588	16.826126	-1.520919
H	7.016825	17.353639	-1.650311
C	10.217605	19.433718	0.046911
H	9.727737	19.646884	0.986599
C	11.395634	18.638618	-0.118375
H	11.966672	18.176408	0.676002
C	11.678593	18.570815	-1.522762
H	12.498528	18.036246	-1.982019
C	10.667199	19.312634	-2.209429
H	10.569558	19.415827	-3.281470
C	9.769833	19.843060	-1.237754
H	8.875822	20.411103	-1.456830
C	11.171404	15.306813	-2.771864
H	11.282187	15.846077	-3.715277
H	10.985759	14.250652	-2.998995
H	12.102097	15.367126	-2.205905
C	10.618534	15.139294	0.417377
C	12.283441	13.827992	1.198231
H	13.274584	14.243260	1.014710
H	12.318280	12.740594	1.235473
C	11.553655	14.487172	2.381566
H	12.243403	15.070799	2.994021
C	10.741657	13.534536	3.279363
H	10.181336	14.180133	3.968429
C	9.745615	12.685651	2.482630
H	9.055843	13.307525	1.901656
H	9.149943	12.069137	3.161662
H	10.260770	12.008721	1.792096
C	11.695617	12.665645	4.108089
H	12.287828	12.004836	3.464164
H	11.126186	12.035153	4.797510
H	12.384221	13.283803	4.693420

Table 18: XYZ coordinates for Optimized structure B3LYP **2**Br

Au	9.641184	17.010754	2.577933
Br	11.773565	17.784940	3.783721
Fe	7.102336	19.789315	2.878897
Au	7.505706	16.271980	1.384608
Br	5.379485	15.527588	0.149481
Fe	9.887225	17.654778	-1.199017
O	5.648166	16.840890	5.187978
N	6.488124	16.163793	3.229610
C	8.531319	18.450911	3.466919
O	11.580898	14.213602	-0.002373
N	10.720217	15.455592	1.645604
C	7.281798	18.276173	4.193109
C	6.961211	19.505416	4.893845
C	8.013502	20.425023	4.591643
H	8.052617	21.452062	4.932124
C	8.959621	19.790909	3.728587
H	9.858691	20.243671	3.335269
C	6.792243	19.617049	0.858053
H	7.320784	18.934179	0.206959
C	5.590531	19.328839	1.577392
H	5.057642	18.387015	1.558163
C	5.253783	20.479116	2.360545
H	4.414463	20.563782	3.037753
C	6.251262	21.480312	2.125656
H	6.298952	22.453663	2.595236
C	7.205655	20.945717	1.200126
H	8.091984	21.452427	0.843740
C	5.791549	19.785060	5.788827
H	5.619156	20.863217	5.852667
H	5.987041	19.409373	6.800948
H	4.880335	19.303239	5.428229
C	6.477837	17.077911	4.154134
C	4.885279	15.626250	4.847289
H	3.875784	15.947308	4.583288
H	4.864721	15.003329	5.741284
C	5.652123	15.020022	3.661472
H	4.973896	14.763590	2.844252
C	6.532799	13.798265	3.986893
H	7.102908	13.596122	3.070991
C	7.524046	14.074592	5.122054
H	8.173071	13.207198	5.277149
H	7.004340	14.269990	6.067414
H	8.159944	14.936687	4.894660
C	5.652649	12.578314	4.283505
H	5.053367	12.733419	5.189023
H	6.273469	11.691193	4.444986
H	4.969480	12.373765	3.451966
C	8.558126	16.361121	-0.342025
C	9.837131	15.726979	-0.626769
C	10.106469	15.813522	-2.049661
C	8.993312	16.500567	-2.626981
H	8.904623	16.761754	-3.673974
C	8.060042	16.833776	-1.597334
H	7.123754	17.355116	-1.737615
C	10.135682	19.284187	0.022457
H	9.621400	19.437223	0.961500
C	11.375199	18.593003	-0.151326
H	11.955967	18.136651	0.639830
C	11.678026	18.566950	-1.550416
H	12.535188	18.090111	-2.006618
C	10.621766	19.242827	-2.243244
H	10.539751	19.364822	-3.314967
C	9.665089	19.682323	-1.271122
H	8.741569	20.203143	-1.483929
C	11.284761	15.276344	-2.804887
H	11.398330	15.812711	-3.751291
H	11.140890	14.212189	-3.029868
H	12.210322	15.370642	-2.233113
C	10.707495	15.165130	0.378435
C	12.399637	13.894075	1.181340
H	13.380906	14.345115	1.021740
H	12.482886	12.808355	1.225748
C	11.630921	14.525928	2.352533
H	12.296474	15.114901	2.987968
C	10.828558	13.548079	3.232519
H	10.242866	14.179787	3.912745
C	9.858427	12.686145	2.418008
H	9.169415	13.305145	1.833811
H	9.263004	12.054347	3.084285
H	10.394845	12.023543	1.728659
C	11.782076	12.691792	4.074249
H	12.398434	12.044477	3.438466
H	11.215062	12.046966	4.753327
H	12.450724	13.319458	4.673410

Table 19: XYZ coordinates for Optimized structure B3LYP **2**I

Au	9.649871	17.017596	2.585171
I	11.908491	17.828405	3.915097
Fe	7.092461	19.790808	2.860160
Au	7.500499	16.268651	1.379671
I	5.249386	15.426917	0.054687
Fe	9.896531	17.674314	-1.193192
O	5.671954	16.838777	5.199561
N	6.496665	16.156364	3.235710
C	8.531370	18.464551	3.460788
O	11.560058	14.204013	-0.002596
N	10.716395	15.450959	1.651457
C	7.279406	18.284314	4.181968
C	6.945109	19.514127	4.875705
C	7.990374	20.441141	4.573662
H	8.019564	21.470158	4.909109
C	8.944536	19.810709	3.717292
H	9.839637	20.271478	3.323962
C	6.791544	19.613116	0.838037
H	7.326584	18.930291	0.192172
C	5.586865	19.323926	1.551992
H	5.055086	18.381530	1.532929
C	5.243437	20.474813	2.330831
H	4.400755	20.558547	3.003983
C	6.239377	21.477791	2.098570
H	6.282014	22.452685	2.565496
C	7.199664	20.943508	1.179132
H	8.086307	21.451655	0.825510
C	5.768703	19.789459	5.763360
H	5.589336	20.866775	5.821928
H	5.960942	19.419407	6.778133
H	4.862303	19.301133	5.399323
C	6.487029	17.077484	4.154070
C	4.917649	15.613371	4.875722
H	3.905345	15.924017	4.610664
H	4.905841	15.000296	5.776478
C	5.686698	15.003151	3.695246
H	5.005687	14.718614	2.889397
C	6.594573	13.805614	4.032338
H	7.169995	13.609746	3.118536
C	7.576794	14.114007	5.167143
H	8.250211	13.265980	5.325190
H	7.050381	14.297171	6.111112
H	8.188522	14.993044	4.937807
C	5.742157	12.568340	4.338277
H	5.136829	12.719090	5.240445
H	6.383231	11.697702	4.509851
H	5.066443	12.340427	3.506760
C	8.558887	16.374046	-0.347008
C	9.841565	15.743895	-0.624838
C	10.122295	15.834922	-2.045421
C	9.013824	16.523163	-2.629299
H	8.932659	16.787710	-3.676046
C	8.073375	16.852619	-1.605389
H	7.140234	17.377935	-1.752312
C	10.149063	19.300650	0.032781
H	9.637886	19.449511	0.974158
C	11.388912	18.612214	-0.149604
H	11.975242	18.153641	0.635963
C	11.684944	18.591193	-1.549879
H	12.540100	18.116201	-2.011780
C	10.624484	19.267669	-2.235156
H	10.537358	19.393696	-3.306035
C	9.671923	19.702361	-1.257080
H	8.746868	20.222769	-1.464023
C	11.307177	15.302108	-2.793642
H	11.425512	15.840752	-3.738161
H	11.167672	14.238156	-3.022242
H	12.228849	15.398302	-2.215878
C	10.701919	15.168445	0.381877
C	12.369950	13.863051	1.182091
H	13.355632	14.308183	1.032860
H	12.442741	12.776327	1.214769
C	11.599099	14.488862	2.353059
H	12.269379	15.051002	3.007933
C	10.764258	13.513574	3.204157
H	10.172398	14.147051	3.877170
C	9.801716	12.672181	2.359553
H	9.137027	13.305075	1.761938
H	9.179855	12.045713	3.006444
H	10.345924	12.005898	1.680141
C	11.687502	12.635742	4.057315
H	12.310002	11.988796	3.427246
H	11.097277	11.989962	4.715408
H	12.349770	13.248198	4.678770

Table 20: XYZ coordinates for Optimized structure B3LYP **2**OAc

Au	9.692458	16.919447	2.548196
O	11.357727	17.272801	3.892034
Fe	7.293656	19.789667	3.010209
Au	7.616162	16.166664	1.284772
O	5.138757	17.165194	-0.222720
Fe	9.902184	17.417440	-1.439895
O	5.564766	16.754578	4.998171
N	6.492229	16.128046	3.062119
C	8.602330	18.310752	3.509394
O	11.809150	14.196687	0.007242
N	10.854775	15.444910	1.598596
C	7.321957	18.152017	4.180494
C	7.055021	19.333407	4.981860
C	8.178032	20.201016	4.803357
H	8.270130	21.187580	5.240342
C	9.111409	19.586966	3.911432
H	10.043720	20.013494	3.569206
C	6.949430	19.699866	0.994477
H	7.334607	18.935536	0.334330
C	5.718106	19.617699	1.716518
H	5.037083	18.779762	1.678395
C	5.588735	20.797623	2.514925
H	4.780860	21.018011	3.200183
C	6.744819	21.613445	2.287086
H	6.961874	22.559092	2.765885
C	7.588180	20.932834	1.348249
H	8.547833	21.281987	0.992498
C	5.872340	19.611728	5.860839
H	5.780482	20.688080	6.032486
H	5.991804	19.119443	6.834190
H	4.943361	19.246682	5.417428
C	6.465214	17.001384	4.025128
C	4.785891	15.578980	4.571360
H	3.796276	15.938043	4.282795
H	4.712980	14.916621	5.433979
C	5.584890	15.004101	3.390679
H	4.937233	14.816093	2.532471
C	6.397668	13.727366	3.687330
H	6.987346	13.537489	2.780664
C	7.365697	13.909551	4.860962
H	7.960158	13.002180	5.004944
H	6.827578	14.104388	5.796188
H	8.055531	14.740455	4.679998
C	5.452961	12.539354	3.903420
H	4.837561	12.681124	4.800217
H	6.026483	11.616462	4.036475
H	4.783212	12.407673	3.046369
C	8.668232	16.150768	-0.430255
C	9.967742	15.551994	-0.689493
C	10.200430	15.521520	-2.122831
C	9.037591	16.091771	-2.729943
H	8.912141	16.248127	-3.794149
C	8.112664	16.475519	-1.709524
H	7.154948	16.953116	-1.861974
C	10.206925	19.079910	-0.285539
H	9.833462	19.213195	0.720035
C	11.454502	18.469236	-0.624475
H	12.161586	18.074537	0.090975
C	11.562665	18.435408	-2.050644
H	12.376969	18.004391	-2.618040
C	10.376834	19.026471	-2.596916
H	10.140100	19.123626	-3.648180
C	9.536592	19.422736	-1.504779
H	8.559627	19.878041	-1.592449
C	11.387445	14.977048	-2.859912
H	11.434566	15.410958	-3.862859
H	11.309677	13.887337	-2.962447
H	12.322521	15.194226	-2.339083
C	10.870853	15.105378	0.343278
C	12.629237	13.967517	1.210134
H	13.586399	14.465847	1.044944
H	12.771455	12.890390	1.296727
C	11.812155	14.598442	2.348125
H	12.435850	15.242634	2.970342
C	11.054713	13.610368	3.258726
H	10.439116	14.233979	3.920505
C	10.124809	12.681950	2.470475
H	9.401278	13.253431	1.879904
H	9.566674	12.036331	3.155436
H	10.690380	12.033227	1.791195
C	12.046586	12.824785	4.124712
H	12.688729	12.183919	3.508310
H	11.509713	12.179635	4.827507
H	12.689228	13.500565	4.699815
C	12.186489	18.203310	3.509484
C	13.338907	18.423281	4.479861
H	12.949803	18.877151	5.397949
H	14.085663	19.085518	4.038956
H	13.796640	17.467882	4.752101
O	12.068943	18.872640	2.472002
C	5.094298	15.925806	-0.245570
C	3.974254	15.186739	-0.964521
H	3.784659	14.210877	-0.512295
H	4.281088	15.027684	-2.005064
H	3.065142	15.791757	-0.962831
O	5.980992	15.139723	0.296440

References