

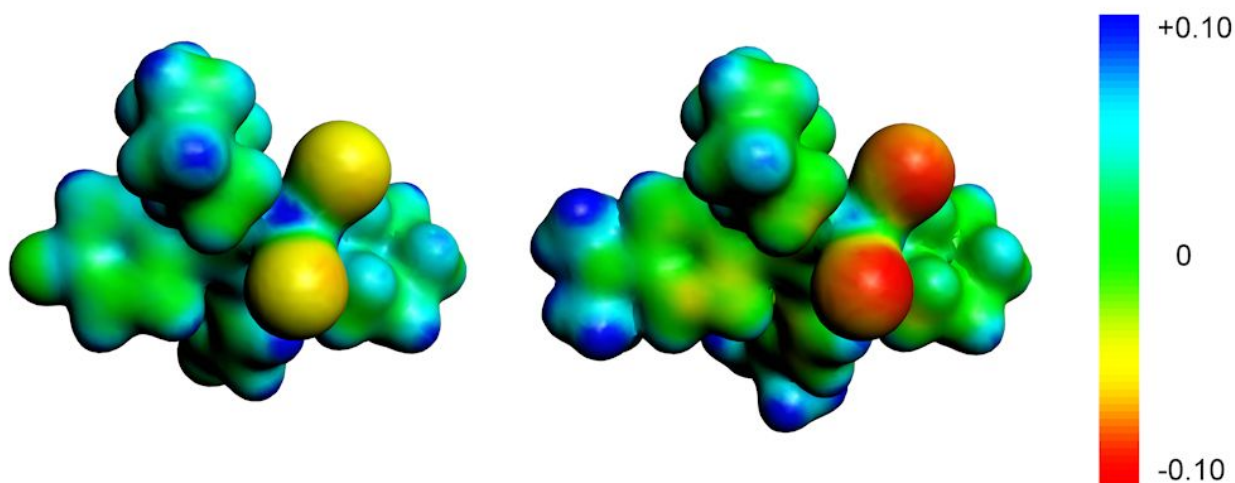
# Modelling the polymerisation mechanism of $\alpha$ -diimine iron catalysts

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The  $\alpha$ -diimine iron complexes have been proposed as the first example outside the realm of biomolecules where the spin-state of the transition metal involved dictates the catalytic behaviour [1]. Here, we study a typical complex of this family,  $R''[N,N]FeCl_2$ , with  $[N,N] = Cy-N=CR''-CR''=N-Cy$  ( $Cy$ =cyclohexyl),  $R''=PhF$  (para-fluorophenyl),  $PhOMe$  (para-methoxyphenyl),  $PhNMe_2$  (para-dimethylaminophenyl). With  $R''=PhF$ ,  $PhOMe$ , polymerisation proceeds as a catalytic chain transfer (CCT) mechanism; with  $R''=PhNMe_2$ , the polymerisation follows an atom transfer radical polymerisation (ATRP) pathway. Contrary to previous suggestions, we show that the spin states of the complexes involved are *not* affected by the  $R''$  group, however. Instead, the different behaviour arises from a subtle interplay between the electron-withdrawing or donating character of the phenyl substituent and the iron centre, located more than 8 Å away. Small but crucial differences in the reorganisation energies effected during the reactions are also noted and discussed.



The electrostatic potential (ESP) for the  $R''=PhF$  (left) and  $R''=PhNMe_2$  (right) complexes.

- [1] M.P. Shaver, L.E.N. Allan, H.S. Rzepa, V.C. Gibson, "Correlation of Metal Spin State with Catalytic Reactivity: Polymerizations Mediated by  $\alpha$ -Diimine-Iron Complexes", *Angew. Chem. Int. Ed.* **45** (2006) 1241–1244.
- [2] M.P. Johansson, M. Swart, "Subtle effects control the polymerisation mechanism in  $\alpha$ -diimine iron catalysts" (submitted)