Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Syntheses, Spectroscopic, Redox, and Structural Properties of Homoleptic Iron(III/II) Dithione Complexes

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Refinement details for [**2**][PF_6]$_2$ and [**3**][$FeCl_4$][PF_6]$_2$

All nonhydrogen atoms were refined anisotropically by full matrix least squares against F^2. H atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.99 and 0.98 Å for CH_2 and CH_3 moieties, respectively. Methyl CH_3 were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C) with 1.5 for CH_3 and 1.2 for CH_2 units, respectively.

The crystal of [**2**][PF_6]$_2$ was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180□ rotation around the reciprocal axis (1 0 0). The two components were integrated using Saint and corrected for absorption using Twinabs. The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.1680(8).

One of the [PF_6]$^-$ anions was found to be disordered by a rotation about the central atom. A two-fold disorder model was used for refinement. The major and minor moieties were restrained to have similar geometries (SAME restraint of Shelxl). For the minor moiety, the P-F distances were restrained to be similar. The ADPs of the major and minor P atoms and of F8 and F8B were each constrained to be identical. U^{ij} components of atomic anisotropic displacement parameters (ADPs) for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratios refined to 0.646(6) to 0.354(6).

In the structure of [**3**][$FeCl_4$][PF_6]$_2$, three of the six isopropyl groups were refined as disordered by a slight rotation around the C-N bond (C5, C6, C7; C8, C9, C10; and C25, C26, C27). The major and minor disordered moieties were each restrained to have similar geometries (SAME and SADI commands of Shelxl). U^{ij} components of ADPs for the disordered atoms closer to each other less than 2.0 Å were restrained to be similar. Subject to these conditions, the occupancy ratios refined to 0.736(18) to 0.264(18), to 0.745(12) to 0.255(12), and to 0.58(3) to 0.42(3).

The two [PF_6]$^-$ and the [$FeCl_4$]$^-$ units were found to be disordered by a rotation about the central atom. A two-fold disorder model was used for all three anions. The [PF_6]$^-$ anions were restrained to be

close to octahedral in shape by restraining all P-F bond distances and all cis-F•••F contacts to be similar in length for each $[PF_6]^-$ anion. The $[FeCl_4]^-$ anion moieties were restrained to be close to tetrahedral by restraining all Fe-Cl bond distances and all Cl•••Cl distances to be similar in length for both moieties. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratios refined to 0.706(6) to 0.294(6) for the first $[PF_6]^-$ anion, to 0.344(8) to 0.656(8) for the second $[PF_6]^-$ anion, and to 0.413(12) to 0.587(12) for the $[FeCl_4]^-$ anion.

Methods for vibrating sample magnetometry of solid-state sample

The raw data were converted to inverse molar magnetic susceptibility (χ_M^{-1}) and fit with Curie-Weiss law: $\chi = C/(T - \theta)$ for T > 75K using $1/\chi = 46.118 + 1.7964(T)$.

Given the equation $1/\chi = A+B \bullet T$, the Weiss temperature (θ), the effective magnetic moment of Fe (μ_{Fe}) can be derived as follows

$\theta = -A/B$, $C = 1/B$, $\mu Fe = 2.828 * \sqrt{C}$

The results are θ = -25.67, C= 0.56 emu K/mol Oe and μ_{Fe} = 2.1 μ_B . A negative value for θ implies antiferromagnetic interactions dominate.
The magnetization data for H = 5 kOe was converted to χ_M^{-1} and fit to the same Curie-Weiss Law for all temperatures (T= 1.9 K - 300 K) using $1/\chi$ = 7.9187 + 2.5817(T). The (μ_{Fe}) was derived using eqn. X with θ = -3.07, C= 0.39 emu K/mol Oe and μ_{Fe} = 1.8 μ_B. The value for θ is negative but smaller than what was observed at H= 1kOe indicating weak antiferromagnetic interactions dominate the system. The μ_{Fe} at both H=1 kOE and 5 kOe support low spin Fe(III).

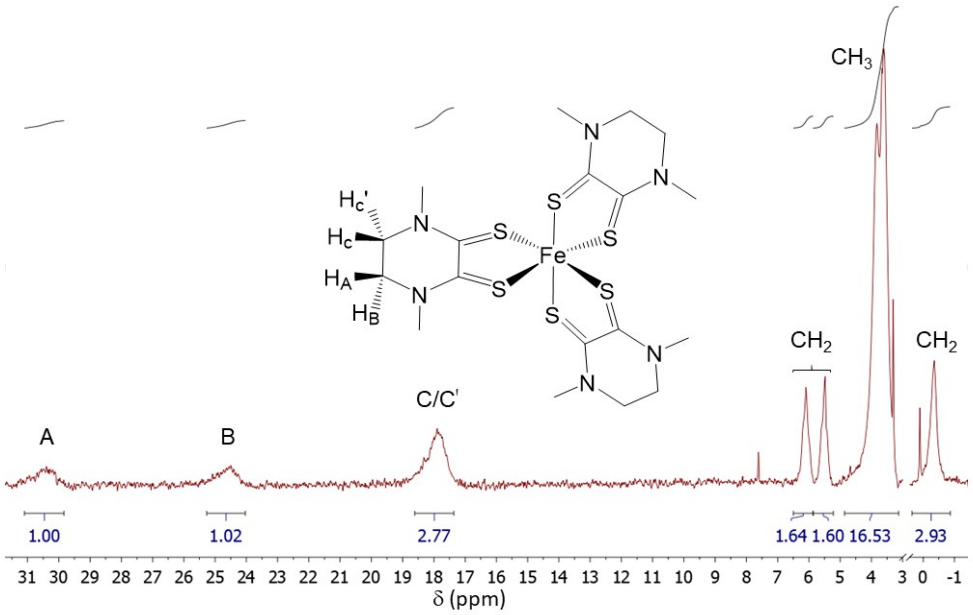

Figure S1. 1H NMR spectrum of [**4**][PF_6]$_3$ collected in CD (δ = 1.93 ppm) at 296 K.

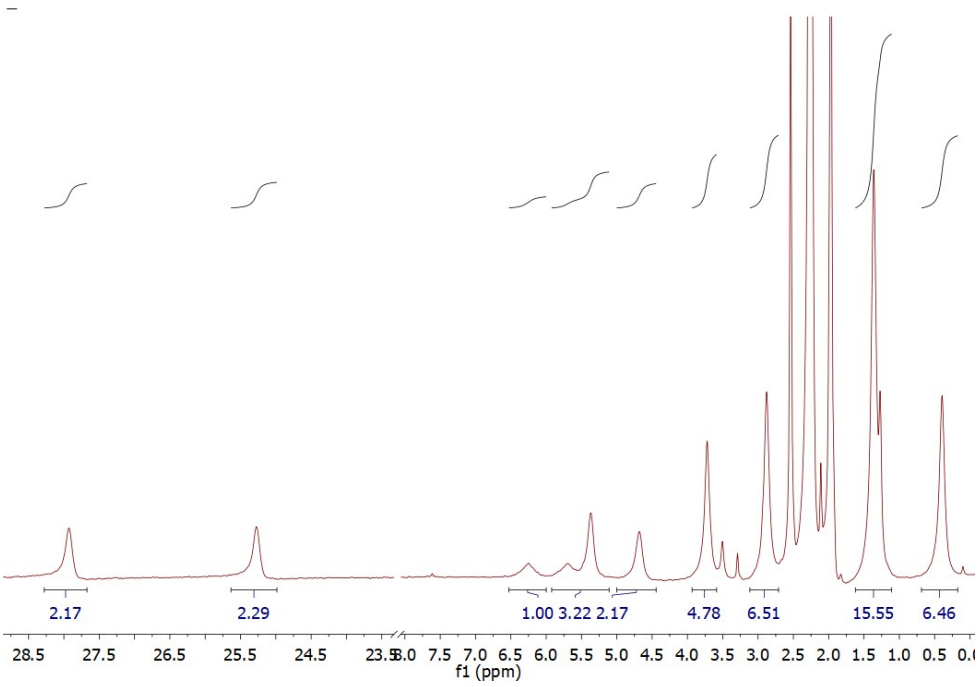

Figure S2. ^{1}H NMR spectrum of [**3**][PF_6]$_3$ recorded as described in Figure S1.

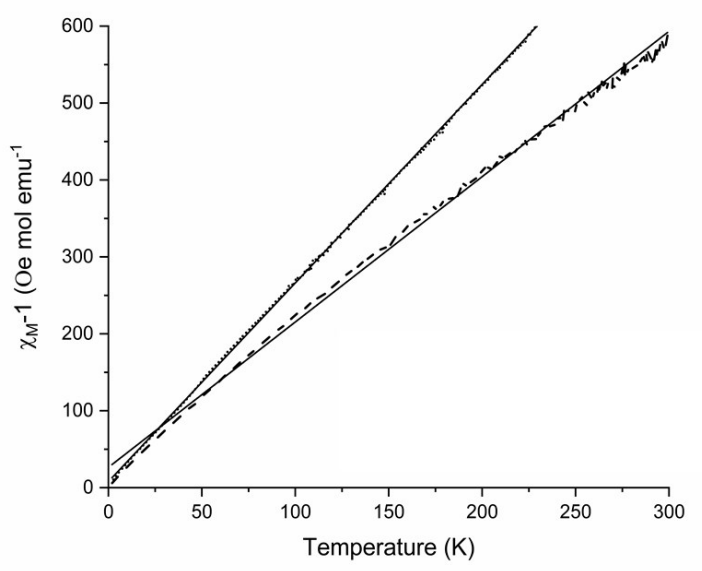

Figure S3. Inverse molar magnetic susceptibility of complex [**4**][PF_6]$_3$ at 1kOe (dashed line) and 5kOe (dotted line) from 1.9K to 300K.

All electrochemical data presented below is recorded as described in Figure 3.

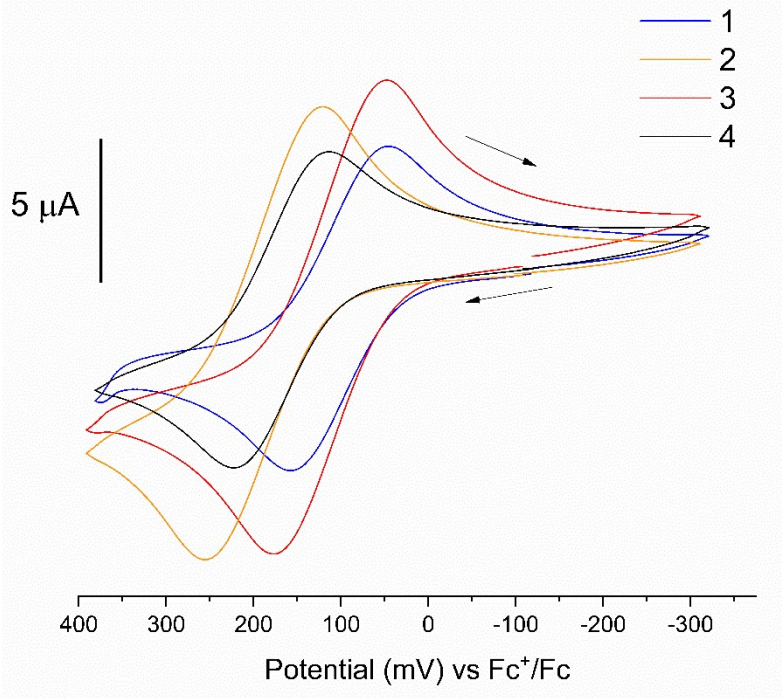

Figure S4. $Fe^{III/II}$ based redox couples for [**1**][PF_6]$_2$ (blue), [**2**][PF_6]$_2$ (orange), [**3**][PF_6]$_3$ (red), and [**4**][PF_6]$_3$ (gray).

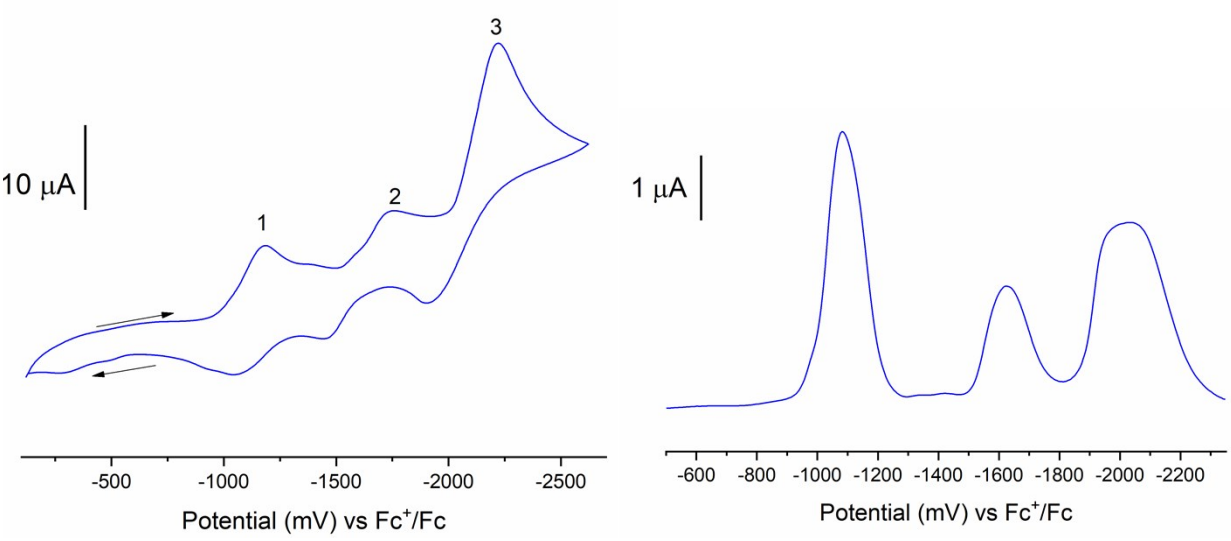

Figure S5. Ligand-based couples (left) and DPV (right) of [**1**][PF_6]$_2$.

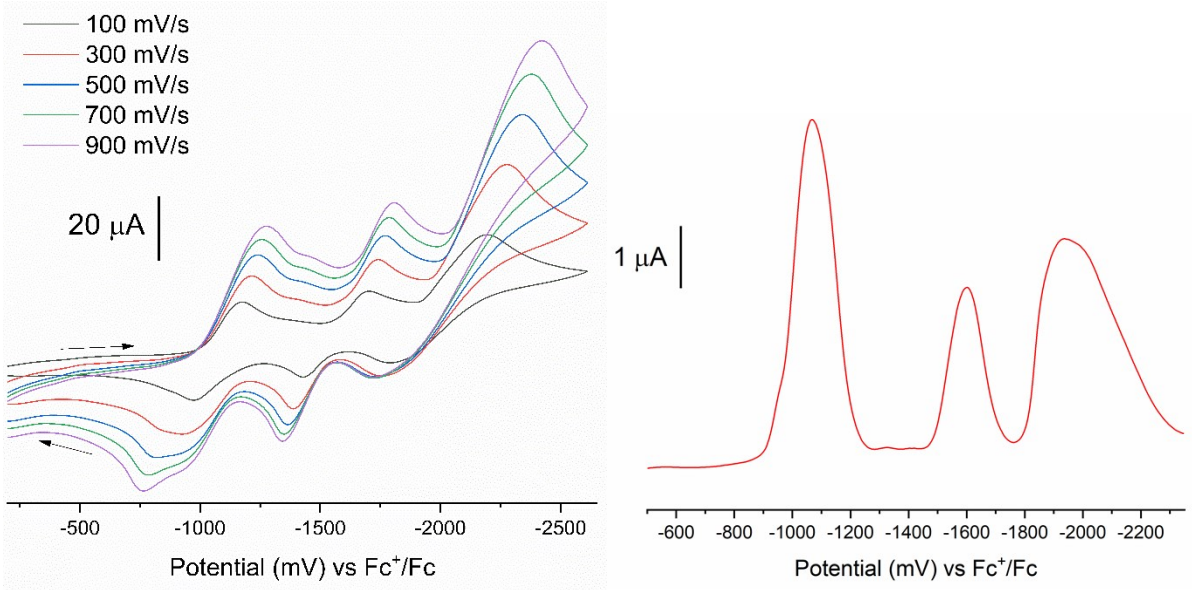

Figure S6. Ligand-based couples at different scan rates (left) and DPV (right) of [**3**][PF_6]$_3$.

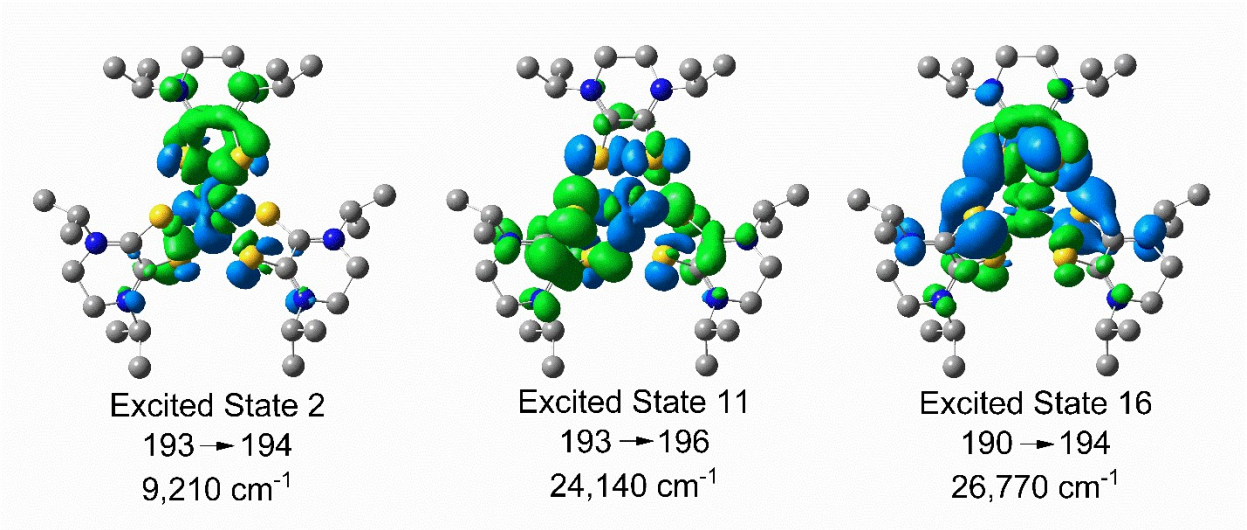

Figure S7. Electron density difference maps (EDDMs) of **1**· PCM-TD-DFT calculations for **1** were performed in acetonitrile using B3LYP with 6-311G* for light atoms and the LANL2DZ effective core potential for Fe. Attempts to model the electronic spectra for **1** with full electron basis sets for Fe were unsatisfactory in both gas and solution phase calculations, and all attempts to model the electronic spectra of **3** were unsuccessful. Electron accepting orbitals are colored green while electron donating orbitals are blue. Transition energies and participating orbitals are included for each EDDM. TD-DFT output for each complex excited state is included in Table S2.

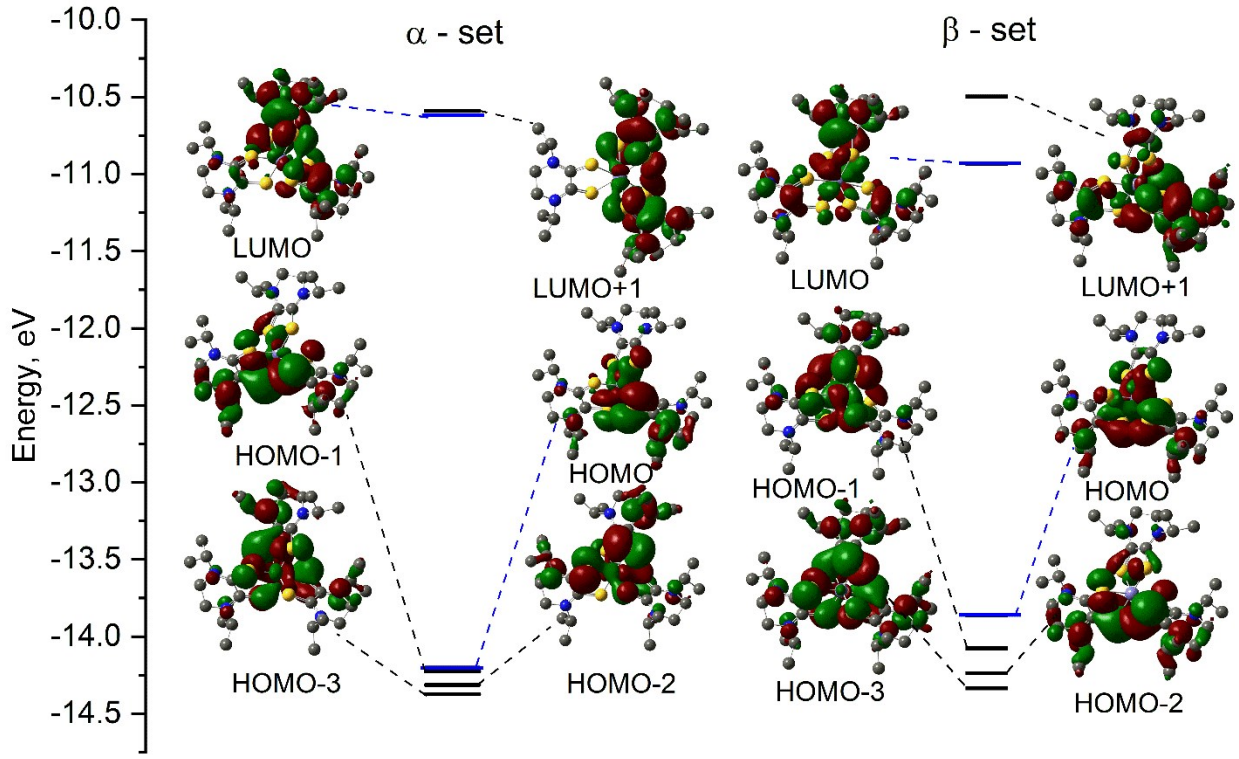

Figure S8. Frontier orbitals and energy diagrams of **3**. Energies are relative and each molecular orbital is paired with its corresponding energy on the diagram. HOMO and LUMO are highlighted blue for clarity.

Table S1. δ_{para} shifts for [**3**][PF_6]$_3$ and [**4**][PF_6]$_3$ at various temperatures.

[**4**][PF_6]$_3$

T (K)	H_A (1H)	H_B (1H)	H_C (2H)	H_D(2H)	H_E(2H)	H_F (9H)	H_G (9H)	H_H (4H)
296	30.88	24.52	17.86	6.06	5.46	3.81	3.55	-0.39
286	31.92	25.56	18.66	6.12	5.54	3.80	3.52	-0.40
273	33.95	26.85	19.66	6.16	5.60	3.80	3.53	-0.41
263	35.53	27.79	20.41	6.20	5.63	3.78	3.51	-0.42
253	37.21	28.79	21.25	6.231	5.66	3.77	3.50	-0.42
243	39.17	29.95	22.14	6.27	5.70	3.78	3.49	-0.43

[**3**][PF_6]$_3$

T (K)	CH_2 (2H)	CH_2 (2H)	CH_2 (1H)	CH_2 (1H)	CH_2 (2H)	CH_2 (2H)	CH_2 (2H)	CH (6H)	CH_3 (12H)	CH_3 (6H)
296	26.70	24.17	6.15	5.60	5.34	4.83	3.72	2.74	1.34	0.45
286	27.90	25.25	6.21	5.66	5.33	4.64	3.68	2.84	1.32	0.35
273	29.53	26.67	6.31	5.76	5.35	4.44	3.69	3.00	1.34	0.26
263	30.83	27.72	6.34	5.79	5.30	4.23	3.64	3.06	1.30	0.13
253	32.28	28.92	6.40	5.86	5.29	4.05	3.63	3.18	1.29	0.03
243	33.76	30.08	6.45	5.93	5.28	3.87	3.62	3.27	1.27	-0.06

Table S2. TD-DFT calculated excited states for **1.**

Excited State 1: Singlet-A 1.1068 eV 1120.25 nm f=0.0004 <S**2>=0.000
180 ->197 0.18776
181 ->198 -0.18484
192 ->194 -0.15289
192 ->198 -0.39899
193 ->195 0.15596
193 ->197 0.40655
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -4017.06446100
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.1419 eV 1085.77 nm f=0.0000 <S**2>=0.000
180 ->197 -0.12010
181 ->198 -0.12330
187 ->197 0.23442
191 ->195 0.13988
191 ->197 0.33114
191 ->198 0.12939
192 ->195 -0.11429
192 ->197 -0.24589
192 ->198 -0.17915
193 ->194 0.11361
193 ->197 -0.17206
193 ->198 0.24673

Excited State 3: Singlet-A 1.1425 eV 1085.22 nm f=0.0000 <S**2>=0.000
180 ->198 0.12194
181 ->197 -0.12146
187 ->198 0.23473
191 ->194 0.13972
191 ->197 -0.13026
191 ->198 0.33103
192 ->194 0.11521
192 ->197 -0.17649
192 ->198 0.24964
193 ->195 0.11248
193 ->197 0.24214
193 ->198 0.17548

Excited State 4: Singlet-A 2.0414 eV 607.34 nm f=0.0000 <S**2>=0.000
180 ->198 0.14802
181 ->197 0.14939
192 ->195 0.24490
192 ->197 0.38817
193 ->194 0.24444
193 ->198 0.38605

Excited State 5: Singlet-A 2.1144 eV 586.38 nm f=0.0002 <S**2>=0.000
180 ->197 0.10640
181 ->198 0.10673
187 ->197 0.22698
191 ->194 -0.14651
191 ->195 0.18801
191 ->197 0.35974

191 ->198 -0.12646
192 ->194 0.10176
192 ->198 0.27856
193 ->195 0.10219
193 ->197 0.27800

Excited State 6: Singlet-A 2.1151 eV 586.19 nm f=0.0002 <S**2>=0.000
180 ->198 -0.10724
181 ->197 0.10593
187 ->198 0.22692
191 ->194 0.18816
191 ->195 0.14655
191 ->197 0.12711
191 ->198 0.36063
192 ->195 0.10054
192 ->197 0.27582
193 ->194 -0.10272
193 ->198 -0.27959

Excited State 7: Singlet-A 2.8249 eV 438.89 nm f=0.0034 <S**2>=0.000
192 ->194 0.48754
192 ->198 -0.16048
193 ->195 -0.44048
193 ->197 0.14560

Excited State 8: Singlet-A 2.8492 eV 435.16 nm f=0.0184 <S**2>=0.000
192 ->194 0.38427
192 ->195 -0.22327
192 ->197 0.11476
192 ->198 -0.10141
193 ->194 0.22208
193 ->195 0.42685
193 ->197 -0.11508
193 ->198 -0.11981

Excited State 9: Singlet-A 2.8497 eV 435.08 nm f=0.0192 <S**2>=0.000
192 ->194 -0.21216
192 ->195 -0.40092
192 ->197 0.10690
192 ->198 0.11319
193 ->194 0.41153
193 ->195 -0.23264
193 ->197 0.12162
193 ->198 -0.11023

Excited State 10: Singlet-A 2.9574 eV 419.24 nm f=0.0000 <S**2>=0.000
192 ->195 0.41833
192 ->197 -0.23136
193 ->194 0.41036
193 ->198 -0.22812

Excited State 11: Singlet-A 2.9931 eV 414.23 nm f=0.0205 <S**2>=0.000
193 ->196 0.68536

Excited State 12: Singlet-A 2.9938 eV 414.13 nm f=0.0211 <S**2>=0.000
192 ->196 0.68493

Excited State 13: Singlet-A 3.0756 eV 403.13 nm f=0.0022 <S**2>=0.000
187 ->198 -0.13418
191 ->194 0.63295
191 ->198 -0.23799

Excited State 14: Singlet-A 3.0781 eV 402.80 nm f=0.0022 <S**2>=0.000
187 ->197 -0.13427
191 ->195 0.63318
191 ->197 -0.23822

Excited State 15: Singlet-A 3.2140 eV 385.77 nm f=0.0038 <S**2>=0.000
187 ->196 0.13154
191 ->196 0.68812

Excited State 16: Singlet-A 3.3187 eV 373.59 nm f=0.1009 <S**2>=0.000
184 ->194 0.12208
184 ->196 -0.14923
185 ->194 -0.10028
185 ->195 -0.11224
186 ->194 0.25164
188 ->195 -0.15387
189 ->194 -0.18197
189 ->195 0.11882
190 ->194 0.50887

Excited State 17: Singlet-A 3.3207 eV 373.37 nm f=0.1009 <S**2>=0.000
184 ->195 -0.11730
185 ->194 -0.11495
185 ->196 -0.15164
186 ->195 0.25234
188 ->194 -0.16477
188 ->195 0.16202
189 ->194 0.12633
189 ->195 0.15147
190 ->195 0.49574

Excited State 18: Singlet-A 3.3751 eV 367.35 nm f=0.0001 <S**2>=0.000
184 ->194 -0.18813
185 ->195 -0.19490
186 ->196 0.17519
188 ->194 0.16242
188 ->195 -0.35905
189 ->194 0.35982
189 ->195 0.15967
190 ->196 0.22942

Excited State 19: Singlet-A 3.3944 eV 365.26 nm f=0.0039 <S**2>=0.000
188 ->194 0.44564
188 ->195 0.18270
189 ->194 -0.21198
189 ->195 0.44001

Excited State 20: Singlet-A 3.4216 eV 362.35 nm f=0.0819 <S**2>=0.000
188 ->195 0.42267
189 ->194 0.41987

190 ->194 0.23054
190 ->195 -0.25258

Excited State 21: Singlet-A 3.4225 eV 362.26 nm f=0.0824 <S**2>=0.000
188 ->194 0.44737
189 ->195 -0.44176
190 ->194 0.18494
190 ->195 0.19882

Excited State 22: Singlet-A 3.5967 eV 344.72 nm f=0.0000 <S**2>=0.000
184 ->194 -0.18999
185 ->195 -0.18664
186 ->196 0.24145
188 ->194 -0.11711
188 ->195 0.26809
189 ->194 -0.26530
189 ->195 -0.11820
190 ->196 0.38414

Excited State 23: Singlet-A 3.6379 eV 340.81 nm f=0.0782 <S**2>=0.000
184 ->194 0.14874
184 ->195 -0.16971
184 ->196 -0.17209
185 ->194 -0.17481
185 ->195 -0.14370
186 ->194 0.23093
189 ->196 0.40774
190 ->194 -0.31469

Excited State 24: Singlet-A 3.6390 eV 340.71 nm f=0.0797 <S**2>=0.000
184 ->194 0.16889
184 ->195 0.14235
185 ->194 0.14298
185 ->195 -0.16872
185 ->196 0.17362
186 ->195 -0.22934
187 ->194 0.10022
188 ->196 0.40991
190 ->195 0.30762

Excited State 25: Singlet-A 3.6895 eV 336.05 nm f=0.0015 <S**2>=0.000
184 ->195 -0.10545
185 ->194 -0.10608
186 ->195 0.11887
187 ->194 0.60682
188 ->196 0.13764
191 ->198 -0.13115

Excited State 26: Singlet-A 3.6907 eV 335.93 nm f=0.0019 <S**2>=0.000
184 ->194 -0.10684
185 ->195 0.10480
186 ->194 -0.12017
187 ->195 0.60141
189 ->196 0.15752
191 ->197 -0.13017

Excited State 27: Singlet-A 3.7425 eV 331.29 nm f=0.0032 <S**2>=0.000
184 ->195 0.15753
185 ->194 0.16458
186 ->194 -0.19680
187 ->195 -0.25875
189 ->196 0.51796
190 ->194 0.11421

Excited State 28: Singlet-A 3.7439 eV 331.17 nm f=0.0033 <S**2>=0.000
184 ->194 -0.16982
184 ->195 -0.10342
185 ->194 -0.10089
185 ->195 0.15442
186 ->195 0.20194
187 ->194 -0.24366
188 ->196 0.51715
190 ->195 -0.11194

Excited State 29: Singlet-A 3.7856 eV 327.51 nm f=0.0000 <S**2>=0.000
184 ->194 0.28972
184 ->195 0.14155
185 ->194 -0.14263
185 ->195 0.30397
190 ->196 0.50416

Excited State 30: Singlet-A 3.8015 eV 326.14 nm f=0.0002 <S**2>=0.000
184 ->194 0.20378
184 ->195 -0.41363
184 ->197 -0.14948
185 ->194 0.42371
185 ->195 0.20312
185 ->198 0.15173

Excited State 31: Singlet-A 3.8481 eV 322.20 nm f=0.0851 <S**2>=0.000
184 ->194 -0.22983
184 ->195 0.22072
185 ->194 0.20773
185 ->195 0.22381
186 ->194 0.52348

Excited State 32: Singlet-A 3.8495 eV 322.08 nm f=0.0845 <S**2>=0.000
184 ->194 0.21436
184 ->195 0.23365
185 ->194 0.21993
185 ->195 -0.22084
186 ->195 0.52071

Excited State 33: Singlet-A 3.9497 eV 313.90 nm f=0.0100 <S**2>=0.000
182 ->194 -0.13235
182 ->195 -0.11529
183 ->194 0.11723
183 ->195 -0.13266
187 ->196 0.61321
191 ->196 -0.11297

Excited State 34: Singlet-A 4.0437 eV 306.61 nm f=0.0059 <S**2>=0.000

180 ->195 0.11322
181 ->194 -0.12087
182 ->194 0.31362
182 ->195 0.25929
183 ->194 -0.28034
183 ->195 0.29989
187 ->196 0.29202

Excited State 35: Singlet-A 4.0619 eV 305.24 nm f=0.0025 <S**2>=0.000
182 ->195 0.15891
183 ->194 0.15039
184 ->196 0.11335
185 ->196 0.57645
186 ->195 0.16469

Excited State 36: Singlet-A 4.0637 eV 305.11 nm f=0.0023 <S**2>=0.000
182 ->194 -0.16034
183 ->195 0.15652
183 ->196 -0.10064
184 ->196 0.57539
185 ->196 -0.11563
186 ->194 0.16017

Excited State 37: Singlet-A 4.0788 eV 303.97 nm f=0.0000 <S**2>=0.000
184 ->194 0.16698
185 ->195 0.15944
186 ->196 0.59964
188 ->197 0.11082
189 ->198 -0.11662
190 ->196 -0.13906

Excited State 38: Singlet-A 4.0930 eV 302.91 nm f=0.0160 <S**2>=0.000
179 ->194 -0.12461
182 ->194 -0.19994
182 ->195 0.30278
182 ->196 0.20231
183 ->194 0.29220
183 ->195 0.21626
183 ->196 -0.16785
184 ->196 -0.11150
185 ->196 -0.23325

Excited State 39: Singlet-A 4.0948 eV 302.78 nm f=0.0160 <S**2>=0.000
179 ->195 0.12434
182 ->194 -0.29456
182 ->195 -0.20758
182 ->196 -0.17085
183 ->194 -0.21053
183 ->195 0.29534
183 ->196 -0.20525
184 ->196 -0.23696
185 ->196 0.10493

Excited State 40: Singlet-A 4.1564 eV 298.30 nm f=0.0214 <S**2>=0.000
188 ->197 0.43519
189 ->198 0.47365

190 ->197 -0.16028

Excited State 41: Singlet-A 4.1565 eV 298.29 nm f=0.0225 <S**2>=0.000
188 ->198 -0.44100
189 ->197 0.49117

Excited State 42: Singlet-A 4.1616 eV 297.92 nm f=0.0000 <S**2>=0.000
186 ->196 -0.15381
188 ->197 0.47028
189 ->198 -0.44740

Excited State 43: Singlet-A 4.1671 eV 297.53 nm f=0.0086 <S**2>=0.000
188 ->198 0.47319
189 ->197 0.41428
192 ->198 0.11080
193 ->197 -0.10088

Excited State 44: Singlet-A 4.2047 eV 294.87 nm f=0.0830 <S**2>=0.000
190 ->197 0.35928
190 ->198 0.54019

Excited State 45: Singlet-A 4.2048 eV 294.86 nm f=0.0845 <S**2>=0.000
188 ->197 0.13530
190 ->197 0.52287
190 ->198 -0.35935

Excited State 46: Singlet-A 4.2800 eV 289.68 nm f=0.0000 <S**2>=0.000
180 ->194 0.17144
180 ->195 0.10770
181 ->194 -0.10966
181 ->195 0.17170
182 ->194 0.27559
182 ->195 -0.31065
183 ->194 0.31373
183 ->195 0.27416
186 ->196 -0.12090

Excited State 47: Singlet-A 4.3116 eV 287.56 nm f=0.0042 <S**2>=0.000
187 ->195 -0.12053
187 ->197 0.55260
187 ->198 0.13190
191 ->197 -0.33731

Excited State 48: Singlet-A 4.3118 eV 287.54 nm f=0.0042 <S**2>=0.000
187 ->194 -0.11995
187 ->197 -0.13177
187 ->198 0.55331
191 ->198 -0.33817

Excited State 49: Singlet-A 4.3221 eV 286.86 nm f=0.0055 <S**2>=0.000
184 ->195 -0.13553
184 ->197 0.45133
185 ->194 0.13351
185 ->198 -0.45107

Excited State 50: Singlet-A 4.4334 eV 279.66 nm f=0.0006 <S**2>=0.000

180 ->194 0.33179
180 ->195 0.16698
181 ->194 -0.26073
181 ->195 0.33859
182 ->194 -0.16867
182 ->195 0.17548
183 ->194 -0.17852
183 ->195 -0.14274
191 ->199 -0.11223

Excited State 51: Singlet-A 4.4418 eV 279.13 nm f=0.0339 <S**2>=0.000
180 ->195 0.40928
181 ->194 0.40408
181 ->195 0.15588
183 ->196 0.18057
186 ->198 0.13130
190 ->198 -0.15658

Excited State 52: Singlet-A 4.4422 eV 279.11 nm f=0.0362 <S**2>=0.000
180 ->194 0.43131
180 ->195 0.11348
181 ->194 0.10987
181 ->195 -0.39366
182 ->196 -0.16304
186 ->197 0.13221
190 ->197 -0.14873

Excited State 53: Singlet-A 4.4540 eV 278.37 nm f=0.0751 <S**2>=0.000
182 ->194 -0.20362
182 ->195 -0.10969
182 ->196 0.24703
183 ->195 0.20867
183 ->196 0.42224
184 ->197 0.19251
185 ->198 0.18836

Excited State 54: Singlet-A 4.4556 eV 278.27 nm f=0.0753 <S**2>=0.000
182 ->194 0.10199
182 ->195 -0.20074
182 ->196 0.42457
183 ->194 -0.19935
183 ->196 -0.24708
184 ->198 -0.19763
185 ->197 0.20079

Excited State 55: Singlet-A 4.4675 eV 277.52 nm f=0.0060 <S**2>=0.000
180 ->194 -0.24064
180 ->195 0.41228
181 ->194 -0.35947
181 ->195 -0.24470
183 ->195 -0.11588

Excited State 56: Singlet-A 4.4940 eV 275.89 nm f=0.0518 <S**2>=0.000
180 ->196 -0.25134
182 ->196 -0.10940
183 ->196 -0.19532

184 ->197 0.35803
184 ->198 -0.14104
185 ->197 0.14009
185 ->198 0.35632
192 ->199 -0.12736

Excited State 57: Singlet-A 4.4942 eV 275.87 nm f=0.0511 <S**2>=0.000
181 ->196 0.25655
182 ->196 -0.20633
183 ->196 0.11587
184 ->197 -0.13954
184 ->198 -0.35214
185 ->197 0.35434
185 ->198 -0.13877
193 ->199 -0.12484

Excited State 58: Singlet-A 4.5804 eV 270.69 nm f=0.0929 <S**2>=0.000
181 ->196 0.14944
186 ->197 0.64562

Excited State 59: Singlet-A 4.5813 eV 270.63 nm f=0.0942 <S**2>=0.000
180 ->196 0.15122
186 ->198 0.64469

Excited State 60: Singlet-A 4.6573 eV 266.22 nm f=0.0035 <S**2>=0.000
181 ->196 0.16726
192 ->199 0.22577
193 ->199 0.61639

Table S3: Electronic spectral data of dithiolene complexes.

Compound	λ_{max}, nm(ε, $M^{-1}cm^{-1}$)	Ref.
$[Fe(IV)(mnt)_3]^{2-}$	806(3,300), 609(1,100), 404(8,000), 247(75,000)	[1]
$[Fe(III)(mnt)_3]^{3-}$	990(700), 714(1,100), 602(sh, 1,200), 363(37,000), 250(84,000)	[1]
[**1**][PF_6]$_2$	923(4,040); 805(3,960); 593 (sh, 7,500); 362 (sh, 15 510); 305 (19 410); 218(33 550)	
[**2**][PF_6]$_2$	887 (3,380); 779 (3,280); 349 (13 310); 292 (23 270); 216 (37 050)	
[**3**][PF_6]$_3$	657 (sh, 3,790); 537 (sh, 4,920); 353 (27 620); 292 (29 010); 228 (33 530)	
[**4**][PF_6]$_3$	882 (4,550); 529 (3,470); 342 (28 900); 281(35 460) 215 (44 030)	

Table S4. Optimization energies (eV) for **3** and **2**

Spin	**Energy (eV)**		
	3	Spin	**2**
HS(S=5/2)	-140303.29442758	HS(S=2)	-127485.38134359
IS(S=3/2)	-140303.80485436	IS(S=1)	-127486.29726489
LS(S=1/2)	-140304.71820637	LS(S=0)	-127487.32960766

Table S5. Optimized coordinates of **1**.

Fe	0.000000	-0.000000	-0.000000
S	1.926000	0.846000	-1.402000
S	-1.754000	-1.160000	1.401000
S	1.882000	-0.939000	1.401000
S	-0.229000	-2.091000	-1.401000
S	-0.127000	2.099000	1.401000
S	-1.695000	1.244000	-1.402000
C	-1.073000	3.174000	0.503000
C	-2.036000	5.304000	-0.013000
H	-1.735000	5.534000	-1.028000
H	-2.121000	6.227000	0.535000
C	-3.358000	4.582000	0.014000
H	-3.715000	4.453000	1.029000
H	-4.089000	5.153000	-0.534000
C	-2.088000	2.620000	-0.504000
C	-0.002000	5.165000	1.481000
H	0.770000	4.435000	1.651000
C	-5.660000	2.915000	-0.719000
H	-5.601000	2.431000	0.250000
H	-6.432000	2.417000	-1.294000
H	-5.981000	3.940000	-0.577000
C	-4.341000	2.796000	-1.481000
H	-4.146000	1.753000	-1.651000
C	0.612000	6.338000	0.719000
H	-0.077000	7.162000	0.577000
H	0.987000	6.027000	-0.250000
H	1.448000	6.718000	1.294000

N	-1.023000	4.471000	0.639000
N	-3.206000	3.280000	-0.638000
C	3.314000	0.498000	-0.504000
C	4.474000	-2.580000	1.482000
H	3.456000	-2.884000	1.652000
C	5.648000	0.616000	0.013000
H	6.508000	0.963000	-0.535000
H	5.714000	0.990000	1.028000
C	3.286000	-0.658000	0.504000
C	5.612000	-0.889000	-0.013000
H	6.454000	-1.277000	0.535000
H	5.660000	-1.266000	-1.028000
C	4.593000	2.361000	-1.482000
H	3.592000	2.713000	-1.652000
C	5.119000	-2.257000	2.828000
H	6.151000	-1.940000	2.721000
H	5.116000	-3.146000	3.447000
H	4.567000	-1.484000	3.348000
N	4.444000	1.136000	-0.639000
N	4.384000	-1.350000	0.639000
N	-1.238000	-4.416000	-0.638000
N	-3.361000	-3.120000	0.639000
C	-1.225000	-3.118000	-0.503000
C	-2.291000	-5.199000	0.013000
H	-2.420000	-6.117000	-0.534000
H	-2.001000	-5.443000	1.028000
C	-3.576000	-4.414000	-0.013000
H	-3.926000	-4.268000	-1.028000

H	-4.334000	-4.949000	0.535000
C	-2.213000	-2.516000	0.504000
C	-4.472000	-2.583000	1.481000
H	-4.226000	-1.550000	1.651000
C	-5.795000	-2.637000	0.719000
H	-6.165000	-3.646000	0.577000
H	-5.713000	-2.157000	-0.250000
H	-6.541000	-2.103000	1.294000
C	-0.252000	-5.158000	-1.481000
H	0.554000	-4.468000	-1.651000
C	5.183000	-3.699000	0.721000
H	4.726000	-3.869000	-0.248000
H	5.093000	-4.613000	1.296000
H	6.241000	-3.515000	0.579000
C	5.356000	3.444000	-0.720000
H	4.907000	3.635000	0.248000
H	5.311000	4.360000	-1.296000
H	6.404000	3.209000	-0.578000
C	-4.350000	3.518000	-2.826000
H	-4.540000	4.581000	-2.720000
H	-5.140000	3.108000	-3.446000
H	-3.410000	3.381000	-3.347000
C	5.223000	2.007000	-2.827000
H	6.239000	1.640000	-2.720000
H	5.263000	2.895000	-3.447000
H	4.634000	1.261000	-3.347000
C	-0.604000	5.562000	2.827000
H	0.167000	6.004000	3.446000

H	-0.998000	4.698000	3.347000
H	-1.395000	6.298000	2.720000
C	-0.873000	-5.527000	-2.826000
H	-0.124000	-6.006000	-3.446000
H	-1.224000	-4.644000	-3.347000
H	-1.699000	-6.222000	-2.720000
C	0.304000	-6.360000	-0.719000
H	-0.424000	-7.150000	-0.577000
H	0.694000	-6.067000	0.250000
H	1.120000	-6.780000	-1.294000
C	-4.516000	-3.303000	2.827000
H	-4.757000	-4.356000	2.720000
H	-5.284000	-2.856000	3.446000
H	-3.570000	-3.212000	3.347000

Table S6. Optimized coordinates for **3**.

Fe	0.021000	-0.250000	-0.146000
S	-0.942000	1.400000	-1.355000
S	1.048000	-1.833000	1.110000
S	1.152000	1.299000	1.027000
S	1.672000	-0.491000	-1.668000
S	-1.614000	-0.220000	1.410000
S	-1.224000	-1.743000	-1.303000
C	-2.900000	-1.075000	0.748000
C	-5.217000	-1.738000	0.590000
H	-5.583000	-1.273000	-0.178000
H	-5.927000	-1.862000	1.238000
C	-4.684000	-3.064000	0.167000
H	-4.421000	-3.574000	0.949000
H	-5.376000	-3.560000	-0.298000
C	-2.636000	-1.968000	-0.422000
C	-4.516000	0.161000	2.129000
H	-3.702000	0.517000	2.542000
C	-3.603000	-5.241000	-1.491000
H	-3.127000	-5.436000	-0.680000
H	-3.291000	-5.819000	-2.191000
H	-4.542000	-5.383000	-1.353000
C	-3.359000	-3.776000	-1.889000
H	-2.428000	-3.704000	-2.190000
C	-5.148000	1.232000	1.313000
H	-5.966000	0.905000	0.932000
H	-4.550000	1.494000	0.608000
H	-5.335000	1.991000	1.870000

N	-4.134000	-0.944000	1.184000
N	-3.520000	-2.887000	-0.723000
C	-0.537000	2.821000	-0.518000
C	2.496000	3.947000	1.514000
H	2.799000	3.019000	1.610000
C	-0.795000	5.118000	0.139000
H	-1.138000	5.921000	-0.284000
H	-1.166000	5.064000	1.033000
C	0.628000	2.788000	0.420000
C	0.669000	5.185000	0.214000
H	0.930000	5.909000	0.804000
H	1.030000	5.371000	-0.667000
C	-2.414000	4.049000	-1.505000
H	-2.660000	3.153000	-1.817000
C	2.282000	4.478000	2.874000
H	1.918000	5.365000	2.818000
H	3.118000	4.505000	3.344000
H	1.667000	3.911000	3.347000
N	-1.201000	3.932000	-0.642000
N	1.226000	3.919000	0.716000
N	4.183000	-0.964000	-1.005000
N	3.419000	-2.933000	0.822000
C	2.928000	-1.167000	-0.761000
C	5.219000	-1.697000	-0.195000
H	6.045000	-1.771000	-0.699000
H	5.404000	-1.212000	0.625000
C	4.699000	-3.042000	0.121000
H	4.579000	-3.546000	-0.699000

H	5.336000	-3.516000	0.677000
C	2.555000	-2.049000	0.409000
C	3.139000	-3.850000	1.957000
H	2.222000	-3.682000	2.258000
C	3.213000	-5.310000	1.474000
H	4.069000	-5.471000	1.070000
H	2.519000	-5.469000	0.829000
H	3.096000	-5.901000	2.222000
C	4.663000	0.059000	-2.006000
H	3.872000	0.424000	-2.457000
C	3.568000	4.690000	0.786000
H	3.608000	4.384000	-0.124000
H	4.414000	4.532000	1.213000
H	3.373000	5.629000	0.799000
C	-3.567000	4.611000	-0.714000
H	-3.373000	4.548000	0.224000
H	-4.364000	4.112000	-0.910000
H	-3.700000	5.532000	-0.952000
C	-4.224000	-3.358000	-3.011000
H	-5.139000	-3.344000	-2.720000
H	-4.129000	-3.979000	-3.737000
H	-3.967000	-2.481000	-3.303000
C	-2.075000	4.893000	-2.709000
H	-1.371000	5.506000	-2.482000
H	-2.851000	5.387000	-2.983000
H	-1.786000	4.326000	-3.428000
C	-5.408000	-0.317000	3.188000
H	-5.469000	0.347000	3.880000

H	-5.062000	-1.132000	3.556000
H	-6.282000	-0.476000	2.822000
C	5.480000	-0.576000	-3.013000
H	5.796000	0.085000	-3.633000
H	4.958000	-1.231000	-3.483000
H	6.229000	-1.006000	-2.593000
C	5.307000	1.163000	-1.284000
H	6.030000	0.819000	-0.754000
H	4.665000	1.589000	-0.712000
H	5.648000	1.802000	-1.914000
C	4.044000	-3.584000	3.098000
H	4.955000	-3.698000	2.817000
H	3.850000	-4.196000	3.811000
H	3.914000	-2.684000	3.405000

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