Electronic Supplementary Information

Designing Air-stable Cyclometalated Fe(II) Complexes: Stabilization via Electrostatic Effects

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1. Computational methodology

All structures were optimized in vacuum with the B3LYP[1-4] functional including Grimme's D2 dispersion correction[5] (B3LYP+D2). The SDD basis set and accompanying pseudopotential were used for Fe,[6] and the 6-311G* basis set[7] was used for all other atoms. Frequencies were calculated for all optimized structures using the harmonic oscillator approximation to verify the nature of the stationary points. The results of these frequency calculations were also used to calculate zero-point energy and entropic corrections to the free energies at 298.15 K and 1.0 atm using standard statistical mechanical conventions. For the purposes of calculating reduction potentials (and subsequently ΔG_{O2}), the electronic energy was determined from PBE[8,9] single point calculations at the B3LYP+D2 optimized geometries. Previous work had shown that PBE is a preferable functional for calculating reduction potentials.[10] These single point calculations employed a larger 6-311+G* basis set for light atoms,[7,11] and also incorporated solvation via the IEF-PCM implicit solvation model to simulate the effect of acetonitrile ($\varepsilon = 37.5$). An ultrafine integral grid was used for all calculations. All DFT calculations were performed with the Gaussian 09 software package Revision D.01.[12]

All structures were confirmed to possess zero imaginary modes with one exception: the quintet state of **4a** possessed a single imaginary mode of ~3 cm^{-1} that despite our best efforts could not be successfully removed. This imaginary mode corresponded to a 'rocking' motion we have seen in a previous study on [Fe(tpy)$_2$]$^{2+}$.[13] There it was found that in the quintet state this rocking potential energy surface was very shallow, and hence it is not surprising that this mode was both very small in magnitude and could be difficult to rigorously remove, both due to the only very small energy penalty for this distortion. Accordingly, we do not expect that this has any significant effects on the electronic energy of quintet **4a**. Note that the omission of a low frequency mode may have a more significant effect on the calculated thermochemical parameters, and hence these are not reported for this complex.

Reduction potentials (E^0) were determined relative to the normal hydrogen electrode (NHE) through equation 1:

$$E^0(eV) = -\frac{\Delta G_{sol}}{nF} - 4.28 \text{ (Eq. 1)}$$

Here, ΔG_{sol} is the change in solvated free energy upon reduction, n is the number of electrons transferred, in our case this is always one, and F is Faraday's constant. The specific reaction in

question is the reduction of the Fe(III) complex (always in the doublet state) to the Fe(II) complex (always in the singlet state). The calculated potentials are referenced to NHE by subtracting the estimated absolute reduction potential of NHE, 4.28 V.[14] Note that much work has been done on determining this value, and not all estimates agree,[14-19] and hence our calculated values may be subject to a modest systematic error. This will have no significant effects on our major conclusions, however, and this general procedure has been shown to work well in previous computational studies.[20] Note that for calculations of ΔG_{O2}, the experimental reduction potential of O_2 was used in place of the calculated reduction potential. This was because while our calculations were capable of matching experimental results for the Fe(II) complexes, matching the O_2 potential was less successful.

$\Delta E_{Q/S}$ was calculated as the electronic energy (using B3LYP+D2) of the optimized quintet state minus the electronic energy of the optimized singlet state. The more positive $\Delta E_{Q/S}$ is, the greater the stability of the singlet state. $\Delta E_{Q/S}$ is notoriously difficult to accurately determine computationally with DFT.[21-28] Jakubikova and coworkers have demonstrated that for complexes that undergo similar structural changes upon spin-state interconversion, the functional dependence, and hence the *relative* values of $\Delta E_{Q/S}$ should be accurate and consistent regardless of functional choice.[29]

Table S1. Calculated $\Delta E_{Q/S}$ (in kcal/mol) for the structures shown in Figure 1 using B3LYP+D2 and PBE functional.

Complex	B3LYP+D2	PBE
1	4.4	24.1
2	10.6	34.5
3	13.5	41.3
4	11.6	35.4
2a	13.6	40.2
3a	14.0	42.5
4a	13.0	38.9

2. Discussion of PBE spin state energetics

To verify that the conclusions regarding spin-state energies presented in the text are not an artifact of method, $\Delta E_{Q/S}$ was also calculated using the PBE functional (Table S1). It is well known that $\Delta E_{Q/S}$ is highly sensitive to the amount of HF exchange in the functional,[28] and it is likely that a functional like B3LYP+D2 (20% HF exchange) will over-stabilize the quintet state,

while a local functional like PBE (0% HF exchange) will over-stabilize the singlet state. Regardless of which method gives the correct answer, it is expected that the trends in the data will be roughly the same, as the functional dependence will be similar for complexes that undergo similar structural distortions upon changing the spin state.[29,30]

The ordering of complexes by $\Delta E_{Q/S}$ was found to be the same regardless of which functional was used. As expected, PBE greatly stabilizes the singlet state compared to B3LYP+D2 as evidenced by the much more positive (by ~20 kcal/mol) values of $\Delta E_{Q/S}$. The only major difference is that the magnitude of the relative differences in $\Delta E_{Q/S}$ was larger for PBE, i.e. PBE predicts a greater effect on $\Delta E_{Q/S}$ due to modifying the ligand. An example of this can be seen when comparing **2** and **3**. For B3LYP+D2 the change in $\Delta E_{Q/S}$ ($\Delta\Delta E_{Q/S}$) between these two compounds is 2.9 kcal/mol, while with PBE it is 6.8 kcal/mol. In the previous work on substituted $[Fe(bpy)_3]^{2+}$ complexes, $\Delta\Delta E_{Q/S}$ between the nitro-substituted and un-substituted complexes was much smaller, only 0.25 kcal/mol.[31] Making direct comparisons is difficult, but it does suggest that the anionic ligand in **2** is more sensitive to ligand effects than a neutral polypyridine. This may be because of stronger covalent interactions between the metal and ligand, but in the absence of detailed electronic structure analysis this is only speculation. Note that even with PBE, $\Delta\Delta E_{Q/S}$ (0.29 eV) is still roughly two times smaller than the change in reduction potential (0.55 eV), suggesting that the changes in metal-ligand electrostatic interactions still dominate over changes in their covalent, orbital-based interactions.

Table S2. Electronic energies calculated with B3LYP+D2 (E), electronic energies calculated with PBE (E′), zero-point energies (ZPE, B3LYP+D2), entropic corrections to free energies (−TS, B3LYP+D2), enthalpies (H, B3LYP+D2), gas phase Gibbs free energies (G, B3LYP+D2), and solvated Gibbs free energies (G_{sol}, PBE and B3LYP+D2) calculated with DFT. E′ was calculated with the IEFPCM correction for solvent (acetonitrile) and therefore contains the effects of solvation already. The only difference between G_{sol} and G is whether E′ or E was used respectively. The temperature (T) was taken as 298.15 K, and the pressure as 1 atm. All values are reported in kcal/mol. Singlet = **S**, quintet = **Q**, and doublet = **D**.

Complex	E	E′	ZPE	−TS	H	G	G_{sol}
1 Fe(II) **S**	-1009660.34	-1008578.51	289.54	-53.24	-1009353.15	-1009406.38	-1008324.55
1 Fe(II) **Q**	-1009655.99	-1008554.37	287.49	-59.61	-1009349.61	-1009409.22	-1008307.61
2 Fe(II) **S**	-988987.48	-987822.13	285.88	-54.00	-988683.72	-988737.73	-987572.38
2 Fe(II) **Q**	-988976.87	-987787.64	283.58	-61.75	-988673.94	-988735.69	-987546.46
3 Fe(II) **S**	-1245725.59	-1244353.38	289.74	-62.25	-1245414.70	-1245476.95	-1244104.74
3 Fe(II) **Q**	-1245712.12	-1244312.08	287.15	-73.65	-1245402.27	-1245475.92	-1244075.89
4 Fe(II) **S**	-1502436.26	-1500854.32	292.33	-71.38	-1502119.42	-1502190.80	-1500608.86
4 Fe(II) **Q**	-1502424.66	-1500818.89	289.90	-78.96	-1502108.84	-1502187.79	-1500582.02
2a Fe(II) **S**	-1699195.28	-1697353.02	343.64	-80.75	-1698822.83	-1698903.58	-1697061.32
2a Fe(II) **Q**	-1699181.65	-1697312.80	341.21	-89.10	-1698810.23	-1698899.33	-1697030.48
3a Fe(II) **S**	-1719189.29	-1717365.03	327.74	-80.42	-1718833.06	-1718913.49	-1717089.23
3a Fe(II) **Q**	-1719175.24	-1717322.50	325.26	-89.13	-1718820.07	-1718909.20	-1717056.46
4a Fe(II) **S**	-1739174.23	-1737365.92	311.61	-80.20	-1738834.44	-1738914.64	-1737106.34
4a Fe(II) **Q**	-1739161.23	-1737327.07	--	--	--	--	--
1⁺ Fe(III) **D**	-1009384.58	-1008446.86	289.94	-53.83	-1009076.93	-1009130.76	-1008193.04
2⁺ Fe(III) **D**	-988880.44	-987728.83	287.66	-54.54	-988574.87	-988629.41	-987477.80
3⁺ Fe(III) **D**	-1245600.87	-1244246.42	290.81	-63.27	-1245288.78	-1245352.05	-1243997.59
4⁺ Fe(III) **D**	-1502301.71	-1500742.70	293.20	-72.43	-1501983.84	-1502056.26	-1500497.26
2a⁺ Fe(III) **D**	-1699071.76	-1697243.78	344.20	-80.16	-1698699.05	-1698779.21	-1696951.22
3a⁺ Fe(III) **D**	-1719056.98	-1717250.62	328.34	-81.55	-1718699.97	-1718781.53	-1716975.16
4a⁺ Fe(III) **D**	-1739033.67	-1737249.01	311.73	-80.13	-1738693.94	-1738774.07	-1736989.41

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