

Photoswitchable electrochemical behaviour of a [FeFe] hydrogenases model with a dithienylethene derivative

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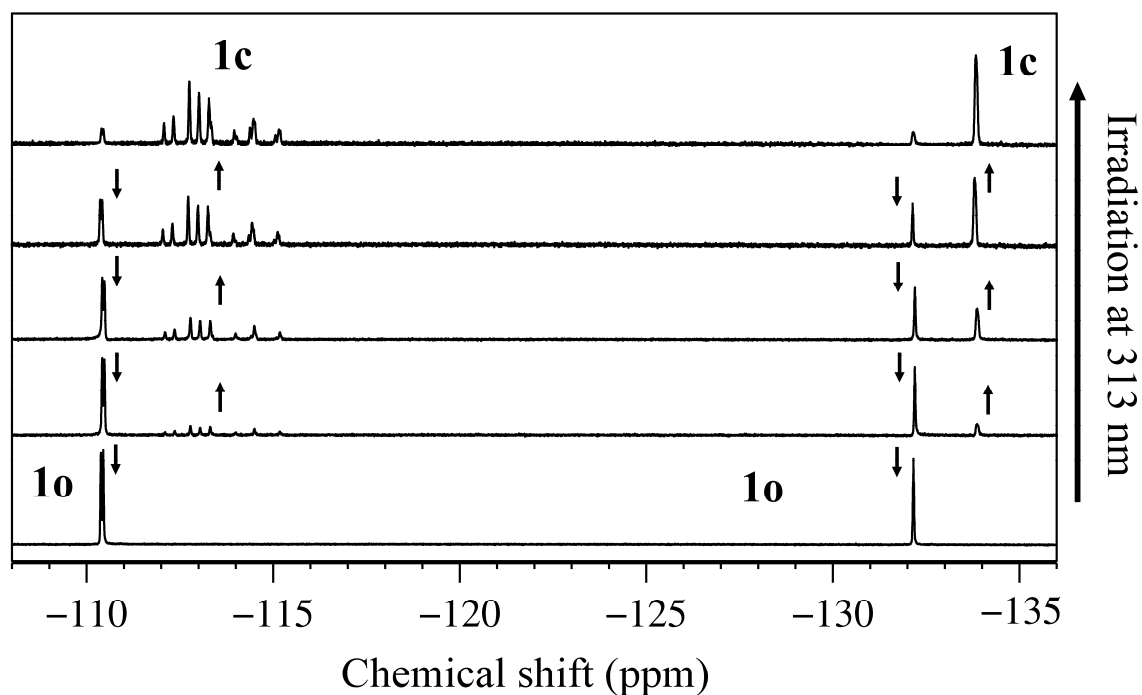


Figure S1. The ^{19}F NMR spectral changes of **1o** in CD_2Cl_2 upon irradiation with 313 nm, showing the conversion of **1o** \rightarrow **1c**.

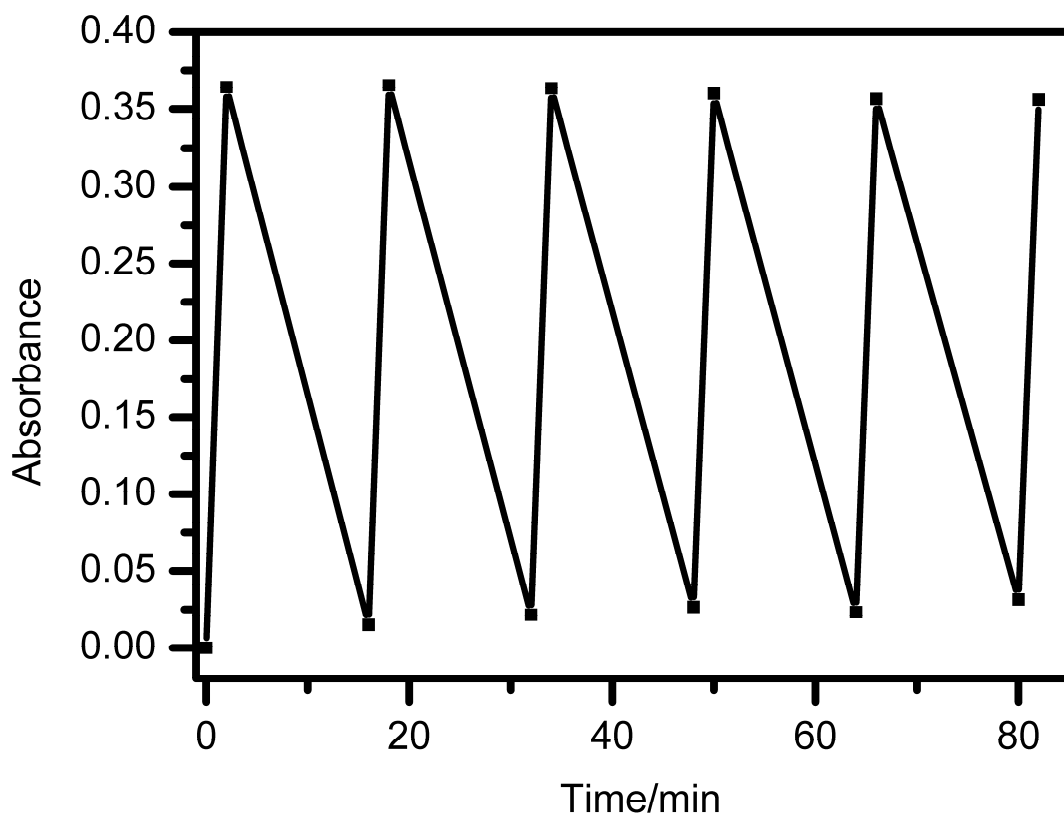


Figure S2. UV-vis absorbance changes of complex **1** (2×10^{-5} M) in CH_3CN at 600 nm on alternate excitation at 313 and > 460 nm over six cycles at room temperature.

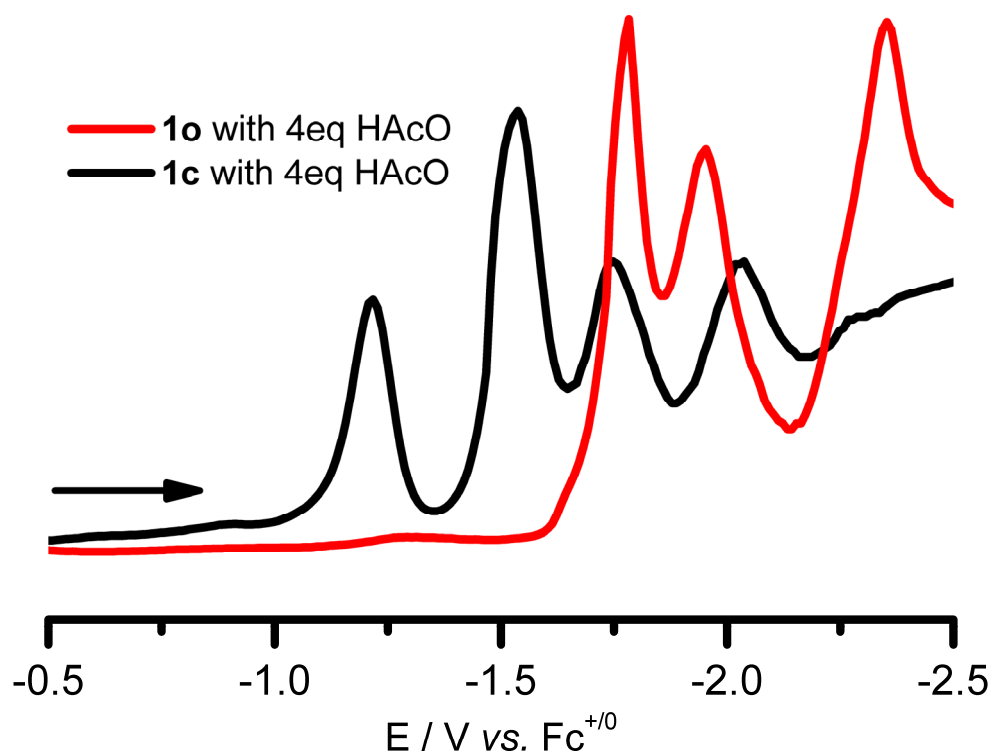


Figure S3. Differential pulse voltammograms of **1o** and **1c** (1.0 mM with 4 mM HAcO) in 0.1 M ⁿBu₄NPF₆/MeCN at a scan rate of 20 mVs⁻¹ vs. Fc^{+/0}.

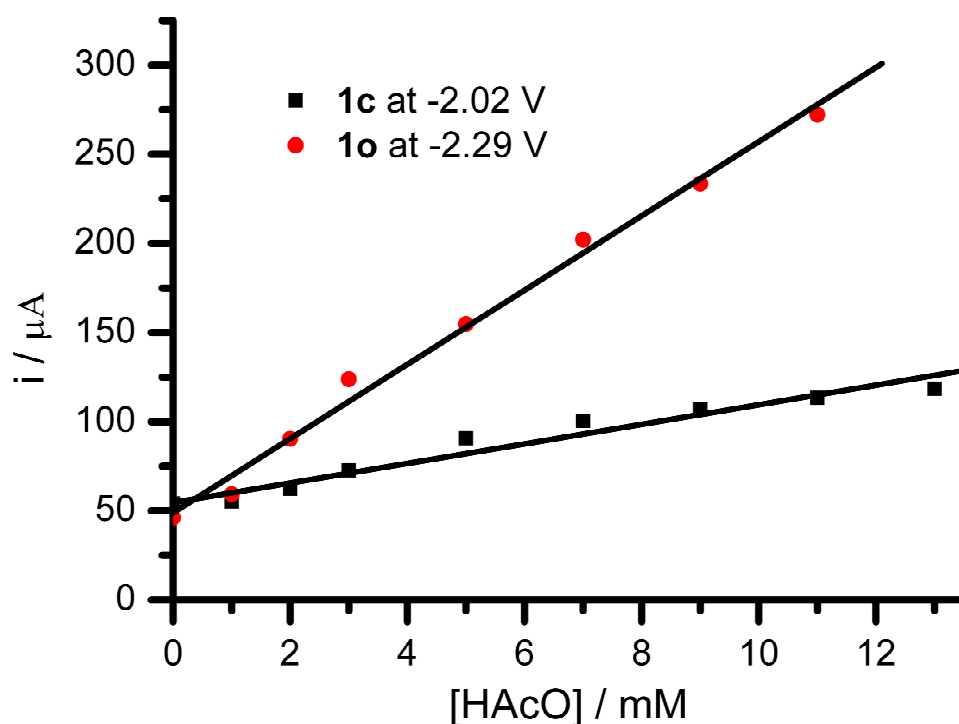


Figure S4. The plots of the current heights of electrocatalytic events for **1o** and **1c** vs. the concentration of HOAc.

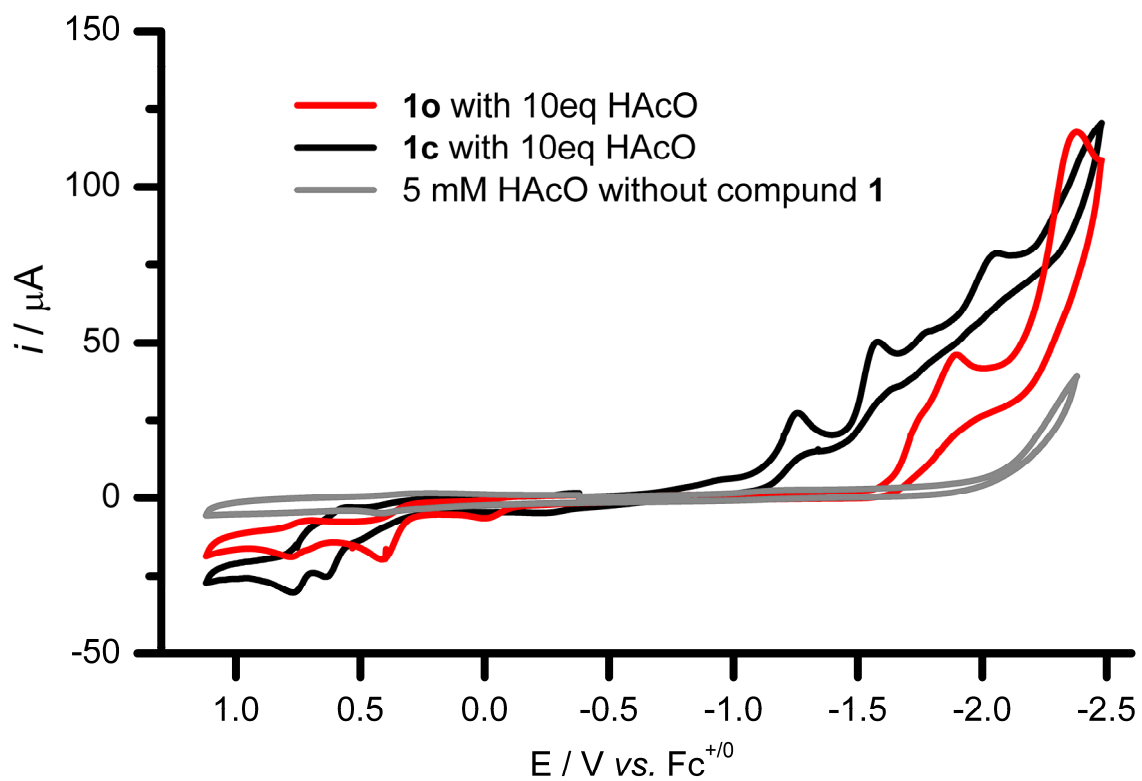
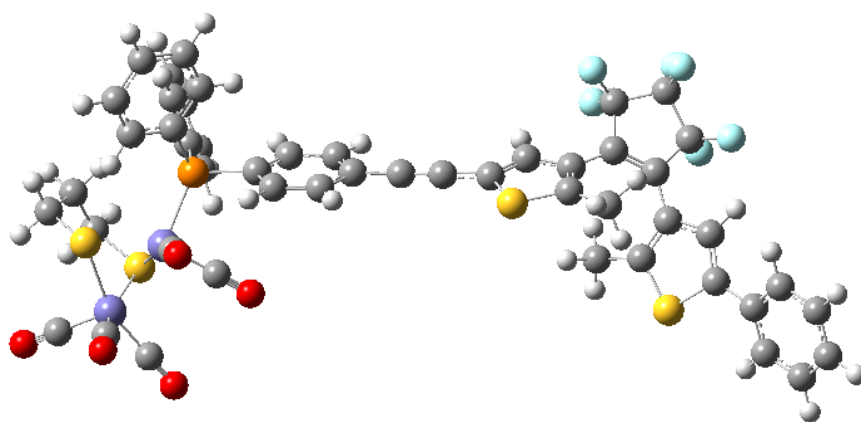
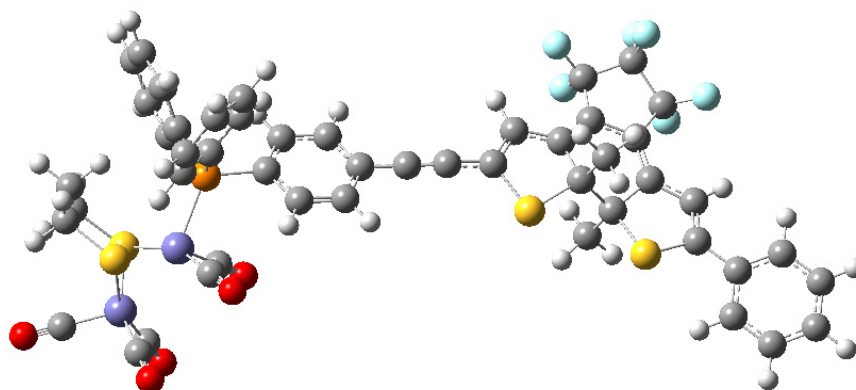


Figure S5. Cyclic voltammetry of **1** in the fourth irradiation cycle, 0.5 mM **1** with 5mM HAcO in 0.1 M $n\text{-Bu}_4\text{NPF}_6/\text{MeCN}$ at a scan rate of 100 mVs^{-1} vs. Fc^+/Fc .

DFT Calculations:



1o

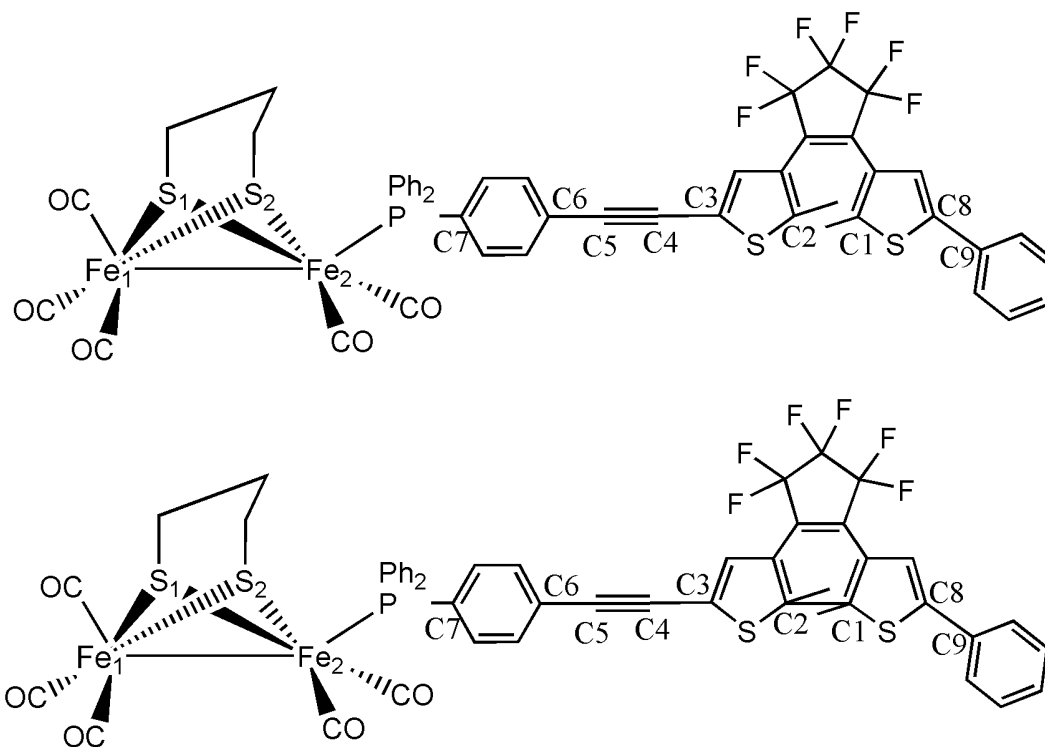


1c

Figure S6. The optimized structures of **1o** and **1c** in the ground state by DFT method at the PBE1PBE level. The purple, orange, yellow, red, light green, gray, and white spheres represent the iron, phosphorus, sulfur, oxygen, fluorine, carbon, and hydrogen atoms, respectively.

Table S1. Selected Bond Length (Å) and Bond Angle (°) of **1o** and **1c** on Calculated Ground State Geometries at the PBE1PBE level

| | 1o | 1c | | 1o | 1c |
|---------|-------------|-----------|------------|-----------|-----------|
| | Bond Length | | Bond Angle | | |
| C1-C2 | 3.5617 | 1.5359 | Fe1-S2-Fe2 | 65.421 | 65.347 |
| C3-C4 | 1.4025 | 1.4002 | Fe1-S1-Fe2 | 65.197 | 65.177 |
| C4-C5 | 1.2169 | 1.2181 | S1-Fe1-S2 | 85.779 | 85.741 |
| C5-C6 | 1.4186 | 1.4173 | S1-Fe2-S2 | 84.581 | 84.543 |
| C7-P | 1.8546 | 1.8564 | Fe2-P-C7 | 112.226 | 112.432 |
| C8-C9 | 1.4635 | 1.4607 | C6-C5-C4 | 179.030 | 179.134 |
| Fe1-Fe2 | 2.4730 | 2.4719 | C5-C4-C3 | 179.314 | 178.135 |
| Fe1-S1 | 2.2784 | 2.2784 | | | |
| Fe1-S2 | 2.2787 | 2.2794 | | | |
| Fe2-S1 | 2.3117 | 2.3107 | | | |
| Fe2-S2 | 2.2975 | 2.2993 | | | |
| S1-S2 | 3.1015 | 3.1009 | | | |
| Fe2-P | 2.2544 | 2.2515 | | | |



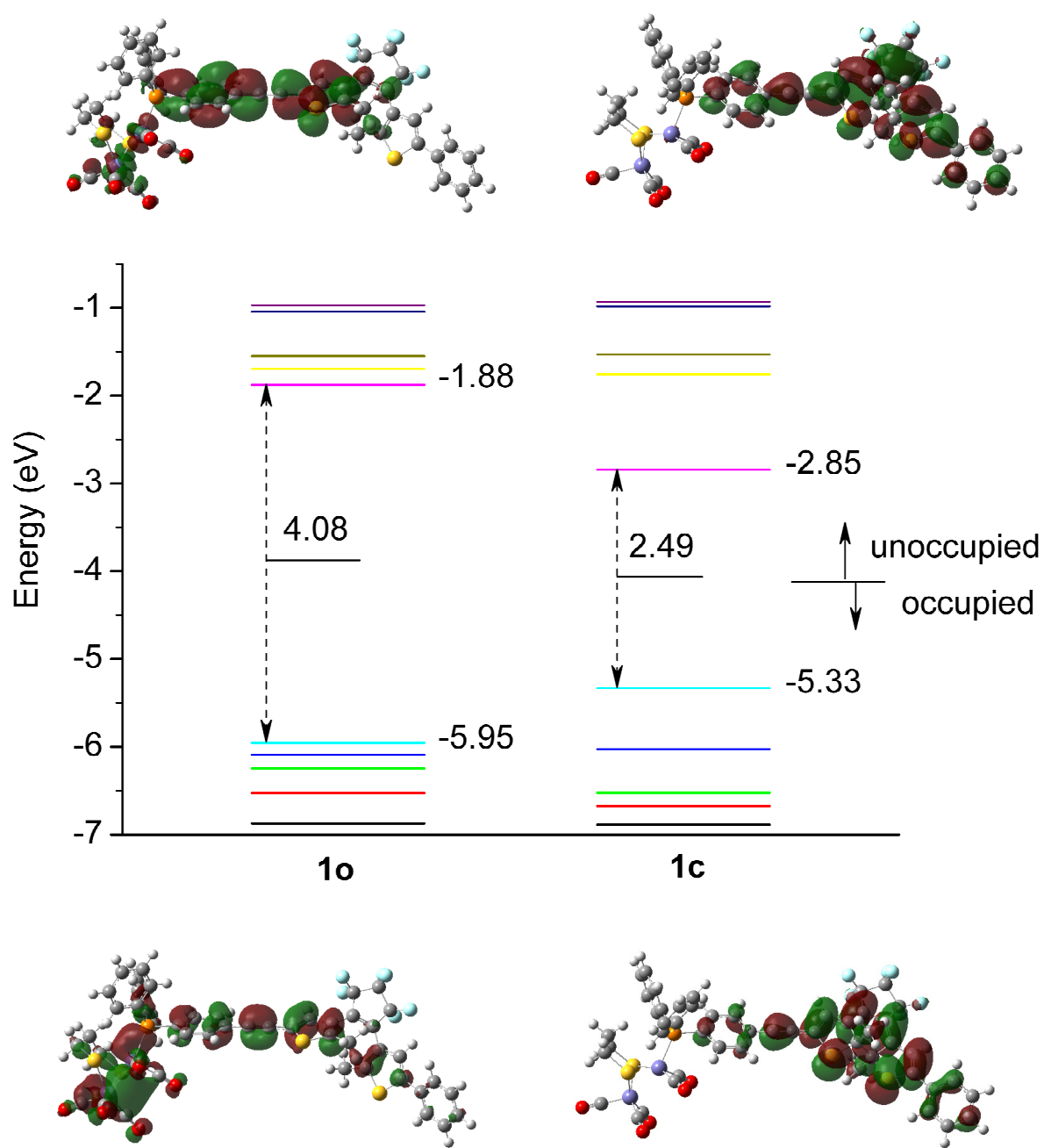


Figure S7. Plots of Energy Level of Frontier Molecular Orbitals HOMO-4 ~ LUMO+4 for ring open compound (**1o**) and ring close compound (**1c**) in the Ground States in Acetonitrile Media by TDDFT method at the PBE1PBE level, together with the electron density diagrams of the HOMO and LUMO orbitals for each compounds (isovalue = 0.02).

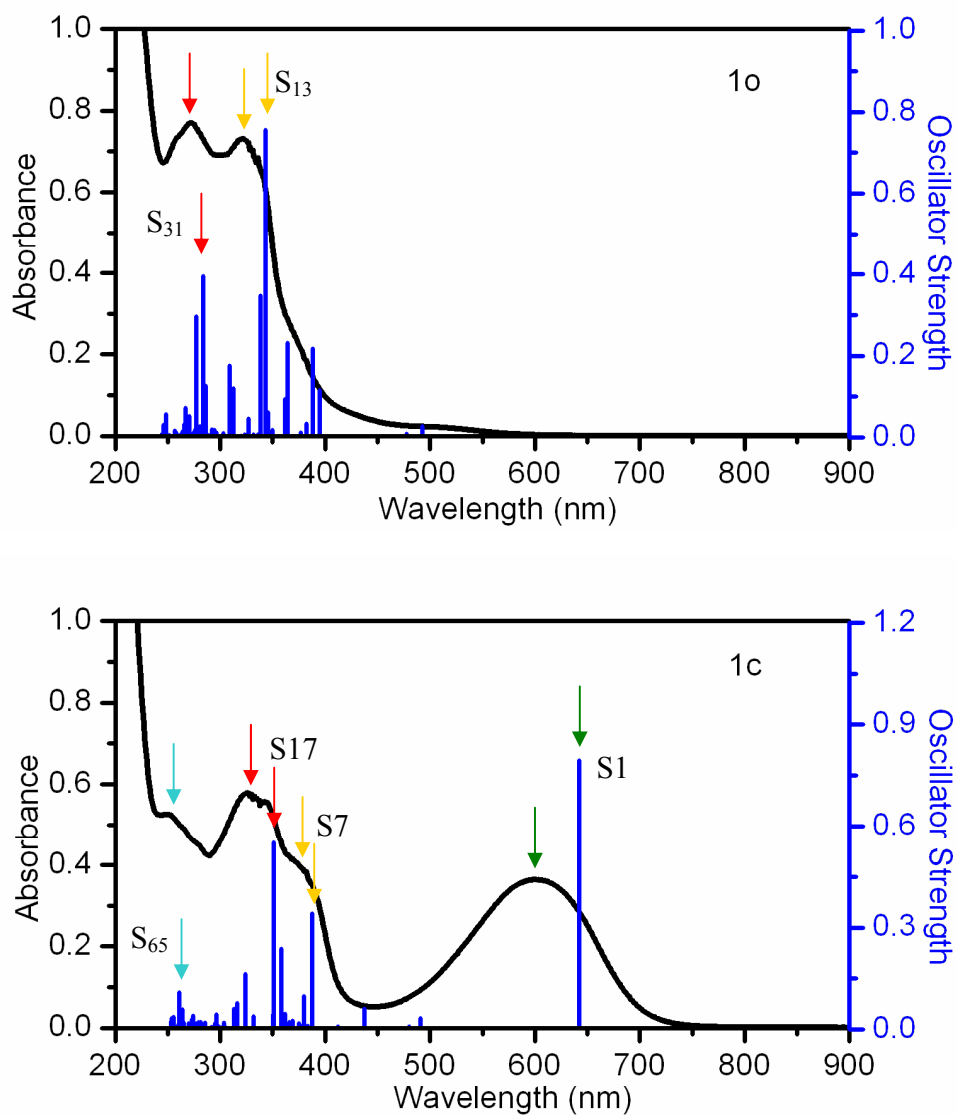
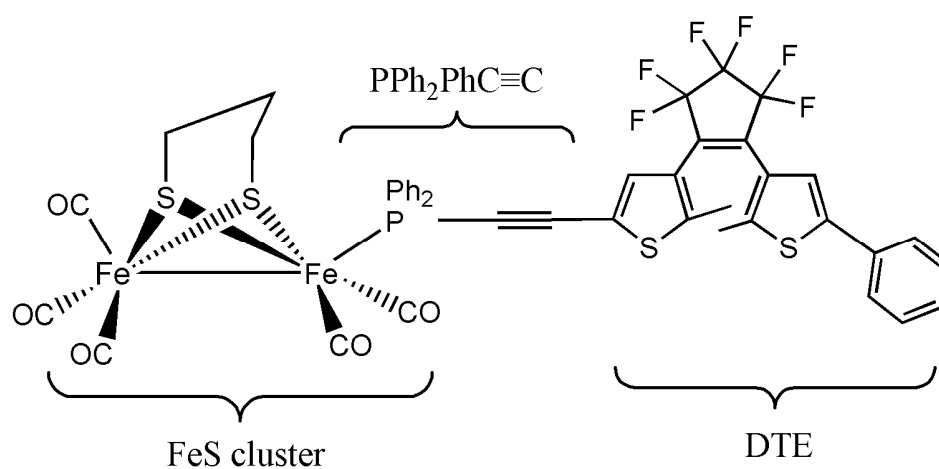


Figure S8. Calculated (blue bars) and measured (black line) UV-vis spectrum of (top) **1o** and (bottom) **1c** in Acetonitrile Media at ambient temperature.

Table S2. The Absorption Transitions for **1o** in Acetonitrile Media Calculated by the TD-DFT Method

| Orbital | Energy (eV) | MO Contribution (%) | | |
|---------|-------------|---------------------|------------------------|-------|
| | | FeS cluster | PPh ₂ PhC≡C | DTE |
| LUMO+3 | -1.0463 | 0.63 | 1.12 | 98.26 |
| LUMO+2 | -1.5513 | 50.90 | 23.01 | 26.08 |
| LUMO+1 | -1.6953 | 27.02 | 4.24 | 68.66 |
| LUMO | -1.8765 | 27.51 | 37.44 | 35.04 |
| HOMO | -5.9541 | 55.74 | 24.60 | 19.66 |
| HOMO-1 | -6.0907 | 36.50 | 11.76 | 51.74 |

| States | E, nm (eV) | O.S. | component | CI coef. | Assignment | Measured Wavelength (nm) |
|-----------------|---------------|--------|---------------|----------|-----------------|--------------------------|
| | | | HOMO→LUMO+2 | 0.3580 | IC/IL | |
| S ₁₃ | 342.89 (3.62) | 0.7568 | HOMO-1→LUMO+1 | -0.2862 | IL/IC/CLCT/LLCT | 321 |
| | | | HOMO→LUMO | -0.2530 | IC/IL/CLCT | |
| | | | HOMO-1→LUMO+3 | 0.4742 | IL/CLCT/LLCT | |
| S ₃₁ | 283.79 (4.37) | 0.3965 | HOMO→LUMO+3 | 0.3776 | CLCT/IL/LLCT | 271 |



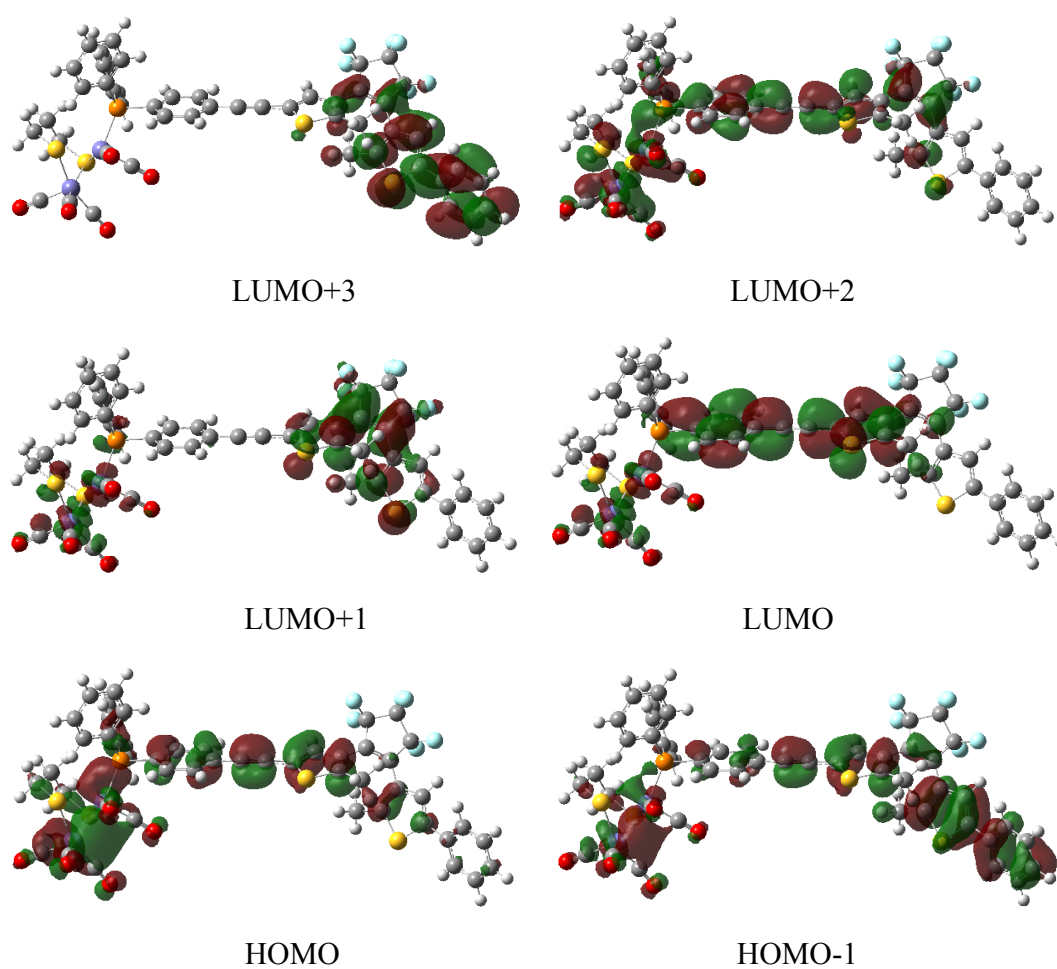


Figure S9. Electron-density diagrams of the frontier molecular orbitals involved in the absorption of compound **10** in Acetonitrile Media (isovalue = 0.02).

Table S3. The Absorption Transitions for **1c** in Acetonitrile Media Calculated by the TD-DFT Method

| Orbital | Energy (eV) | MO Contribution (%) | | |
|---------|-------------|---------------------|------------------------|-------|
| | | FeS cluster | PPh ₂ PhC≡C | DTE |
| LUMO+2 | -1.5309 | 39.02 | 26.20 | 34.78 |
| LUMO+1 | -1.7598 | 63.60 | 21.16 | 15.24 |
| LUMO | -2.8463 | 1.08 | 15.61 | 83.31 |
| HOMO | -5.3343 | 0.53 | 8.62 | 90.85 |
| HOMO-1 | -6.0238 | 88.21 | 10.96 | 0.83 |
| HOMO-4 | -6.8858 | 91.10 | 4.83 | 4.07 |
| HOMO-5 | -6.9941 | 33.09 | 36.25 | 30.66 |

| States | E, nm (eV) | O.S. | component | CI coef. | Assignment | Measured Wavelength (nm) |
|-----------------|---------------|--------|---------------|----------|-----------------|--------------------------|
| S ₁ | 641.90 (1.93) | 0.7951 | HOMO→LUMO | 0.6272 | IL | 600 |
| S ₇ | 387.74 (3.20) | 0.3424 | HOMO-1→LUMO+1 | 0.3472 | IC/CLCT/IL | Sh |
| | | | HOMO→LUMO+1 | 0.2615 | LCCT/IL/LLCT | |
| S ₁₇ | 351.13 (3.53) | 0.5512 | HOMO-5→LUMO | 0.4977 | IL/CLCT/LLCT | 326 |
| | | | HOMO-4→LUMO | -0.2394 | CLCT | |
| | | | HOMO-5→LUMO+1 | 0.2858 | IC/LCCT/IL | |
| S ₆₅ | 261.15 (4.75) | 0.1094 | HOMO-5→LUMO+2 | -0.2214 | IC/IL/LLCT/LCCT | 249 |
| | | | HOMO-4→LUMO+2 | 0.2087 | IC/CLCT | |

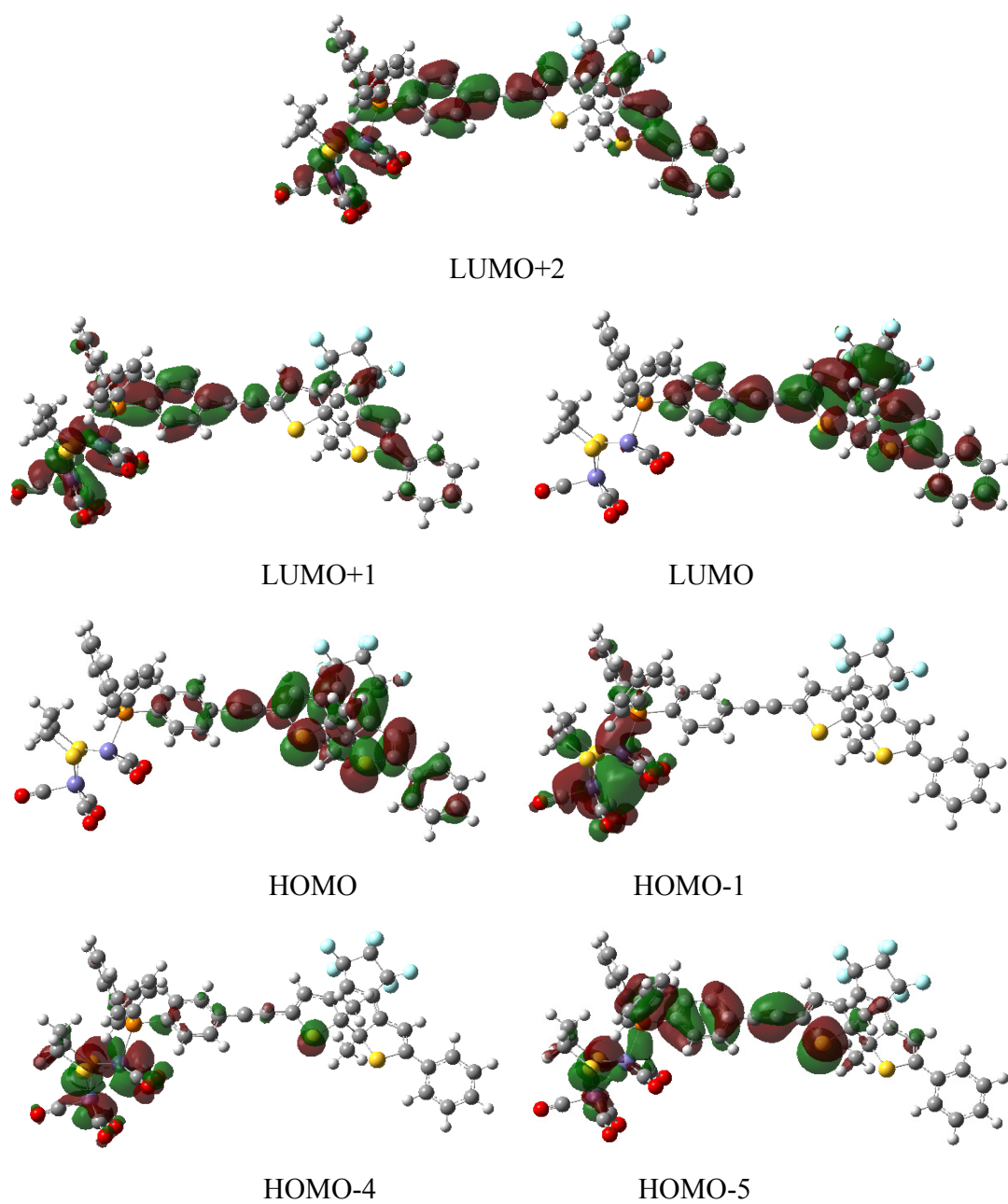


Figure S10. Electron-density diagrams of the frontier molecular orbitals involved in the absorption of compound **1c** in Acetonitrile Media (isovalue = 0.02).

Table S4. Geometry coordinates

Compound 1o

| | | | |
|---|--------------|-------------|-------------|
| C | -0.95824800 | -0.90497000 | 0.77857200 |
| C | -2.17040400 | -0.83833700 | 0.86254300 |
| C | -3.56611800 | -0.74559300 | 0.96437500 |
| C | -4.52715800 | -1.37964800 | 0.21667400 |
| S | -4.31861200 | 0.28854700 | 2.16237900 |
| C | -5.86000700 | -1.02657700 | 0.57937200 |
| H | -4.28695800 | -2.07343000 | -0.57929700 |
| C | -5.91307400 | -0.13421800 | 1.63564600 |
| C | -7.02258400 | -1.61254600 | -0.08253800 |
| C | -7.09984300 | 0.42897000 | 2.34013000 |
| C | -8.18186700 | -1.03767900 | -0.48588500 |
| C | -7.00415400 | -3.07719700 | -0.42941600 |
| H | -7.43892500 | 1.36270700 | 1.87674300 |
| H | -7.93361500 | -0.27679500 | 2.29503500 |
| H | -6.87734000 | 0.63160300 | 3.39109600 |
| C | -9.12349200 | -2.07206600 | -1.04869300 |
| C | -8.54223700 | 0.37862200 | -0.53032100 |
| C | -8.47991700 | -3.42867700 | -0.69612000 |
| F | -6.48286500 | -3.84583500 | 0.54556600 |
| F | -6.27157200 | -3.30376800 | -1.55488700 |
| F | -10.37005100 | -1.98853000 | -0.52393700 |
| F | -9.24499200 | -1.95262100 | -2.38962600 |
| C | -7.72044400 | 1.36398500 | -1.04281200 |
| C | -9.80899800 | 0.88291200 | -0.09690000 |
| F | -9.02792100 | -3.90491200 | 0.43683000 |
| F | -8.62741600 | -4.33443200 | -1.67109000 |
| S | -8.50303400 | 2.90870600 | -0.95589700 |

| | | | |
|----|--------------|-------------|-------------|
| C | -6.36082300 | 1.25276300 | -1.64505200 |
| C | -9.95032400 | 2.23532300 | -0.24446200 |
| H | -10.59328700 | 0.24655700 | 0.29280600 |
| H | -6.21774600 | 0.25654800 | -2.07201200 |
| H | -6.21967200 | 1.98879100 | -2.44105100 |
| H | -5.57230600 | 1.40535200 | -0.89888700 |
| C | -11.09012900 | 3.08172800 | 0.11099300 |
| C | -11.34487400 | 4.28569300 | -0.56012100 |
| C | -12.43624500 | 5.07354100 | -0.21423700 |
| H | -10.69237700 | 4.59580800 | -1.37240400 |
| C | -13.05668200 | 3.47606800 | 1.47536300 |
| C | -13.29915100 | 4.67116100 | 0.80183700 |
| H | -12.61794800 | 6.00180900 | -0.74808300 |
| H | -13.71872200 | 3.15771300 | 2.27549400 |
| H | -14.15344200 | 5.28595800 | 1.06913600 |
| P | 5.10387700 | -1.15782900 | 0.27307700 |
| Fe | 7.58369400 | 2.70249400 | -0.42268700 |
| Fe | 5.97094700 | 0.92001300 | 0.15845000 |
| S | 6.88693800 | 1.14800500 | -1.93621600 |
| S | 8.16707900 | 0.92672700 | 0.88010300 |
| O | 10.20236200 | 3.39026200 | -1.51112400 |
| O | 7.54593800 | 4.29499600 | 2.03382900 |
| O | 5.89519200 | 4.62398000 | -1.84629100 |
| O | 5.28648100 | 1.71462900 | 2.87397800 |
| O | 3.58662400 | 2.16884600 | -0.95393100 |
| C | 9.16581500 | 3.13537100 | -1.08055600 |
| C | 7.55729000 | 3.67244700 | 1.06814500 |
| C | 6.55307200 | 3.86982500 | -1.28204000 |
| C | 5.54820100 | 1.38462800 | 1.80041500 |
| C | 4.51856600 | 1.65989700 | -0.50900300 |

| | | | |
|---|------------|-------------|-------------|
| C | 3.25344200 | -1.14003900 | 0.39538100 |
| C | 2.67103900 | -0.45807500 | 1.47332600 |
| H | 3.29646800 | 0.01778700 | 2.22300000 |
| C | 1.29447200 | -0.38300700 | 1.60716600 |
| H | 0.85642400 | 0.14881400 | 2.44557100 |
| C | 0.45268800 | -0.98948500 | 0.65774900 |
| C | 1.03640400 | -1.67954300 | -0.41547100 |
| H | 0.39680700 | -2.15641500 | -1.15125900 |
| C | 2.41799600 | -1.75445300 | -0.54103700 |
| H | 2.84172000 | -2.29609100 | -1.38023300 |
| C | 5.39157200 | -2.27736100 | -1.17190100 |
| C | 5.15751400 | -1.76894500 | -2.45679700 |
| H | 4.83910500 | -0.73736500 | -2.58130900 |
| C | 5.34550200 | -2.57284700 | -3.57656400 |
| H | 5.15354300 | -2.16807100 | -4.56613800 |
| C | 5.78670400 | -3.88688700 | -3.42859600 |
| H | 5.94197800 | -4.51125500 | -4.30370600 |
| C | 6.03044400 | -4.39396200 | -2.15632000 |
| H | 6.37728400 | -5.41599700 | -2.03347600 |
| C | 5.82860800 | -3.59714800 | -1.03065800 |
| H | 6.01695300 | -4.00588900 | -0.04301200 |
| C | 5.53291000 | -2.19882400 | 1.73969100 |
| C | 4.71840000 | -3.27721800 | 2.11077100 |
| H | 3.81992900 | -3.49852300 | 1.54114300 |
| C | 5.04998200 | -4.05916100 | 3.21175800 |
| H | 4.41125500 | -4.89160400 | 3.49276000 |
| C | 6.19164700 | -3.76897700 | 3.95748900 |
| H | 6.44456200 | -4.37630600 | 4.82188300 |
| C | 6.99815100 | -2.69374400 | 3.59979100 |
| H | 7.88102000 | -2.45380000 | 4.18519900 |

| | | | |
|---|--------------|-------------|-------------|
| C | 6.67074900 | -1.90963400 | 2.49537300 |
| H | 7.28865100 | -1.05646700 | 2.22924000 |
| C | 8.23490200 | -0.03840400 | -2.33559800 |
| H | 7.83130600 | -0.65550800 | -3.14346200 |
| H | 9.05251600 | 0.56169900 | -2.74905700 |
| C | 8.72002400 | -0.92466800 | -1.20683200 |
| H | 7.89871300 | -1.55991100 | -0.86036500 |
| H | 9.48586000 | -1.60154500 | -1.61217000 |
| C | 9.31674900 | -0.18094400 | -0.03193300 |
| H | 10.16562700 | 0.43986500 | -0.33723500 |
| H | 9.68036900 | -0.89101500 | 0.71728100 |
| C | -11.95992200 | 2.69238000 | 1.14008300 |
| H | -11.76080600 | 1.77777800 | 1.69081500 |

Compound 1c

| | | | |
|---|-------------|-------------|-------------|
| C | -1.10116100 | -0.76793000 | 0.53288300 |
| C | -2.31574400 | -0.71011400 | 0.46002500 |
| C | -3.70809700 | -0.60098900 | 0.36069100 |
| C | -4.58058000 | -1.58376100 | -0.02093800 |
| S | -4.47995300 | 0.96145700 | 0.70963300 |
| C | -5.93620600 | -1.16393600 | -0.06701500 |
| H | -4.25241400 | -2.57570300 | -0.30635300 |
| C | -6.16561200 | 0.17974400 | 0.62920900 |
| C | -7.03266400 | -1.79086000 | -0.57542500 |
| C | -6.61577900 | -0.10898800 | 2.07187100 |
| C | -8.32169800 | -1.15205000 | -0.61086500 |
| C | -7.15498000 | -3.17385300 | -1.12822700 |

| | | | |
|---|--------------|-------------|-------------|
| H | -6.73500200 | 0.81583900 | 2.63941600 |
| H | -7.56906900 | -0.64590200 | 2.07207900 |
| H | -5.86427900 | -0.73095600 | 2.56329800 |
| C | -9.36789200 | -2.13231700 | -1.03410000 |
| C | -8.46625000 | 0.17360900 | -0.33392900 |
| C | -8.65382400 | -3.50199300 | -0.92144300 |
| F | -6.36133500 | -4.08294200 | -0.52100900 |
| F | -6.88312600 | -3.22242900 | -2.45807500 |
| F | -10.48926200 | -2.09677300 | -0.27662300 |
| F | -9.75451100 | -1.94558800 | -2.32212900 |
| C | -7.18536400 | 0.99216900 | -0.18255100 |
| C | -9.63958600 | 0.96573900 | -0.22379100 |
| F | -8.81987400 | -3.97849600 | 0.32859600 |
| F | -9.11483100 | -4.39978600 | -1.79997200 |
| S | -7.73572400 | 2.55587000 | 0.65533000 |
| C | -6.69665500 | 1.36524900 | -1.59317400 |
| C | -9.43028100 | 2.22521700 | 0.26171100 |
| H | -10.61963900 | 0.58712500 | -0.48880200 |
| H | -6.43503800 | 0.46335600 | -2.15439800 |
| H | -7.49700100 | 1.88652400 | -2.12310000 |
| H | -5.82055400 | 2.01450600 | -1.54555100 |
| C | -10.43701000 | 3.25822700 | 0.49198600 |
| C | -10.07607200 | 4.61044900 | 0.58996500 |
| C | -11.04113400 | 5.58835400 | 0.79661500 |
| H | -9.03310700 | 4.89470600 | 0.48057200 |
| C | -12.75345200 | 3.89423700 | 0.82763700 |
| C | -12.38265100 | 5.23544500 | 0.91451600 |
| H | -10.74326600 | 6.63055200 | 0.86245000 |
| H | -13.79647300 | 3.60966200 | 0.92991700 |
| H | -13.13622600 | 6.00006700 | 1.07819400 |

| | | | |
|----|-------------|-------------|-------------|
| P | 4.97704300 | -0.98307100 | 0.76385500 |
| Fe | 7.54901100 | 2.30419600 | -1.26332300 |
| Fe | 5.87469500 | 0.87209400 | -0.14269300 |
| S | 6.93992600 | 0.26871000 | -2.08892100 |
| S | 8.01419300 | 1.19148900 | 0.66967000 |
| O | 10.23122200 | 2.53148900 | -2.39020800 |
| O | 7.41880200 | 4.74224100 | 0.35299000 |
| O | 5.95809900 | 3.49151400 | -3.41523800 |
| O | 5.00761100 | 2.71565100 | 1.93611300 |
| O | 3.59529900 | 1.51282100 | -1.83995300 |
| C | 9.17085200 | 2.45796100 | -1.94897200 |
| C | 7.46496700 | 3.78698800 | -0.28353100 |
| C | 6.57853500 | 3.02772000 | -2.56695100 |
| C | 5.34380100 | 1.97085200 | 1.12228600 |
| C | 4.48403500 | 1.24776200 | -1.15802800 |
| C | 3.12212200 | -0.98172300 | 0.68922400 |
| C | 2.44079700 | 0.10785500 | 1.25029600 |
| H | 2.99344300 | 0.91061600 | 1.72911500 |
| C | 1.05854900 | 0.17983300 | 1.20796000 |
| H | 0.54163400 | 1.03013800 | 1.64074400 |
| C | 0.31244100 | -0.84527000 | 0.59874700 |
| C | 0.99367000 | -1.94232900 | 0.04901900 |
| H | 0.42607500 | -2.74050300 | -0.41855200 |
| C | 2.38049200 | -2.00712000 | 0.09564800 |
| H | 2.88366200 | -2.86501600 | -0.33794600 |
| C | 5.39443100 | -2.60902200 | -0.01500100 |
| C | 5.28028400 | -2.72396200 | -1.40728100 |
| H | 4.96598000 | -1.86797600 | -1.99854500 |
| C | 5.57962200 | -3.92592900 | -2.04030900 |
| H | 5.47928100 | -4.00381500 | -3.11914000 |

| | | | |
|---|--------------|-------------|-------------|
| C | 6.01407300 | -5.02088500 | -1.29481900 |
| H | 6.25629200 | -5.95618400 | -1.79106100 |
| C | 6.13907000 | -4.90959700 | 0.08614600 |
| H | 6.47965600 | -5.75752900 | 0.67347300 |
| C | 5.82521700 | -3.71210000 | 0.72673600 |
| H | 5.92212300 | -3.63868400 | 1.80525200 |
| C | 5.24149100 | -1.27560200 | 2.57051000 |
| C | 4.37330900 | -2.10612900 | 3.29199200 |
| H | 3.53012700 | -2.57467500 | 2.79196600 |
| C | 4.58067600 | -2.32664000 | 4.64913500 |
| H | 3.90054900 | -2.96986200 | 5.20007900 |
| C | 5.65119800 | -1.71668700 | 5.30126900 |
| H | 5.80700100 | -1.88392300 | 6.36320400 |
| C | 6.51171100 | -0.88537300 | 4.59201500 |
| H | 7.34019400 | -0.39713700 | 5.09692200 |
| C | 6.30868300 | -0.66337500 | 3.23138500 |
| H | 6.97063500 | 0.00116300 | 2.68295400 |
| C | 8.31459200 | -0.93980400 | -1.90239500 |
| H | 7.98152700 | -1.82801200 | -2.44678400 |
| H | 9.16576500 | -0.51492400 | -2.44490600 |
| C | 8.69640800 | -1.31919600 | -0.48725500 |
| H | 7.84084900 | -1.78859100 | 0.00709700 |
| H | 9.48330600 | -2.08526100 | -0.54101800 |
| C | 9.20712800 | -0.17401800 | 0.35958200 |
| H | 10.09480900 | 0.28960900 | -0.08349200 |
| H | 9.48634700 | -0.53674500 | 1.35367800 |
| C | -11.79297400 | 2.91457400 | 0.62144600 |
| H | -12.09095600 | 1.87144100 | 0.58267900 |