Supplementary Information

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

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Refinement details for $[2][\text{PF}_6]_2$ and $[3][\text{FeCl}_4][\text{PF}_6]_2$

Methods for vibrating sample magnetometry of solid-state sample.

Figure S1. $^1$H NMR spectrum of $[4][\text{PF}_6]_3$.

Figure S2. $^1$H NMR spectrum of $[3][\text{PF}_6]_3$.

Figure S3. Inverse molar magnetic susceptibility of $[4][\text{PF}_6]_3$.

Figure S4. Fe$^{III}$ based couples of $[1][\text{PF}_6]_2$, $[2][\text{PF}_6]_2$, $[3][\text{PF}_6]_3$, and $[4][\text{PF}_6]_3$.

Figure S5. Ligand-based couples and DPV of $[1][\text{PF}_6]_2$.

Figure S6. Ligand-based couples at different scan rates and DPV of $[3][\text{PF}_6]_3$.

Figure S7. EDDMs of 1.

Figure S8. Molecular orbital diagram for 3.

Table S1. Temperature dependent $\delta_{\text{para}}$ for $[3][\text{PF}_6]_3$ and $[4][\text{PF}_6]_3$.

Table S2. TD-DFT predicted excited states transitions of 1.

Table S3. Electronic spectra for 1, $[2][\text{PF}_6]_2$, $[3][\text{PF}_6]_3$, and $[4][\text{PF}_6]_3$.

Table S4. Optimization energies of high and low spin states of 2 and 3.

Table S5. Optimized coordinates of 1.

Table S6. Optimized coordinates 3.
Refinement details for [2][PF₆]₂ and [3][FeCl₄][PF₆]₂

All nonhydrogen atoms were refined anisotropically by full matrix least squares against F². 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 CH₂ and CH₃ moieties, respectively. Methyl CH₃ were allowed to rotate but not to tip to best fit the experimental electron density. Uᵦₒ(H) values were set to a multiple of Uₑₒ(C) with 1.5 for CH₃ and 1.2 for CH₂ units, respectively.

The crystal of [2][PF₆]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 [PF₆]⁻ 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. Uᵦᵦ 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][FeCl₄][PF₆]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). Uᵦᵦ 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 [PF₆]⁻ and the [FeCl₄]⁻ 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 [PF₆]⁻ 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 \([\text{PF}_6]^-\) anion. The \([\text{FeCl}_4]^-\) 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 \([\text{PF}_6]^-\) anion, to 0.344(8) to 0.656(8) for the second \([\text{PF}_6]^-\) anion, and to 0.413(12) to 0.587(12) for the \([\text{FeCl}_4]^-\) anion.

Methods for vibrating sample magnetometry of solid-state sample

The raw data were converted to inverse molar magnetic susceptibility \((\chi_M^{-1})\) and fit with Curie-Weiss law: 

\[ \chi = C/(T - \theta) \]

for \(T > 75\text{K}\) using \(1/\chi = 46.118 + 1.7964(T)\).

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

\[ \theta = -A/B, \quad C = 1/B, \quad \mu_{Fe} = 2.828 \times \sqrt{C} \]

The results are \(\theta = -25.67\), \(C = 0.56 \text{ emu K/mol Oe}\) and \(\mu_{Fe} = 2.1 \mu_B\). A negative value for \(\theta\) implies antiferromagnetic interactions dominate. The magnetization data for \(H = 5\) kOe was converted to \(\chi_M^{-1}\) 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 \((\mu_{Fe})\) was derived using eqn. X with \(\theta = -3.07\), \(C = 0.39 \text{ emu K/mol Oe}\) and \(\mu_{Fe} = 1.8 \mu_B\). The value for \(\theta\) is negative but smaller than what was observed at \(H = 1\) kOe indicating weak antiferromagnetic interactions dominate the system. The \(\mu_{Fe}\) at both \(H = 1\) kOe and 5 kOe support low spin Fe(III).
Figure S1. $^1$H NMR spectrum of $[4][\text{PF}_6]_3$ collected in CD ($\delta = 1.93$ ppm) at 296 K.

Figure S2. $^1$H NMR spectrum of $[3][\text{PF}_6]_3$ recorded as described in Figure S1.
All electrochemical data presented below is recorded as described in Figure 3.

Figure S4. Fe^{III} based redox couples for [1][PF₆]₂ (blue), [2][PF₆]₂ (orange), [3][PF₆]₃ (red), and [4][PF₆]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. \( \delta_{\text{para}} \) 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) | \( \text{CH}_2 \) | \( \text{CH}_2 \) | \( \text{CH}_2 \) | \( \text{CH}_2 \) | \( \text{CH}_2 \) | \( \text{CH}_2 \) | \( \text{CH} \) (6H) | \( \text{CH}_3 \) | \( \text{CH}_3 \) (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 | Singlet-A    | E (eV)   | λ (nm)  | f  | <S^2> |
|---------------|--------------|----------|---------|----|-------|
| 1             | Singlet-A    | 1.1068   | 1120.25 | 0.0004 | 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 | Singlet-A    | E (eV)   | λ (nm)  | f  | <S^2> |
|---------------|--------------|----------|---------|----|-------|
| 2             | Singlet-A    | 1.1419   | 1085.77 | 0.0000 | 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 | Singlet-A    | E (eV)   | λ (nm)  | f  | <S^2> |
|---------------|--------------|----------|---------|----|-------|
| 3             | Singlet-A    | 1.1425   | 1085.22 | 0.0000 | 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 | Singlet-A    | E (eV)   | λ (nm)  | f  | <S^2> |
|---------------|--------------|----------|---------|----|-------|
| 4             | Singlet-A    | 2.0414   | 607.34  | 0.0000 | 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 | Singlet-A    | E (eV)   | λ (nm)  | f  | <S^2> |
|---------------|--------------|----------|---------|----|-------|
| 5             | Singlet-A    | 2.1144   | 586.38  | 0.0002 | 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      |
| Energy (eV) | Wavelength (nm) | Oscillator Strength | Transition Probability | sq. Overlap |
|------------|----------------|---------------------|------------------------|-------------|
| 2.1151     | 586.19         | 0.0002              | 0.000                  | 0.000       |
| 2.8249     | 438.89         | 0.0034              | 0.000                  | 0.000       |
| 2.8492     | 435.16         | 0.0184              | 0.000                  | 0.000       |
| 2.8497     | 435.08         | 0.0192              | 0.000                  | 0.000       |
| 2.9574     | 419.24         | 0.0000              | 0.000                  | 0.000       |
| 2.9931     | 414.23         | 0.0205              | 0.000                  | 0.000       |
| 2.9938     | 414.13         | 0.0211              | 0.000                  | 0.000       |
| Excited State | Singlet-A | Energy (eV) | Wavelength (nm) | f | \( <S^2> \) |
|---------------|-----------|-------------|-----------------|---|-----------|
| 13            | 3.0756    | 403.13      | 0.0022          | 0.000 |
| 14            | 3.0781    | 402.80      | 0.0022          | 0.000 |
| 15            | 3.2140    | 385.77      | 0.0038          | 0.000 |
| 16            | 3.3187    | 373.59      | 0.1009          | 0.000 |
| 17            | 3.3207    | 373.37      | 0.1009          | 0.000 |
| 18            | 3.3751    | 367.35      | 0.0001          | 0.000 |
| 19            | 3.3944    | 365.26      | 0.0039          | 0.000 |
| 20            | 3.4216    | 362.35      | 0.0819          | 0.000 |
Excited State 21: Singlet-A

190 -> 194  0.23054
190 -> 195  -0.25258

Energy: 3.4225 eV  Wavelength: 362.26 nm  Oscillator Strength: 0.0824  

Excited State 22: Singlet-A

188 -> 194  0.44737
189 -> 195  -0.25258
190 -> 194  0.18494
190 -> 195  0.19882

Energy: 3.5967 eV  Wavelength: 344.72 nm  Oscillator Strength: 0.0000

Excited State 23: Singlet-A

184 -> 194  -0.18999
185 -> 195  -0.18664
186 -> 196  0.24145
188 -> 194  -0.11711
188 -> 195  -0.11820
190 -> 196  0.38414

Energy: 3.6379 eV  Wavelength: 340.81 nm  Oscillator Strength: 0.0782

Excited State 24: Singlet-A

184 -> 194  0.14874
184 -> 195  -0.16971
184 -> 196  -0.17209
185 -> 194  -0.17481
185 -> 195  -0.14370
186 -> 194  0.23093
186 -> 196  0.40774
190 -> 194  -0.31469

Energy: 3.6390 eV  Wavelength: 340.71 nm  Oscillator Strength: 0.0797

Excited State 25: Singlet-A

184 -> 194  0.16889
184 -> 195  0.14235
185 -> 194  0.14298
185 -> 195  -0.16872
186 -> 195  0.17362
186 -> 196  -0.22934
187 -> 194  0.10022
188 -> 196  0.40991
190 -> 195  0.30762

Energy: 3.6895 eV  Wavelength: 336.05 nm  Oscillator Strength: 0.0015

Excited State 26: Singlet-A

184 -> 195  -0.10545
185 -> 194  -0.10608
186 -> 195  0.11887
187 -> 194  0.60682
188 -> 196  0.13764
191 -> 198  -0.13115

Energy: 3.6907 eV  Wavelength: 335.93 nm  Oscillator Strength: 0.0019

Excited State 27: Singlet-A

184 -> 194  -0.10684
185 -> 195  0.10480
186 -> 194  -0.12017
187 -> 195  0.60141
189 -> 196  0.15752
191 -> 197  -0.13017

Energy: 3.6907 eV  Wavelength: 335.93 nm  Oscillator Strength: 0.0019
| Excited State | Energy (eV) | Wavelength (nm) | f | \langle S^2 \rangle |
|--------------|-------------|----------------|---|-----------------|
| 27: Singlet-A | 3.7425 | 331.29 | 0.0032 | 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 |
| 28: Singlet-A | 3.7439 | 331.17 | 0.0033 | 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 |
| 29: Singlet-A | 3.7856 | 327.51 | 0.0000 | 0.000 |
| 184 -> 194 | 0.28972 |
| 184 -> 195 | 0.14155 |
| 185 -> 194 | -0.14263 |
| 185 -> 195 | 0.30397 |
| 190 -> 196 | 0.50416 |
| 30: Singlet-A | 3.8015 | 326.14 | 0.0002 | 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 |
| 31: Singlet-A | 3.8481 | 322.20 | 0.0851 | 0.000 |
| 184 -> 194 | -0.22983 |
| 184 -> 195 | 0.22072 |
| 185 -> 194 | 0.20773 |
| 185 -> 195 | 0.22381 |
| 186 -> 194 | 0.52348 |
| 32: Singlet-A | 3.8495 | 322.08 | 0.0845 | 0.000 |
| 184 -> 194 | 0.21436 |
| 184 -> 195 | 0.23365 |
| 185 -> 194 | 0.21993 |
| 185 -> 195 | -0.22084 |
| 186 -> 195 | 0.52071 |
| 33: Singlet-A | 3.9497 | 313.90 | 0.0100 | 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 |
| 34: Singlet-A | 4.0437 | 306.61 | 0.0059 | 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  -0.10006 
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
| Excited State | Type       | Energy (eV) | Wavelength (nm) | f | S^2 |
|--------------|------------|-------------|-----------------|---|-----|
| 51           | Singlet-A  | 4.4418      | 279.13          | 0.0339 | 0.000 |
| 52           | Singlet-A  | 4.4422      | 279.11          | 0.0362 | 0.000 |
| 53           | Singlet-A  | 4.4540      | 278.37          | 0.0751 | 0.000 |
| 54           | Singlet-A  | 4.4556      | 278.27          | 0.0753 | 0.000 |
| 55           | Singlet-A  | 4.4675      | 277.52          | 0.0060 | 0.000 |
| 56           | Singlet-A  | 4.4940      | 275.89          | 0.0518 | 0.000 |
| Transition | Coefficient | Energy (eV) | Wavelength (nm) | Oscillator Strength (f) | Squared Transition Dipole Moment (S^2) |
|------------|-------------|-------------|-----------------|------------------------|-------------------------------------|
| 184 -> 197 | 0.35803     | 4.4942      | 275.87          | 0.0511                 | 0.000                               |
| 184 -> 198 | -0.14104    | 4.5804      | 270.69          | 0.0929                 | 0.000                               |
| 185 -> 197 | 0.14009     | 4.5813      | 270.63          | 0.0942                 | 0.000                               |
| 185 -> 198 | 0.35632     | 4.6573      | 266.22          | 0.0035                 | 0.000                               |

Excited State 57: Singlet-A
Excited State 58: Singlet-A
Excited State 59: Singlet-A
Excited State 60: Singlet-A
Table S3: Electronic spectral data of dithiolene complexes.

| Compound                  | $\lambda_{\text{max}}$ (nm) | $\varepsilon$ (M$^{-1}$ cm$^{-1}$) | Ref. |
|---------------------------|------------------------------|-----------------------------------|------|
| [Fe(IV)(mnt)$_2$]$^{2-}$ | 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)  | Spin  | Energy (eV)  |
|-------|--------------|-------|--------------|
| 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.

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| 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   |
|   |      X   |       Y   |       Z   |
|---|---------|---------|---------|
| 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 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| 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.

| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| 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
1. Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Walton, J. R., Spectroelectrochemical (electronic and FTIR) studies of trismaleonitriledithiolate) complexes. *Inorg. Chem.* **1988**, 27 (5), 884-90.