Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**SUPPORTING INFORMATION**

# Heme isomers substantially affect heme electronic structure and function

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**Table S1. Electronic energies ($E_{el}$) and zero-point energies (ZPE) from numerically computed frequencies of geometry-optimized states (BP/def2-SVP COSMO, ε = 10); in atomic units. Q = total charge; M = multiplicity; and thermodynamic corrections to the energy $\Delta E_{therm}$, entropy ΔS, and free energy ΔG.**

| Model | State | Q | M | $E_{el}$ (a.u.) | ZPE (a.u.) | $\Delta E_{therm}$ (kJ/mol) | ΔS (kJ/molK) | ΔG (kJ/mol) |
|---|---|---|---|---|---|---|---|---|
| EE0 | Fe(II) LS | -2 | 1 | -3096.5373 | 0.5529 | 1546.0 | 1.015 | 1245.9 |
| | Fe(II) HS | -2 | 5 | -3096.5313 | 0.5647 | 1566.2 | 0.885 | 1304.8 |
| | Fe(III) LS | -1 | 2 | -3096.4030 | 0.5525 | 1545.6 | 1.019 | 1244.2 |
| | Fe(III) HS | -1 | 6 | -3096.3864 | 0.5648 | 1566.9 | 0.890 | 1304.2 |
| | | | | | | | | |
| EEO2 | Fe(II) LS | -2 | 1 | -3512.2062 | 0.6631 | 1851.1 | 1.110 | 1522.6 |
| | Fe(II) HS | -2 | 5 | -3512.1731 | 0.6510 | 1826.9 | 1.229 | 1463.0 |
| | Fe(III) LS | -1 | 2 | -3512.0657 | 0.6601 | 1847.2 | 1.164 | 1502.7 |
| | Fe(III) HS | -1 | 6 | -3512.0248 | 0.6571 | 1842.0 | 1.191 | 1489.5 |
| | | | | | | | | |
| EEcpdI | doublet | -1 | 2 | -3436.9559 | 0.6550 | 1829.8 | 1.128 | 1495.9 |
| | quartet | -1 | 4 | -3436.9565 | 0.6571 | 1835.5 | 1.123 | 1503.3 |
| | | | | | | | | |
| EZ0 | Fe(II) LS | -2 | 1 | -3096.5396 | 0.5511 | 1540.2 | 1.021 | 1238.2 |
| | Fe(II) HS | -2 | 5 | -3096.5326 | 0.5495 | 1537.4 | 1.023 | 1234.8 |
| | Fe(III) LS | -1 | 2 | -3096.4051 | 0.5518 | 1542.2 | 1.004 | 1245.3 |
| | Fe(III) HS | -1 | 6 | -3096.3884 | 0.5501 | 1540.9 | 1.036 | 1234.4 |
| | | | | | | | | |
| EZO2 | Fe(II) LS | -2 | 1 | -3512.2079 | 0.6612 | 1848.1 | 1.133 | 1512.7 |
| | Fe(II) HS | -2 | 5 | -3512.1748 | 0.6509 | 1829.1 | 1.258 | 1456.6 |
| | Fe(III) LS | -1 | 2 | -3512.0672 | 0.6603 | 1847.1 | 1.148 | 1507.2 |
| | Fe(III) HS | -1 | 6 | -3512.0266 | 0.6573 | 1839.4 | 1.143 | 1501.2 |
| | | | | | | | | |
| EZcpdI | doublet | -1 | 2 | -3436.9575 | 0.6563 | 1834.2 | 1.137 | 1497.8 |
| | quartet | -1 | 4 | -3436.9578 | 0.6525 | 1827.8 | 1.188 | 1476.1 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ZE0 | Fe(II) LS | -2 | 1 | -3096.5383 | 0.5507 | 1540.1 | 1.042 | 1232.0 |
| | Fe(II) HS | -2 | 5 | -3096.5332 | 0.5493 | 1539.5 | 1.054 | 1227.8 |
| | Fe(III) LS | -1 | 2 | -3096.4037 | 0.5516 | 1541.6 | 1.011 | 1242.7 |
| | Fe(III) HS | -1 | 6 | -3096.3859 | 0.5493 | 1537.3 | 1.036 | 1230.8 |
| | | | | | | | | |
| ZEO2 | Fe(II) LS | -2 | 1 | -3512.2079 | 0.6608 | 1847.4 | 1.139 | 1510.2 |
| | Fe(II) HS | -2 | 5 | -3512.1750 | 0.6592 | 1844.0 | 1.138 | 1507.3 |
| | Fe(III) LS | -1 | 2 | -3512.0673 | 0.6603 | 1847.1 | 1.151 | 1506.5 |
| | Fe(III) HS | -1 | 6 | -3512.0266 | 0.6577 | 1842.3 | 1.161 | 1498.7 |
| | | | | | | | | |
| ZEcpdI | doublet | -1 | 2 | -3436.9576 | 0.6569 | 1835.2 | 1.126 | 1502.0 |
| | quartet | -1 | 4 | -3436.9578 | 0.6582 | 1837.1 | 1.107 | 1509.5 |
| | | | | | | | | |
| ZZ0 | Fe(II) LS | -2 | 1 | -3096.5396 | 0.5523 | 1545.0 | 1.043 | 1236.4 |
| | Fe(II) HS | -2 | 5 | -3096.5343 | 0.5608 | 1558.6 | 0.910 | 1289.6 |
| | Fe(III) LS | -1 | 2 | -3096.4055 | 0.5523 | 1543.1 | 1.004 | 1246.1 |
| | Fe(III) HS | -1 | 6 | -3096.3899 | 0.5503 | 1541.3 | 1.035 | 1235.1 |
| | | | | | | | | |
| ZZO2 | Fe(II) LS | -2 | 1 | -3512.2133 | 0.6549 | 1838.3 | 1.243 | 1470.1 |
| | Fe(II) HS | -2 | 5 | -3512.1760 | 0.6513 | 1829.6 | 1.249 | 1459.6 |
| | Fe(III) LS | -1 | 2 | -3512.0737 | 0.6551 | 1836.4 | 1.196 | 1482.4 |
| | Fe(III) HS | -1 | 6 | -3512.0280 | 0.6578 | 1842.4 | 1.162 | 1498.5 |
| | | | | | | | | |
| ZZcpdI | doublet | -1 | 2 | -3436.9568 | 0.6582 | 1837.0 | 1.108 | 1509.0 |
| | quartet | -1 | 4 | -3436.9584 | 0.6580 | 1837.0 | 1.114 | 1507.4 |

**Table S2. Electronic energies ($E_{el}$) in atomic units of models and states computed by TPSSh, B3LYP, and PBE with and without dispersion D3 corrections, using the def2-TZVPP basis set. Q = total charge; M = multiplicity.**

| Model | State | Q | M | TPSSh-D3 | D3 | B3LYP-D3 | D3 | PBE-D3 | D3 |
|---|---|---|---|---|---|---|---|---|---|
| EE0 | Fe(II) LS | -2 | 1 | -3098.5947 | -0.0750 | -3097.3200 | -0.0918 | -3096.0069 | -0.0550 |
| | Fe(II) HS | -2 | 5 | -3098.5900 | -0.0745 | -3097.3265 | -0.0912 | -3095.9955 | -0.0547 |
| | Fe(III) LS | -1 | 2 | -3098.4427 | -0.0753 | -3097.1687 | -0.0922 | -3095.8645 | -0.0552 |
| | Fe(III) HS | -1 | 6 | -3098.4269 | -0.0748 | -3097.1589 | -0.0916 | -3095.8476 | -0.0549 |
| | | | | | | | | | |
| EEO2 | Fe(II) LS | -2 | 1 | -3514.7051 | -0.1001 | -3513.1753 | -0.1210 | -3511.6622 | -0.0748 |
| | Fe(II) HS | -2 | 5 | -3514.6693 | -0.0983 | -3513.1587 | -0.1189 | -3511.6099 | -0.0734 |
| | Fe(III) LS | -1 | 2 | -3514.5585 | -0.1003 | -3513.0336 | -0.1213 | -3511.5155 | -0.0749 |
| | Fe(III) HS | -1 | 6 | -3514.5222 | -0.0982 | -3513.0112 | -0.1187 | -3511.4667 | -0.0734 |
| | | | | | | | | | |
| EEcpdI | doublet | -1 | 2 | -3439.3659 | -0.0977 | -3437.8742 | -0.1183 | -3436.3901 | -0.0728 |
| | quartet | -1 | 4 | -3439.3660 | -0.0977 | -3437.8737 | -0.1183 | -3436.3918 | -0.0728 |
| | | | | | | | | | |
| EZ0 | Fe(II) LS | -2 | 1 | -3098.5938 | -0.0757 | -3097.3199 | -0.0927 | -3096.0074 | -0.0555 |
| | Fe(II) HS | -2 | 5 | -3098.5901 | -0.0743 | -3097.3264 | -0.0910 | -3095.9958 | -0.0545 |
| | Fe(III) LS | -1 | 2 | -3098.4416 | -0.0750 | -3097.1687 | -0.0918 | -3095.8660 | -0.0550 |
| | Fe(III) HS | -1 | 6 | -3098.4287 | -0.0757 | -3097.1610 | -0.0928 | -3095.8493 | -0.0555 |
| | | | | | | | | | |
| EZO2 | Fe(II) LS | -2 | 1 | -3514.7078 | -0.0999 | -3513.1784 | -0.1209 | -3511.6647 | -0.0745 |
| | Fe(II) HS | -2 | 5 | -3514.6735 | -0.0979 | -3513.1635 | -0.1184 | -3511.6136 | -0.0731 |
| | Fe(III) LS | -1 | 2 | -3514.5597 | -0.1000 | -3513.0348 | -0.1210 | -3511.5168 | -0.0746 |
| | Fe(III) HS | -1 | 6 | -3514.5239 | -0.0979 | -3513.0129 | -0.1184 | -3511.4684 | -0.0731 |
| | | | | | | | | | |
| EZcpdI | doublet | -1 | 2 | -3439.3673 | -0.0975 | -3437.8755 | -0.1180 | -3436.3911 | -0.0726 |
| | quartet | -1 | 4 | -3439.3668 | -0.0976 | -3437.8745 | -0.1181 | -3436.3928 | -0.0727 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| ZE0 | Fe(II) LS | -2 | 1 | -3098.5951 | -0.0746 | -3097.3226 | -0.0914 | -3096.0091 | -0.0548 |
| | Fe(II) HS | -2 | 5 | -3098.5919 | -0.0743 | -3097.3284 | -0.0910 | -3095.9973 | -0.0545 |
| | Fe(III) LS | -1 | 2 | -3098.4427 | -0.0750 | -3097.1693 | -0.0919 | -3095.8660 | -0.0550 |
| | Fe(III) HS | -1 | 6 | -3098.4297 | -0.0747 | -3097.1610 | -0.0915 | -3095.8497 | -0.0548 |
| | | | | | | | | | |
| ZEO2 | Fe(II) LS | -2 | 1 | -3514.7072 | -0.0998 | -3513.1775 | -0.1207 | -3511.6642 | -0.0745 |
| | Fe(II) HS | -2 | 5 | -3514.6712 | -0.0982 | -3513.1605 | -0.1188 | -3511.6117 | -0.0733 |
| | Fe(III) LS | -1 | 2 | -3514.5595 | -0.0998 | -3513.0345 | -0.1208 | -3511.5166 | -0.0745 |
| | Fe(III) HS | -1 | 6 | -3514.5233 | -0.0978 | -3513.0116 | -0.1183 | -3511.4709 | -0.0731 |
| | | | | | | | | | |
| ZEcpdI | doublet | -1 | 2 | -3439.3675 | -0.0974 | -3437.8759 | -0.1180 | -3436.3917 | -0.0725 |
| | quartet | -1 | 4 | -3439.3672 | -0.0975 | -3437.8750 | -0.1181 | -3436.3928 | -0.0726 |
| | | | | | | | | | |
| ZZ0 | Fe(II) LS | -2 | 1 | -3098.5965 | -0.0744 | -3097.3216 | -0.0911 | -3096.0089 | -0.0545 |
| | Fe(II) HS | -2 | 5 | -3098.5922 | -0.0739 | -3097.3285 | -0.0906 | -3095.9977 | -0.0542 |
| | Fe(III) LS | -1 | 2 | -3098.4416 | -0.0746 | -3097.1691 | -0.0914 | -3095.8660 | -0.0547 |
| | Fe(III) HS | -1 | 6 | -3098.4296 | -0.0766 | -3097.1612 | -0.0937 | -3095.8499 | -0.0562 |
| | | | | | | | | | |
| ZZO2 | Fe(II) LS | -2 | 1 | -3514.7080 | -0.0995 | -3513.1787 | -0.1205 | -3511.6651 | -0.0742 |
| | Fe(II) HS | -2 | 5 | -3514.6791 | -0.0977 | -3513.1712 | -0.1182 | -3511.6130 | -0.0729 |
| | Fe(III) LS | -1 | 2 | -3514.5691 | -0.1057 | -3513.0438 | -0.1277 | -3511.5239 | -0.0790 |
| | Fe(III) HS | -1 | 6 | -3514.5253 | -0.1036 | -3513.0132 | -0.1251 | -3511.4726 | -0.0729 |
| | | | | | | | | | |
| ZZcpdI | doublet | -1 | 2 | -3439.3689 | -0.0973 | -3437.8765 | -0.1179 | -3436.3914 | -0.0724 |
| | quartet | -1 | 4 | -3439.3674 | -0.0972 | -3437.8752 | -0.1177 | -3436.3928 | -0.0724 |

**Table S3. Relative Energies (kJ/mol) of Isomers in Different Spin and Redox States (relative to the corresponding EE isomers = 0 kJ/mol).**

| | | TPSSh-D3 | TPSSh | B3LYP-D3 | B3LYP | PBE-D3 | PBE |
|---|---|---|---|---|---|---|---|
| EE0 | Fe(II) LS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(II) HS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(III) LS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(III) HS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | |
| EE O2 | Fe(II) LS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(II) HS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(III) LS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Fe(III) HS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | |
| EEcpdI | doublet | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | quartet | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | |
| EZ0 | Fe(II) LS | 2.2 | 4.1 | 0.5 | 2.8 | -1.3 | -0.1 |
| | Fe(II) HS | -0.3 | -0.7 | 0.4 | -0.1 | -0.9 | -1.3 |
| | Fe(III) LS | 2.9 | 2.2 | -0.1 | -1.0 | -4.0 | -4.6 |
| | Fe(III) HS | -4.9 | -2.5 | -5.6 | -2.5 | -4.5 | -2.9 |
| | | | | | | | |
| EZ O2 | Fe(II) LS | -7.1 | -7.7 | -8.0 | -8.5 | -6.4 | -7.0 |
| | Fe(II) HS | -10.9 | -12.0 | -12.6 | -13.8 | -9.7 | -10.6 |
| | Fe(III) LS | -3.3 | -4.0 | -3.2 | -3.9 | -3.6 | -4.3 |
| | Fe(III) HS | -4.6 | -5.3 | -4.5 | -5.2 | -4.5 | -5.1 |
| | | | | | | | |
| EZcpdI | doublet | -3.7 | -4.2 | -3.5 | -4.1 | -2.6 | -3.1 |
| | quartet | -2.3 | -2.6 | -2.1 | -2.6 | -2.6 | -2.9 |
| | | | | | | | |
| ZE0 | Fe(II) LS | -1.1 | -1.9 | -6.8 | -7.7 | -5.9 | -6.6 |
| | Fe(II) HS | -5.0 | -5.7 | -4.9 | -5.6 | -4.9 | -5.5 |
| | Fe(III) LS | 0.0 | -0.6 | -1.6 | -2.4 | -3.9 | -4.5 |
| | Fe(III) HS | -7.4 | -7.7 | -5.6 | -5.9 | -5.7 | -6.0 |
| | | | | | | | |
| ZE O2 | Fe(II) LS | -5.5 | -6.3 | -5.8 | -6.6 | -5.2 | -6.1 |
| | Fe(II) HS | -5.0 | -5.3 | -4.8 | -5.1 | -4.8 | -5.1 |
| | Fe(III) LS | -2.6 | -3.8 | -2.2 | -3.6 | -2.9 | -4.0 |
| | Fe(III) HS | -3.0 | -4.0 | -1.1 | -2.1 | -11.1 | -12.0 |
| | | | | | | | |
| ZEcpdI | doublet | -4.0 | -4.8 | -4.6 | -5.3 | -4.2 | -4.9 |
| | quartet | -3.1 | -3.6 | -3.5 | -4.1 | -2.6 | -3.1 |
| | | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ZZ0 | Fe(II) LS | -4.9 | -6.4 | -4.1 | -5.9 | -5.3 | -6.6 |
| | Fe(II) HS | -5.8 | -7.3 | -5.2 | -6.8 | -6.0 | -7.3 |
| | Fe(III) LS | 2.9 | 1.3 | -1.2 | -3.1 | -3.9 | -5.2 |
| | Fe(III) HS | -7.2 | -2.7 | -6.2 | -0.6 | -6.1 | -2.7 |
| | | | | | | | |
| ZZ O2 | Fe(II) LS | -7.5 | -9.0 | -8.8 | -10.1 | -7.5 | -9.1 |
| | Fe(II) HS | -25.6 | -27.2 | -32.8 | -34.5 | -8.0 | -9.4 |
| | Fe(III) LS | -28.0 | -13.9 | -26.8 | -10.0 | -22.1 | -11.4 |
| | Fe(III) HS | -8.2 | 6.1 | -5.3 | 11.6 | -15.5 | -16.7 |
| | | | | | | | |
| ZZcpdI | doublet | -7.8 | -8.8 | -6.1 | -7.1 | -3.5 | -4.5 |
| | quartet | -3.8 | -5.3 | -4.0 | -5.6 | -2.6 | -3.9 |

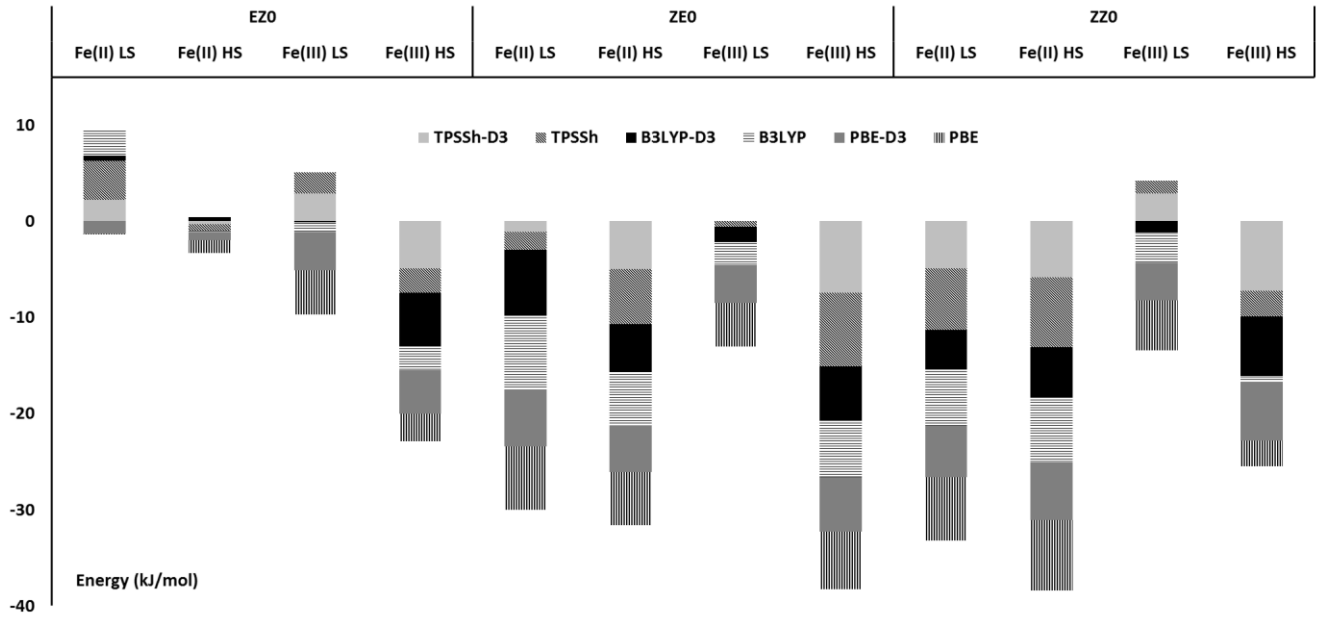


**Figure S1.** Stability (in kJ/mol) relative to EE0 isomer for the four electronic states of EZ0, ZE0, and ZZ0, with various bars representing TPSSh-D3, TPSSh, B3LYP-D3, B3LYP, PBE-D3, and PBE; most methods give energies within 5 kJ/mol and of similar sign.

**Table S4. Computed Half Reduction Potentials vs. SHE (V) for Fe(III) + $e^- \rightarrow$ Fe(II), Corrected for Vibrational and Thermal Free energy Contributions.**

| System | State | TPSSh-D3 | B3LYP-D3 | PBE-D3 |
|---|---|---|---|---|
| EE0 | LS | 0.32 | 0.34 | 0.59 |
| | HS | 0.01 | -0.12 | 0.42 |
| | | | | |
| EE O2 | LS | 0.66 | 0.79 | 0.65 |
| | HS | 0.16 | 0.15 | 0.27 |
| | | | | |
| EZ0 | LS | 0.22 | 0.25 | 0.52 |
| | HS | 0.05 | -0.05 | 0.46 |
| | | | | |
| EZ O2 | LS | 0.47 | 0.59 | 0.47 |
| | HS | -0.09 | -0.12 | 0.03 |
| | | | | |
| ZE0 | LS | 0.18 | 0.16 | 0.44 |
| | HS | 0.00 | -0.15 | 0.39 |
| | | | | |
| ZE O2 | LS | 0.46 | 0.59 | 0.46 |
| | HS | 0.51 | 0.48 | 0.70 |
| | | | | |
| ZZ0 | LS | 0.12 | 0.19 | 0.45 |
| | HS | 0.58 | 0.45 | 0.98 |
| | | | | |
| ZZ O2 | LS | 0.54 | 0.64 | 0.47 |
| | HS | -0.15 | -0.26 | 0.22 |

**Table S5. Fe–O, Fe–$N_{ax}$, and O–O bond lengths (Å) of optimized geometries.**

| System | State | Q | M | Fe–O | Fe–$N_{ax}$ | O–O |
|---|---|---|---|---|---|---|
| | | | | | | |
| EE O2 | Fe(II) LS | -2 | 1 | 1.757 | 2.074 | 1.282 |
| | Fe(II) HS | -2 | 5 | 1.895 | 2.130 | 1.282 |
| | Fe(III) LS | -1 | 2 | 1.859 | 2.062 | 1.272 |
| | Fe(III) HS | -1 | 6 | 1.983 | 2.109 | 1.265 |
| | | | | | | |
| EE cpdI | doublet | -1 | 2 | 1.631 | 2.132 | |
| | quartet | -1 | 4 | 1.645 | 2.124 | |
| | | | | | | |
| EZ O2 | Fe(II) LS | -2 | 1 | 1.757 | 2.076 | 1.282 |
| | Fe(II) HS | -2 | 5 | 1.898 | 2.148 | 1.281 |
| | Fe(III) LS | -1 | 2 | 1.857 | 2.063 | 1.272 |
| | Fe(III) HS | -1 | 6 | 1.984 | 2.112 | 1.265 |
| | | | | | | |
| EZ cpdI | doublet | -1 | 2 | 1.630 | 2.134 | |
| | quartet | -1 | 4 | 1.645 | 2.130 | |
| | | | | | | |
| ZE O2 | Fe(II) LS | -2 | 1 | 1.757 | 2.074 | 1.282 |
| | Fe(II) HS | -2 | 5 | 1.895 | 2.133 | 1.282 |
| | Fe(III) LS | -1 | 2 | 1.859 | 2.062 | 1.272 |
| | Fe(III) HS | -1 | 6 | 1.983 | 2.110 | 1.265 |
| | | | | | | |
| ZE cpdI | doublet | -1 | 2 | 1.630 | 2.133 | |
| | quartet | -1 | 4 | 1.645 | 2.128 | |
| | | | | | | |
| ZZ O2 | Fe(II) LS | -2 | 1 | 1.825 | 2.057 | 1.285 |
| | Fe(II) HS | -2 | 5 | 1.899 | 2.151 | 1.281 |
| | Fe(III) LS | -1 | 2 | 1.898 | 2.069 | 1.266 |
| | Fe(III) HS | -1 | 6 | 1.981 | 2.124 | 1.265 |
| | | | | | | |
| ZZ cpdI | doublet | -1 | 2 | 1.631 | 2.138 | |
| | quartet | -1 | 4 | 1.644 | 2.132 | |

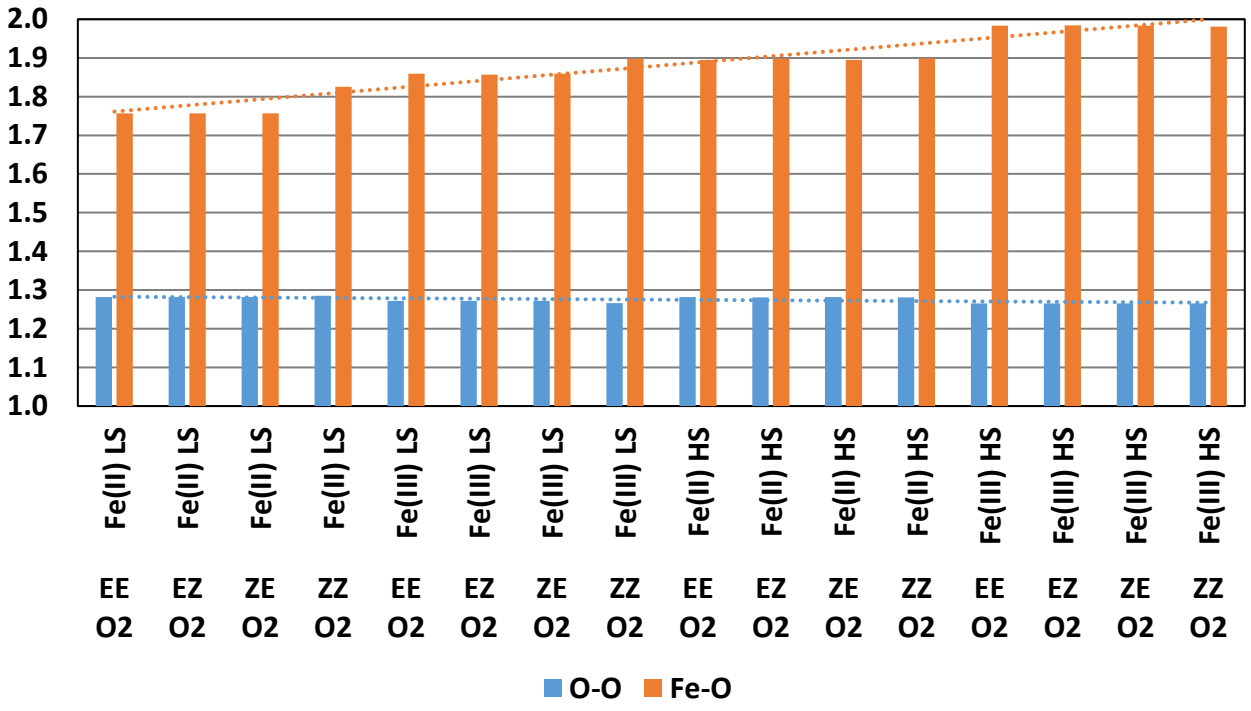


**Figure S2. Differences in equilibrium Fe-O and O-O bond lengths of $O_2$-adduct isomer states (Å). Notice the high-spin effect on Fe-O bonds and the inverse relationship of Fe-O and O-O due to back-bonding.**

**Table S6. Energy Separations (def2-TZVPP, in kJ/mol) between High-Spin and Low-Spin States, Corrected for Zero-Point Energies, for Planar 4-Coordinate Models.**

| Model | State | Q | TPSSh-D3 | B3LYP-D3 | PBE-D3 |
|---|---|---|---|---|---|
| EE0 | Fe(II) | -2 | -43.3 | -13.9 | -60.9 |
| | Fe(III) | -1 | -73.9 | -58.2 | -76.9 |
| | | | | | |
| EZ0 | Fe(II) | -2 | -5.6 | 21.3 | -26.2 |
| | Fe(III) | -1 | -29.1 | -15.7 | -39.4 |
| | | | | | |
| ZE0 | Fe(II) | -2 | -4.7 | 18.9 | -27.4 |
| | Fe(III) | -1 | -28.0 | -15.8 | -36.8 |
| | | | | | |
| ZZ0 | Fe(II) | -2 | -33.8 | -4.2 | -51.6 |
| | Fe(III) | -1 | -26.1 | -15.5 | -37.1 |

**Table S7. Energy Separations (def2-TZVPP, in kJ/mol) between High-Spin and Low-Spin States, Corrected for Zero-Point Energies, for $O_2$-Adducts (all favor low-spin).**

| Model | State | Q | TPSSh-D3 | B3LYP-D3 | PBE-D3 |
|---|---|---|---|---|---|
| EE O2 | Fe(II) | -2 | -62.4 | -12.0 | -105.8 |
| | Fe(III) | -1 | -87.6 | -51.3 | -120.4 |
| | | | | | |
| EZ O2 | Fe(II) | -2 | -63.0 | -11.9 | -107.0 |
| | Fe(III) | -1 | -86.1 | -49.7 | -119.3 |
| | | | | | |
| ZE O2 | Fe(II) | -2 | -90.2 | -40.4 | -133.6 |
| | Fe(III) | -1 | -88.0 | -53.3 | -113.0 |
| | | | | | |
| ZZ O2 | Fe(II) | -2 | -66.4 | -10.2 | -127.5 |
| | Fe(III) | -1 | -122.3 | -87.6 | -141.9 |

**Table S8. Doublet-Quartet Separations (def2-TZVPP, in kJ/mol), Corrected for Zero-Point Energies, for Compound I. (Positive number means that the quartet is favored).**

| Model | TPSSh-D3 | B3LYP-D3 | PBE-D3 |
|---|---|---|---|
| EEcpdI | -5.4 | -6.8 | -1.0 |
| | | | |
| EZcpdI | 8.5 | 7.1 | 14.3 |
| | | | |
| ZEcpdI | -4.2 | -5.8 | -0.4 |
| | | | |
| ZZcpdI | -3.5 | -3.1 | 4.0 |

**Table S9. Electronic energies of fully geometry-relaxed BP86/def2_SVP potential energy surfaces for ZE0 used for computing single-point TPSSh-D3/def2-TZVPP energies in Figure 2.**

| | 2-vinyl | | 4-vinyl | |
|---|---|---|---|---|
| Torsion angle | BP86/def2-SVP | TPSSh-D3/def2-TZVPP | BP86/def2-SVP | TPSSh-D3/def2-TZVPP |
| -105 | -3096.52825 | -3098.58922 | -3096.52952 | -3098.59164 |
| -90 | -3096.52744 | -3098.58592 | -3096.52877 | -3098.59083 |
| -75 | -3096.52819 | -3098.58669 | -3096.52947 | -3098.58785 |
| -60 | -3096.52956 | -3098.58824 | -3096.53121 | -3098.58974 |
| -45 | -3096.53099 | -3098.58981 | -3096.53272 | -3098.59130 |
| -30 | -3096.53147 | -3098.59031 | -3096.53329 | -3098.59174 |
| -15 | -3096.53105 | -3098.59291 | -3096.53284 | -3098.59110 |
| 0 | -3096.53047 | -3098.59229 | -3096.53207 | -3098.59028 |
| 15 | -3096.53141 | -3098.59335 | -3096.53282 | -3098.59126 |
| 30 | -3096.53178 | -3098.59388 | -3096.53328 | -3098.59189 |
| 45 | -3096.53121 | -3098.59365 | -3096.53261 | -3098.59134 |
| 60 | -3096.52957 | -3098.58818 | -3096.53117 | -3098.58973 |
| 75 | -3096.52744 | -3098.58572 | -3096.52945 | -3098.58787 |
| 90 | -3096.52715 | -3098.58577 | -3096.52867 | -3098.58687 |
| 105 | -3096.52764 | -3098.58997 | -3096.52951 | -3098.58779 |
| 120 | -3096.52983 | -3098.59223 | -3096.53113 | -3098.58939 |
| 135 | -3096.53163 | -3098.59404 | -3096.53289 | -3098.59124 |
| 150 | -3096.53285 | -3098.59509 | -3096.53390 | -3098.59241 |
| 165 | -3096.53324 | -3098.59535 | -3096.53453 | -3098.59289 |
| 180 | -3096.53320 | -3098.59511 | -3096.53424 | -3098.59266 |
| 195 | -3096.53313 | -3098.59523 | -3096.53442 | -3098.59624 |
| 210 | -3096.53272 | -3098.59507 | -3096.53393 | -3098.59583 |
| 225 | -3096.52958 | -3098.59180 | -3096.53308 | -3098.59526 |
| 240 | -3096.52828 | -3098.59042 | -3096.53083 | -3098.59296 |
| 255 | -3096.52709 | -3098.58922 | -3096.52930 | -3098.59132 |

**Table S10. Electronic energies of 5-coordinate systems geometry optimized at the BP86/def2-SVP level and thermodynamic terms and zero-point energies. The Fe(II) HS states were used for computing $O_2$-affinities as described in the main text.**

| Model | State | Q | M | E(BP86/def2-SVP) (a.u.) | ZPE (a.u.) | ΔE (kJ/mol) | ΔS (kJ/molK) | ΔG (kJ/mol) | ΔH (kJ/mol) |
|---|---|---|---|---|---|---|---|---|---|
| EE5 | Fe(II) HS | -2 | 5 | -3361.93481 | 0.6489 | 1814.53 | 1.147 | 1475.09 | 1817.03 |
| | Fe(III) HS | -1 | 6 | -3361.80462 | 0.6506 | 1817.93 | 1.133 | 1482.73 | 1820.43 |
| | | | | | | | | | |
| EZ5 | Fe(II) HS | -2 | 5 | -3361.93556 | 0.6467 | 1811.11 | 1.195 | 1457.34 | 1813.61 |
| | Fe(III) HS | -1 | 6 | -3361.80520 | 0.6484 | 1812.4 | 1.147 | 1473.01 | 1814.9 |
| | | | | | | | | | |
| ZE5 | Fe(II) HS | -2 | 5 | -3361.93603 | 0.6467 | 1811.33 | 1.199 | 1456.35 | 1813.83 |
| | Fe(III) HS | -1 | 6 | -3361.80566 | 0.6510 | 1818.53 | 1.127 | 1484.92 | 1821.03 |
| | | | | | | | | | |
| ZZ5 | Fe(II) HS | -2 | 5 | -3361.93613 | 0.6462 | 1811.05 | 1.219 | 1449.99 | 1813.55 |
| | Fe(III) HS | -1 | 6 | -3361.80629 | 0.6520 | 1820.28 | 1.1150 | 1490.33 | 1822.78 |

**Table S11. Electronic energies of 5-coordinate systems; The Fe(II) HS states were used for computing $O_2$-affinities as described in the main text.**

| Model | State | Q | M | TPSSh-D3 | D3 | B3LYP-D3 | D3 | PBE-D3 | D3 |
|---|---|---|---|---|---|---|---|---|---|
| EE5 | Fe(II) HS | -2 | 5 | -3364.29235 | -0.09275 | -3362.85481 | -0.11255 | -3361.35855 | -0.06896 |
| | Fe(III) HS | -1 | 6 | -3364.15842 | -0.09303 | -3362.71857 | -0.11285 | -3361.22621 | -0.06920 |
| | | | | | | | | | |
| EZ5 | Fe(II) HS | -2 | 5 | -3364.29184 | -0.09255 | -3362.85377 | -0.11233 | -3361.35925 | -0.06877 |
| | Fe(III) HS | -1 | 6 | -3364.15980 | -0.09333 | -3362.71993 | -0.11326 | -3361.22748 | -0.06939 |
| | | | | | | | | | |
| ZE5 | Fe(II) HS | -2 | 5 | -3364.29587 | -0.09260 | -3362.85673 | -0.11239 | -3361.35978 | -0.06882 |
| | Fe(III) HS | -1 | 6 | -3364.15903 | -0.09273 | -3362.71900 | -0.11250 | -3361.22702 | -0.06896 |
| | | | | | | | | | |
| ZZ5 | Fe(II) HS | -2 | 5 | -3364.29377 | -0.09133 | -3362.85559 | -0.11086 | -3361.36112 | -0.06786 |
| | Fe(III) HS | -1 | 6 | -3364.15951 | -0.09124 | -3362.71931 | -0.11070 | -3361.22786 | -0.06782 |