

On the Innocence of Bipyridine Ligands: How Well Do DFT Functionals Fare for These Challenging Spin Systems?

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The electronic structures of a number of iron, cobalt, vanadium, and titanium complexes with the 2,2'-bipyridine (bpy) ligand were considered using the multireference CASSCF and NEVPT2 methods.[1,2] Many of these systems have been studied in the past using B3LYP and were found to contain the bpy ligand as a radical anion. For many of the cases, this is contradicted both by our chemical intuition and by our multireference calculations. While there are instances where the ligand is indeed a radical anion resulting from electron transfer from the metal centre, in many cases it remains neutral and is involved in π -backbonding from the metal centre.

Since there are many cases where CASSCF is too costly, a number of DFT functionals, including the newer double-hybrid functionals, were evaluated against the CASSCF data. It was found that nonhybrid functionals, especially those containing the kinetic energy density τ (*i.e.*, meta-GGA functionals), were the best at predicting the electronic nature of the complexes. The τ -HCTH and HCTH functionals were the top performers, correctly predicting all eleven out of eleven test cases and with the lowest mean unsigned errors (MUE, 7.6 and 7.8 kcal/mol, respectively); the M06-L, N12, BLYP, PBE, and TPSS functionals also did well, while B3LYP had significant shortcomings.

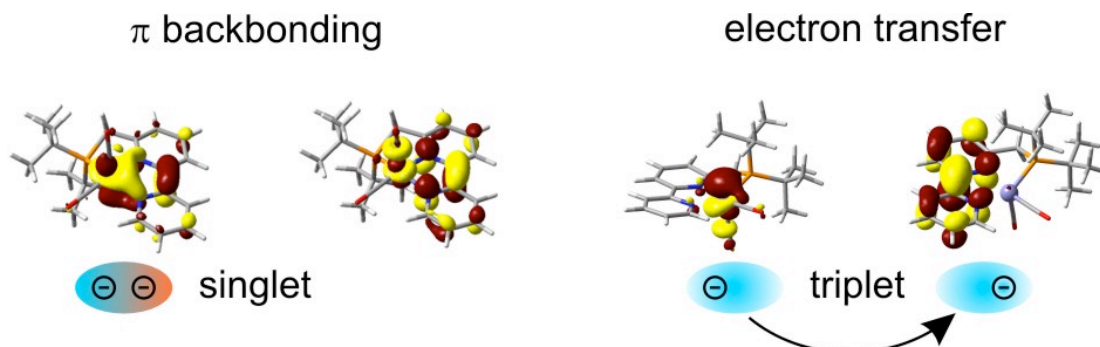


Figure 1: HOMO and LUMO of $(\eta^3\text{-PNN-}t\text{Bu}_2\text{PCH}_2\text{-bpy})\text{Fe}(\text{CO})_2$ showing the π -backbonding in the closed-shell singlet state and the electron transfer triplet state.

[1] P. Milko and M. A. Iron, *J. Chem. Theory Comput.*, **10**, 220 (2014).

[2] T. Zell, P. Milko, K. L. Fillman, Y. Diskin-Posner, T. Bendikov, M. A. Iron, G. Leitun, Y. Ben-David, M. L. Neidig and D. Milstein, *Chem. Eur. J.*, 4403 (2014).