## Supporting Information

Determining the Inherent Selectivity for Carbon Radical Hydroxylation versus Halogenation with High-Spin Oxoiron(IV)−Halide Complexes: A Concerted Rebound Step

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**Tests of the functionals**: The unrestricted hybrid density functional method unrestricted Becke, three-parameter, Lee–Yang–Parr (UB3LYP) we have used is commonly accepted and applied for the mononuclear non-heme iorn complexes, meanwhile, gives the reliable results in many theoretical investigations[1-5]. To ascertain the choice of UB3LYP, the functional test is carried out. We have used the extra UM06L and UPBE1PBE functionals to optimize the structure of $[Fe^{IV}(O)(TQA)(X)]^+$ (X=Cl and Br). All the functionals tests show that the quintet state is more stable than triplet state. As expected, the UM06L/B1//UM06L/B2 and UPBE1PBE/B1//UPBE1PBE/B2 results are comparable with those obtained from UB3LYP/B1//UB3LYP/B1. Therefore, we selected UB3LYP as the method of choice.

**Table S1. UM06L/B1-, UM06L/B2-, UPBE1PBE/B1- and UPBE1PBE/B2-calculated the relative energies (kcal/mol), mulliken charge and spin densities for the Fe and O atoms and the important bond lengths (Å).**

| X | | | $\Delta E_{(T-Q)}$ | Mulliken charge | | Spin densities | | $r_{Fe-O}$ | $r_{Fe-X}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Fe | O | Fe | O | | |
| Cl | UM06L/B1 | T | 4.20 | 0.84 | -0.47 | 1.16 | 0.89 | 1.64 | 2.37 |
| | | Q | | 0.85 | -0.46 | 2.94 | 0.71 | 1.64 | 2.34 |
| | UM06L/B2 | T | 7.84 | 0.41 | -0.54 | 1.25 | 0.83 | 1.64 | 2.37 |
| | | Q | | 0.68 | -0.55 | 3.14 | 0.58 | 1.64 | 2.93 |
| | UPBE1PBE/B1 | T | 4.08 | 0.61 | -0.44 | 1.15 | 0.90 | 1.62 | 2.34 |
| | | Q | | 0.72 | -0.43 | 3.03 | 0.68 | 1.61 | 2.37 |
| | UPBE1PBE/B2 | T | 6.71 | 0.04 | -0.51 | 1.24 | 0.83 | 1.62 | 2.34 |
| | | Q | | 0.38 | -0.50 | 3.17 | 0.59 | 1.61 | 2.37 |
| Br | UM06L/B1 | T | 4.71 | 0.74 | -0.47 | 1.18 | 0.88 | 1.64 | 2.53 |
| | | Q | | 0.75 | -0.47 | 2.93 | 0.73 | 1.64 | 2.50 |
| | UM06L/B2 | T | 7.34 | 0.33 | -0.53 | 1.27 | 0.83 | 1.64 | 2.53 |
| | | Q | | 0.62 | -0.55 | 3.13 | 0.58 | 1.64 | 2.50 |
| | UPBE1PBE/B1 | T | 6.46 | 0.52 | -0.44 | 1.17 | 0.89 | 1.62 | 2.48 |
| | | Q | | 0.61 | -0.43 | 3.06 | 0.67 | 1.62 | 2.50 |

T for triplet; Q for quintet

NOTE: Whether using the UM06L or UPBE1PBE, the quintet state is more stable than triplet state

**Tests of the basis set**: We have used a basis set TZVP, B2 in brief, to calculate single-point energy on the LACVP-optimized geometry. To ascertain the choice of TZVP, we have used higher basis set def2-TZVPP on the calculation of LACVP-optimized geometry of $[Fe^{IV}(O)(TQA)(X)]^+$ (X=Cl and Br), the basis set test shows that the quintet state is more stable than triplet state.

**Table S2. UB3LYP/def2-TZVPP-calculated the relative energies (kcal/mol), mulliken charge and spin densities for the Fe and O atoms and the important bond lengths (Å).**

| X | | | $\Delta E_{(T-Q)}$ | Mulliken charge | | Spin densities | | $r_{Fe-O}$ | $r_{Fe-NCME}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Fe | O | Fe | O | | |
| Cl | UB3YP/def2-TZVPP | T | 6.78 | 0.49 | -0.50 | 1.24 | 0.82 | 1.64 | 2.50 |
| | | Q | | 0.78 | -0.50 | 3.10 | 0.63 | 1.63 | 2.51 |
| Br | UB3YP/def2-TZVPP | T | 6.97 | 0.48 | -0.49 | 1.24 | 0.82 | 1.64 | 2.34 |
| | | Q | | 0.75 | -0.49 | 3.10 | 0.63 | 1.63 | 2.34 |

T for triplet; Q for quintet

NOTE: Even if using the higher basis set def2-TZVPP, the quintet state is more stable than triplet state.
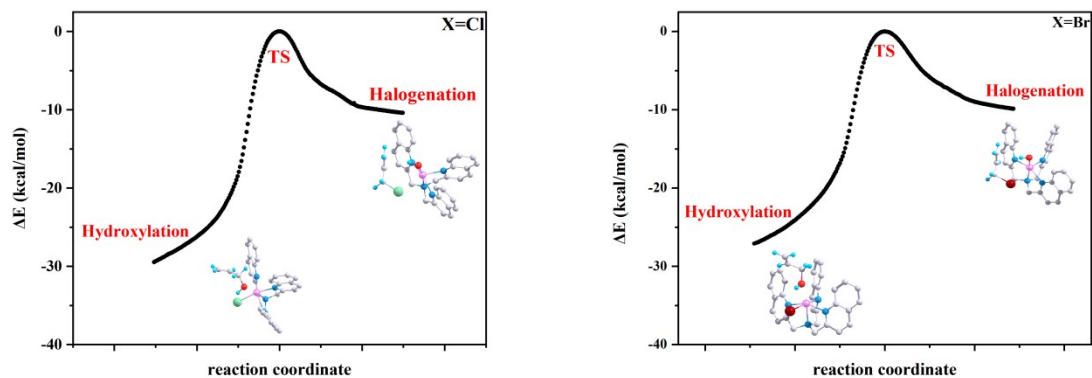


**Fig. S1. The intrinsic reaction coordinate for [Fe$^{IV}$(O)(TQA)(X)] $^+$ (X=Cl and Br)**

**Reference**

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