# Supplementary Materials: Structural Dynamics of Spin Crossover in Iron(II) Complexes with Extended-Tripod Ligands

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**Table S1.** Pertinent geometric parameters of DFT-optimized **ls-[FeL]$^{2+}$**.

| | B3LYP | | | | | | BP86 | PBE | TPSS0 | TPSSh |
|---|---|---|---|---|---|---|---|---|---|---|
| | $a_0$ = | | | | | | | | | |
| | **0.00** | **0.05** | **0.10** | **0.15** | **0.20** | **0.25** | | | | |
| Bond lengths [Å] | | | | | | | | | | |
| $d_{Fe-N(ald)}$ | 1.935 | 1.942 | 1.948 | 1.957 | 1.970 | 1.981 | 1.930 | 1.929 | 1.943 | 1.931 |
| $d_{Fe-N(py)}$ | 1.976 | 1.984 | 1.993 | 2.001 | 2.016 | 2.024 | 1.974 | 1.976 | 1.988 | 1.977 |
| $d_{Fe-N}$ | 1.955 | 1.969 | 1.970 | 1.979 | 1.993 | 2.002 | 1.952 | 1.952 | 1.965 | 1.954 |
| distortion | | | | | | | | | | |
| $\Sigma_{cis}$ / ° [b] | 58.2 | 59.2 | 59.9 | 61.3 | 64.8 | 68.0 | 57.9 | 58.5 | 59.8 | 59.2 |
| $\theta$ / ° [c] | **44.9** | **44.4** | **44.3** | **43.8** | **43.4** | **43.2** | **45.0** | **45.0** | **44.0** | **44.5** |
| $S(O_h)$ [d] | 1.19 | 1.25 | 1.28 | 1.36 | 1.44 | 1.48 | 1.17 | 1.17 | 1.32 | 1.24 |
| $S$(TP) [d] | 9.92 | 9.76 | 9.71 | 9.50 | 9.31 | 9.28 | 10.01 | 10.01 | 9.57 | 9.77 |

[a] *amount of exact exchange;* [b] *summed deviation from 90° of twelve N-Fe-N* cis *angles;* [c] *trigonal distortion;* [d] *continuous shape measures* $S(O_h)$ *and* $S$(TP) *with reference to the octahedron and the trigonal prism, respectively.*

**Table S2.** Pertinent geometric parameters of DFT-optimized **ls-[Fe(tren)py$_3$]$^{2+}$**.

| | B3LYP | | | | | Exp. [b] |
|---|---|---|---|---|---|---|
| | $a_0$ [a] = | | | | | |
| | **0.00** | **0.05** | **0.10** | **0.15** | **0.20** | |
| distances [Å] | | | | | | |
| $d_{Fe-N(ald)}$ | 1.942 | 1.952 | 1.965 | 1.977 | 1.995 | 1.942 |
| $d_{Fe-N(py)}$ | 1.981 | 1.990 | 1.998 | 2.009 | 2.021 | 1.967 |
| $d_{Fe-N}$ | 1.961 | 1.971 | 1.981 | 1.993 | 2.008 | 1.955 |
| $d_{Fe-N7}$ | 3.530 | 3.511 | 3.490 | 3.469 | 3.441 | 3.439 |
| distortion | | | | | | |
| $\Sigma_{cis}$ / ° [c] | 60.8 | 61.6 | 61.9 | 62.2 | 62.9 | - |
| $\theta$/ ° [d] | **54.1** | **54.0** | **53.7** | **53.5** | **53.1** | **53.97** |
| $S(O_h)$ [e] | 0.60 | 0.62 | 0.64 | 0.67 | 0.71 | - |
| $S$(TP) [e] | 15.08 | 14.99 | 14.90 | 14.76 | 14.62 | - |

[a] *amount of exact exchange;* [b] *Cation in* ***[Fe(tren)py$_3$](BF$_4$)$_2$****, data taken from Ref. [53] in the manuscript;* [c] *summed deviation from 90° of twelve N-Fe-N* cis *angles;* [d] *trigonal distortion;* [e] *continuous shape measures* $S(O_h)$ *and* $S$(TP) *with reference to the octahedron and the trigonal prism, respectively.*

**Table S3.** Pertinent geometric parameters of DFT-optimized **hs-[Fe(tren)py$_3$]$^{2+}$**.

| | B3LYP $a_0$ [a] = | | | | | BP86 | Exp. [b] |
|---|---|---|---|---|---|---|---|
| | **0.00** | **0.05** | **0.10** | **0.15** | **0.20** | **[Zn(tren)py$_3$]$^{2+}$** | **[Zn(tren)py$_3$]$^{2+}$** |
| distances [Å] | | | | | | | |
| $d_{Fe-N(ald)}$ | 2.118 | 2.133 | 2.147 | 2.161 | 2.173 | 2.158 | 2.128 |
| $d_{Fe-N(py)}$ | 2.252 | 2.256 | 2.257 | 2.261 | 2.265 | 2.244 | 2.226 |
| $d_{Fe-N}$ | 2.185 | 2.195 | 2.202 | 2.211 | 2.219 | 2.201 | 2.180 |
| $d_{Fe-N7}$ | 2.800 | 2.795 | 2.834 | 2.876 | 2.923 | 3.053 | 3.013 |
| distortion | | | | | | | |
| $\Sigma_{cis}$ / ° [c] | 112.7 | 111.8 | 109.4 | 108.3 | 109.9 | 92.4 | - |
| $\theta$ / ° [d] | **47.5** | **47.5** | **47.2** | **46.8** | **46.3** | **46.3** | **45.9** |
| $S(O_h)$ [e] | 2.07 | 2.12 | 2.12 | 2.13 | 2.15 | 1.74 | - |
| $S(TP)$ [e] | 12.71 | 12.79 | 12.62 | 12.40 | 12.15 | 11.66 | - |

[a] *amount of exact exchange;* [b] *Cation in* ***[Zn(tren)py$_3$](BF$_4$)$_2$****, data taken from Ref. [53] in the manuscript;* [c] *summed deviation from 90° of twelve N-Fe-N* cis *angles;* [d] *trigonal distortion;* [e] *continuous shape measures* $S(O_h)$ *and* $S(TP)$ *with reference to the octahedron and the trigonal prism, respectively.*

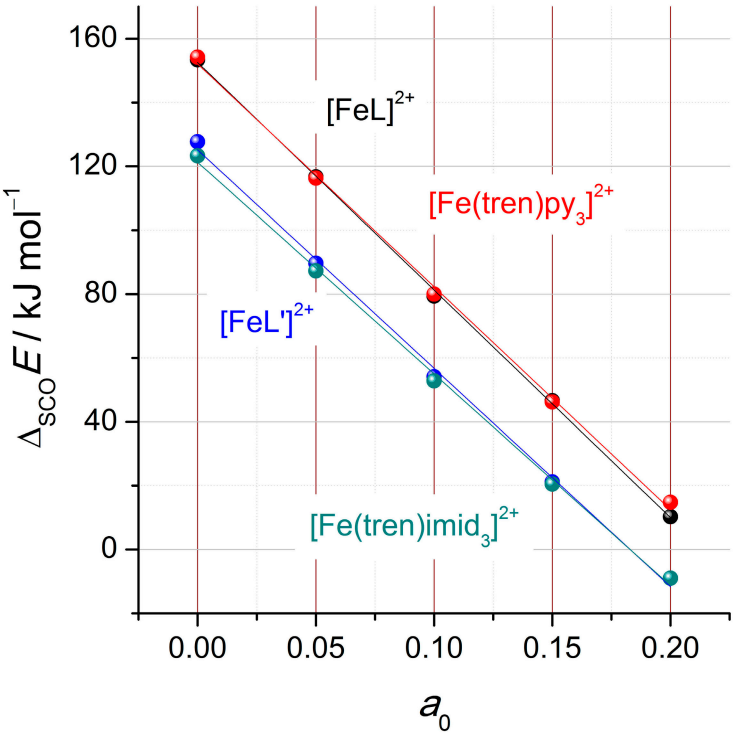


**Figure S1.** Dependence of DFT-derived apparent SCO energies $\Delta_{SCO}E$ on exact exchange $a_0$; symbols: computed energies; lines: linear regressions.

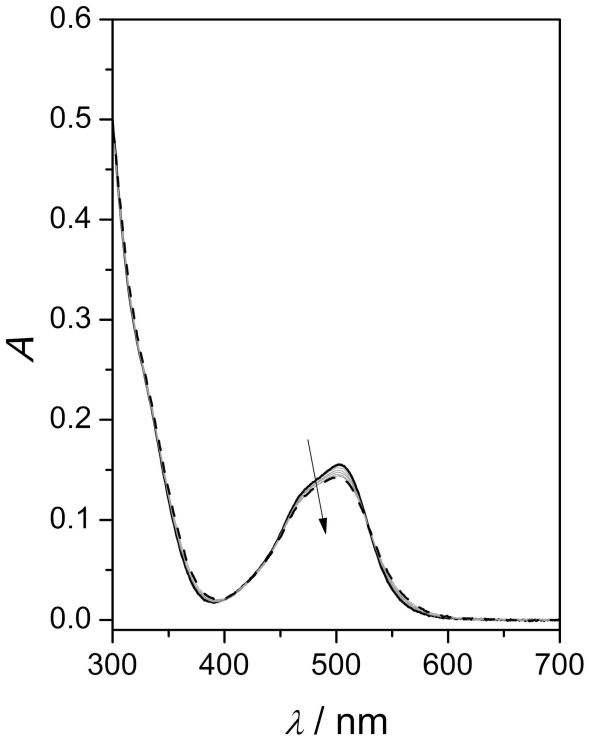


**Figure S2.** VT-UV-Vis spectra of **[FeL]**$(BF_4)_2$ in MeCN between 273 K < $T$ < 350 K; arrow denotes the MLCT intensity loss with increasing temperature (effects of volume density have been accounted for).

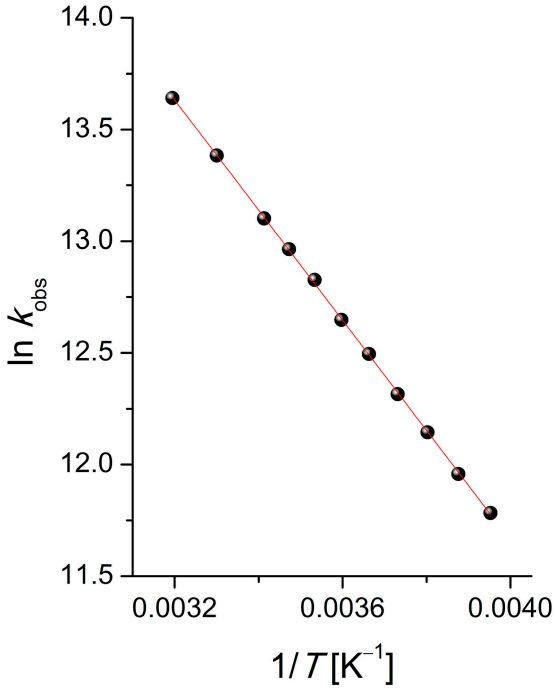


**Figure S3.** Arrhenius plot of transient decay rate constants of **[FeL]**$^{2+}$ in MeCN; symbols: experimental data; line: linear fit with $E_a$ = 'slope' × $R$ = 22.2(3) kJ mol$^{-1}$ and $A_0$ = exp('intercept') = 2.9(2) × $10^9$ s$^{-1}$ ($R^2$ = 0.9998)

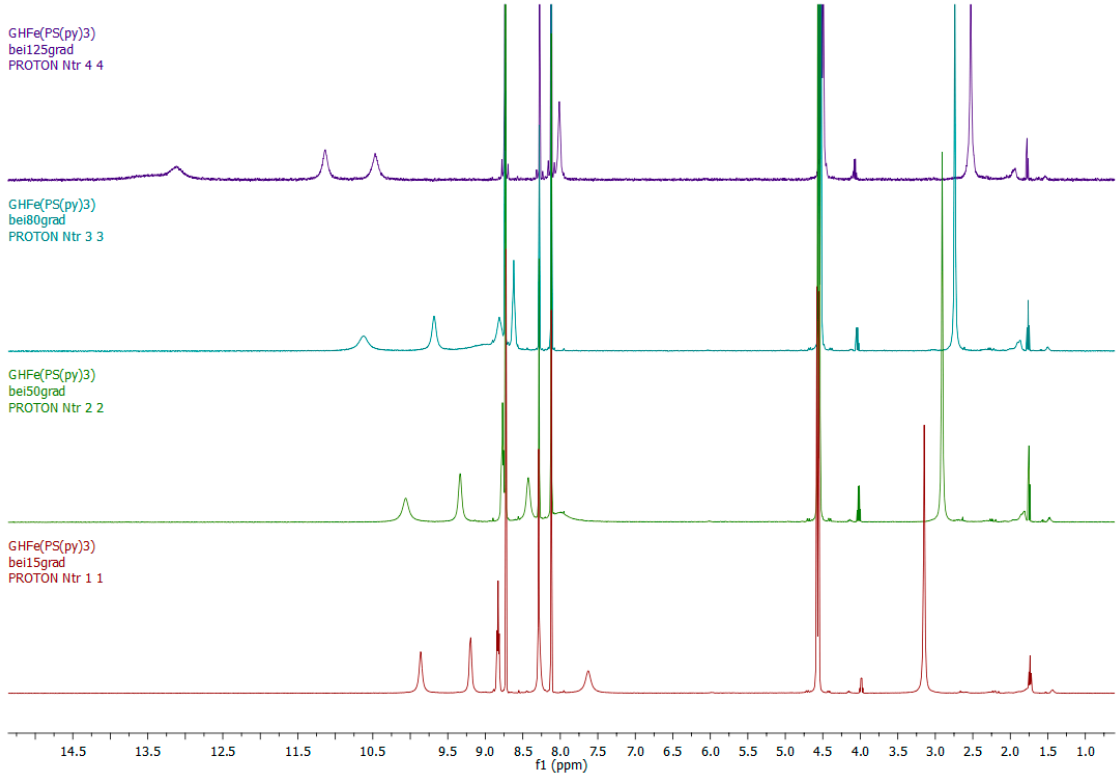


**Figure S4.** VT-$^1$H NMR spectra of **[FeL]**$(BF_4)_2$ (500 MHz; [$D_5$]nitrobenzene).

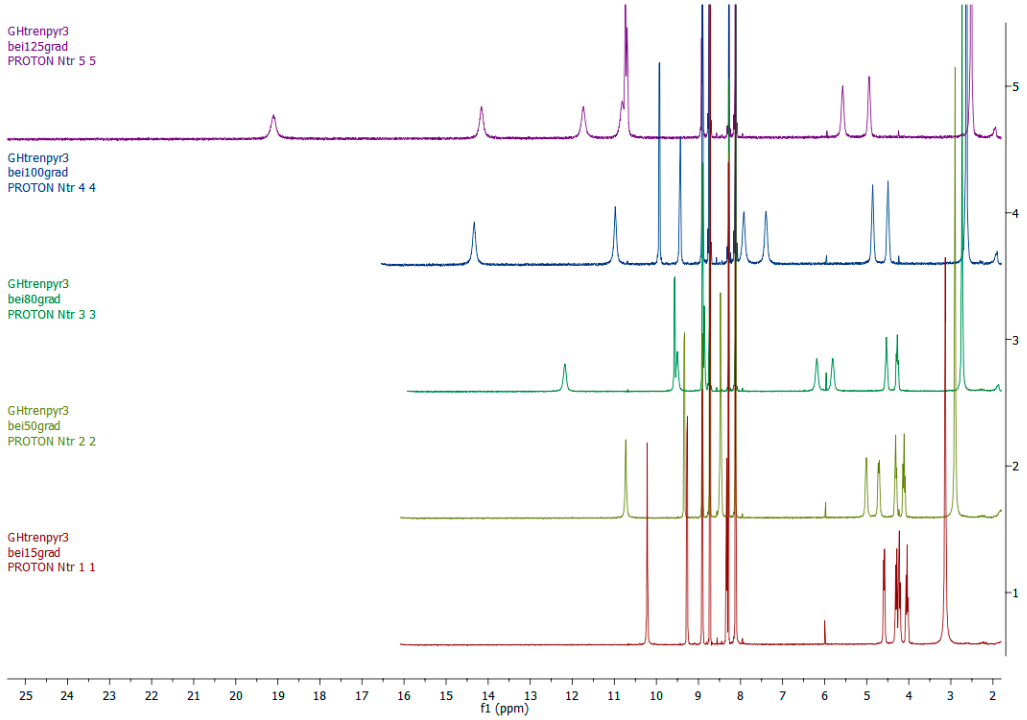


**Figure S5.** VT-$^1$H NMR spectra of **[Fe(tren)py$_3$]**$(ClO_4)_2$ (500 MHz; [$D_5$]nitrobenzene).

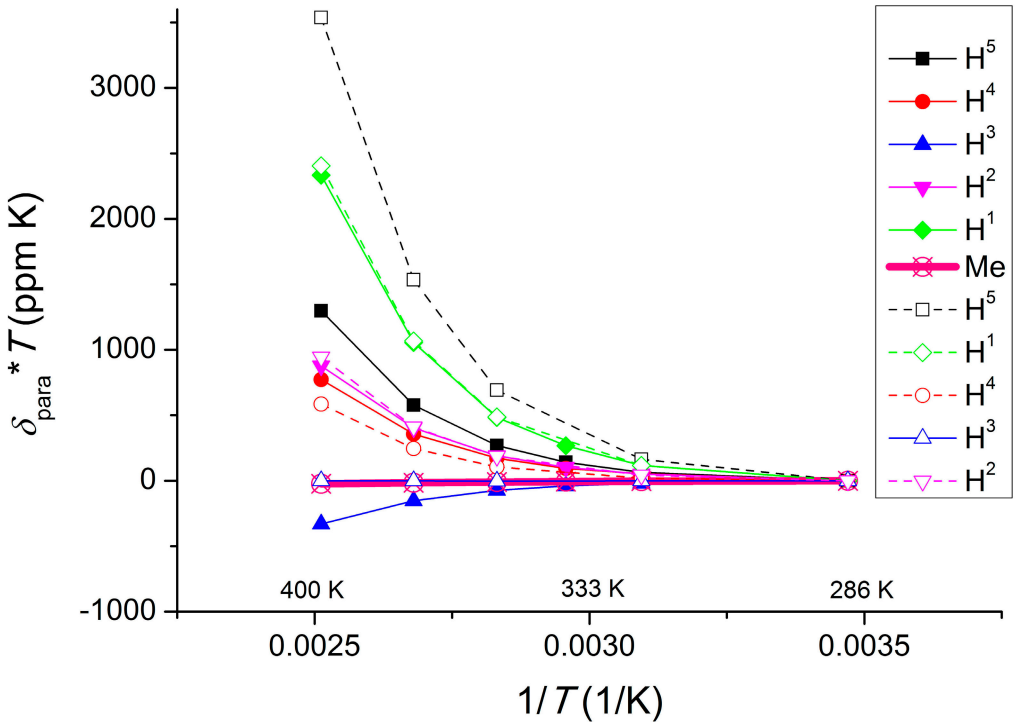


**Figure S6.** Curie plot of the proton chemical shifts in NMR spectra of **[Fe(tren)py$_3$]**$(ClO_4)_2$ (open symbols) and **[FeL]**$(BF_4)_2$ (filled symbols) (500 MHz; [$D_5$]nitrobenzene); for proton assignment, see Scheme 1 in the Manuscript.

**Table S4.** Cartesian coordinates of DFT-optimized **ls-[FeL]**$^{2+}$ (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| C | 2.193278 | -1.271660 | -3.308945 |
| C | 2.884631 | -2.409438 | -2.910318 |
| C | -0.221419 | 3.258077 | -2.903877 |
| C | 0.782202 | 0.680919 | -2.655366 |
| C | 1.446745 | -0.570524 | -2.365997 |
| C | 2.809087 | -2.807293 | -1.578572 |
| C | -2.492531 | -3.140544 | -1.444357 |
| C | -3.712580 | -2.782219 | -0.877496 |
| C | 2.034720 | -2.066365 | -0.692886 |
| C | -1.399752 | -2.294597 | -1.291090 |
| C | -3.802535 | -1.578296 | -0.189044 |
| C | -2.670109 | -0.774694 | -0.083386 |
| C | -2.684138 | 0.538611 | 0.521527 |
| C | -2.586124 | 3.201262 | 1.301727 |
| C | 2.231519 | 3.490222 | 1.243390 |
| C | -0.218904 | -2.144179 | 1.985869 |
| C | 1.800130 | 0.837152 | 1.937622 |
| C | 1.358324 | -0.479355 | 2.341445 |
| C | 0.243059 | -2.866370 | 3.080179 |
| C | 1.879398 | -1.155992 | 3.441472 |
| C | 1.315165 | -2.369751 | 3.816100 |
| H | 2.232685 | -0.918398 | -4.332036 |
| H | 3.475626 | -2.971667 | -3.623249 |
| H | -0.754394 | 2.726714 | -3.695867 |
| H | 0.915779 | 1.178958 | -3.607542 |
| H | 0.828576 | 3.393752 | -3.187709 |
| H | -0.682906 | 4.229723 | -2.746999 |
| H | 3.339893 | -3.680496 | -1.221558 |
| H | -2.379730 | -4.063106 | -1.999135 |
| H | -4.578923 | -3.425351 | -0.975539 |
| H | -0.436716 | -2.551958 | -1.709643 |
| H | -4.734186 | -1.253475 | 0.257574 |
| H | 1.946122 | -2.358366 | 0.344546 |
| H | -3.359701 | 3.224315 | 0.525015 |
| H | -3.610864 | 1.001499 | 0.836207 |
| H | 2.222103 | 4.475319 | 0.783801 |
| H | 3.235313 | 3.064079 | 1.166740 |
| H | -2.289468 | 4.217333 | 1.549702 |
| H | -1.043379 | -2.511048 | 1.389068 |
| H | -2.973585 | 2.709280 | 2.196995 |
| H | 1.943419 | 3.576602 | 2.298182 |
| H | 2.503079 | 1.401480 | 2.537163 |
| H | -0.235163 | -3.800657 | 3.344344 |
| H | 2.706033 | -0.725257 | 3.993060 |
| H | 1.699871 | -2.913729 | 4.670171 |
| N | -0.346398 | 2.476256 | -1.668346 |
| N | 0.136398 | 1.200305 | -1.658766 |
| N | 1.358786 | -0.972475 | -1.066008 |
| N | -1.471284 | -1.136389 | -0.622672 |
| N | -1.537779 | 1.143365 | 0.540730 |
| N | -1.398687 | 2.463460 | 0.855667 |
| N | 1.310075 | 2.620069 | 0.504244 |
| N | 1.201407 | 1.317175 | 0.892470 |
| N | 0.321639 | -0.978174 | 1.609161 |
| P | -0.189639 | 3.264894 | -0.117451 |
| S | -0.303870 | 5.169435 | -0.155653 |
| Fe | 0.001414 | 0.090923 | -0.050540 |

**Table S5.** Cartesian coordinates of DFT-optimized **hs-[FeL]**$^{2+}$ (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| C | 2.286655 | -1.177572 | -3.569293 |
| C | 2.790818 | -2.458544 | -3.373377 |
| C | 0.198710 | 3.421297 | -2.877184 |
| C | 1.091742 | 0.803664 | -2.671289 |
| C | 1.564877 | -0.570373 | -2.543924 |
| C | 2.560280 | -3.093521 | -2.157070 |
| C | -2.822535 | -3.390828 | -0.958056 |
| C | -4.049959 | -2.818428 | -0.638269 |
| C | 1.812396 | -2.428854 | -1.190810 |
| C | -1.676375 | -2.610730 | -0.848750 |
| C | -4.087658 | -1.488087 | -0.234479 |
| C | -2.896134 | -0.770789 | -0.156325 |
| C | -2.886729 | 0.640378 | 0.207463 |
| C | -2.801440 | 3.318362 | 0.924731 |
| C | 2.004235 | 3.645739 | 1.609405 |
| C | 0.374204 | -2.405197 | 2.039103 |
| C | 1.649770 | 0.977687 | 2.282214 |
| C | 1.449541 | -0.432287 | 2.593749 |
| C | 0.891367 | -3.056110 | 3.154214 |
| C | 2.020134 | -1.018086 | 3.721446 |
| C | 1.736399 | -2.349994 | 4.005390 |
| H | 2.459018 | -0.643663 | -4.496009 |
| H | 3.360984 | -2.948273 | -4.153732 |
| H | -0.375315 | 2.897014 | -3.647088 |
| H | 1.237489 | 1.317772 | -3.615577 |
| H | 1.236179 | 3.537524 | -3.208072 |
| H | -0.233430 | 4.402747 | -2.702897 |
| H | 2.945242 | -4.084898 | -1.956551 |
| H | -2.748470 | -4.418810 | -1.288001 |
| H | -4.964394 | -3.395369 | -0.708780 |
| H | -0.702511 | -3.015933 | -1.094961 |
| H | -5.024990 | -1.003208 | 0.010360 |
| H | 1.605511 | -2.890419 | -0.232270 |
| H | -3.582479 | 3.352664 | 0.157337 |
| H | -3.824197 | 1.122081 | 0.464006 |
| H | 1.975973 | 4.626089 | 1.141650 |
| H | 3.005835 | 3.216305 | 1.504792 |
| H | -2.499026 | 4.331586 | 1.175050 |
| H | -0.285811 | -2.917919 | 1.349716 |
| H | -3.186792 | 2.819209 | 1.818687 |
| H | 1.756343 | 3.746309 | 2.671993 |
| H | 2.320968 | 1.564815 | 2.899969 |
| H | 0.635448 | -4.090412 | 3.344556 |
| H | 2.661517 | -0.431189 | 4.368079 |
| H | 2.161728 | -2.825644 | 4.880856 |
| N | 0.142841 | 2.642097 | -1.636419 |
| N | 0.566384 | 1.361628 | -1.631813 |
| N | 1.312138 | -1.203700 | -1.374739 |
| N | -1.700184 | -1.335413 | -0.448611 |
| N | -1.755258 | 1.257923 | 0.162792 |
| N | -1.635445 | 2.571434 | 0.440589 |
| N | 1.044358 | 2.761760 | 0.940080 |
| N | 0.969550 | 1.466715 | 1.300686 |
| N | 0.648432 | -1.128558 | 1.753651 |
| P | -0.197298 | 3.370908 | -0.102761 |
| S | -0.323319 | 5.281064 | -0.146624 |
| Fe | 0.024388 | -0.072609 | -0.034711 |

**Table S6.** Cartesian coordinates of DFT-optimized **[ZnL]**$^{2+}$ (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| C | 2.362389 | -1.119418 | -3.537243 |
| C | 2.854169 | -2.404001 | -3.335708 |
| C | 0.230482 | 3.487365 | -2.873735 |
| C | 1.137730 | 0.860463 | -2.670755 |
| C | 1.618496 | -0.511000 | -2.528091 |
| C | 2.600029 | -3.041385 | -2.125023 |
| C | -2.825518 | -3.424046 | -0.897426 |
| C | -4.052120 | -2.838691 | -0.598054 |
| C | 1.842693 | -2.373022 | -1.170776 |
| C | -1.677768 | -2.644578 | -0.810314 |
| C | -4.085707 | -1.498004 | -0.231994 |
| C | -2.890833 | -0.783719 | -0.162886 |
| C | -2.880968 | 0.634307 | 0.184029 |
| C | -2.828853 | 3.322389 | 0.853149 |
| C | 2.025269 | 3.594051 | 1.569878 |
| C | 0.292600 | -2.449779 | 2.065068 |
| C | 1.620880 | 0.924761 | 2.239126 |
| C | 1.400734 | -0.481521 | 2.563108 |
| C | 0.808268 | -3.084774 | 3.189968 |
| C | 1.969802 | -1.052906 | 3.699907 |
| C | 1.671577 | -2.372923 | 4.016815 |
| H | 2.557832 | -0.584677 | -4.458857 |
| H | 3.434617 | -2.895376 | -4.107264 |
| H | -0.303979 | 2.980006 | -3.681708 |
| H | 1.320986 | 1.379654 | -3.606073 |
| H | 1.279340 | 3.625745 | -3.156131 |
| H | -0.223305 | 4.457813 | -2.690688 |
| H | 2.976200 | -4.035000 | -1.919540 |
| H | -2.754411 | -4.461204 | -1.198498 |
| H | -4.968026 | -3.414567 | -0.656332 |
| H | -0.704463 | -3.058668 | -1.046924 |
| H | -5.022331 | -1.003481 | -0.004552 |
| H | 1.622054 | -2.830782 | -0.213364 |
| H | -3.587626 | 3.329800 | 0.062787 |
| H | -3.821408 | 1.107128 | 0.446623 |
| H | 2.015884 | 4.570994 | 1.094590 |
| H | 3.016383 | 3.143642 | 1.459162 |
| H | -2.540596 | 4.343929 | 1.084942 |
| H | -0.381972 | -2.970325 | 1.396310 |
| H | -3.237636 | 2.846730 | 1.749048 |
| H | 1.786352 | 3.709678 | 2.632769 |
| H | 2.298632 | 1.499614 | 2.861741 |
| H | 0.534389 | -4.109036 | 3.407665 |
| H | 2.620793 | -0.460016 | 4.330829 |
| H | 2.099619 | -2.834971 | 4.898252 |
| N | 0.125240 | 2.674206 | -1.657238 |
| N | 0.563957 | 1.402566 | -1.654276 |
| N | 1.351716 | -1.144966 | -1.364722 |
| N | -1.700775 | -1.361041 | -0.437777 |
| N | -1.757123 | 1.260991 | 0.132325 |
| N | -1.644828 | 2.572494 | 0.419042 |
| N | 1.042410 | 2.726938 | 0.911745 |
| N | 0.950121 | 1.430433 | 1.262609 |
| N | 0.588186 | -1.186244 | 1.744872 |
| P | -0.199460 | 3.372184 | -0.105251 |
| S | -0.299440 | 5.285328 | -0.102565 |
| Zn | 0.011031 | -0.133733 | -0.048471 |

**Table S7.** Cartesian coordinates of DFT-optimized **ls-[Fe(tren)py$_3$]$^{2+}$** (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| Fe | -5.241944 | 2.663158 | 3.567574 |
| N | -6.384012 | 4.019024 | 4.430049 |
| N | -6.991966 | 2.221404 | 2.683666 |
| N | -5.636811 | 1.229343 | 4.880700 |
| N | -4.274586 | 1.140046 | 2.684776 |
| N | -3.536819 | 3.269045 | 4.366075 |
| N | -4.701984 | 4.016114 | 2.185527 |
| N | -4.991981 | 3.272514 | 6.973181 |
| C | -7.622693 | 4.004517 | 4.080965 |
| C | -8.028930 | 2.981441 | 3.134916 |
| C | -9.339197 | 2.777452 | 2.711706 |
| C | -9.598818 | 1.762092 | 1.793170 |
| C | -8.536192 | 0.994876 | 1.324736 |
| C | -7.250393 | 1.254763 | 1.793746 |
| C | -5.231540 | 0.056316 | 4.541851 |
| C | -4.447747 | -0.049465 | 3.326206 |
| C | -3.916610 | -1.240325 | 2.841602 |
| C | -3.170118 | -1.214798 | 1.665811 |
| C | -2.971690 | 0.005214 | 1.025419 |
| C | -3.540686 | 1.157602 | 1.564936 |
| C | -2.888619 | 4.141557 | 3.677320 |
| C | -3.511776 | 4.620851 | 2.458421 |
| C | -2.962170 | 5.591091 | 1.626409 |
| C | -3.654290 | 5.960427 | 0.475708 |
| C | -4.876620 | 5.351389 | 0.205662 |
| C | -5.364049 | 4.383089 | 1.081199 |
| C | -5.920790 | 5.010552 | 5.393655 |
| C | -5.830911 | 4.428388 | 6.826753 |
| C | -6.415830 | 1.386504 | 6.103571 |
| C | -5.576076 | 1.989656 | 7.252321 |
| C | -2.947009 | 2.753827 | 5.596148 |
| C | -3.566656 | 3.397918 | 6.858750 |
| H | -8.343383 | 4.727966 | 4.463213 |
| H | -10.134741 | 3.404395 | 3.099802 |
| H | -10.609266 | 1.573468 | 1.447390 |
| H | -8.692847 | 0.200981 | 0.603441 |
| H | -6.402272 | 0.676666 | 1.449911 |
| H | -5.464334 | -0.831263 | 5.131003 |
| H | -4.092010 | -2.165930 | 3.379509 |
| H | -2.746102 | -2.127473 | 1.261660 |
| H | -2.389884 | 0.071960 | 0.113585 |
| H | -3.414231 | 2.121170 | 1.087584 |
| H | -1.907531 | 4.508887 | 3.978924 |
| H | -2.009370 | 6.042458 | 1.880326 |
| H | -3.249619 | 6.711289 | -0.194077 |
| H | -5.450215 | 5.613080 | -0.675937 |
| H | -6.306129 | 3.882313 | 0.897369 |
| H | -6.592404 | 5.876545 | 5.412034 |
| H | -4.931398 | 5.343583 | 5.076787 |
| H | -5.482472 | 5.252495 | 7.465143 |
| H | -6.840557 | 4.169487 | 7.161286 |
| H | -6.820097 | 0.422439 | 6.433806 |
| H | -7.251072 | 2.053746 | 5.882108 |
| H | -6.244379 | 2.036750 | 8.124243 |
| H | -4.773263 | 1.289884 | 7.504361 |
| H | -1.865449 | 2.936575 | 5.609811 |
| H | -3.123024 | 1.675997 | 5.619102 |
| H | -3.059216 | 2.930370 | 7.714888 |
| H | -3.306437 | 4.461273 | 6.873908 |

**Table S8.** Cartesian coordinates of DFT-optimized **hs-[Fe(tren)py$_3$]$^{2+}$** (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| Fe | -5.154130 | 2.721159 | 3.808125 |
| N | -6.614343 | 4.115147 | 4.525715 |
| N | -7.060448 | 2.261191 | 2.654503 |
| N | -5.636058 | 0.991531 | 5.017449 |
| N | -4.271215 | 0.960408 | 2.735508 |
| N | -3.238712 | 3.534206 | 4.445840 |
| N | -4.492995 | 4.108397 | 2.145327 |
| N | -4.977506 | 3.234392 | 6.632835 |
| C | -7.808645 | 4.023165 | 4.079416 |
| C | -8.113718 | 3.004866 | 3.074492 |
| C | -9.409221 | 2.798279 | 2.604008 |
| C | -9.631157 | 1.793679 | 1.663962 |
| C | -8.546827 | 1.043763 | 1.218851 |
| C | -7.281875 | 1.312801 | 1.740145 |
| C | -5.358496 | -0.158787 | 4.539117 |
| C | -4.624343 | -0.232240 | 3.272899 |
| C | -4.276531 | -1.444860 | 2.685583 |
| C | -3.528105 | -1.429670 | 1.509096 |
| C | -3.152161 | -0.204743 | 0.967321 |
| C | -3.551644 | 0.967049 | 1.611382 |
| C | -2.662160 | 4.357020 | 3.660525 |
| C | -3.312053 | 4.721269 | 2.395462 |
| C | -2.758273 | 5.660459 | 1.531931 |
| C | -3.446251 | 5.983112 | 0.361603 |
| C | -4.662024 | 5.359136 | 0.107980 |
| C | -5.145655 | 4.423923 | 1.026805 |
| C | -6.296637 | 5.044800 | 5.603336 |
| C | -6.026458 | 4.225448 | 6.872539 |
| C | -6.224226 | 1.129102 | 6.340072 |
| C | -5.245746 | 1.920571 | 7.217242 |
| C | -2.672634 | 3.207484 | 5.747261 |
| C | -3.617379 | 3.733782 | 6.834328 |
| H | -8.615598 | 4.668967 | 4.436641 |
| H | -10.223304 | 3.412645 | 2.974342 |
| H | -10.628682 | 1.600671 | 1.284393 |
| H | -8.671604 | 0.259205 | 0.481062 |
| H | -6.418094 | 0.744870 | 1.414215 |
| H | -5.617275 | -1.088637 | 5.053074 |
| H | -4.584822 | -2.378129 | 3.145078 |
| H | -3.237186 | -2.358066 | 1.029654 |
| H | -2.562586 | -0.149661 | 0.059534 |
| H | -3.291749 | 1.942011 | 1.213370 |
| H | -1.700850 | 4.819660 | 3.903118 |
| H | -1.810304 | 6.129255 | 1.773333 |
| H | -3.041024 | 6.712038 | -0.331840 |
| H | -5.233100 | 5.585304 | -0.785121 |
| H | -6.087560 | 3.911914 | 0.862654 |
| H | -7.105625 | 5.764004 | 5.778596 |
| H | -5.393351 | 5.595911 | 5.319369 |
| H | -5.773345 | 4.903886 | 7.698902 |
| H | -6.947854 | 3.706218 | 7.150480 |
| H | -6.447375 | 0.157379 | 6.797047 |
| H | -7.159602 | 1.689155 | 6.239359 |
| H | -5.654851 | 1.993244 | 8.236130 |
| H | -4.305449 | 1.365532 | 7.277751 |
| H | -1.670600 | 3.634498 | 5.879139 |
| H | -2.602006 | 2.116406 | 5.814366 |
| H | -3.214960 | 3.464267 | 7.821756 |
| H | -3.634833 | 4.826307 | 6.776654 |

**Table S9.** Cartesian coordinates of DFT-optimized **[Zn(tren)py$_3$]$^{2+}$** (B3LYP*-D/TZVPP).

| | | | |
|---|---|---|---|
| Zn | -5.23310 | 2.68063 | 3.78940 |
| N | -6.64694 | 4.09422 | 4.59891 |
| N | -7.14351 | 2.27161 | 2.66773 |
| N | -5.52954 | 0.97326 | 5.07827 |
| N | -4.28590 | 0.97830 | 2.68181 |
| N | -3.33618 | 3.46674 | 4.45388 |
| N | -4.60235 | 4.06046 | 2.14342 |
| N | -4.99857 | 3.22739 | 6.78406 |
| C | -7.81934 | 4.08357 | 4.08298 |
| C | -8.14795 | 3.10417 | 3.03874 |
| C | -9.42445 | 3.03351 | 2.47401 |
| C | -9.67259 | 2.06734 | 1.49380 |
| C | -8.63819 | 1.21101 | 1.11540 |
| C | -7.38638 | 1.35078 | 1.72918 |
| C | -5.12929 | -0.15321 | 4.61850 |
| C | -4.44153 | -0.20723 | 3.32185 |
| C | -3.96537 | -1.40930 | 2.79217 |
| C | -3.30202 | -1.38530 | 1.56125 |
| C | -3.13738 | -0.16313 | 0.90863 |
| C | -3.64964 | 0.99593 | 1.50591 |
| C | -2.74072 | 4.25628 | 3.63966 |
| C | -3.38945 | 4.62147 | 2.37326 |
| C | -2.79325 | 5.50617 | 1.47118 |
| C | -3.47574 | 5.82641 | 0.29351 |
| C | -4.72587 | 5.25222 | 0.06288 |
| C | -5.25062 | 4.36950 | 1.01582 |
| C | -6.31671 | 5.00522 | 5.68388 |
| C | -6.06334 | 4.19780 | 6.97188 |
| C | -6.14213 | 1.07146 | 6.39346 |
| C | -5.23093 | 1.89798 | 7.32261 |
| C | -2.75457 | 3.14753 | 5.74822 |
| C | -3.63885 | 3.73301 | 6.86669 |
| H | -8.60547 | 4.78517 | 4.40243 |
| H | -10.20549 | 3.72230 | 2.80057 |
| H | -10.65911 | 1.98443 | 1.03613 |
| H | -8.79012 | 0.44438 | 0.35511 |
| H | -6.54822 | 0.70524 | 1.45932 |
| H | -5.27245 | -1.09499 | 5.17024 |
| H | -4.11215 | -2.34291 | 3.33782 |
| H | -2.91722 | -2.30678 | 1.12290 |
| H | -2.62430 | -0.10046 | -0.05095 |
| H | -3.55099 | 1.97175 | 1.02708 |
| H | -1.75191 | 4.68668 | 3.85993 |
| H | -1.81489 | 5.93509 | 1.69311 |
| H | -3.03876 | 6.51705 | -0.42907 |
| H | -5.29204 | 5.47785 | -0.84099 |
| H | -6.22153 | 3.89193 | 0.87308 |
| H | -7.11294 | 5.74987 | 5.85491 |
| H | -5.38980 | 5.53396 | 5.40678 |
| H | -5.85385 | 4.91086 | 7.79251 |
| H | -6.98816 | 3.66309 | 7.23585 |
| H | -6.33464 | 0.07883 | 6.83492 |
| H | -7.10257 | 1.59911 | 6.27762 |
| H | -5.68998 | 1.91703 | 8.33045 |
| H | -4.26483 | 1.37967 | 7.41572 |
| H | -1.72341 | 3.52934 | 5.84297 |
| H | -2.73582 | 2.04994 | 5.84602 |
| H | -3.15679 | 3.51263 | 7.83996 |
| H | -3.66137 | 4.82782 | 6.75635 |