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# Fine-Tuning of the Spin-Crossover properties on Fe(III) Complexes via Ligand design

# Supporting Information

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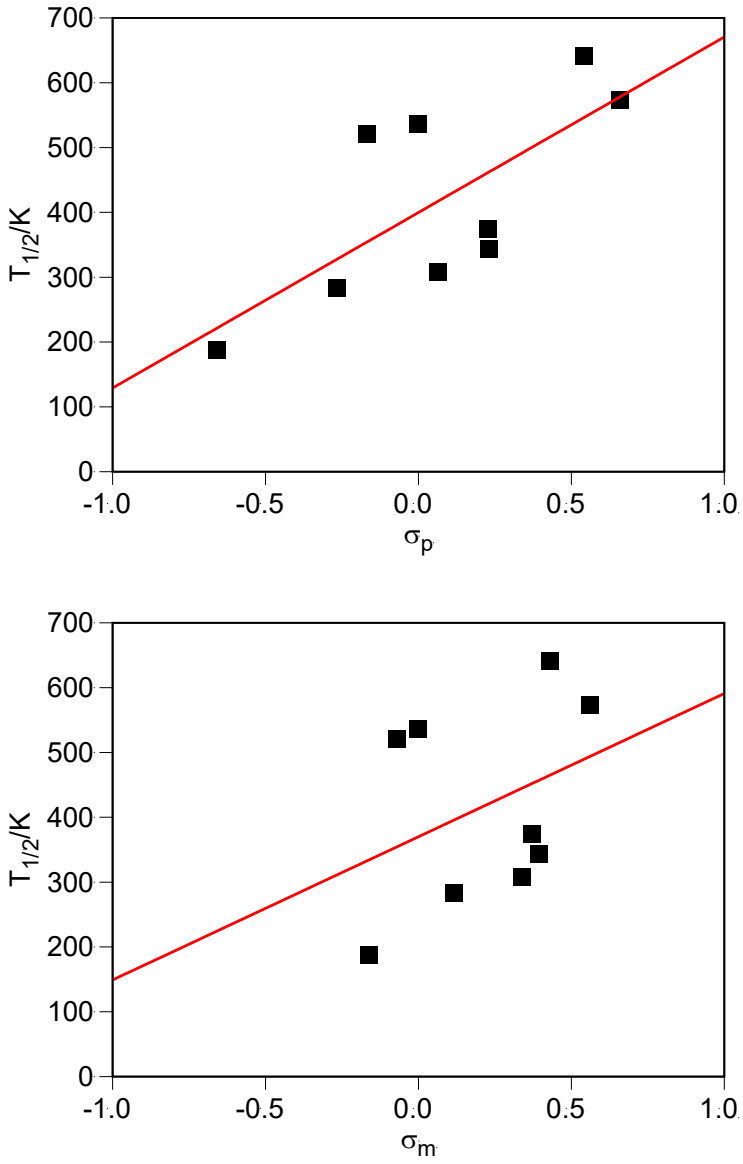
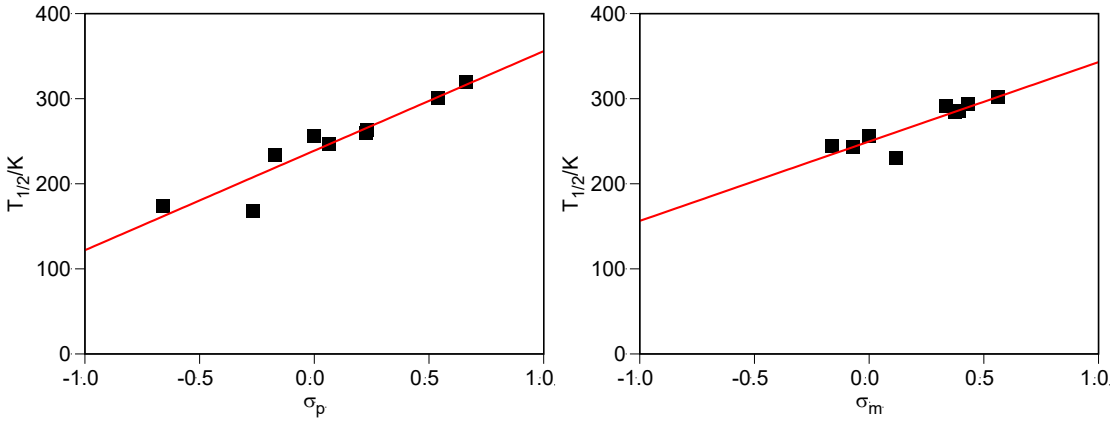
S1. $T_{1/2}$ for $[Fe(L_1^R)(im)_2]^+$ vs. $\sigma_p/\sigma_m$ constant correlation




Top, scatterplot between the computed $T_{1/2}$ and the Hammett $\sigma_p$ constant ($R^2 = 0.51$)
Bottom, scatterplot between the computed $T_{1/2}$ and the Hammett $\sigma_m$ constant ($R^2 = 0.13$)

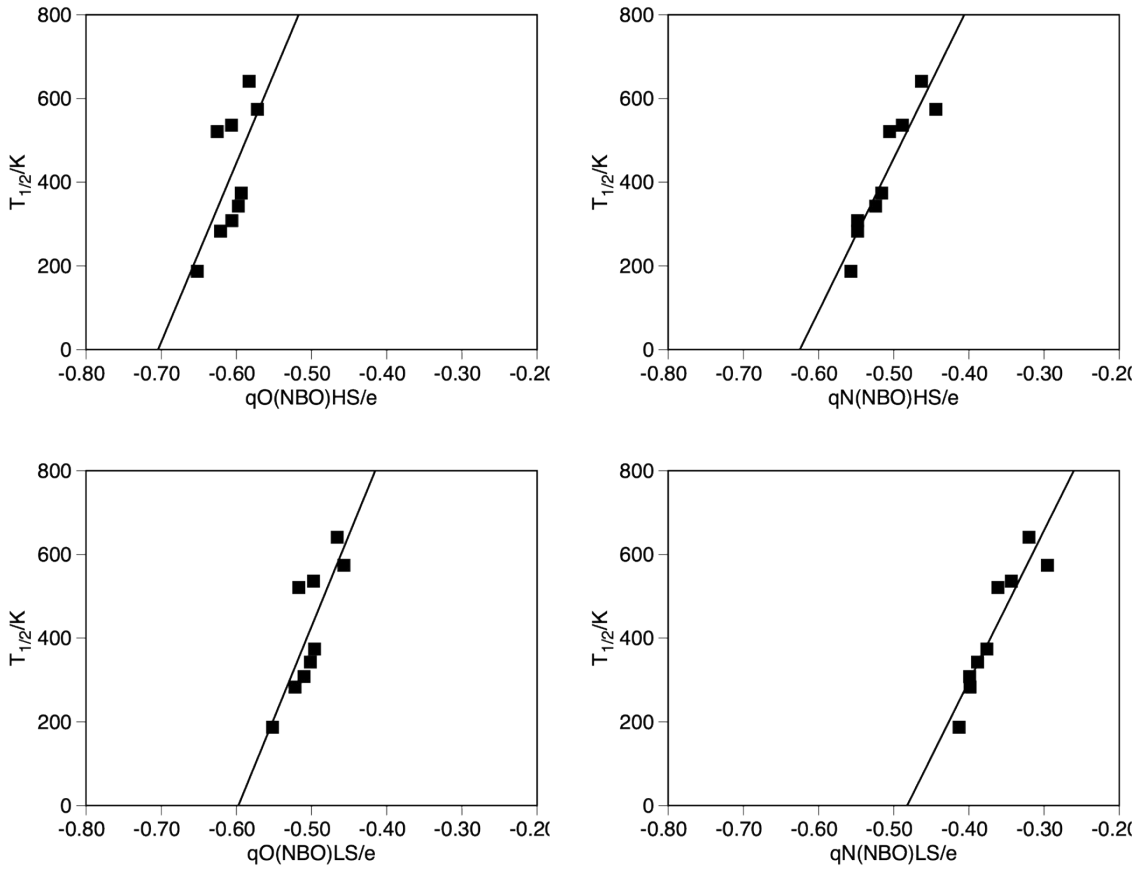
S2: $T_{1/2}$ for the $[Fe(L_2^{Rp/Rm})(im)_2]^+$ vs. $\sigma_p/\sigma_m$ constant correlation




Left, correlation between the computed $T_{1/2}$ and the $\sigma_p$ Hammett constant ($R^2 = 0.88$), and right, correlation between the computed $T_{1/2}$ and the $\sigma_m$ Hammett constant ($R^2 = 0.79$).

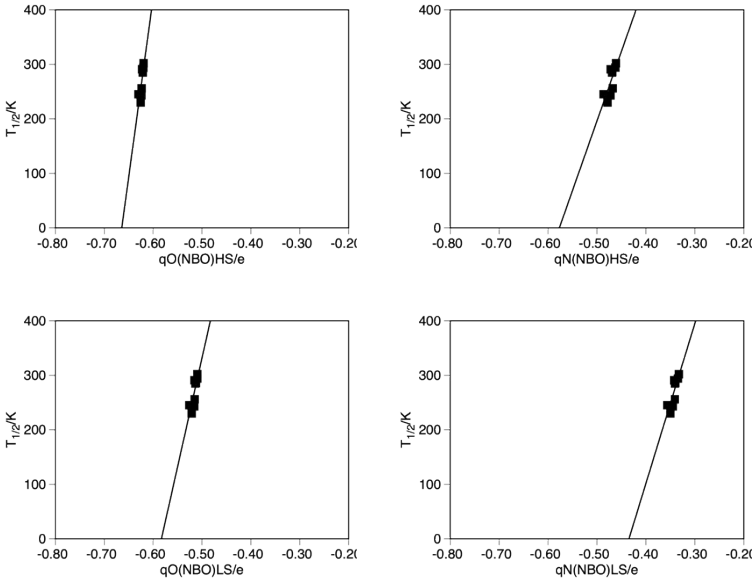
S3. NBO charges correlations for $[Fe(L_1^R)(im)_2]^+$ and $[Fe(L_2^{Rp/Rm})(im)_2]^+$ systems. The following plots provide with correlations of the average NBO charge on donor oxygen atoms, qO(NBO), or on donor nitrogen atoms, qN(NBO), against $T_{1/2}$. The charges of both the high-spin (HS) and low-spin (LS) states are considered.

$[Fe(L_1^R)(im)_2]^+$ vs $T_{1/2}$



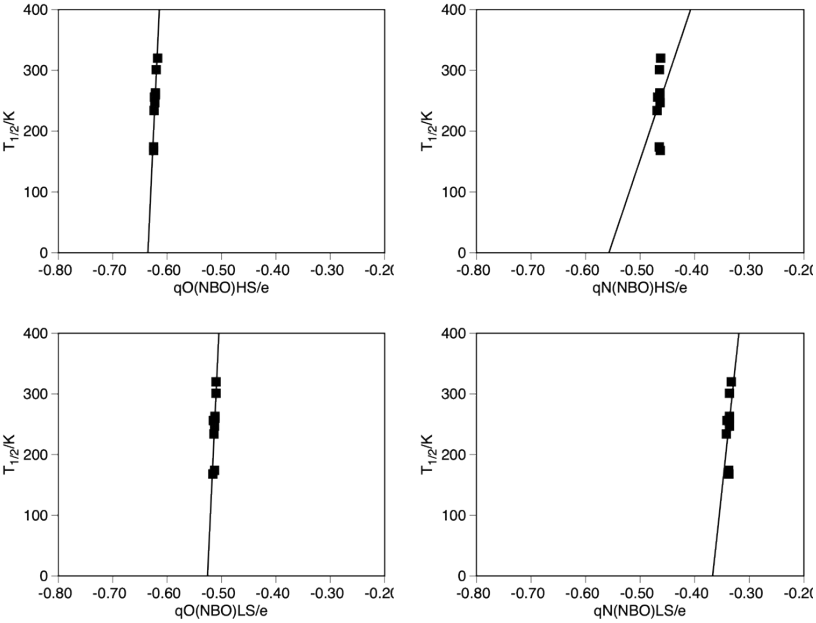

Left-Right, Top-Bottom correlation coefficients: $R^2 = 0.44$, $R^2 = 0.87$, $R^2 = 0.67$ and $R^2 = 0.86$

$[Fe(L_2^{Rm})(im)_2]^+$ vs $T_{1/2}$



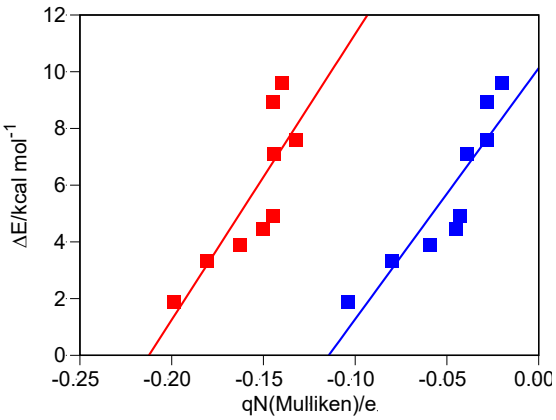

Left-Right, Top-Bottom correlation coefficients: $R^2 = 0.65$, $R^2 = 0.65$, $R^2 = 0.64$ and $R^2 = 0.66$

$[Fe(L_2^{Rp})(im)_2]^+$ vs $T_{1/2}$

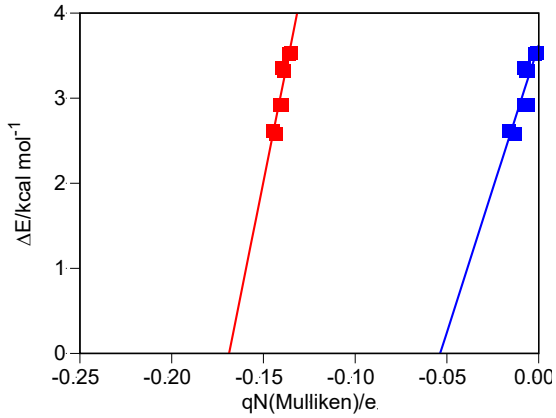



Left-Right, Top-Bottom correlation coefficients: $R^2 = 0.85$, $R^2 = 0.85$, $R^2 = 0.60$ and $R^2 = 0.19$.

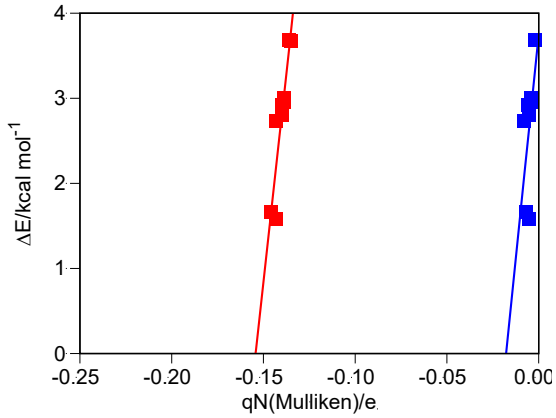
S4 Mulliken charges correlations for $[Fe(L_1^{R})(im)_2]^+$ and $[Fe(L_2^{Rp/Rm})(im)_2]^+$ . Blue for low-spin (S=1/2) and red for high-spin (S=5/2)




Correlation between the average N Mulliken charge and the spin-state energy gap for the $[Fe(L_1^{R})(im)_2]^+$ systems. ($R^2$ = 0.67 and 0.82 for high- and low-spin states respectively)

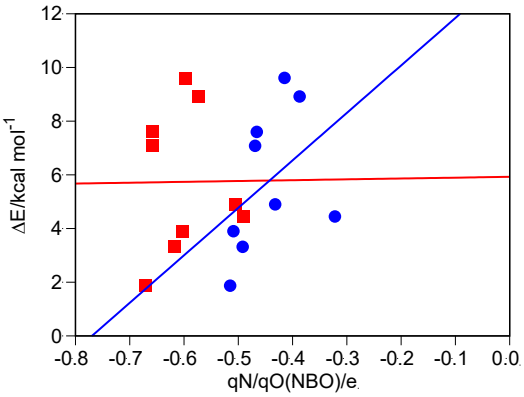



Correlation between the average N Mulliken charge and the spin-state energy gap for the $[Fe(L_2^{Rm})(im)_2]^+$ systems. ($R^2$ = 0.82 and 0.76 for high- and low-spin states respectively)

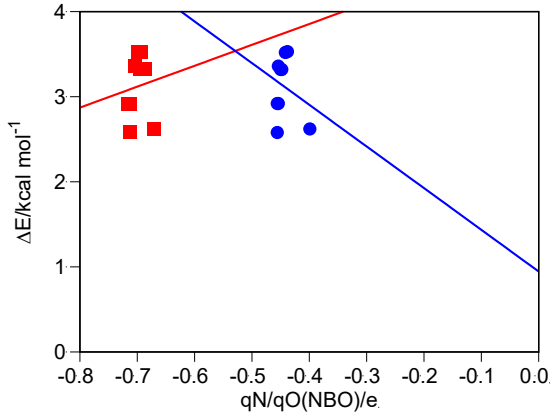



Correlation between the average N Mulliken charge and the spin-state energy gap for the $[Fe(L_2^{Rp})(im)_2]^+$ systems. ($R^2$ = 0.86 and 0.48 for high- and low-spin states respectively)

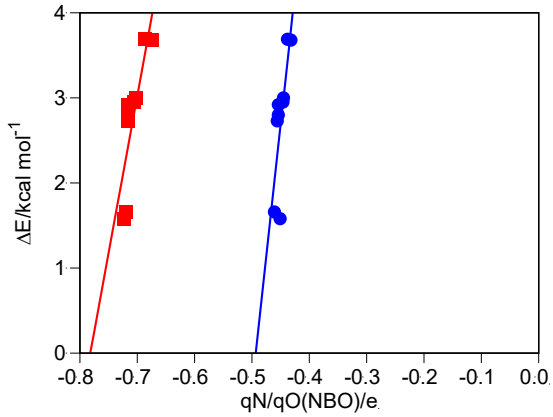
S5 NBO charges correlations for ($L_1^R$) and ($L_2^{Rp/Rm}$). Circle for the average NBO charge of the N-donor atoms, and squares for the average O-donor atom.




Correlation between the average N (circle) or O (squares) NBO charge of the free $L_1^R$ ligand and the spin-state energy gap for the $[Fe(L_1^R)(im)_2]^+$ systems. ($R^2$ = 0.00 and 0.17 for oxygen and nitrogen respectively)

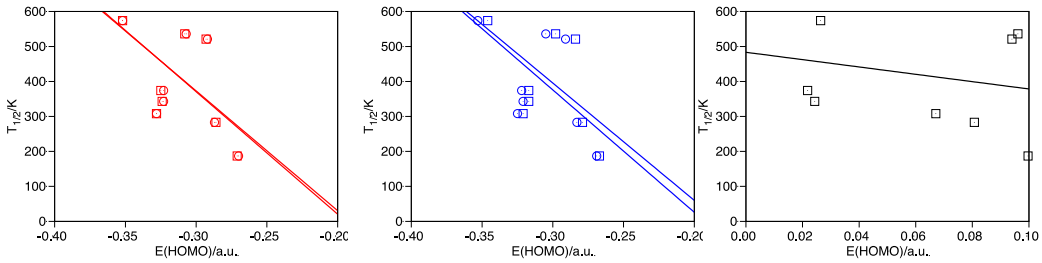



Correlation between the average N (circle) or O (squares) NBO charge of the free $L_2^{Rm}$ ligand and the spin-state energy gap for the $[Fe(L_2^{Rm})(im)_2]^+$ systems. ($R^2$ = 0.01 and 0.05 for oxygen and nitrogen respectively)

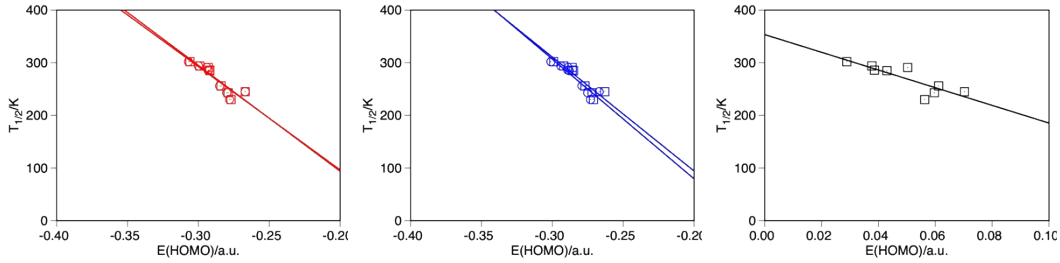



Correlation between the average N (circle) or O (squares) NBO charge of the free $L_2^{Rp}$ ligand and the spin-state energy gap for the $[Fe(L_2^{Rp})(im)_2]^+$ systems. ($R^2$ = 0.67 and 0.58 for oxygen and nitrogen respectively)

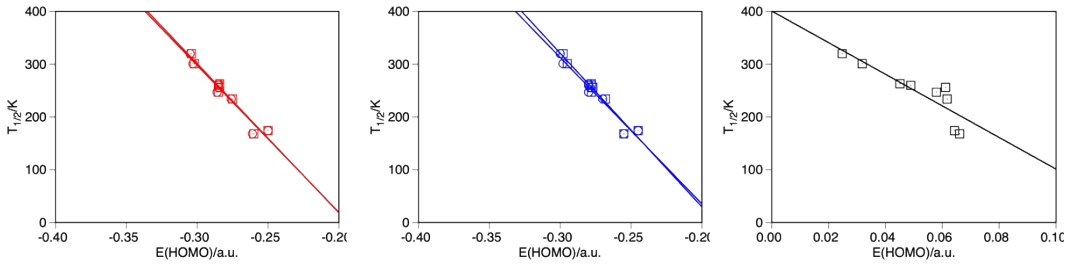
S6 HOMO energy vs. $T_{1/2}$ correlations. Red for high-spin, Blue for low-spin and black for the ligand. For the high-spin and low-spin situation, both alpha (circle) and beta (squares) HOMO energies have been used.




Energy of the HOMO vs the computed $T_{1/2}$ for the $[Fe(L_1^{R})(im)_2]^+$ systems. $R^2$ values are 0.38 and 0.43 (high-spin alpha and beta), 0.39 and 0.45 (low-spin alpha and beta), and 0.07 (free ligand)

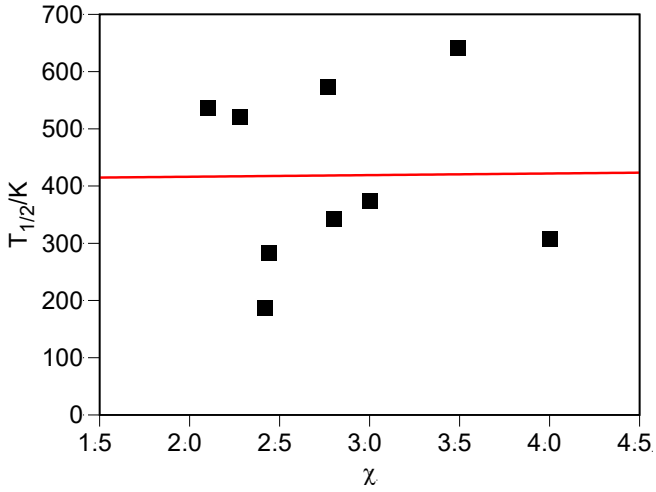



Energy of the HOMO vs the computed $T_{1/2}$ for the $[Fe(L_2^{Rm})(im)_2]^+$ systems. $R^2$ values are 0.89 and 0.89 (high-spin alpha and beta), 0.91 and 0.92 (low-spin alpha and beta), and 0.78 (free ligand)



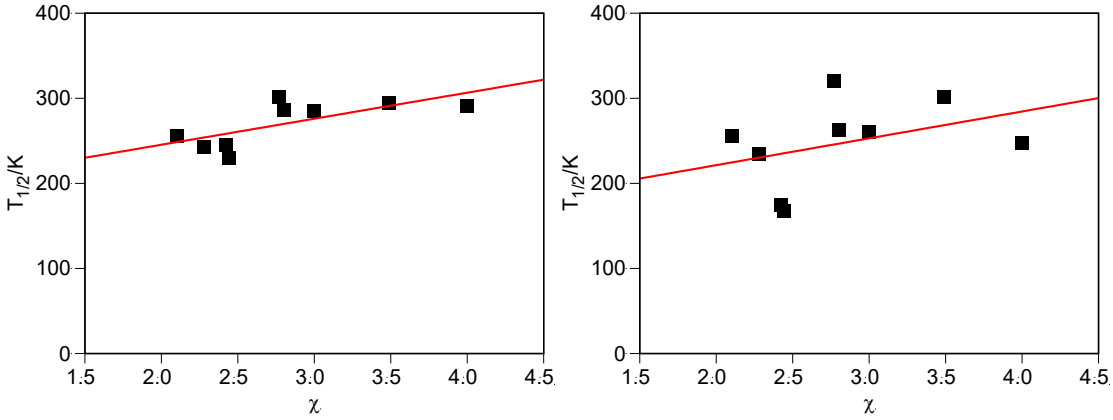

Energy of the HOMO vs the computed $T_{1/2}$ for the $[Fe(L_2^{Rp})(im)_2]^+$ systems. $R^2$ values are 0.95 and 0.95 (high-spin alpha and beta), 0.95 and 0.95 (low-spin alpha and beta), and 0.71 (free ligand)

S7. $T_{1/2}$ for the $[Fe(L_1^R)(im)_2]^+$ vs. electronegativity correlation




Scatterplot of the substituent electronegativity[1] and the computed $T_{1/2}$ for $[Fe(L_1^R)(im)_2]^+$ ($R^2 = 0.00$)

S8. $T_{1/2}$ for the $[Fe(L_2^{Rp/Rm})(im)_2]^+$ vs. electronegativity correlation




Scatterplot of the substituent electronegativity[1] and the computed $T_{1/2}$ for $[Fe(L_2^{Rm})(im)_2]^+$ (left, $R^2 = 0.49$) and $[Fe(L_2^{Rp})(im)_2]^+$ (left, $R^2 = 0.14$) and

S9 A data set collection of computational results is available in the ioChem-BD repository[2] and can be accessed via https://doi.org/10.19061/iochem-bd-6-197

S10 Available experimental data

Experimental data for the $[Fe(L_1^R)(im)_2]^+$ systems

| *Substituent* | *Counterion* | *$T_{1/2}$ (K)* | *Reference* |
|---|---|---|---|
| $CH_3$[a] | $[BPh_4]^-$ | LS at all T | [3] |

[a] In addition to ESR data in powder samples, ESR measurements in DMSO frozen solutions show that the compound is LS at 298 K, which is consistent with our predicted $T_{1/2}$ value of 521 K (see Table 1 in the main text).

Experimental data for the $[Fe(L_2^{Rp/Rm})(im)_2]^+$ systems

| *Substituent* | *Counterion* | *$T_{1/2}$ (K)* | *Reference* |
|---|---|---|---|
| H | $PF_6^-$ | 78 | [4] |
| H | $CF_3SO_3^-$ | Gradual transition. $T_{1/2}$ not given | [4] |
| H | $BPh_4^-$ | Gradual transition. $T_{1/2}$ not given | [4] |
| H | $ClO_4^-$ | HS at all T | [4] |
| H | $BF_4^-$ | HS at all T | [4] |
| H | $AsF_6^-$ | 69.4 - 74.0 | [5] |
| H | $SbF_6^-$ | 105 | [6] |
| OMe (*meta*)[b] | $PF_6^-$ | ~ 150 | [7] |
| OMe (*para*)[b] | $PF_6^-$ | ~ 150 | [7] |
| OMe (*meta*) | $CF_3SO_3^-$ | 192-193 | [8] |

[b] Ethanolic solutions of these compounds feature thermochromism when going from liquid nitrogen temperature to room temperature, which is in line with our predicted $T_{1/2}$ values of 230 K (*meta*, Table 2 in the main text) and 168 K (*para*, Table 3 in the main text).

**References:**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