Supporting information for:
Linear scaling relationships to predict $pK_a$’s and reduction potentials for bio-inspired hydrogenase catalysis

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Supporting Information Available

Biomimetic catalyst complexes

Fe$_2$(bd)CO$_2$  Fe$_2$(bd)CO$_2$PPh$_2$  Fe$_2$(bd)CO$_2$PPh$_3$  Fe$_2$(bd)CO$_2$PPh$_4$

Fe$_2$(bd)CO$_3$PPh$_2$  Fe$_2$(bd)CO$_3$PPh$_3$  Fe$_2$(bd)CO$_3$PPh$_4$

Fe$_2$(bd)CO$_4$PPh$_2$  Fe$_2$(bd)CO$_4$PPh$_3$  Fe$_2$(bd)CO$_4$PPh$_4$

Fe$_2$(bd)CO$_5$PPh$_2$  Fe$_2$(bd)CO$_5$PPh$_3$  Fe$_2$(bd)CO$_5$PPh$_4$
Figure S1: Chemical structures of the 80 biomimetic diiron hydrogenase complexes investigated in this study. For the bridgehead ligands iPr$_2$-pdt and Pr$_2$-pdt, some structures with PPhMe$_2$ terminal ligands were found to be unstable and hence not included in this study.

**Plots of p$K_a$ versus $E$ for catalytic cycle II**

The plots below show the same data points shown in Figure 7 in the main text, but here subdivided into the data subset of the ”less bulky bridgehead ligands” (middle panels) and the data subset of the ”bulky bridgehead ligands” (bottom panels). The top panels show the complete data sets from all 80 complexes (similar to shown in Figure 7), but here showing the fit functions using the entire data set. Note the significantly poorer squared correlation coefficients of $R^2 = 0.79$ for p$K_{a1}$ versus $E_1$ and $R^2 = 0.71$ for p$K_{a3}$ versus $E_3$ in this case.
Figure S2: Acidity constant versus reduction potential computed for 80 diiron complexes for catalytic cycle II. Left panel: $pK_{a1}$ versus $E_1$; Right panel: $pK_{a3}$ versus $E_3$. Red lines show the linear fit functions to the data. Top panels: computed data from all complexes. Middle panels: subset containing only the less bulky bridgehead ligands: pdt, odt, bdt, edt, Me-pdt, cl$_2$-bdt, and iPr-pdt. Bottom panels: subset containing only the bulky bridgehead ligands, Me$_2$-pdt, iPr$_2$-pdt, and Pr$_2$-pdt. Reduction potentials are shown in V.
Relation between reduction potentials

Figure S3: Correlation amongst all pairs of reduction potentials, $E_1$ to $E_4$, for the complexes with the less bulky bridgehead ligands. Reduction potentials are shown in V.
Figure S4: Correlation amongst all pairs of reduction potentials, $E_1$ to $E_4$, for the complexes with the bulky bridgehead ligands. Reduction potentials are shown in V.
Effect of change in geometry

Figure S5: Correlation between the four acidity constants $pK_{a1}$ to $pK_{a4}$ and the four reduction potentials $E_1$ to $E_4$ for the edt complexes. The $AH^-$ state is calculated using the optimized structure of the complex. Reduction potentials are shown in V.
Figure S6: Correlation between the four acidity constants $pK_{a1}$ to $pK_{a4}$ and the four reduction potentials $E_1$ to $E_4$ for the edt complexes. The AH$^-$ state is calculated as the single point energy of the optimized AH structure. Reduction potentials are shown in Volt.
Figure S7: Correlation between the reduction potentials for the complexes with the edt bridgehead ligand. The AH⁻ state is calculated using the optimized structure of the complex. Reduction potentials are shown in V.
Figure S8: Correlation between the reduction potentials for the complexes with the edt bridgehead ligand. The AH\(^{-}\) state is calculated as the single point energy of the optimized AH structure. Reduction potentials are shown in V.
Figure S9: Side view of the spatial geometries of the Fe$_2$(edt)(CO)$_3$(PMe$_3$)$_3$ complex in the AH$^-$ (left) and AH (right) states. Note the broken Fe-S bond in the AH$^-$ complex, resulting in a somewhat rotated dithiolate ligand and an under-coordinated iron ion (purple balls).

**Plots for the individual bridgehead ligands**

Below, we show the plots for the individual bridgehead ligands. Violet data points are from complexes with PMe$_3$ terminal ligands and green data points denote complexes with PPhMe$_2$ terminal ligands. For pdt and the less bulky derivatives of the pdt bridgehead ligands, there exist very clear linear correlations between the different properties. Thus for complexes with pdt, Me-pdt, iPr-pdt, and odt bridgehead ligands, we can accurately predict the properties by changing the terminal ligands (see Figures S10, S11, S12, S13, S14, S15, S16, and S17). The complexes with bdt, cl$_2$-bdt, edt, and bulky bridgehead ligands, the plots with E$_4$ or p$K_a$$_4$ do not show a good linear relationship (except for the E$_4$ vs p$K_a$$_4$) for reasons discussed in the main text, see Figures S18, S19,S20, S21, S22, S23, S24, S25, S26, S27.
Figure S10: Correlation between pK\textsubscript{a}'s and reduction potentials for the pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S11: Correlation between reduction potentials for the pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S12: Correlation between pK_a’s and reduction potentials for the Me-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S13: Correlation between reduction potentials for the Me-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S14: Correlation between p\(K_a\)'s and reduction potentials for the iPr-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S15: Correlation between reduction potentials for the iPr-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S16: Correlation between pKₐ’s and reduction potentials for the odt bridgehead ligand. Reduction potentials are shown in V.
Figure S17: Correlation between reduction potentials for the odt bridgehead ligand. Reduction potentials are shown in V.
Figure S18: Correlation between p$K_a$'s and reduction potentials for the bdt bridgehead ligand. Reduction potentials are shown in V.
Figure S19: Correlation between reduction potentials for the bdt bridgehead ligand. Reduction potentials are shown in V.
Figure S20: Correlation between pK_a’s and reduction potentials for the cl_2-bdt bridgehead ligand. Reduction potentials are shown in V.
Figure S21: Correlation between reduction potentials for the cl₂-bdt bridgehead ligand. Reduction potentials are shown in V.
Figure S22: Correlation between $pK_a$’s and reduction potentials for the Me$_2$-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S23: Correlation between reduction potentials for the Me₂-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S24: Correlation between pK_a’s and reduction potentials for the iPr_2-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S25: Correlation between reduction potentials for the iPr₂-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S26: Correlation between pKₐ’s and reduction potentials for the Pr₂-pdt bridgehead ligand. Reduction potentials are shown in V.
Figure S27: Correlation between reduction potentials for the Pr$_2$-pdt bridgehead ligand. Reduction potentials are shown in V.
Comparison with experimental values

The below table shows the comparison of redox potentials and acidity constants with available experimental data.

Table S1: The values of redox potentials and acidity constants are taken from corresponding literature. The values in brackets are from this study.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>E1 (V)</th>
<th>E2 (V)</th>
<th>E4 (V)</th>
<th>pK\textsubscript{a2}</th>
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<tr>
<td>Fe\textsubscript{2}(bdt)(CO)\textsubscript{6}</td>
<td></td>
<td>-1.32\textsuperscript{S1} (-1.50)</td>
<td></td>
<td>12.70\textsuperscript{S2} (10.38)</td>
</tr>
<tr>
<td>Fe\textsubscript{2}(cl\textsubscript{2}bdt)(CO)\textsubscript{6}\textsuperscript{S3}</td>
<td></td>
<td>-1.20 (-1.33)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{2}(edt)CO\textsubscript{6}\textsuperscript{S4}</td>
<td>1.29 (1.27)</td>
<td>-1.30 (-1.50)</td>
<td>-1.84 (-1.61)</td>
<td></td>
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<tr>
<td>Fe\textsubscript{2}(pdt)CO\textsubscript{6}\textsuperscript{S4}</td>
<td>1.14 (1.16)</td>
<td>-1.34 (-1.52)</td>
<td>-1.95 (-1.61)</td>
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<tr>
<td>Fe\textsubscript{2}(pdt)(CO)\textsubscript{5}PMe\textsubscript{3}\textsuperscript{S4}</td>
<td>0.34 (0.42)</td>
<td>-1.85 (-1.67)</td>
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<tr>
<td>Fe\textsubscript{2}(edt)(CO)\textsubscript{5}PMe\textsubscript{3}\textsuperscript{S4}</td>
<td>0.34 (0.52)</td>
<td>-1.87 (-1.77)</td>
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<td></td>
</tr>
</tbody>
</table>

References


(S4) Chong, D.; Georgakaki, I. P.; Mejia-Rodriguez, R.; Sanabria-Chinchilla, J.; Sorriaga, M. P.; Daresbourg, M. Y. Electrocatalysis of hydrogen production by active

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