Effect of *meso*-Substitution on the Selectivity of the Propene Reaction by Fe(IV)OCl–Porphyrin: a Density Functional Theory Mechanistic Study

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We have performed density functional theory (DFT) calculations of C=C epoxidation and C−H hydroxylation of propene using a model of Fe(IV)OCl–porphyrin cation radical complexes with fluorine and methyl groups as *meso*-substituents of the porphyrin ring. By gas-phase DFT calculations, it is found that fluorine substitution enhances the reactivity. According to detailed electronic feature analysis of the reactant complexes and transition states, electron-withdrawing groups at the *meso*-position stabilize the electron acceptor orbital of the complex more than the electron donation orbital of the substrate, leading to a decrease in the energy gap between these orbitals, and a lower energy barrier. More importantly, fluorine substitution for the *pull effect* makes hydroxylation favorable, whereas methyl substitution makes epoxidation preferable. The selective oxidation reactivity of Fe(IV)OCl–porphyrin is largely ascribed to the effect of *meso*-substitution on the amount of electron transfer from propene to Fe(IV)OCl–porphyrin. Additionally, we analyzed intersystem crossing between the quartet and sextet spin states using the potential energy surfaces (PESs), and the crossing seam between the quartet and sextet PESs occurs at around transition state TS1.

Keywords: Density functional theory, *meso*-substitution effect, Oxoiron(IV)–porphyrin, Electronic structure, Molecular orbital

1 INTRODUCTION

Heme enzymes are versatile and important enzymes, and they are responsible for oxygen transport and oxygenation of substrates, such as hydroxylation and epoxidation [1]. In particular, the cytochrome P450s (P450) enzyme is involved in monooxygenation for biosynthesis of hormones, in which one oxygen atom is transferred to the substrate, generating hydrocarbon products [2]. The main active form of the P450 enzyme (compound I) is in the Fe = O region, which is verified by the kinetic isotope effects and product in experiments [3]. The Fe = O active center of the P450 enzyme has been used as a template to generate new catalysts by synthetic chemists in the biinorganic or inorganic chemistry fields [4]. They focused on enhancing the activity and efficiency by modifying the axial ligands and substituents. For example, oxoiron–porphyrin complexes have been studied using different axial ligands bound to the iron atom [5–12]. In some compound I complexes, the iron atom is bound to nitrate or imidazole, but in other compound I complexes the iron is bound to fluorine or chlorine. These axial ligands cause a push effect or electron-withdrawing effect (pull effect) during the reaction process [13, 14]. As a result, oxoiron–porphyrin complexes with various axial ligands show great differences in the catalysis mechanisms and electronic properties. From experiment, the dramatic difference is shown in the frequency of the Fe = O bond \(v_{\text{Fe} = \text{O}}\). Fluorine or chlorine axial ligands show low \(v_{\text{Fe} = \text{O}}\) frequencies (801 cm\(^{-1}\)) compared with the nitrate axial ligand \(v_{\text{Fe} = \text{O}} = 821 \text{ cm}^{-1}\) [15].

Another important factor is substitution of the porphyrin ring, such as *meso*-substitution and pyrrole beta-substitution, which greatly affects the catalytic activity and electronic structure of oxoiron–porphyrin complexes. Bulky substituents restrict substrate binding to the active center, thereby affecting the reaction rate of hydroxylation or epoxidation [16–18]. In general, the radical elec-
tron on porphyrin is located in the $a_{2u}$ orbital for meso-substitution, but the beta-substituted porphyrin has an $a_{1u}$ radical state. With increasing electron-withdrawing effect at the meso-position, the $a_{2u}$ radical state shifts to the $a_{1u}$ radical state [19]. Additionally, a positive charge on the meso-substituent of the porphyrin ring greatly enhances the hydroxylation reactivity of oxoiron(IV)–porphyrin complexes, which is ascribed to the peripheral charges creating an attractive potential that lowers the electron acceptor orbital [20]. By thermodynamic analysis based on the redox potential, Fujii et al. [21] reported that meso-substitution affects heterolytic versus hemolytic cleavage of the O–Cl bond.

Recently, we studied the effect of peripheral fluorine atoms on the epoxidation reaction of ethylene using beta-substituted and phenyl-substituted oxoiron(IV)–porphyrin π-cation radical complexes [22]. With increasing number of fluorine atoms, the energy barrier decreased for both beta-substitution and phenyl-substitution, which is in agreement with the experimental results. Moreover, the sextet spin surface energy is lower than the quartet spin surface energy for beta-substituted complexes. By contrast, for phenyl-substituted complexes, the quartet spin surface energy is lower than the sextet spin surface energy. We also investigated the effects of axial ligands and environmental perturbation (e.g., an external electric field) on olefin epoxidation by oxoiron(IV)–porphyrin complexes [23]. The axial ligands affected the pattern of electron transfer during the reaction. The strong interaction between the axial ligand and iron enhances the reactivity. The external electric field directing in electron transfer flow catalyzes the oxidation reaction. In addition, a study of phenyl-beta-substitution effects on the electronic structures and reactivity of oxoiron(IV)–porphyrin complexes has been performed by combining experiments with density functional theory (DFT) calculations [24]. Spectroscopic analysis of the phenyl-substituted complexes showed that the porphyrin radical state changes from the $A_{2u}$ radical state to the $A_{1u}$ radical state with increasing number of the fluorine atoms in the meso-phenyl group, which occurs at introduction of four fluorine atoms. Based on the above reports, we wanted to answer the following two questions. (1) Do groups at the meso-position with the ability to donate or withdraw electrons affect the ratios of epoxidation and hydroxylation of an alkene? (2) Do they affect the location of intersystem crossing (ISC) between various spin states? To answer these questions, we performed DFT calculations of alkene reactions by Fe(IV)OCl–porphyrin complexes with fluorine (F) atoms and methyl (Me) groups as the meso-substituents. The reaction pathway and some key species are shown in Scheme 1. Propene was chosen as a model alkene, and the results for propene are used to determine a model trend and make a prediction on relevant reactions. A similar model of oxoiron–porphyrin in experiments showed that the ground state of the reactants is the quartet state ($S = 3/2$), whereas the ground state of the products is the sextet state ($S = 5/2$) [15], so this system was investigated in the quartet and sextet spin states.

## 2 Computational Methods

All of the DFT calculations were performed with the Gaussian 16 program [25]. From our previous calculations of the Fe(IV) OCl–porphyrin model [22], the PBE0 functional is reasonable to assess its energy, which is in agreement with a CASPT2 calculation and experimental results. In the present model of Fe(IV)OCl–porphyrin, we used the unrestricted PBE0 hybrid functional [26] in combination with the cc-PVTZ basis set [27] for the iron atom and the 6-31G basis set [28] for the other atoms. Initially, geometry scans were performed in which one variable acted as the coordinate, and then all of the remaining degrees of freedom were fully optimized. The geometry scans were performed to both search for the transition state and connect the transition state with the local minima. All of the energy profiles of the geometry scans are shown in Figures S1–S4 in the Supporting Information. All of the geometric structures were fully optimized in the gas-phase and frequency
analysis was performed to check whether they were local minima or saddle points. All of the reactants, intermediate species, and products were located on local minima, and the transition states were characterized to have only one imaginary frequency for the transition state vector. The two-dimensional (2D) potential energy surface (PES) was also scanned using the Gaussian 16 program.

3 RESULTS AND DISCUSSION

3.1 Geometric and Electronic Structures

The molecular geometries and Mulliken spin populations ($P$) of Fe(IV)OCl–porphyrin with fluoride (F) and methyl (Me) groups as the meso-substituents, which are designated Comp-F and Comp-Me, respectively, are shown in Figure 1. In agreement with our previous report, the meso-substituents (F or Me) hardly affect the Fe = O bond. Note that the Fe–Cl bond is affected by the electronegativity of the meso-substituents. The electron-donating methyl groups at the meso-positions cause elongation of the Fe–Cl bond, whereas the electron-withdrawing fluoride atoms shorten the Fe–Cl bond in the quartet and sextet spin states. Rearrangement of the electronic structures is probably exerted by the pull effect of the F atom at the meso-position, resulting in enhancement of the oxidation reactivity, which is explained in detail in the following section of the energy profiles.

For Comp-Me in the quartet state, the spin populations $P_{\text{Fe}}$ and $P_{\text{O}}$ are 1.16 and 0.89, respectively, while for Comp-F, $P_{\text{Fe}}$ and $P_{\text{O}}$ are 1.10 and 0.92, respectively. This indicates that the Fe = O moiety has two spin-up electrons, and another spin-up electron is located on the porphyrin ring. For Comp-Me in the sextet spin state, the spin populations $P_{\text{Fe}}$ and $P_{\text{O}}$ are 3.20 and 0.59, respectively, while for Comp-F, $P_{\text{Fe}}$ and $P_{\text{O}}$ are 3.18 and 0.62, respectively. This means that the Fe = O moiety has almost four spin-up electrons, and one spin-up electron is located on the porphyrin ring. The pull effect of the fluorine groups clearly causes larger spin population of the O atom relative to the push effect of the methyl groups, whereas the spin populations of iron and porphyrin-$\pi$ are the opposite. Other geometric parameters, the charges, and the spin populations are summarized in Tables S1–S4 in the Supporting Information.

Based on the above discussion, Fe(IV)OCl–porphyrin has three

![Figure 1. Typical bond lengths (in Å) and Mulliken spin populations ($P$) of Comp-Me and Comp-F in the ground quartet ($S = 3/2$) and excited sextet ($S = 5/2$) spin states.

- Unpaired electrons in the quartet spin state, which are expressed as $(a_{1u}^*)^2(b_{2g}^*)^2$, doubly occupied orbitals $(a_{1u})^2(b_{2g})^2$, and unoccupied orbitals $(d_{x^2−y^2})^2(d_{xy})^2$ (see Figure 2). The $a_{1u}$ and $b_{2g}$ orbitals represent the bonding and antibonding combinations of the $3a_{1u}$ orbital on iron and the $2p_{xy}$ orbitals on oxygen. By analysis of the molecular orbital composition, the $a_{1u}$ orbitals mix with the $\sigma$ orbitals on nitrogen and $\pi$ orbital on chlorine. The nonbonding $d_{xy}$ orbital on iron is located in the plane of porphyrin.

Another orbital in the porphyrin plane is the antibonding orbital $d_{x^2−y^2}$, which is mixing of the $3d_{x^2−y^2}$ orbital on iron with the $\sigma$ orbitals on nitrogen. The $d_{x^2−y^2}$ orbital is affected by the F atoms and Me groups at the meso-positions. The pull effect of the F atoms makes the contribution of the $a_{1u}$ orbital small, which mixes with the $\pi$ orbital on the F atom (see Figure 2).

Another difference between Comp-F and Comp-Me is the orbital energies. The electron-withdrawing fluoride groups result in all of the orbitals being more stable compared with the methyl groups in both the quartet and sextet spin states. The sextet spin state is formed by one electron excitation from the $\beta-d_{xy}$ orbital to the $\alpha-d_{x^2−y^2}$ orbital, leading to the $\alpha-d_{xy}$ and $\alpha-d_{x^2−y^2}$ orbitals of the sextet spin state becoming more stable relative to the quartet spin state.

The key orbitals shown in Figure 2 are occupied by 11 electrons. However, because experimental results show that the $a_{1u}$ radical state shifts to the $a_{1u}$ radical state with an increase in the electron-withdrawing effect at the meso-position [19], we analyzed the typical electronic states in the quartet and sextet spin states (see Table 1), such as the $A_{2u}$ and $A_{1u}$ states. The single electron lies in the $a_{1u}$ orbital, such as $(a_{1u})^2(b_{2g}^*)^2(b_{1g})^2$, which is designated as the $A_{2u}$ state. Similarly, $(a_{1u})^2(b_{2g}^*)^2(a_{1g})^2$ is designated as the $A_{1u}$ state. Comparing the energies of the $A_{2u}$ and $A_{1u}$ states, all of the $A_{1u}$ states are at least 5 kcal/mol higher in energy than the $A_{2u}$ ground state. The $4A_{1u}$ states of Fe(IV)OCl–porphyrin are high in energy and not expected to play an important role in catalysis.
and oxidation. However, the $^4A_{2u}$ state is well separated from the other electronic states, and it will be a critical state for catalysis or oxidation of substrates.

The state ordering of Comp-\textit{Me} is different from that of Comp-\textit{F}. In the gas-phase, the $^6A_{2u}$-\textit{Me} states are below the $^6A_{2u}$-\textit{Me} states in energy, and the energy gap between these two states is around 3 kcal/mol. Nevertheless, the $^6A_{1u}$-\textit{Me} states are higher lying than $^6A_{1u}$-\textit{Me} in energy, and the energy gap between the $^6A_{1u}$-\textit{Me} and $^6A_{1u}$-\textit{F} states is around 2 kcal/mol. This difference between the state orders may result from interaction of the $a_{2u}$ orbitals with the meso-substituents. In the bare porphyrin in $D_{4h}$ symmetry, the $a_{1u}$ and $a_{2u}$ orbitals are nearly degenerate. However, in the Fe(IV) OCI–porphyrin with meso-substitution, the $a_{2u}$ orbital mixes with the $\sigma$ orbital on the chlorine atom and the $\pi$ orbital of the meso-substituted groups. In particular, for Comp-\textit{F}, the $a_{1u}$ orbital is shown to favorably mix with the $\pi$ orbital on the fluorine atom,
but this mixing is very small on the methyl group (see Figure 2). Therefore, the energy gap between $A_{2u}$ and $A_{1u}$ is large.

### 3.2 Oxidation Reactivity

From our previous work, Fe(IV)OCl–porphyrin complexes react with olefins by a stepwise mechanism, where the C=C and Fe = O bonds are initially activated, resulting in formation of a radical intermediate ($\text{Int}^E$), and then the radical attacks the oxygen atom to form the epoxide product ($\text{P}^E$) [22]. Bond activation is completed by overcoming the energy barrier of $\text{TS}1^E$ and is accompanied by electron transfer from C=C to the Fe(IV)OCl–porphyrin catalyst. Similarly, hydroxylation of propene occurs by a stepwise mechanism, in which the initial hydrogen transfer reaction leads to formation of an iron-hydroxo intermediate ($\text{Int}^H$) through $\text{TS}1^H$, and then the radical rebinds to the oxygen atom to generate the hydroxylation product ($\text{P}^H$). First, we compared the energies between unsubstituted complex (Comp-H) and substituted complexes (Comp-Me and Comp-F) shown in Table S5 of Supporting Information. Clearly, the potential energies of Comp-Me are higher than that of Comp-H, whereas the potential energies of Comp-F are lower than that of Comp-H. To compare the donate or withdraw electron effects on potential energies, the gas-phase energy profiles for epoxidation and hydroxylation of propene by Comp-F and Comp-Me in the quartet and sextet spin states are shown in Figure 3, and the corresponding potential energy profiles are designated $^\lambda$Comp-Me and $^\lambda$Comp-F in the quartet and sextet states. The initial reactant (R) is in the center of the Figure. The energy profiles of propene epoxidation are shown on the left-hand side, while the energy profiles of propene hydroxylation are shown on the right-hand side. By analysis of the overall energy profiles, the rate-determining step is formation of the first transition state ($\text{TS}1^E/\text{TS}1^H$).

#### Epoxidation of Propene

Starting from reactant (R) to intermediate ($\text{Int}^E$) through transition state ($\text{TS}1^E$), the energy barriers are affected by the meso-substituents (Me and F). The activation energies are 14.9, 13.0, 11.4, and 10.5 kcal/mol for $^4$Comp-Me, $^4$Comp-Me, $^4$Comp-F, and $^4$Comp-F, respectively. This means that the fluorine group as a meso-substituent enhances propene epoxidation. Methyl and fluorne groups at the meso-positions of the Fe(IV) OCl–porphyrin complexes also affect the spin energy surface. For Comp-Me with the methyl group as a meso-substituent, the sextet energy barrier is higher than the quartet energy barrier, which suggests that ISC from a quartet to a sextet spin state occurs after $\text{TS}1^E$. However, for Comp-F with fluorine as a meso-substituent, the sextet energy barrier is lower than the quartet energy barrier, indicating that ISC occurs before $\text{TS}1^E$. In addition, ring closure from $\text{Int}^H$ to $\text{P}^H$ through $\text{TS}2^H$ is barrierless in the quartet spin state. However, for $\text{TS}2^E$ in the sextet spin state, there are barriers of 4.6 and 8.6 kcal/mol for Comp-Me and Comp-F, respectively.

#### Hydroxylation of Propene

The energy profiles along the reaction pathway for hydroxylation of propene are shown on the right-hand side of Figure 3. Similar to the epoxidation potential energy, the energy barriers are affected by the meso-substituents. The activation energies of $\text{TS}1^H$ for $^4$Comp-Me, $^4$Comp-Me, $^4$Comp-F, and $^4$Comp-F, are 16.3, 14.2, 11.9, and 9.9 kcal/mol, respectively. Additionally, the energy barrier of $^4$Comp-Me is higher than that of $^4$Comp-Me, which suggests that ISC occurs after $\text{TS}1^H$. Conversely, the energy barrier of $^4$Comp-F is lower than that of $^4$Comp-F, indicating that ISC occurs before $\text{TS}1^H$. Differing from epoxidation transition state $\text{TS}2^E$, hydroxylation transition state $\text{TS}2^H$ in both the quartet and sextet spin states has an energy barrier from 0.4 to 2.4 kcal/mol for conversion from $\text{Int}^H$ to $\text{P}^H$ by Comp-Me and Comp-F.

To explore the effect of meso-substitution on the selectivity of
the propene reaction by Comp-Me and Comp-F, we compared the energy barriers of the rate-determining steps (TS1E and TS1H) for epoxidation and hydroxylation. First, comparing the energies of TS1E and TS1H for Comp-Me in both the quartet and sextet spin states, the TS1E energy of 4 Comp-Me (13.0 kcal/mol) is lower than the TS1H energies of 4 Comp-Me, which means that epoxidation of propene is favorable over hydroxylation. In the same manner, we also compared the TS1E and TS1H energies of 4 Comp-F. Note that the TS1H energy of 6 Comp-F (9.9 kcal/mol) is the lowest of all of the TS1 energies, which suggests that hydroxylation of propene by 6 Comp-F is favorable over epoxidation.

In summary, for Comp-Me, ISC from a quartet to a sextet spin state occurs after TS1E,H, and propene epoxidation is favorable over propene hydroxylation. Conversely, for Comp-F, ISC occurs before TS1E,H, and hydroxylation of propene is favorable over epoxidation of propene. Additionally, fluorine as a meso-substituent lowers the reaction PES. The reasons are discussed in detail in the following section.

### 3.3 meso-Substitution Effect of Fe(IV)OCl–Porphyrin

meso-Substitution of Fe(IV)OCl–porphyrin systems affects the geometries and fine-tunes the electronic properties, which controls the properties of the catalyst. The geometric structures and electronic features of 4,6 TS1E and 4,6 TS1H for Comp-Me and Comp-F are compared in Figure 4. There is a significant difference in the bond lengths between iron and oxygen/chlorine. The Fe–O
and Fe–Cl bonds of Comp-F are shorter than those of Comp-Me. Furthermore, the effect of meso-substitution can be seen from the spin populations and Mulliken charges. For Comp-F, the spin population on the iron atom \( P_{\text{Fe}} = 1.37/3.84 \) is approximately 0.1 lower than that for Comp-Me \( P_{\text{Fe}} = 1.48/3.87 \) in the quartet and sextet spin states (see top of Figure 4). The changes in the Mulliken charges are similar to those of the spin populations. The pull effect of the fluorine meso-substituent accelerates electron transfer from the substrate (propene) to Fe(IV)OCl–porphyrin, making the reaction process easier. Therefore, Fe(IV)OCl–porphyrin with fluorine as a meso-substituent has low epoxidation and hydroxylation barriers. In addition, the pull effect of fluorine meso-substitution also causes the spin population of the Cl atom \( P_{\text{Cl}} = 0.13 \) to increase by 0.02 units in comparison with Comp-Me \( P_{\text{Cl}} = 0.11 \), while that of porphyrin-\( \pi \) (Por) decreases by the same amount \( P_{\text{Por}} = 0.24 \) of Comp-F vs \( P_{\text{Por}} = 0.26 \) of Comp-Me, which is consistent with the short Fe–Cl bond (2.296 of Comp-F vs 2.321 of Comp-Me, see top of Figure 4). Hence, the pull effect of electron-withdrawing groups at the meso-positions make the barrier of Fe(IV)OCl–porphyrin low, thus enhancing the reactivity. In the Hydroxylation shown bottom of Figure 4, the changes of spin populations and Charges are similar to that of epoxidation.

As mentioned above, electron-withdrawing fluorine groups at the meso-positions lower the propene activation barriers by Fe(IV)OCl–porphyrin catalysts. This can be explained by the effect of fluorine groups at the meso-position on the compositions of the frontier orbitals and the energy gaps between the electron donation orbital and electron acceptor orbital. The compositions of the frontier orbitals and the energy gaps between the electron donation orbital and electron acceptor orbital for propene epoxidation by Comp-Me and Comp-F at the transition state (TS1) are shown in Figure 5. The electron donation orbital \( \psi_{\text{CC}} \) is the \( \pi \)-orbital of propene, and \( a_{2u} \) and \( d_{x^2-y^2}^\ast \) are the electron acceptor orbitals in the quartet and sextet spin states, respectively. The \( a_{2u} \) and \( d_{x^2-y^2}^\ast \) orbitals are stabilized by the Comp-F system relative to the Comp-Me system, such as \( a_{2u} \) and \( \psi_{\text{CC}} \) orbital energies of \( ^4\text{Comp-Me} \) are \(-3.52 \) and \(-5.06 \) eV with energy gap of 1.54 eV, whereas that of \( ^4\text{Comp-F} \) are \(-4.28 \) and \(-5.76 \) eV with energy gap of 1.48, respectively, the Comp-F reduces the orbital energy gap by 0.06 eV. Therefore, in the Comp-F system, \( a_{2u} \) and \( \psi_{\text{CC}} \) mixing becomes

Figure 5. Orbital energy levels at TS1E and the corresponding compositions of the frontier orbitals for propene epoxidation by Comp-Me and Comp-F in the quartet and sextet spin states.
easier than in the Comp-Me system, which is revealed by the composition of the frontier orbital. For example, the virtual orbitals \( a_{2u} \) mix with 21% and 26% C=C compositions in \(^4\text{Comp-Me}\) and \(^4\text{Comp-F}\), respectively. In the sextet spin state, the change trend of orbital energy is similar to that of quartet spin state. These data explain that because of the pull effect, TS1 is reached earlier and with a lower barrier by Comp-F than by Comp-Me. This fact is also observed by the change in the Fe−O bond (see Figure 4).

Reduction of the energy gap between the electron donation orbital and electron acceptor orbital also occurs at TS1 for propene hydroxylation, and \( \sigma_{C−H} \) mixes with the C=C composition (Figure 6). By analysis of the frontier molecular orbitals, for example, \( a_{2u} \) and \( \sigma_{C−H} \) orbital energies of \(^4\text{Comp-Me}\) are −3.62 and −5.11 eV with energy gap of 1.49 eV, whereas that of \(^4\text{Comp-F}\) are −4.35 and −5.80 eV with energy gap of 1.45, respectively, the energy gap in the Comp-F system is 0.04 eV smaller than that in the Comp-Me system. Thus, the occupied \( \sigma_{C−H} \) orbital mixes with the virtual \( a_{2u} \) and \( d_{z^2} \) orbitals in the former earlier and with a lower barrier than in the latter, as confirmed by the compositions of the frontier molecular orbitals. For instance, the virtual orbitals \( a_{2u} \) mix with 16% of C=C and 18% of C−H in the Comp-F system, and 12% of C=C and 16% of C−H in the Comp-Me system, respectively. The case of \(^6\text{Comp-Me/F}\) is similar to that of \(^4\text{Comp-Me/F}\).

To compare the effect of meso-substitution on the barriers of TS1, the relative energy barriers for Comp-Me and Comp-F are shown in Figure 7. In the Comp-Me system, the \(^4\text{TS}^E\) barrier is the lowest, whereas in the Comp-F system, the \(^6\text{TS}^H\) barrier is the lowest. By analyzing energy barrier, the former is preferable for epoxidation and the latter is preferable for hydroxylation. The origin can be revealed by the electron transfer from the reactant to the transition state. The amounts of electron transfer are given in Table 2. The amount of electron transfer from propene to Fe(IV) OC1–porphyrin for Comp-F (0.125–0.247) is more than that for Comp-Me (0.048–0.109). Furthermore, the highest amounts of electrons transferred from propene to Fe(IV)OC1–porphyrin are 0.247 in \(^4\text{TS}^H\) of Comp-F and 0.109 in \(^4\text{TS}^H\) of Comp-Me. Therefore, the electron-withdrawing groups at the meso-positions enhance the reactivity, this is because electron-withdrawing fluorene reduces molecular orbital energy gaps between donor and acceptor orbitals, therefore it is easy to occur for electron transfers.
Because the oxoiron–porphyrin complex changes the spin state along the reaction coordination, PES crossing must occur. Furthermore, by analysis of the energy profile along the reaction path, ISC may be located around TS1 for Comp-F, while for Comp-Me, ISC may be located after TS1. To investigate this process, we calculated the 2D PESs from R to Imt through TS1 for Comp-F in the quartet and sextet spin states. An overlay of the quartet and sextet PESs is shown in Figure 8, where the O–C bond is scanned from 0.8 to 2.0 Å in 0.1 Å increments and the Fe–O is scanned from 1.64 to 1.78 Å in 0.01 Å increments. The crossing seam between the quartet and sextet PESs occurs around TS1. Note that there are two crossing seams. The first crossing seam is located at a Fe–O distance of about 1.68 Å in the left Figure, and the second crossing seam is located at a Fe–O distance of about 1.74 Å in the right Figure. There is a minimum energy point on the second crossing seam, and its approximate position is indicated by a black solid dot at a Fe–O distance of about 1.74 Å and an O–H distance of about 1.6 Å. At the minimum energy crossing point, the energy is about 9.5 kcal/mol. After quartet to sextet crossover, the system proceeds along the minimum energy path to the stable sextet intermediate. Other 2D PESs are shown in Figures S5 and S6.

5 CONCLUSIONS

The effects of meso-substitution of the model Fe(IV)OCl–porphyrin complex on epoxidation and hydroxylation of propene have been investigated by DFT, and the changes in the energy profiles under the meso-substitution effect have been explained by the electron transfer and frontier molecular orbitals.

We analyzed the electronic configurations of Comp-F and Comp-Me. Comparing the energies of the A_{1u} and A_{2u} states, the A_{2u} state is always stable in the Comp-F and Comp-Me systems. meso-Substitution hardly affects the electronic configurations of Fe(IV)OCl–porphyrin. Additionally, we analyzed ISC between the quartet and sextet spin states using the PESs. The crossing seam between the quartet and sextet PESs occurs around TS1. According to detailed electronic feature analysis of the reactant complexes and transition states, electron-withdrawing groups at the meso-positions stabilize the electron acceptor orbital of the

![Figure 7](image_url)

**Figure 7.** Relative energy barrier heights of the rate-determining steps (4,6TS1) in the gas-phase for propene activation by Comp-Me and Comp-F. The energies are in kcal/mol relative to the energy of 4TS1E.

![Figure 8](image_url)

**Figure 8.** 2D PESs of the quartet (light blue) and sextet (red) spin states of C–H hydroxylation (from R to Imt through TS1) by Comp-F.

|     | 4TS1E | 5TS1E | 4TS1H | 5TS1H |
|-----|-------|-------|-------|-------|
| Comp-Me | 0.109 | 0.098 | 0.103 | 0.048 |
| Comp-F  | 0.205 | 0.214 | 0.125 | 0.247 |

Table 2. Amount of electron transfer from propene to Fe(IV)OCl–porphyrin with fluorine and methyl groups as the meso-substituents in the quartet and sextet spin states.
complex more than the electron donation orbital of the substrate, leading to a decrease in the energy gap between these orbitals, and thus lowering the energy barrier. More importantly, the pull effect of fluorine meso-substitution makes hydroxylation favorable, whereas methyl meso-substitution makes epoxidation preferable. The selective oxidation reactivity of Fe(IV)OCl–porphyrin is ascribed to the effect of meso-substitution on the amount of electron transfer from propene to Fe(IV)OCl–porphyrin.

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