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COMMUNICATION

## Designing air-stable cyclometalated Fe(II) complexes: Stabilization via electrostatic effects

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**Designing efficient Fe(II) chromophores requires optimization of numerous, at times conflicting, properties. It has been suggested that replacement of polypyridine ligands with cyclometalated analogs will be effective at destabilizing the quintet state and therefore extending the lifetime of photoactive metal-to-ligand charge transfer states. However, cyclometalated Fe(II) complexes are not oxidatively stable due to the strong electron-donating nature of this ligand, which limits their applicability. Here we use density functional theory calculations to show how simple addition of nitro and carboxylic acid groups to these cyclometalated complexes can engender a less oxidizable Fe(II) center while maintaining, or even improving, the favorable ligand field strength.**

One of the most interesting features of Fe(II) complexes is their ability to readily access multiple spin states.<sup>1-5</sup> Being able to predict and control the energetic ordering of these states is of great interest for developing novel multifunctional materials that possess spin crossover capabilities.<sup>6</sup> Different spin states also can display very different reactivity, making spin state control a powerful tool for catalyst design.<sup>7-9</sup> In some cases, however, low energy electronic states of higher multiplicity are an undesirable feature. Hence the design strategy needs to focus on stabilizing the low spin singlet state relative to the high spin quintet state; i.e. creating complexes with large values of  $\Delta E_{Q/S}$ , where  $\Delta E_{Q/S} = E(\text{quintet}) - E(\text{singlet})$ . One such challenge is the utilization of Fe(II) complexes as photosensitizers in dye-sensitized solar cells (DSSCs)<sup>10-13</sup> or dye-sensitized photoelectrosynthesis cells (DSPECs).<sup>14, 15</sup> DSSCs typically make use of Ru(II) based dyes, which form a metal-to-ligand charge-transfer (MLCT) state upon photoexcitation that can undergo interfacial electron transfer (IET) to an attached

semiconductor.<sup>16</sup> As Fe is cheaper and more abundant than Ru, it would be an economically and environmentally preferable alternative.<sup>17</sup> However, due to the presence of low-lying metal-centered (MC) triplet and quintet states in Fe(II) polypyridines, the lifetime of their photoactive MLCT states is on the order of  $\sim 100$  fs.<sup>18, 19</sup>

Extensive computational<sup>20-25</sup> and experimental work has suggested that synthesizing Fe(II) complexes with strong  $\sigma$ -donating ligands can significantly destabilize the quintet and triplet MC states and therefore increase MLCT state lifetimes. Wärnmark and coworkers have shown that complexes which possess Fe-C bonds resulting from NHC ligands lead to dramatically lengthened MLCT lifetimes, on the order of picoseconds.<sup>26-31</sup> This has also been demonstrated computationally by comparing the calculated  $\Delta E_{Q/S}$  for typical Fe(II) polypyridine complexes to similar cyclometalated complexes where the pyridines are systematically substituted by anionic aryl groups.<sup>20, 22, 24</sup> Fundamental ligand field theory considerations suggest that the aryl ligands are better  $\sigma$ -donors than pyridines, and that their presence raises the energy of the antibonding  $e_g^*$  orbitals that become occupied in the quintet state.<sup>20</sup> Increasing the ligand  $\sigma$ -donor strength should therefore be a useful strategy for increasing  $\Delta E_{Q/S}$ . Unfortunately, use of strong  $\sigma$ -donating ligands makes the Fe(II) center easier to oxidize to Fe(III),<sup>32</sup> and Fe(II) complexes with aryl ligands are much less air-stable than their polypyridine counterparts.<sup>33</sup>

A recent computational study on substituted  $[\text{Fe}(\text{bpy})_3]^{2+}$  complexes (where bpy = 2,2'-bipyridine) demonstrated that keeping the ligand framework the same but only varying the functional groups para to the coordinating pyridine nitrogens allows for large variations ( $\sim 2$  eV) in the Fe(III/II) reduction potential, with only small changes ( $\sim 0.3$  eV) in the calculated  $\Delta E_{Q/S}$ .<sup>34</sup> This was attributed to large changes in metal-ligand electrostatic interactions but only minor changes in metal-ligand orbital interactions. Effects such as these can explain why increasing the ligand  $\sigma$ -donor strength in other Fe(II) complexes significantly shifts Fe(III/II) reduction potentials despite the fact that the ligand  $\sigma$ -orbitals do not directly interact with the Fe  $t_{2g}$

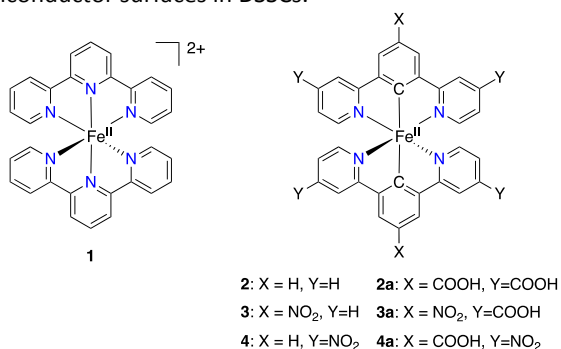
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orbitals.<sup>32</sup> Knowledge of these electrostatic effects can thus be exploited to design Fe(II) complexes with strong  $\sigma$ -donating ligands that produce a desirable  $\Delta E_{Q/S}$ , and electron withdrawing substituents that control their oxidative stability.

To investigate this issue further, the complexes shown in Figure 1 were studied using density functional theory (DFT) to evaluate how ligand modifications affect both  $\Delta E_{Q/S}$  and the oxidative stability. The complexes under consideration were  $[\text{Fe}(\text{tpy})_2]^{2+}$  (**1**, tpy = 2,2';6',2''-terpyridine) and its cyclometalated analogs where both axial nitrogens were replaced by carbons (**2-4**). Complex **2** was of great interest due to the fact that it has been experimentally demonstrated to be unstable in the Fe(II) state and undergo oxidation to Fe(III).<sup>33</sup> Additionally, an experimental estimate of the Fe(II) reduction potential is known. Compounds **3** and **4** have nitro substituents on the axial and equatorial rings, respectively. Compounds **2a-4a** are similar, except they also include functionalization with carboxylic acid groups. In addition to being electron-withdrawing, these groups are often employed as linking groups for attaching transition metal chromophores to the semiconductor surfaces in DSSCs.<sup>13</sup>



**Figure 1.** Fe(II) complexes investigated for their redox properties.

All molecules were optimized at the B3LYP<sup>35-38</sup>+D2<sup>39</sup> level of theory. The D2 correction was employed since it has been used for Fe(II) polypyridine complexes previously and, in combination with B3LYP, reproduces well both the experimental structure as well as spin-state energetics of these complexes.<sup>40-42</sup> Although DFT is known for being unreliable at predicting  $\Delta E_{Q/S}$  with quantitative accuracy, it can perform well for predicting *relative* values of  $\Delta E_{Q/S}$  in a series of structurally similar complexes.<sup>5, 43</sup> The oxidative stability of Fe(II) complexes was gauged by calculating the Fe(III/II) reduction potentials ( $E_{\text{Fe}}$ ) using the PBE<sup>44</sup> functional on the B3LYP+D2 optimized structures, as PBE has been shown to perform better for quantitatively matching reduction potentials.<sup>45</sup> This data can be used to determine if it is possible to maintain a strong ligand field (large  $\Delta E_{Q/S}$ ) by controlling the nature of the iron-ligand covalent bonding, and at the same time tune the oxidative stability (indicated by  $E_{\text{Fe}}$ ) by changing the metal-ligand electrostatic interactions via ligand substituents.

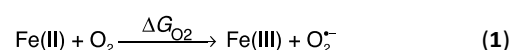
First, we tackle the question of whether the compounds investigated are stable in air, and how this stability is affected by ligand substitution. The  $E_{\text{Fe}}$  are listed in Table 1, reported vs. the Normal Hydrogen Electrode (NHE).<sup>46</sup> Compounds **1** and **2** have had  $E_{\text{Fe}}$  experimentally determined to be 1.37<sup>47</sup> and

-0.20<sup>33</sup> eV, respectively. Comparing this to our calculated values of 1.42 and -0.18 eV shows that the employed methodology is performing well. These two compounds are important as an experimental frame of reference: **1** is air stable, and does not spontaneously oxidize to Fe(III), while **2** is not air stable.

**Table 1.** Calculated  $E_{\text{Fe}}$  values (in eV vs. NHE),  $\Delta G_{\text{O}_2}$  (in kcal/mol) and  $\Delta E_{Q/S}$  (in kcal/mol) for the structures shown in Figure 1. The  $\Delta E_{Q/S}$  were calculated with B3LYP+D2. The electronic energies for  $E_{\text{Fe}}$  and  $\Delta G_{\text{O}_2}$  were calculated with PBE. Note the experimental values of  $E_{\text{Fe}}$  for **1** and **2** are 1.37<sup>47</sup> and -0.20<sup>33</sup> eV, respectively.

| Compound  | $E_{\text{Fe}}$ | $\Delta G_{\text{O}_2}$ | $\Delta E_{Q/S}$ |
|-----------|-----------------|-------------------------|------------------|
| <b>1</b>  | 1.42            | 37.0                    | 4.4              |
| <b>2</b>  | -0.18           | 0.0                     | 10.6             |
| <b>3</b>  | 0.37            | 12.6                    | 13.5             |
| <b>4</b>  | 0.56            | 17.1                    | 11.6             |
| <b>2a</b> | 0.49            | 15.5                    | 13.6             |
| <b>3a</b> | 0.67            | 19.5                    | 14.0             |
| <b>4a</b> | 0.79            | 22.4                    | 13.0             |

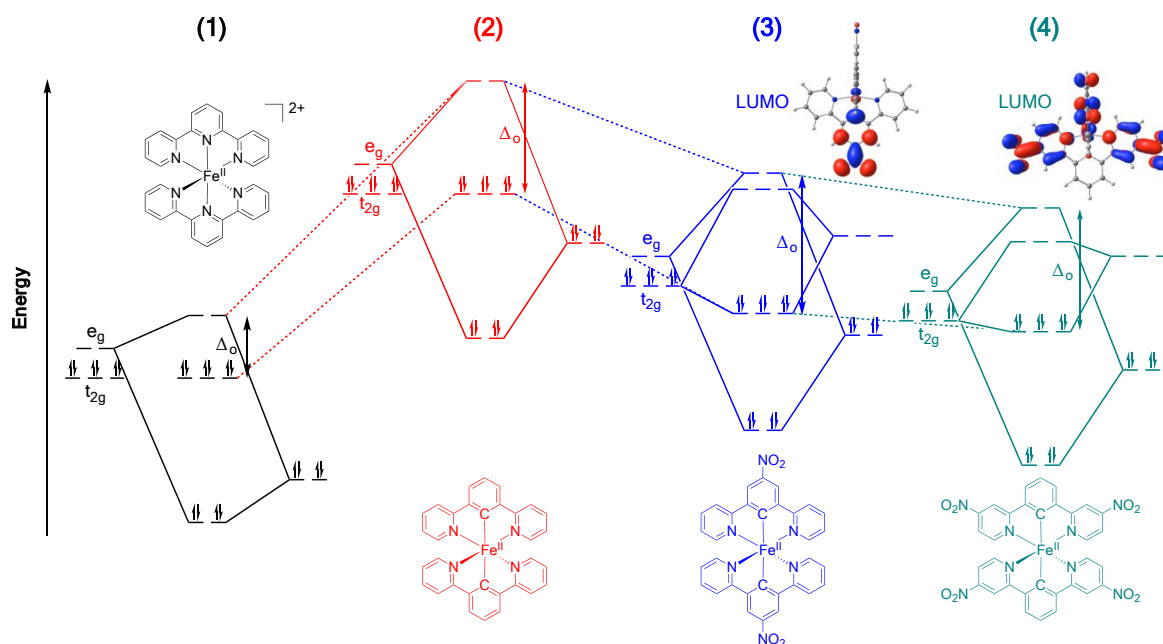
As  $E_{\text{Fe}}$  potentials reflect how easy it is to reduce the Fe(III) center, the more positive the value, the harder it is to oxidize the Fe(II) complex. From a simple thermodynamic standpoint then, the way to make a complex more stable in an oxidizing environment is to make  $E_{\text{Fe}}$  more positive. As expected, the presence of the strong  $\sigma$ -donating aryl ligands has the opposite effect, as they make  $E_{\text{Fe}}$  significantly more negative relative to **1**. In compound **2** the  $E_{\text{Fe}}$  is -0.18 eV compared to 1.42 eV for compound **1**. While these relative changes in Fe(II/III) reduction potentials are informative, a more useful measure is whether O<sub>2</sub> itself will be able to oxidize the complex. As oxidation by O<sub>2</sub> is likely an outer sphere process, the rate-determining step will be an initial electron transfer to O<sub>2</sub> to form O<sub>2</sub><sup>•-</sup> as shown in Equation 1.<sup>48</sup>



To simplify this analysis, initially just the driving force of the electron-transfer ( $\Delta G_{\text{O}_2}$ ) can be considered as a way of screening for potentially air-stable complexes (Table 1). Regardless of the complexities of the mechanism of electron transfer involved, if  $\Delta G_{\text{O}_2}$  is excessively unfavorable, then electron transfer simply cannot occur. Using our calculated redox potentials and the experimentally measured reduction potential of O<sub>2</sub>/O<sub>2</sub><sup>•-</sup> ( $E_{\text{O}_2}$  = -0.18 V),<sup>49</sup>  $\Delta G_{\text{O}_2}$  can be calculated via Equation 2:

$$\Delta G_{\text{O}_2} = -\frac{[E_{\text{O}_2} - E_{\text{Fe}}]}{nF} \quad (2)$$

where  $n$  is the number of electrons transferred (always one in this reaction), and  $F$  is Faraday's constant. The calculated  $E_{\text{Fe}}$  for **2** (-0.18 eV, see Table 1) is similar to  $E_{\text{O}_2}$  which leads to a thermodynamically viable oxidation by O<sub>2</sub> with  $\Delta G_{\text{O}_2}$  = 0.0 kcal/mol. Compare this to the air-stable **1**, which has a calculated  $\Delta G_{\text{O}_2}$  of 37.0 kcal/mol.



**Figure 2.** Qualitative MO diagrams of **1-4** illustrating the combined effects of electrostatic and orbital-based metal-ligand interactions. The MO diagram is always depicted for  $O_h$  symmetry for simplicity's sake. The LUMO for **3** and **4** are doubly degenerate, however, only one isosurface is shown (isovalue = 0.03  $e/\text{\AA}^3$ ).

As can be seen in Table 1, incorporation of electron withdrawing groups (EWGs) makes the Fe complex less susceptible to oxidation and stabilizes it in the Fe(II) oxidation state. In particular, substitution of  $\text{NO}_2$  moieties onto the aryl ligands (**3**) significantly increases  $\Delta G_{\text{O}_2}$  from 0.0 to 12.6 kcal/mol. If twice the number of  $\text{NO}_2$  groups are added to the pyridines (**4**) instead, the complex is further oxidatively stabilized ( $\Delta G_{\text{O}_2} = 17.1$  kcal/mol). Addition of carboxylic acid linker groups (**2a-4a**) has very similar results. Based on the calculated increases of  $\Delta G_{\text{O}_2}$ , the substitution of EWGs on to the ligand scaffold of cyclometalated Fe(II) complexes is a viable pathway to air-stabilization of the Fe(II) oxidation state. The remaining question is how these EWGs affect the ligand field strength. If the primary effect of these EWGs is to make the  $\sigma$ -donating strength of the ligands weaker, then  $\Delta E_{\text{Q/S}}$  would become smaller, cancelling out the beneficial effect of using the cyclometalated complexes in the first place. On the other hand, if the primary effect is to decrease  $\pi$ -donation from the ligand and/or increase  $\pi$ -backbonding to the ligand, then  $\Delta E_{\text{Q/S}}$  would become larger.

Table 1 also shows the calculated values of  $\Delta E_{\text{Q/S}}$  for all of the considered complexes. Going from **1** to **2** causes a significant increase in  $\Delta E_{\text{Q/S}}$  of  $\sim 7$  kcal/mol, consistent with the expected stronger  $\sigma$ -donation from the aryl groups. Addition of  $\text{NO}_2$  groups to the aryl ligands (**3**) causes a small increase of  $\Delta E_{\text{Q/S}}$  by  $\sim 3$  kcal/mol relative to **2**. Addition of twice the number of  $\text{NO}_2$  groups to the pyridine rings (**4**) counter-intuitively causes a smaller shift in  $\Delta E_{\text{Q/S}}$  of only  $\sim 1$  kcal/mol. This relatively small increase in  $\Delta E_{\text{Q/S}}$  upon substitution of pyridine rings agrees well with the previously mentioned computational study on  $[\text{Fe}(\text{bpy})_3]^{2+}$ ,<sup>34</sup> although the ligand effects on  $[\text{Fe}(\text{bpy})_3]^{2+}$  were even smaller. Finally, note that addition of carboxylic acid groups in combination with  $\text{NO}_2$  groups (complexes **2a-4a**)

causes further small increases in  $\Delta E_{\text{Q/S}}$ , with the largest overall  $\Delta E_{\text{Q/S}}$  belonging to the complex with  $\text{NO}_2$  groups on the aryl rings and carboxylic acid groups on the pyridine rings, **3a**.

The greater sensitivity of the cyclometalated complex to orbital-based effects as compared to the  $[\text{Fe}(\text{bpy})_3]^{2+}$  system,<sup>34</sup> i.e. the more pronounced changes in  $\Delta E_{\text{Q/S}}$  upon ligand substitution, may be related to the increased covalency of the Fe-C bond. This is even more evident when considering calculations of  $\Delta E_{\text{Q/S}}$  with PBE (Table S1; being a GGA functional, PBE is a better comparison to the prior work on  $[\text{Fe}(\text{bpy})_3]^{2+}$  which was performed with BP86<sup>34</sup>), which although they completely preserve the trends seen in Table 1, they also show roughly twice as large changes in  $\Delta E_{\text{Q/S}}$  upon ligand substitution than the hybrid B3LYP+D2 method. Without a more rigorously benchmarked DFT method it is difficult to predict how sensitive  $\Delta E_{\text{Q/S}}$  actually is to ligand modification, but in all cases, changes in  $\Delta E_{\text{Q/S}}$  are always significantly smaller than the effect of ligand modifications on  $E_{\text{Fe}}$ .

In conclusion, ligand substituents modify both the Fe(III/II) reduction potential,  $E_{\text{Fe}}$ , and quintet-singlet energy gap  $\Delta E_{\text{Q/S}}$ . The impact on the  $E_{\text{Fe}}$  and thus the oxidative stability of the Fe(II) complex is, however, more pronounced than the corresponding influence on  $\Delta E_{\text{Q/S}}$ . The orbital-induced effects on  $\Delta E_{\text{Q/S}}$  and electrostatic effects on the oxidative stability are illustrated in Figure 2. While the inclusion of strong, negatively charged  $\sigma$ -donors (i.e., aryl groups) increases the  $\Delta_o$  and  $\Delta E_{\text{Q/S}}$  of the Fe(II) complexes, it also destabilizes their orbital energies, making the complexes easier to oxidize to Fe(III). Substitution of nitrate or carboxylic acid onto the ligand scaffold stabilizes the orbital energies via electrostatic effects, making  $E_{\text{Fe}}$  more positive and Fe(II) more difficult to oxidize. While this result is perhaps unsurprising based on our previous work,<sup>34</sup> as far as we are aware this strategy has not been attempted to specifically

remediate problems with oxidative stability of cyclometalated Fe(II) complexes. Similar effects on  $E_{Fe}$  and  $\Delta E_{Q/S}$  can be achieved via ligand substitution by other EWGs, and based on previous work it is expected that these effects will scale with the Hammett parameter for a particular EWG.<sup>34</sup> From a practical standpoint, these results are highly encouraging, and suggest a pathway toward designing air-stable cyclometalated Fe(II) complexes. Inclusion of EWG groups may promote other decomposition pathways such as ligand loss due to the expected weaker metal-ligand bonds, especially for Fe polypyridine complexes. However, the strong Fe-C bonds of the cyclometalated ligand may help maintain the coordinative stability, even with EWGs present. Furthermore, the strongly electron-withdrawing nitro groups are not absolutely necessary, as compound **2a** is predicted to be oxidatively stable and only makes use of carboxylic acid groups, which are frequently used as anchoring groups for known Fe(II) polypyridine complexes. Finally, because this strategy for tuning the reduction potential of the metal center is based on simple electrostatics rather than complex orbital interactions, it is likely transferable to other types of transition metal complexes.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgments

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### Notes and references

1. P. Gamez, J. S. Costa, M. Quesada and G. Aromi, *Dalton Trans.*, 2009, **0**, 7845-7853.
2. O. Sato, J. Tao and Y. Z. Zhang, *Angew. Chem.*, 2007, **46**, 2152-2187.
3. A. Bousseksou, G. Molnár and G. Matouzenko, *Eur. J. Inorg. Chem.*, 2004, **2004**, 4353-4369.
4. A. Bousseksou, G. Molnar, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313-3335.
5. D. C. Ashley and E. Jakubikova, *Coord. Chem. Rev.*, 2017, **337**, 97-111.
6. A. B. Gaspar, V. Ksenofontov, M. Seredyuk and P. Gülich, *Coord. Chem. Rev.*, 2005, **249**, 2661-2676.
7. D. Schröder, S. Shaik and H. Schwarz, *Acc. Chem. Res.*, 2000, **33**, 139-145.
8. D. Mandal and S. Shaik, *J. Am. Chem. Soc.*, 2016, **138**, 2094-2097.
9. Y. Sun, H. Tang, K. Chen, L. Hu, J. Yao, S. Shaik and H. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 3715-3730.
10. B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737-740.
11. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595-6663.
12. M. Grätzel, *Inorg. Chem.*, 2005, **44**, 6841-6851.
13. E. Jakubikova and D. N. Bowman, *Acc. Chem. Res.*, 2015, **48**, 1441-1449.
14. Z. Yu, F. Li and L. Sun, *Energy Environ. Sci.*, 2015, **8**, 760-775.
15. M. K. Brennaman, R. J. Dillon, L. Alibabaei, M. K. Gish, C. J. Dares, D. L. Ashford, R. L. House, G. J. Meyer, J. M. Papanikolas and T. J. Meyer, *J. Am. Chem. Soc.*, 2016, **138**, 13085-13102.
16. S. Ardo and G. J. Meyer, *Chem. Soc. Rev.*, 2009, **38**, 115-164.
17. S. Enthaler, K. Junge and M. Beller, *Angew. Chem.*, 2008, **47**, 3317-3321.
18. J. E. Monat and J. K. McCusker, *J. Am. Chem. Soc.*, 2000, **122**, 4092-4097.
19. W. Zhang, R. Alonso-Mori, U. Bergmann, C. Bressler, M. Chollet, A. Galler, W. Gawelda, R. G. Hadt, R. W. Hartsock, T. Kroll, K. S. Kjaer, K. Kubicek, H. T. Lemke, H. W. Liang, D. A. Meyer, M. M. Nielsen, C. Purser, J. S. Robinson, E. I. Solomon, Z. Sun, D. Sokaras, T. B. van Driel, G. Vanko, T. C. Weng, D. Zhu and K. J. Gaffney, *Nature*, 2014, **509**, 345-348.
20. S. Mukherjee, D. N. Bowman and E. Jakubikova, *Inorg. Chem.*, 2015, **54**, 560-569.
21. D. N. Bowman, A. Bondarev, S. Mukherjee and E. Jakubikova, *Inorg. Chem.*, 2015, **54**, 8786-8793.
22. I. M. Dixon, F. Alary, M. Boggio-Pasqua and J.-L. Heully, *Dalton Trans.*, 2015, **44**, 13498-13503.
23. I. M. Dixon, F. Alary, M. Boggio-Pasqua and J. L. Heully, *Inorg. Chem.*, 2013, **52**, 13369-13374.
24. I. M. Dixon, S. Khan, F. Alary, M. Boggio-Pasqua and J. L. Heully, *Dalton Trans.*, 2014, **43**, 15898-15905.
25. I. M. Dixon, G. Boissard, H. Whyte, F. Alary and J. L. Heully, *Inorg. Chem.*, 2016, **55**, 5089-5091.
26. Y. Liu, T. Harlang, S. E. Canton, P. Chabera, K. Suarez-Alcantara, A. Fleckhaus, D. A. Vithanage, E. Goransson, A. Corani, R. Lomoth, V. Sundstrom and K. Warnmark, *Chem. Commun.*, 2013, **49**, 6412-6414.
27. L. A. Fredin, M. Pápai, E. Rozsályi, G. Vankó, K. Wärnmark, V. Sundström and P. Persson, *J. Phys. Chem. Lett.*, 2014, **5**, 2066-2071.
28. T. C. B. Harlang, Y. Liu, O. Gordivska, L. A. Fredin, C. S. Ponseca Jr, P. Huang, P. Chábera, K. S. Kjaer, H. Mateos, J. Uhlig, R. Lomoth, R. Wallenberg, S. Styring, P. Persson, V. Sundström and K. Wärnmark, *Nat. Chem.*, 2015, **7**, 883-889.
29. Y. Liu, P. Persson, V. Sundstrom and K. Warnmark, *Acc Chem Res*, 2016, **49**, 1477-1485.
30. W. Zhang, K. S. Kjaer, R. Alonso-Mori, U. Bergmann, M. Chollet, L. A. Fredin, R. G. Hadt, R. W. Hartsock, T. Harlang, T. Kroll, K. Kubicek, H. T. Lemke, H. W. Liang, Y. Liu, M. M. Nielsen, P. Persson, J. S. Robinson, E. I. Solomon, Z. Sun, D. Sokaras, T. B. van Driel, T.-C. Weng, D. Zhu, K. Warnmark, V. Sundstrom and K. J. Gaffney, *Chem. Sci.*, 2017, **8**, 515-523.
31. P. Chábera, K. S. Kjaer, O. Prakash, A. Honarfar, Y. Liu, L. A. Fredin, T. C. B. Harlang, S. Lidin, J. Uhlig, V. Sundström, R. Lomoth, P. Persson and K. Wärnmark, *J. Phys. Chem. Lett.*, 2018, **9**, 459-463.
32. Y. Liu, K. S. Kjaer, L. A. Fredin, P. Chabera, T. Harlang, S. E. Canton, S. Lidin, J. Zhang, R. Lomoth, K. E. Bergquist, P. Persson, K. Warnmark and V. Sundstrom, *Chem. Eur. J.*, 2015, **21**, 3628-3639.

33. S. Estrada-Montaño Aldo, D. Ryabov Alexander, A. Gries, C. Gaiddon and R. Le Lagadec, *Eur. J. Inorg. Chem.*, 2017, **2017**, 1673-1678.
34. D. C. Ashley and E. Jakubikova, *Inorg. Chem.*, 2018, **57**, 9907-9917.
35. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
36. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
37. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
38. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
39. S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787-1799.
40. D. C. Ashley and E. Jakubikova, *Inorg. Chem.*, 2018, **57**, 5585-5596.
41. S. Mukherjee, D. E. Torres and E. Jakubikova, *Chem. Sci.*, 2017, **8**, 8115-8126.
42. J. Nance, D. N. Bowman, S. Mukherjee, C. T. Kelley and E. Jakubikova, *Inorg. Chem.*, 2015, **54**, 11259-11268.
43. D. N. Bowman and E. Jakubikova, *Inorg. Chem.*, 2012, **51**, 6011-6019.
44. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
45. L. E. Roy, E. Jakubikova, M. G. Guthrie and E. R. Batista, *J. Phys. Chem. A*, 2009, **113**, 6745-6750.
46. C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2006, **110**, 16066-16081.
47. L. L. Jamula, A. M. Brown, D. Guo and J. K. McCusker, *Inorg. Chem.*, 2014, **53**, 15-17.
48. S. Fallab, *Angew. Chem.*, 1967, **6**, 496-507.
49. W. H. Koppenol, D. M. Stanbury and P. L. Bounds, *Free Radic. Biol. Med.*, 2010, **49**, 317-322.

Substitution of EWGs onto the cyclometalated iron complexes electrostatically stabilizes Fe(II) center while still preserving the increased ligand field strength.

