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An In Silico Design Tool for Fe(II) Spin Crossover and Light-Induced Excited Spin State-Trapped Complexes

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The bistability of spin crossover (SCO) and light-induced excited spin state trapping (LIESST) materials is of great interest for molecular electronics, data storage, and display devices.[1] However, the energetics of SCO and LIESST are delicate, and discovering new materials is challenging.[2] For example, since the serendipitous discovery of the first Fe(II) SCO complexes [Fe(phen)$_2$(NCE)$_2$] (E = S, Se),[3,4] hundreds of species have been reported,[5] but the vast majority retain the original FeN$_6$ motif. Only recently have mixed-donor sets such as FeN$_4$O$_2$ been found.[6]

Since SCO and LIESST are "ligand field" problems, Tanabe−Sugano diagrams have been used to give at least a qualitative theoretical interpretation. For d^6 Fe(II), the crossover point from high-spin (HS) $^5T_{2g}$ to low-spin (LS) $^1A_{1g}$ is a balance between the ligand field, which favors LS, and d−d interelectron repulsion, which favors HS. The main variable is Δ_{oct},[7,8] and SCO occurs around the amine/imine point, hence the FeN$_6$ paradigm.

To break free of this restraint, a more quantitative treatment of SCO and LIESST is desirable. The assumption of O_h symmetry implicit in Tanabe−Sugano diagrams is too severe, but modern quantum chemistry is more flexible. Density functional theory (DFT), for example, is general enough and can predict spin-state energy differences fairly reliably.[9−15] However, *all* quantum-mechanical (QM) approaches are too expensive for molecular discovery, where screening, conformational searching, and dynamics may require thousands or even millions of calculations.

In contrast, empirical ligand-field molecular mechanics (LFMM) treats both d-orbital splitting and interelectron repulsion and thus can deliver DFT-like accuracy up to 4 orders of magnitude faster.[16] Here we demonstrate in principle how LFMM could be used to design new SCO and LIESST complexes.

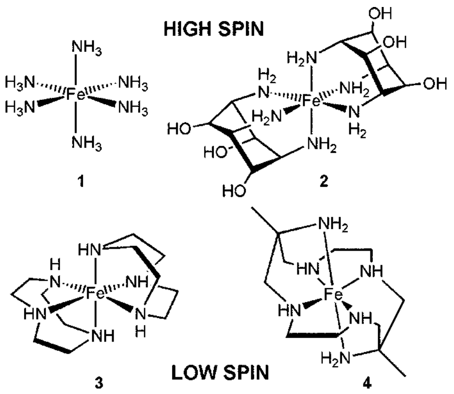

Figure 1. Schematic diagrams of Fe(II) am(m)ine complexes. In the solid state, **1** and **2** are high-spin while **3** and **4** are low-spin.

The am(m)ine complexes shown in Figure 1 span the SCO divide. In the solid state, [Fe(NH$_3$)$_6$]$^{2+}$ (**1**) and [Fe(htach)$_2$]$^{2+}$ (**2**) (htach =1,3,5-triamino-2,4,6-trihydroxycyclohexane[17]) are HS while [Fe([9]aneN$_3$)$_2$]$^{2+}$ (**3**) ([9]aneN$_3$ = 1,4,7-triazacyclononane) and [Fe(diammac)]$^{2+}$ (**4**) (diammac = *exo*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazatetradecane) are LS. Using Swart's DFT protocol (OPBE functional, TZP basis sets[15]) plus the conductor-like screening model to include condensed-phase effects,[18] we computed HS and LS structures and spin-state energy differences for these complexes (see the Supporting Information).

DFT correlates perfectly with experiment. Hence, we can harness the power of DFT, which can access *both* spin states, and use these eight calculations as training data for optimizing the LFMM parameters (see the Supporting Information) via a penalty-function procedure similar to that of Norrby.[19]

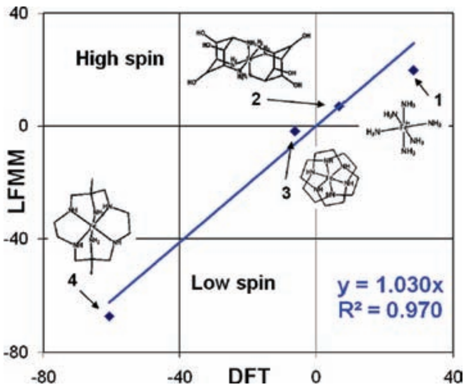

Figure 2. Comparison of theoretical spin-state energy differences (kJ mol^{-1}) for complexes **1**−**4**.

LFMM gives virtually the same results as DFT for **1**−**4** (Figure 2), but in contrast to DFT, we can use LFMM in discovery mode to rapidly carry out multistep conformational searches and screen for SCO behavior. Starting from **4**, which is strongly LS, 19 derivatives were tested in a few hours using a laptop. Two were predicted to be near the SCO boundary (Figure 3; also see the Supporting Information).

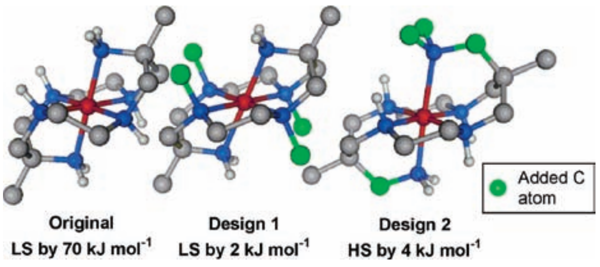

Figure 3. Molecular design of modified versions of **4** near the SCO divide. LFMM spin-state energy differences are given. Added carbon atoms are shown in green. (Nonpolar H atoms have been removed for clarity.)

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The spin-state energy differences for these new designs were reevaluated with DFT and found to be within about ±5 kJ mol^{-1}. LFMM does not perfectly reproduce the DFT values for species not in the training set, and since packing effects in the solid state may further perturb the energetics, a sufficient number of complexes should be screened to obtain a series that spans the SCO divide by 10−15 kJ mol^{-1} in order to increase the likelihood of getting a "hit".

LFMM also appears to capture the dynamics of thermal SCO. In solution, **3** undergoes a spin equilibrium between 360 and 220 K dominated by intramolecular structural changes.[20] Likewise, single-molecule ligand-field molecular dynamics (LFMD) favors the HS state by ~4 kJ mol^{-1} at 360 K and the LS state by ~3 kJ mol^{-1} at 220 K (Figure 4).[21] The small (~0.02 Å) increase in the Fe−N bond lengths with rising temperature gives an energy change of the correct magnitude, although more sophisticated MD simulations are required to test this more fully.

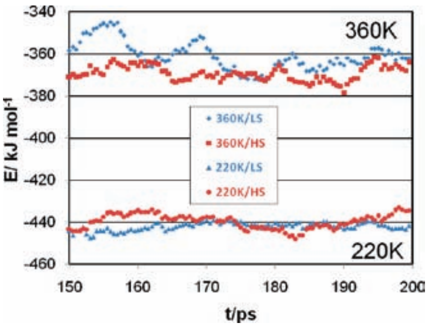

Figure 4. LFMD-averaged energies for the final 50 ps of a 200 ps LFMD run for molecule **3**.

Finally, LIESST depends on the barrier for spin-state conversion (usually HS to LS), which we derived in an approximate way from the minimum-energy crossing point[22,23] (MECP, Figure 5). Here we made an intriguing discovery. The SCO analysis generally found that HS and LS versions have the same conformation, but stochastic conformational searches for **4** showed that the "staggered" conformation of the two ethylene links between equatorial N donors is ~20 kJ mol^{-1} lower than the "eclipsed" form for LS but ~44 kJ mol^{-1} higher for HS (Figure 6, top).

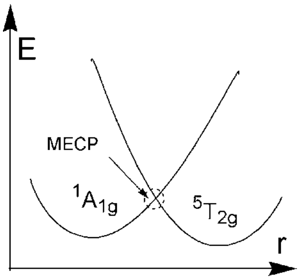

Figure 5. Schematic illustration of the minimum-energy crossing point (MECP) for a typical Fe(II) complex as a function of the average Fe−L bond length, *r*.

The staggered LS−HS energy difference is large, so the MECP barrier is negligible. However, if the complex could relax to the lower-energy eclipsed form (the red dotted curve in Figure 6), the predicted MECP barrier would increase to ~9 kJ mol^{-1}. The relaxation mechanism might be complex, possibly involving other spin states,[24] and in the case of **4**, the small barrier suggests that the HS state may be too short-lived. However, since LFMM enables conformational searching, alternative structures that might have an effect on LIESST can and should be included in the search.

In summary, the quest for new SCO and LIESST systems needs better theoretical tools. QM can never be as fast as MM, but MM can be designed to be as accurate as QM. For TM complexes, LFMM treats the crucial d-electron effects and is also fast enough for screening, conformational searches, and dynamics. With support from high-level QM results, accurate, tailored, and transferable force fields can be derived that will help discovery efforts break free of the FeN$_6$ paradigm completely and perhaps reveal new classes of complexes previously believed incapable of supporting SCO or LIESST.

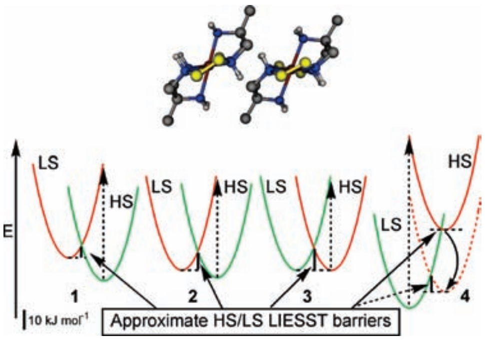

Figure 6. (top) Orientation of ethylene bridges in **4**: (left) eclipsed; (right) staggered. (bottom) Schematic depiction of the approximate LIESST barriers between the HS and LS states (black bars). For **4**, the curved arrow represents the hypothetical change from the staggered to the eclipsed conformation and the concomitant increase in the LIESST barrier.

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Supporting Information Available: ADF-optimized coordinates and binding energies; LFMM parameters; and LFMM spin-state energy differences for 19 modifications of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Létard, J. F.; Guionneau, P.; Goux-Capes, L. *Top. Curr. Chem.* **2004**, *235*, 221.
(2) Carbonera, C.; Kilner, C. A.; Létard, J. F.; Halcrow, M. A. *Dalton Trans.* **2007**, 1284.
(3) Baker, W. A.; Bobonich, H. M. *Inorg. Chem.* **1964**, *3*, 1184.
(4) Koenig, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.
(5) Halcrow, M. A. *Polyhedron* **2007**, *26*, 3523.
(6) Weber, B.; Kaps, E.; Weigand, J.; Carbonera, C.; Létard, J. F.; Achterhold, K.; Parak, F. G. *Inorg. Chem.* **2008**, *47*, 487.
(7) Guetlich, P.; Spiering, H.; Hauser, A. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley and Sons: New York, 1999; Vol. 2, pp 575−622.
(8) Sohrin, Y.; Kokusen, H.; Matsui, M. *Inorg. Chem.* **1995**, *34*, 3928.
(9) Sorkin, A.; Iron, M. A.; Truhlar, D. G. *J. Chem. Theory Comput.* **2008**, *4*, 307.
(10) Remacle, F.; Grandjean, F.; Long, G. J. *Inorg. Chem.* **2008**, *47*, 4005.
(11) Deeth, R. J.; Fey, N. *J. Comput. Chem.* **2004**, *25*, 1840.
(12) Baranovic, G. *Chem. Phys. Lett.* **2003**, *369*, 668.
(13) Reiher, M. *Inorg. Chem.* **2002**, *41*, 6928.
(14) Respondek, I.; Bressel, L.; Saalfrank, P.; Kampf, H.; Grohmann, A. *Chem. Phys.* **2008**, *347*, 514.
(15) Swart, M. *J. Chem. Theory Comput.* **2008**, *4*, 2057.
(16) Deeth, R. J.; Anastasi, A.; Diedrich, C.; Randell, K. *Coord. Chem. Rev.* **2009**, *253*, 795.
(17) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.
(18) Hocking, R. K.; Deeth, R. J.; Hambley, T. W. *Inorg. Chem.* **2007**, *46*, 8238.
(19) Norrby, P. O.; Brandt, P. *Coord. Chem. Rev.* **2001**, *212*, 79.
(20) Turner, J. W.; Schultz, F. A. *Inorg. Chem.* **2001**, *40*, 5296.
(21) Average energy for the last 50 ps of a 200 ps LFMD *NVT* run.
(22) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95.
(23) Jensen, F.; Norrby, P. O. *Theor. Chem. Acc.* **2003**, *109*, 1.
(24) Suaud, N.; Bonnet, M. L.; Boilleau, C.; Labeguerie, P.; Guihery, N. *J. Am. Chem. Soc.* **2009**, *131*, 715.

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