The structure, catalytic activity and reaction mechanism modeling for halogenated iron-tetraphenylporphyrin complexes

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Abstract

The geometric structure optimization of iron-tetraphenylporphyrin chloride (Fe(TPP)Cl) and a number of its halogenated complexes have been performed by PM3 semi-empirical quantum calculations. Using molecular modelling based on HF/6-31G* ab initio calculation the activation of O_2 on the surfaces of these complexes has been modeled. The negative Mulliken charge on the Fe atoms obtained in the complexes studied meet the condition of attraction of O_2 molecules to the activation center in molecular modeling of the activation of O_2 on the surface of the complexes. These results were compared with the modeling of Fe(TPP)Cl with a positive Mulliken charge on Fe atom given by ZINDO/1. The similar modeling for the latter case shows even if the O_2 molecule was put closely over the Fe atom, O_2 would also depart away from the Fe atom. When hydrogen atoms on Fe(TPP)Cl are replaced by fluorine or bromine atoms, the electronic densities on Fe are increased. The spin population shows that partial spin is transferred from the Fe atom to the porphyrin ring. The data also indicate the spin transfer increases with increasing degree of halogenation on the porphyrin ring. A low HOMO and high electronic density on Fe atom have been shown to favor the enhanced catalytic activity of halogenated iron-tetraporphyrin complexes, with a paddle structure especially preferred holding the phenyl groups crossing with the porphyrin's saddle surface. The chemometric quantitative structure activity relationship (QSAR) studies using quantum chemistry parameters as feature variables have been shown as very promising for catalyst design.
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1. Introduction

The metalloporphyrin complexes are widely used as model compounds simulating the catalytic behavior of cytochrome P450 enzymes in life process [1,2]. These complexes can catalyze the oxidative hydroxylation of alkanes in a biomimetic manner

simulating the function of P-450. Metalloporphyrin complexes have been the subjects of a number of investigations [3–10] as they can be introduced as catalysts in selective oxidation of alkanes with molecular oxygen to produce alcohol or carbonyl compounds. Many works have shown that halogenated metalloporphyrin complexes are very efficient catalysts for the direct reaction of alkanes with molecular oxygen under very mild conditions [11–13]. The iron complexes with *meso*-pentafluorophenyl groups, in particular Fe(TPPF$_{20}$)Cl, Fe(TPPF$_{20}$β-Br$_8$)Cl and

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Fe(TPPF$_{20}$)OH show very high catalytic activity as reported by Lyons et al. [12]. These authors showed the high yield oxidation reaction of isobutane at 80 °C in benzene solutions of metallotetraphenylporphyrin complexes with molecular oxygen as the oxidant and *tert*-butyl alcohol the predominant product. The most important step in the catalyzing mechanism is the step of oxygen activation by the iron-porphyrin complexes. Although some mechanistic studies have been reported [12,14], the complex microstructure and oxygen activation mechanism are still not very clear by now. The iron-porphyrin complexes studied in this work are of very complicated geometry structure containing about 80 atoms including Fe, C, N, O, F, Cl and Br. The quantum chemistry calculation in general, the ab initio calculation in particular involving these complexes is extremely difficult. To our knowledge, no theoretical calculations concerning halogenated iron tetraphenylporphyrin complexes have been published so far, though some calculations of simplified four-coordinate iron(II) porphyrin complexes (Fe(P)) containing 37 atoms were made [15,16] and some restrictive assumptions on the geometry were introduced [16]. Recently the structures and electronic spectra of Fe^{2+}- and Fe^{3+}-porphyrin (Fe(P)) were calculated with intermediate neglect of differential overlap (INDO) quantum chemical procedure in the ZINDO program [17]. All the calculations of the simplified four-coordinate Fe(P) led to a positive Muliken charge on the central atom Fe with ZINDO or density functional theory (DFT) based methods. As the DFT calculation involving the complexes is very time-consuming, the geometry was optimized with a semi-empirical method SAM1 [15]. Rovira et al. [16] considered the DFT calculation involving Fe(P) a 'semi-empirical' one as including only the valence electrons. Actually, in a preliminary experiment the present authors found that the geometry of Fe(P) obtained by Rovira et al. was very close to or almost identical with the geometry obtained by ZINDO/1 semi-empirical calculation. The positive Mulliken charge on Fe of Fe(TPP)Cl calculated by ZINDO/1 contradicts the condition of attraction of the O$_2$ molecule to the activation center when one performs the molecular modeling with molecular dynamics based on HF/6-31G*. Compared with five-coordinate halogenated Fe(TPP)X ($X =$ Cl or OH), the electronic structure of tetra-coordinate

iron(II) porphyrin complexes Fe(P) is very simple and different from the former. The outstanding catalytic activity in oxygen oxidative reaction under mild reaction conditions of the five-coordinate halogenated iron tetraphenylporphyrin complexes [11,12] must have special mechanisms. In industry, the metallotetraphenylprophyrin complexes have been applied to catalysts in oxidation of isobulane, cyclohexane, *n*-hexane, and ethylbenzene. Searching high effective and stable catalysts is very important for the oxidation reaction. The theoretical study of the reaction mechanism, the geometry and electronic structure of the halogenated iron tetraphenylporphyrin complexes is of considerable interest.

In this work the molecular structures of halogenated iron-tetraphenylporphyrin complexes were studied by PM3 quantum calculation by Stewart [18] and molecular mechanics MM+ methods. A comprehensive comparison concerning the geometry and electronic parameters including electronic population, spin population, HOMO, etc. has been performed for eight halogenated iron-tetraphenylporphyrin complexes to shed some light on the relationship between the quantum chemistry parameters and the special properties of the complexes possessing high catalytic activity. As an example, the relationship between the catalytic turnovers in reactions of isobutane oxidation and electronic structure parameters of the complexes were studied in a search of the ways for pursuing better new catalysts of this kind of metalloporphyrin complexes. The activation of the molecular oxygen on the complexes were modeled by molecular mechanics force field (MM+) and molecular dynamics based on HF/6-31G* calculation in order to provide a deeper sight of the mechanisms of the activation of molecular oxygen in the reactions involved.

2. Selection of calculation procedures

In preliminary tries we found the calculation involving these halogenated Fe(TPP)X could hardly be done by empirical methods, such as CNDO, MINDO, MNDO/d and AM1. The molecular systems including Br atoms could not be treated by ZINDO/1 empirical quantum calculation either. For the complexes which can be calculated by ZINDO/1, it turned out that the

ZINDO/1 calculation was associated with very heavy computational burden to give reasonable geometry for these complexes without geometry restriction. The geometry optimization of Fe(TPP)Cl which is the most simple one among the complexes studied, for example, took several days to calculate with ZINDO/1 on Pentium4/1.5 GHz PC without reaching an optimum geometry of it. The Hatree–Fock ab initio quantum calculation seems not be able to accomplish the single point calculation for these complexes. Using Hyperchem-6 and selecting STO-6G* basic set for Fe and Br atoms and 6-31G*, 3-21G* or 6-31G for the remaining atoms the single point calculation processes failed to converge. The calculation of each of halogenated Fe(TPP)X involves about 1000 basis functions and more than 2000 Gaussian functions which result in too heavy computational burden. Considering aforementioned aspects, the PM3 in Hyperchem is a good selection for us to study the halogenated iron tetraphenylporphyrin complexes. So far there is no similar calculation study of these complexes using the PM3 method. This work is also a test of PM3 for this kind of research. Although the HF/6-31G* can not accomplish single point calculation for the iron-porphyrins studied, we found it still useful to perform calculations for oxygen molecule in the O_2-complex system when the complexes were frozen.

3. Calculation method

The geometric structure optimization was conducted by semi-empirical quantum calculation PM3 [18] UHF method using HYPERCHEM6 (Hypercube Inc.) without any molecular geometry restriction on a Pentium4/(1.5 GHz and 256 M RAM) PC computer. The SCF control parameters selected were 0.001 kcal/mol for the convergence limit and 100 cycles for the iteration limit. Termination condition was set to an RMS gradient of 0.005 kcal/mol or maximum 3000 cycles. Considering the steepest descent algorithm may give incorrect geometry structures for these complexes of complicated structure, the Polak–Ribiere conjugate gradient algorithm was selected to optimize geometry structures of the halogenated iron-tetraphenylporphyrin complexes. Because each of the molecules contains 78 or 79 atoms

with many electrons, each molecule should take up about 24 h or more time to optimize the geometry under the condition for a preliminary geometry optimization by the molecular mechanics (MM+) method. In modeling the activation of O_2 on these complexes surfaces, the Hatree-Fock SCF method with the 6-31G* basis set was selected for C, H, O, F, N and Cl atoms and STO-6G* basis set for Fe and Br atoms. The molecular oxygen was first calculated at the UHF + MP2/6-31G*//HF/6-31G* level. The O_2 molecule was put into the surrounding environment of the optimized complex and selected to perform molecular modeling with MM+ and HF methods. Hyperchem permits selected molecule(s) as a part of a molecular system to be processed. In the systems studied in this work, because the iron-tetraphenloporphyrin complexs are difficult to be calculated by Hatree–Fock SCF, the O_2 molecule was selected to calculate the O_2-complex system.

4. The geometry of iron tetraphenylporphyrin chloride[Fe(TPP)Cl]

Fe(TPP)Cl possesses the least number of electrons among the halogenated complexes. In order to make certain the geometry of its ground state, Fe(TTP)Cl was optimized in spin multiplicities of S of $\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$. The geometric structures of the three spin states are similar to each other. The optimized structure of spin S $= \frac{1}{2}$ state complex is plotted in Fig. 1 with C_2 symmetry. Two phenyl planes bend shoulder to shoulder to one side of the porphyrin's saddle-type surface and the other pair of phenyl groups bend to another side. The dihedral angles of the phenyl planes of the two pairs are ϕ (bending to Fe–Cl band side) $= 24.35°$ and $\theta = 33.45°$ in S $= \frac{5}{2}$ complex which has the lowest energy compared with the complexes with S $= \frac{1}{2}$ and $\frac{3}{2}$. It was found that the phenyl planes lie across the porphyrin saddle surface except for the phenyl planes that are almost face to face bending to Fe–Cl band side in the complex with S $= \frac{3}{2}$ whose geometric structure was very difficult to optimize. All the energies for the three spin states of Fe(TPP)Cl are given in Table 1. The enthalpy of formation ΔH_f, the total energy and bonding energy of S $= \frac{5}{2}$ state are by about 20.4 and 30.1 kcal/mol lower than those of the other two complexes. So the most stable state
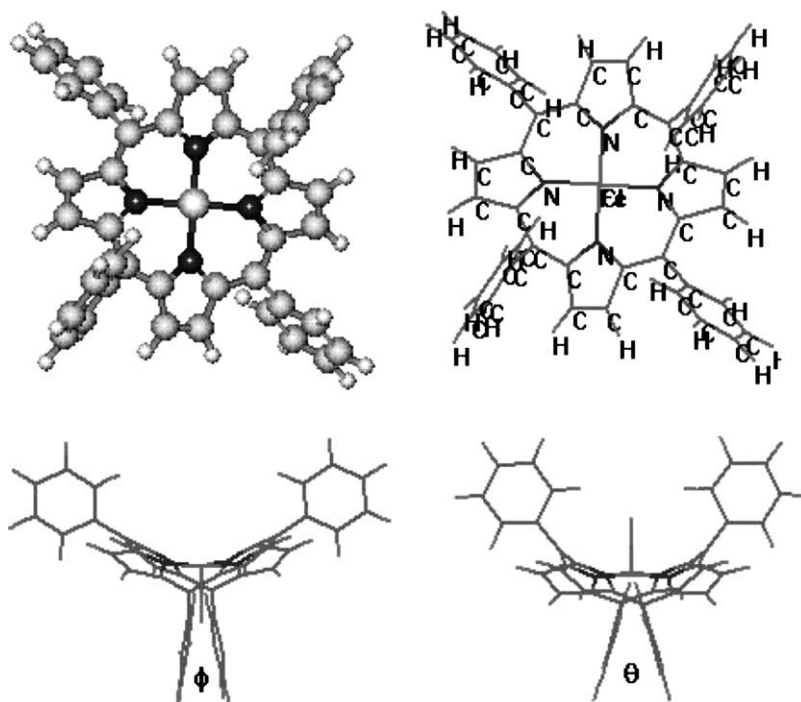
Fig. 1. The geometric structure of Fe(TPP)Cl ($S = \frac{5}{2}$) ($\phi = 24.35°$; $\theta = 33.45°$).

of Fe(TPP)Cl is the state with a spin of $\frac{5}{2}$. Similar results were reported for deoxyhemoglobin which contains high spin d-electron configuration of iron [19]. Collman et al. [20] proved the five-coordinate geometry Fe(TPP)X being in high-spin state. Silva et al. [21] also found the resonance Raman spectrum of Fe(TPP)Cl$^-$ was quite similar to other high-spin five-coordinate ferrous porphyrin complexes, such as Fe(TPP)(OH)$^-$. Fe^{III}(TPP)Cl and Fe^{III}(TPPBr$_4$)Cl were reported as possessing high-spin magnetic property [22].

Table 1
The PM3 energies of Fe(TPP)Cl in $S = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ states (kcal/mol)

	Spin		
	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
Total E	−164716.1	−164706.5	−164736.5
Bonding E	−9603.64	−9594.03	−9624.05
ΔH_f	−45.33	−35.68	−65.74

5. The structure of the halogenated iron tetraphenylporphyrin complexes

There are seven halogenated iron tetraphenylporphyrin complexes namely Fe(TPPCl$_8$)Cl, Fe(TPPF$_{20}$)Cl, Fe(TPPβ-Br$_4$)Cl, Fe(TPPCl$_8$β-Br$_4$)Cl, Fe(TPPF$_{20}$β-Br$_8$)Cl, Fe(TPPCl$_8$)OH and Fe(TPPF$_{20}$)OH calculated with the PM3 semi-empirical quantum mechanics method. TPPCl$_8$ is TPP in which four phenyls are replaced by four *ortho*-C$_6$H$_4$Cl$_2$; TPPF$_{20}$ is TPP in which four phenyls are replaced by four –C$_6$F$_5$; β-Br refers to Br substituting β-H on the porphyrin ring. For the β-Br$_4$ structure, C$_4$ symmetry structure of porphyrinato ligand was adopted at the start of geometry optimization. Considering that the ground state of Fe(TPP)Cl is in a spin of $S = \frac{5}{2}$ and the result of Collman [20], spin states for all the five-coordinate Fe porphyrin complexes were set to $S = \frac{5}{2}$ arbitrarily. Their optimized geometric structures are all approximately similar to that of ground state of Fe(TPP)Cl except for the geometry of Fe(TPPβ-Br$_4$)Cl which is

Table 2
Important geometric parameters of iron-porphyrin complexes

Complexes	ϕ (°)	θ (°)	Symmetry
Fe(TPP)Cl	24.35	33.45	C_2
Fe(TPPCl$_8$)Cl	1.55	11.88	C_2
Fe(TPPF$_{20}$)Cl	24.36	2.93	C_2
Fe(TPPβ-Br$_4$)Cl	127.8	31.82	C_2
Fe(TPPCl$_8$β-Br$_4$)Cl	12.79	16.11	C_2
Fe(TPPF$_{20}$β-Br$_8$)Cl	32.07	30.15	C_2
Fe(TPPCl$_8$)OH	1.44	6.09	C_1
Fe(TPPF$_{20}$)OH	20.47	9.91	C_1

very similar to that of the Fe(TPP)Cl in the spin state of $S = \frac{3}{2}$ with two phenyl planes bending to Fe–Cl band side almost face to face. Some of their important geometric parameters are given in Table 2 along with the parameters of Fe(TPP)Cl ($S = \frac{5}{2}$) for the convenience of comparison between the complexes. The angles of ∠(Cl–Fe–N) and ∠(O–Fe–N) are not listed in Table 2 since they are not important parameters. The angles of ∠(Cl–Fe–N) are all slightly larger than 90° (about 93–95°). The angles of ∠(O–Fe–N) are about 97° in the direction of bond O–H and about 91–92° in the opposite direction in the two hydroxo complexes. The H atom of O–H bond seems to tend to form hydrogen bonds with the halogen elements on the phenyl groups considering the bending of O–H bond toward one of the halogenated phenyl groups. All the bond lengths of Fe–N in these complexes are about 1.88 Å and seem not to be greatly affected by the halogen atoms. These bond length values are all shorter than the value in Fe(P) calculated by ZINDO [17] (about 1.97 Å) and DFT [16] (about 2.0 Å); only the valence electrons included in DFT computation

and the value from X-ray data for Mn–Np bond in Mn(TPP)Cl is about 2.0 Å [23]. The parameters of ϕ and θ angles are similar to those in Fe(TPP)Cl mentioned for Fig. 1. The large ϕ value of Fe(TPPβ-Br$_4$)Cl indicates its structure being different from the others.

Important quantum chemical parameters of the complexes are given in Table 3. From the data of the table some interesting phenomena could be observed. At the first sight one notices the prominent negative Mulliken charge ranging from −0.27 to −0.34 on Fe atoms and miraculous positive Mulliken charge greater than 0.4 on each nitrogen atom in all the complexes. These results are very different from the Mulliken charges of Fe(P) reported in literature [16,17] with a value of about −0.42 on N atoms and 0.73 or 0.98 on Fe atom with ZINDO/1 and DFT calculations. These at first sight unreasonable results obtained by PM3 unexpectedly circumvent the contradiction concerning the condition of attraction of O_2 molecules to the activation center in molecular modeling of the activation of O_2 on the surface of the complexes (vide infra). It turned out that with a positive Mulliken charge on Fe atom the molecular modeling would predict the complexes studied not possessing catalytic activity to activate the molecular oxygen. When hydrogen atoms are replaced by halogens except for Cl atoms the Mulliken charges on Fe become more negative. When the auxiliary ligand Cl bonding to Fe is replaced by OH the same trends are observed when one compare Fe(TPPCl$_8$)OH, Fe(TPPF$_{20}$)OH with Fe(TPPCl$_8$)Cl, Fe(TPPF$_{20}$)Cl in Table 3. That is to say, the results of the two kinds of substitution all make more electrons attracted to Fe atom from the porphyrin ring in spite of the introduction of the

Table 3
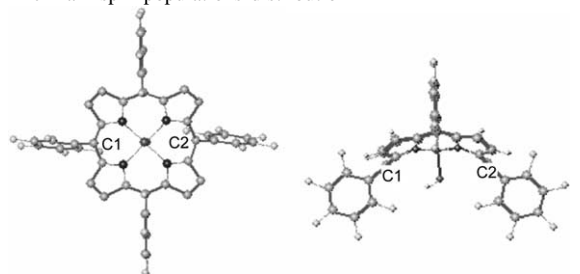Important quantum chemistry parameters of iron-porphyrin complexes

Complexes	Net charge		Bond order of Fe–N	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔH_f (kcal/mol)
	Fe	N				
Fe(TPP)Cl	−0.275	0.436, 0.441	0.8316, 0.8319	−7.626	−2.346	−65.74
Fe(TPPCl$_8$)Cl	−0.270	0.443, 0.446	0.8292, 0.8317	−7.638	−2.518	−102.1
Fe(TPPF$_{20}$)Cl	−0.295	0.446, 0.469	0.8283, 0.8302	−8.332	−3.202	−888.0
Fe(TPPβ-Br$_4$)Cl	−0.295	0.441, 0.450	0.8283, 0.8284	−8.030	−2.451	−16.35
Fe(TPPCl$_8$β-Br$_4$)Cl	−0.274	0.435, 0.446	0.8275, 0.8317	−7.982	−2.726	−47.16
Fe(TPPF$_{20}$β-Br$_8$)Cl	−0.298	0.429, 0.464	0.8279, 0.8266	−8.691	−3.535	−775.2
Fe(TPPCl$_8$)OH	−0.329	0.460, 0.478	0.810–0.815	−7.446	−2.278	−117.9
Fe(TPPF$_{20}$)OH	−0.340	0.462, 0.493	0.8220, 0.8060	−8.200	−3.011	−907.7

electron-withdrawing halo-groups into the macrocycle ring of the complexes. Goff et al. [24] studied the nuclear magnetic resonance of ferrous porphyrin complexes and pointed out that the contact shifts are consistent only with spin transfer via P (porphyrin ring) $\rightarrow$ Fe π charge transfer. The electron transfer was considered to give a greater tendency for the active catalyst to behave as an oxo-centered radical (P)Fe–O$^{\bullet}$ in alkanes oxidative reaction [12,14].

Besides the Mulliken charge on Fe and N atoms, some regularities associated with the data in other columns of Table 3 also contain some interesting information. The bond orders of Fe–N in the halogenated complexes are all slightly less than those in Fe(TPP)Cl but the polarity of the Fe–N bonds are all enhanced. All complexes with C_2 symmetry and Fe(TPPF$_{20}$)OH possess two pairs of identical bond orders. A comparison of the values of E_{HOMO} and E_{LUMO} of Fe(TPP)Cl with other halogenated complexes shows that halogenation lowers both E_{HOMO} and E_{LUMO}. Comparing the E_{HOMO} and E_{LUMO} values of Fe(TPPCl$_8$)OH and Fe(TPPF$_{20}$)OH with Fe(TPPCl$_8$)Cl and Fe(TPPF$_{20}$)Cl, one notices that when the auxiliary ligand Cl is replaced by OH the values of E_{HOMO} and E_{LUMO} increase slightly. At the same time the hydroxo complexes always have lower Fe–N bond orders and higher positive Mulliken charge on N atoms compared to chloro complexes. As far as the enthalpy of formation is concerned, substitutions in the porphyrin rings and the auxiliary ligands lower the ΔH_f values except for Br substituted complexes. When each H atom on the porphyrin ring is substituted by a Br atom, the value of ΔH_f will be increased by about 14 kcal/mol though this does not prevent the brominated complexes from achieving a relatively higher catalytic turnover.

The spin density on all the atoms except for Fe and two C atoms is nearly close to zero. The spin populations on Fe and the two C atoms are listed in Table 4. The C_1 or C_2 is the carbon connected with the phenyl group bending to Fe–Cl or Fe–OH side of the saddle surface. The high spin Fe-porphyrin complex can be realized as a five-coordinate Fe(III) in d^5 configuration. But the spin population on Fe is about 3.0 and the spin population on the two C atoms is about 0.83–0.93. The population data show that partial spin is transferred from the Fe atom to the porphyrin macrocycle. Apparently there are two unpaired electrons diverted

Table 4
The main spin populations distribution

Complexes	Spin population		
	Fe	C_1	C_2
Fe(TPP)Cl	3.210	0.935	0.935
Fe(TPPCl$_8$)Cl	3.211	0.885	0.885
Fe(TPPF$_{20}$)Cl	3.184	0.905	0.905
Fe(TPPβ-Br$_4$)Cl	3.185	0.827	0.827
Fe(TPPCl$_8$β-Br$_4$)Cl	3.207	0.910	0.910
Fe(TPPF$_{20}$β-Br$_8$)Cl	3.176	0.902	0.902
Fe(TPPCl$_8$)OH	3.060	0.887	0.888
Fe(TPPF$_{20}$)OH	3.048	0.882	0.920

onto the porphyrin ligand. This condition infers the single occupied d$_\pi$ orbitals of Fe and the π-type group orbitals of the porphyrin ring being recombined. The data in Table 4 also indicate the spin transfer increases with increasing degree of halogenation on the macrocycle of porphyrin. Considering the Mulliken charges on Fe atoms of these complexes shown in Table 3, one notices the correlation between the Mulliken charge and the spin population on Fe atom. The decrease in the spin population and increase with negative Mulliken charge on Fe indicate that electrons of opposite spin transfer from the macrocycle to the Fe atom. Similar spin transfer and Fe–P π bonding in ferrous-porphyrin complexes were reported in the literature [22,24]. The high spin population on Fe atom indicates the complexes are all iron-centered radicals. At the same time, considering the Mulliken charge on N atoms and π-type HOMO distributed on the porphyrin ring of these complexes described in the following section, the macrocycles of the complexes are also all π-radical. Silva et al. [22] studied the resonance Raman spectrum of Fe(TPP)$^{2-}$ and found the complex being probably not a pure π-anion radical. There is a significant back bonding between the d$_\pi$-orbital of the iron to the e$_g^*$ orbital of the porphyrin. The π-electron transfer is an important characteristic

of iron-porphyrin complexes which could provide reasonable explanation of Mulliken charge on Fe and N atoms in these complexes or the trend of electrons transfer from porphyrin ring toward the iron atom.

6. The relationship between activity and parameters of the complexes

The data of catalytic turnovers for isobutane oxidation listed in Table 5 were taken from the reference [12]. The data were obtained in solutions of the 25 ml of benzene containing 7 g of isobutane and given amounts of catalysts stirred at 80 °C under 100 psig of O_2 for 6 h. The relationships between the catalytic turnover and E_{HOMO}, E_{LUMO} and ΔH_f together with the relationship between E_{HOMO} and E_{LUMO} are shown in Fig. 2.

From Fig. 2a and b, one notices a general trend of relatively high turnover for low E_{HOMO} and E_{LUMO}. Two hydroxo complexes located above the line and Fe(TPPβ-Br$_4$)Cl below the line greatly deviate from the linear relationship in Fig. 2a. The two hydroxo complexes are distinguished by their relatively high HOMO and LUMO compared to those of their chloro counterparts. The electronic density on Fe atoms in both hydroxo complexes are the highest ones (Table 3). High electron density on Fe atom seems favorable for a higher catalyst turnover. The complex Fe(TPPβ-Br$_4$)Cl has a relatively low turnover though it has low HOMO and LUMO. The electron density on its Fe atom is relatively high, though not so high as those on the Fe atoms of the two hydroxo complexes. The structure of Fe(TPPβ-Br$_4$)Cl is different from the others. Probably a structure characteristic of all porphyrin complexes except Fe(TPPβ-Br$_4$)Cl is crucial for high catalytic turnover, i.e. holding the phenyl planes lying across with the porphyrin's saddle surface as a paddle structure. The geometrical structure is important for the morphology of HOMO as depicted in Fig. 3. All the HOMOs are π-type orbitals which are similar to each other except for that of Fe(TPPβ-Br$_4$)Cl, though there are some minor difference between in the HOMO structure Fe(TPP)Cl and the corresponding fluorinated and chlorinated complexes. The HOMO structure of Fe(TPPβ-Br$_4$)Cl extends to the two phenyl planes that has a dihedral angle $\phi = 127.8°$. Its HOMO region enlarged to the two phenyls making the energies of HOMO and LUMO lower, which should favor the enhancement of catalytic turnover. On the other hand, the aforementioned morphology of HOMO would enhance the chance of reaction with all other molecules at the phenyls with its HOMO. Then the catalytic turnover with respect to molecule O_2 is reduced. The correlation between TO and ΔH_f is rather poor, though it is obvious that a much negative ΔH_f is essential for a high catalytic turnover (Fig. 2c). Fig. 2d shows the values of E_{HOMO} and E_{LUMO} follow a nice linear relationship only with Fe(TPPβ-Br$_4$)Cl as an outlier. The solid line in Fig. 2d gives a correlation coefficient $r = 0.9431$ and the dotted line gives a $r = 0.9924$ when the outlier point of Fe(TPPβ-Br$_4$)Cl was not taken into account.

Quantitative structure activity relationship (QSAR) based on quantum chemistry parameters as feature variables is an important branch of chemometrics very useful for catalyst design. In this respect we tried to model the quantum chemistry parameters E_{HOMO}, Mulliken charge on Fe atom and ϕ parameter for predicting the catalytic turnovers in the form of following equation.

$$TO = -2312.7 \times E_{HOMO} - 0.26604\phi^2 - 14235 \times netcharge_{Fe} - 21354 \quad (1)$$

The prediction of TO has a correlation coefficient $r = 0.9931$. The calculated and experimental catalytic turnovers are presented in Table 5 and Fig. 4. A lower HOMO and much higher electronic density on Fe atom seem essential for enhanced catalytic activity

Table 5
The isobutane oxidation activity of porphyrinatoiron complexes

Complexes	TO[a]	Calculated TO
Fe(TPP)Cl	–	146.8
Fe(TPPCl$_8$)Cl	263	153.8
Fe(TPPF$_{20}$)Cl	2040	2075.3
Fe(TPPβ-Br$_4$)Cl	155	152.7
Fe(TPPCl$_8$β-Br$_4$)Cl	865	949.3
Fe(TPPF$_{20}$β-Br$_8$)Cl	3090	2919.3
Fe(TPPCl$_8$)OH	711	549.6
Fe(TPPF$_{20}$)OH	2245	2422.2

[a] Mol O_2 consumed/mol catalyst used.
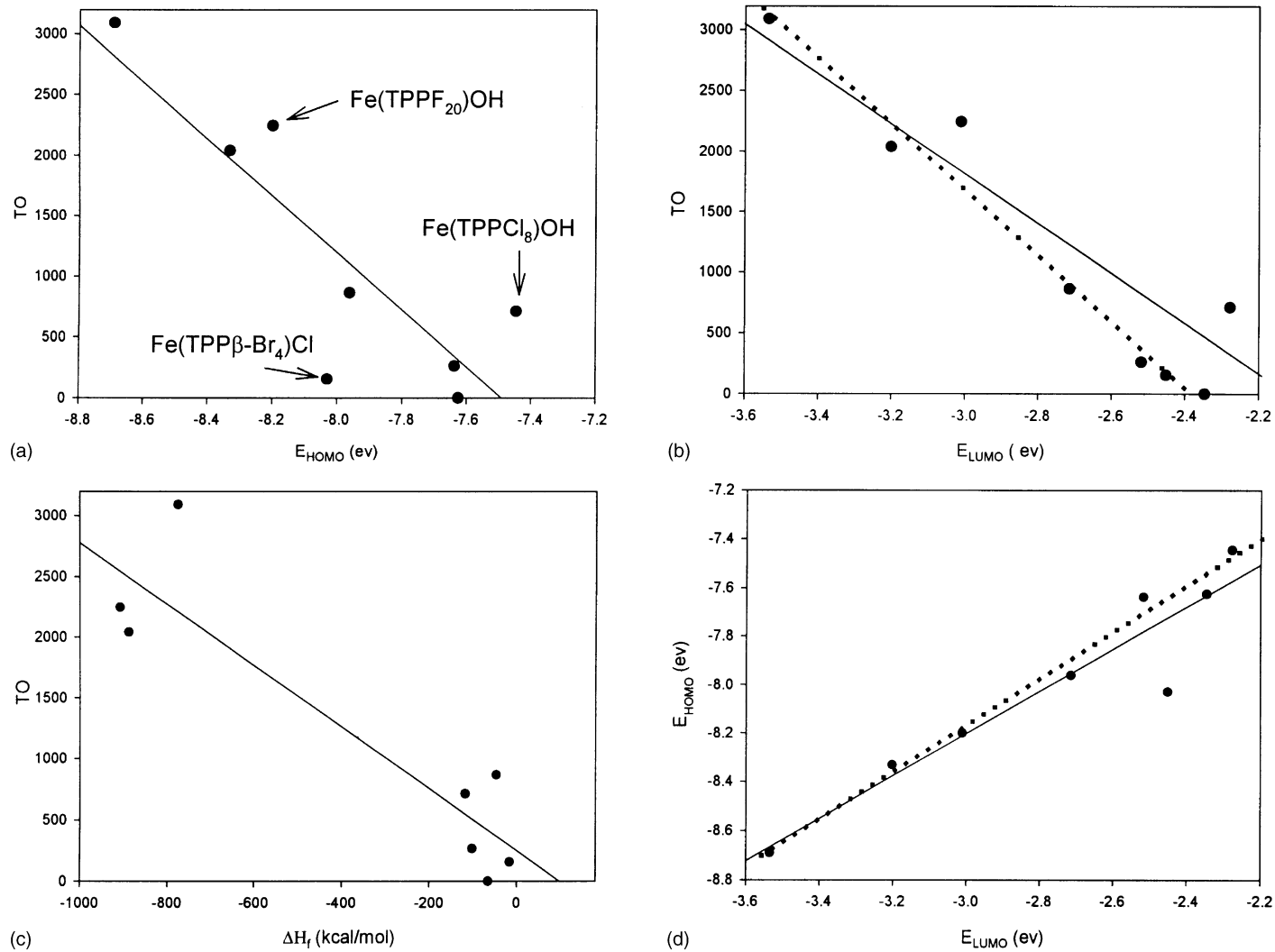
Fig. 2. The relationships of turnover vs. E_{HOMO} (a), E_{LUMO} (b), ΔH_f (c) and E_{HOMO} vs. E_{LUMO} (d).
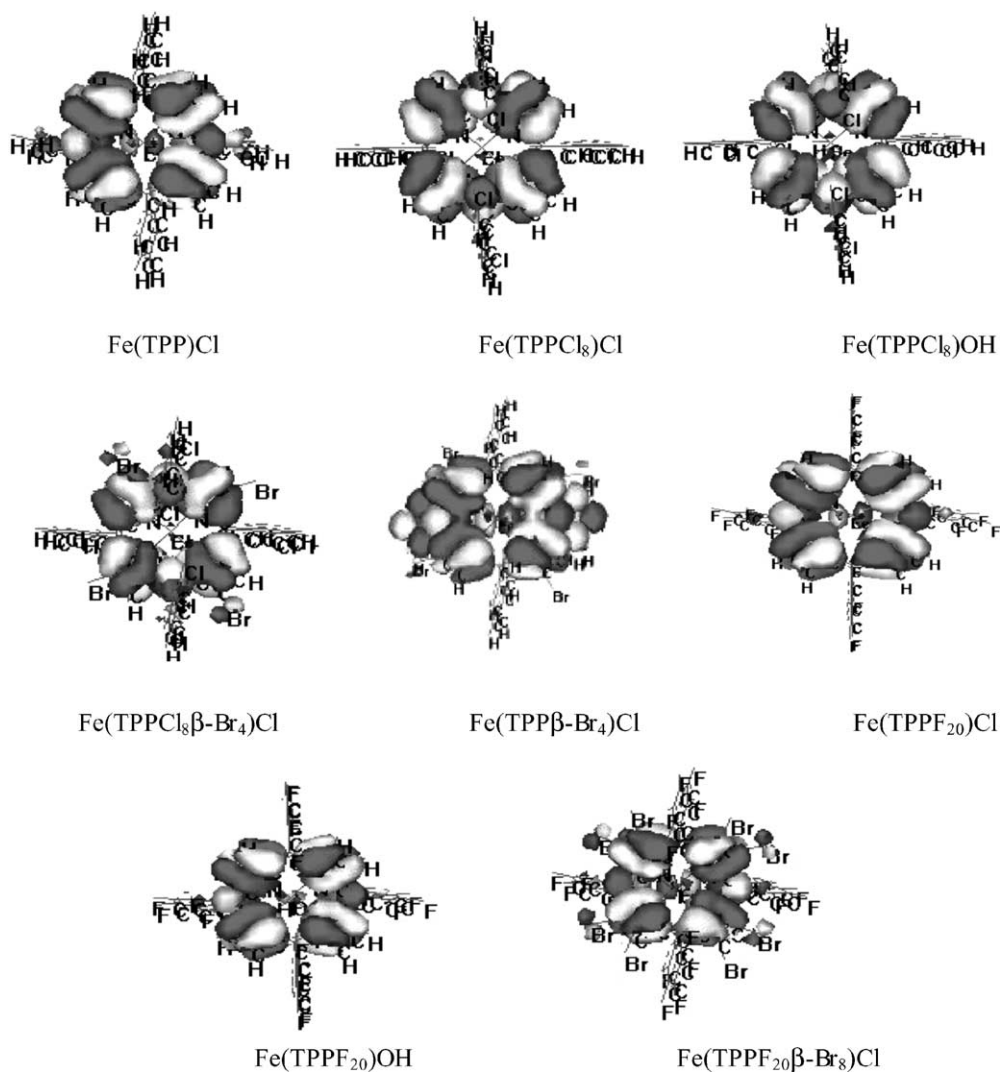
Fig. 3. The overlook graphs of HOMOs of iron-porphyrin complexes.

of these complexes. The value of ϕ is included in the regression equation showing that the structure of the complexes holding the phenyl planes lying across with the inner porphyrin ring is important for high catalytic activity. Among HOMO and LUMO only E_{HOMO} of the complexes is included in the equation. The values of E_{SOMO} of O_2 are -11.7052, and $-14.5639\,\text{eV}$ as calculated by PM3 and MP2 + HF/6-31G^* methods, respectively. According to the frontier molecular orbital theory, considering the energy of single electron occupied molecular orbital (E_{SOMO}) of O_2 being very low, it would be much easier for a complex with a lower E_{HOMO} to interact with the SOMO of O_2 by its HOMO. The QSAR studies concerning the catalytic activity of halogenated iron tetraphenyl-porphyrins presented here is just an example showing the ways for searching high efficient catalysts using quantum chemistry parameters. For practical applications of this chemometric approach an experimental data base of sufficient size is needed.
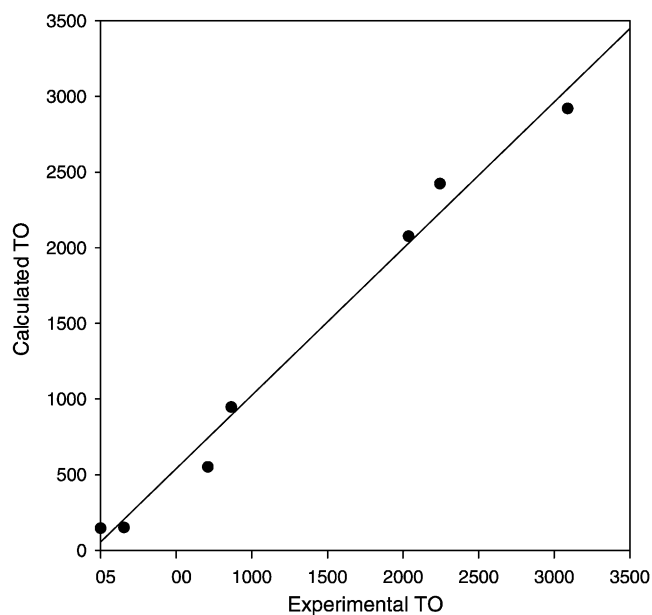
Fig. 4. The calculated turnovers vs. experimental turnovers.

7. Simulation for catalysis mechanism of molecular oxygen activation

All geometric structures of the complexes were optimized at first with the PM3 method as before. In order to simulate the catalysis of the complexes in molecular oxygen activation, the geometry structures of O_2 in a spin of $S = 1$ was optimized with HF/6-31G* ab initio calculation. Simulations were processed with molecular mechanics force field (MM+) and ab initio methods. The basis set for different atoms used were given in the Calculation Method section. The molecular dynamics modeling temperature was set at 353 K according to the practical reaction temperature (80 °C).

When the molecular oxygen was selected to perform geometry optimization in O_2-complex system with the MM+ method, it might get into the complex by approaching one of the phenyl groups holding a distance about 3.4 Å or by approaching the Fe atom keeping a distance about 3.3 Å. For the convinience of explanation, the latter position is denoted as Q point (Fig. 5a). The Q point is the place where all eight complexes would move to in the first step of modeling (vide infra). When the simulation is done by the MM+ method, the O_2 molecule would move to the Q position only in the cases of Fe(TPP)Cl, Fe(TPPβ-Br$_4$)Cl, Fe(TPPF$_{20}$)Cl, Fe(TPPF$_{20}$β-Br$_8$)Cl and Fe(TPPF$_{20}$)OH. When the three chlorinated complexes, i.e. Fe(TPPCl$_8$)Cl, Fe(TPPCl$_8$β-Br$_8$)Cl and Fe(TPPCl$_8$)OH were simulated with the MM+ method, even starting by putting O_2 at the Q point, the oxygen molecule would come out from the Q point and stop near the center of the three *ortho*-Cl atoms on three phenyls, respectively. This might be caused by the repulsion coming from the two *ortho*-Cl atoms on the phenyl groups and/or the electrostatic potential field formed by the complex. The electrostatic potential three-dimensional surfaces for the complexes are given in Fig. 5b–i at a contour value of 0.01. In each electrostatic potential surface the negative potential region is marked with shallow grey tint. For three fluorinated complexes as simulated by the MM+ method the molecular oxygen can get to the Q point very easily. When the HF/6-31G* method was used to optimize the selected O_2 molecule in the O_2-complex system from a starting position of the Q point, we observed for all the complexes the O_2 gradually moving toward the Fe atom. Molecular dynamics modeling based on the ab
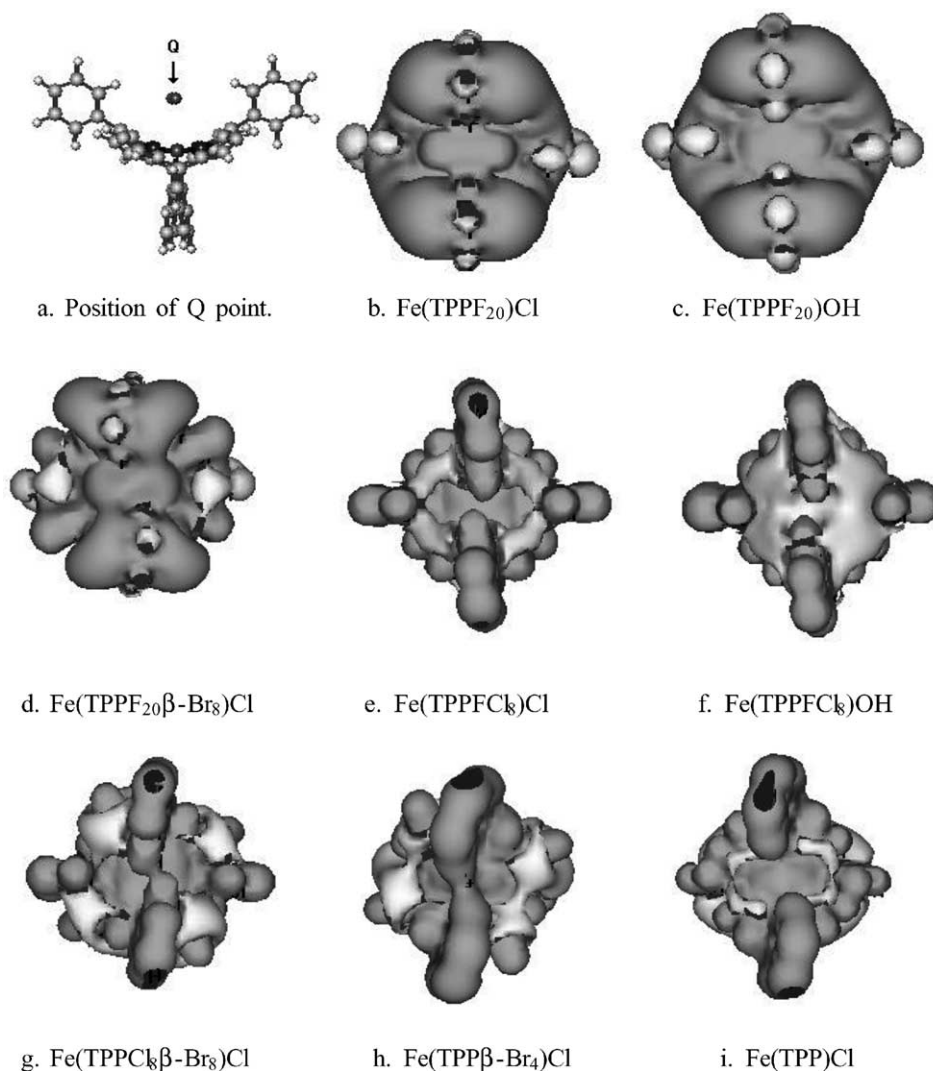
a. Position of Q point.   b. Fe(TPPF$_{20}$)Cl   c. Fe(TPPF$_{20}$)OH

d. Fe(TPPF$_{20}$β-Br$_8$)Cl   e. Fe(TPPFCl$_8$)Cl   f. Fe(TPPFCl$_8$)OH

g. Fe(TPPCl$_8$β-Br$_8$)Cl   h. Fe(TPPβ-Br$_4$)Cl   i. Fe(TPP)Cl

Fig. 5. The Q point and the overlook of electrostatic potential surfaces (contour value: 0.01) of the complexes.

initio HF/6-31G* method presents similar behavior of O_2 molecule compared to the optimization operation by the ab initio method. When O_2 was close to Fe atom, the eight complexes studied can be classified into three groups as explained later.

The group of three fluorinated complexes is explained in Fig. 6 with Fe(TPPF$_{20}$)Cl as an example. The oxygen molecule is approaching the complex (Figs. 6 and 1), first reaching the Q point (2) and then approaching the Fe atom (3, 4). Fig. 6 refers to the case when the O–O band is parallel to the saddle sur-face of the porphyrin (3, 4, 5). At the same time the O–O bond stretches (4, 4a, 5). The two oxygen atoms sit in the middle between two N atoms of the complex (4a, 5). The stretching of O–O bond finally results in the break down of the bond (6, 6a) and release of activated atomic oxygen for participating in the oxidation reaction. Besides the case as demonstrated in Fig. 6, the simulation shows a case when the O–O bond is not parallel to the saddle surface of porphyrin, one oxygen atom holds on over the Fe atom at a distance about 1.5 Å and the another oxygen atom moves
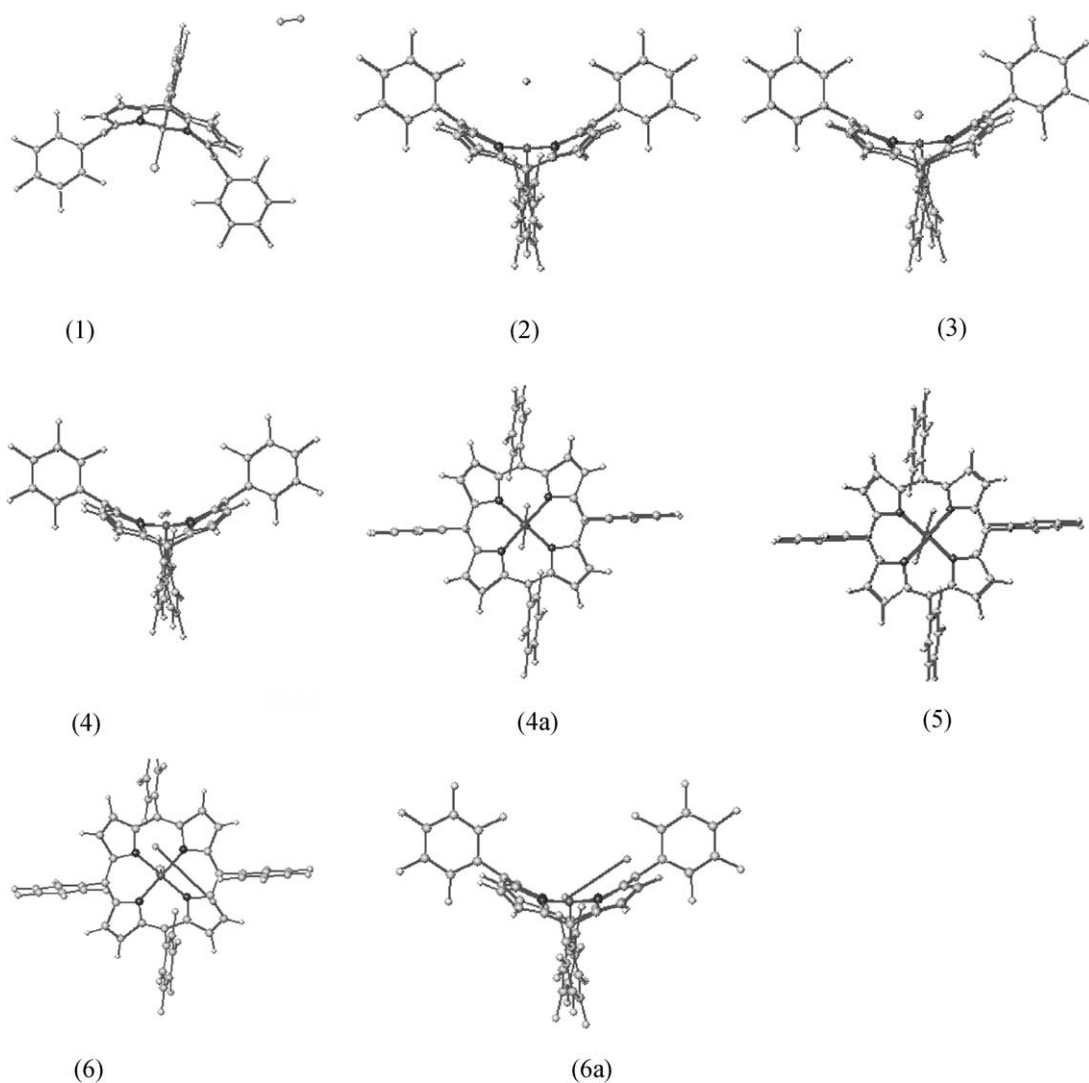
Fig. 6. Modeling process of O_2–Fe(TPPF$_{20}$)Cl system (see the text for the details of the process (1–6)).

very close to one N atom and then releases away from the complex after complicated interaction with the porphyrin ring by O–O bond stretching and breaking down.

The three chlorinated complexes belong to the second group. The situation was similar to the previous group. The O_2 was slightly difficult to move to the Q point with ab initio method for this group. When O_2 moved close to Fe atom, the interaction between the O and N atoms takes a longer time compared to the fluorinated complex group. The O atom touches with

the N atom and escapes away from the complex, or it moves close to the H atom of the complex on the phenyl group.

The third group covers Fe(TPP)Cl and Fe(TPPβ-Br$_4$)Cl. The O_2 could easily get to the Q point. Then the O_2 moves toward the Fe atom. Gradually one O atom turns close to the Fe atom. When the distance between this O atom and the Fe atom becomes very short, the other O atom turns over approaching the N atom, and the bond of O–O stretches. Then both O atoms interact with the N atoms at two sides of the Fe
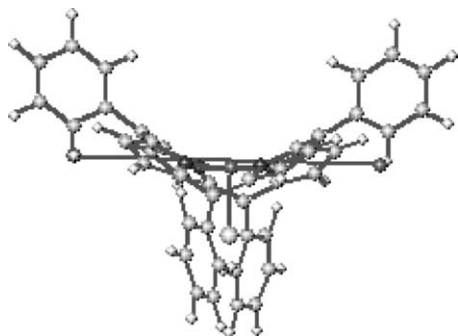
Fig. 7. Modeling of O_2–Fe(TPP)Cl system (O attacking the H atom).

atom and the O–O bond breaks down with the O atoms approaching the O–H atoms on phenyl groups (Fig. 7) or released away. For Fe(TPP)Cl both the O atoms always tend to attack the H atoms on the phenyl groups. It is very possible that the interaction between the O and the H atoms on the catalyst complexes would destroy the complexes and cause them to lose the catalytic activity.

A similar modeling was done with the Fe(TPP)Cl calculated with the ZINDO/1 program based on a geometry optimized by MM+ with a Mulliken charge of about 0.203 on Fe and −0.168 on N atoms. We found the O_2 could not approach Fe-centered Fe(TPP)Cl in this condition by HF/6-31G* ab initio modeling. Even if the O_2 was put closely over the Fe atom, simulation results in the O_2 molecule departing away from the Fe atom. So we can conclude that our calculation resulting in negative Mulliken charge on the Fe atom provides a reasonable explanation why the iron tetraphenylporphyrin complexes possess catalytic activity toward oxygen oxidative reactions.

Considering the π-type HOMO structures of the complexes studied, the interaction between SOMO of O_2 (an anti-bonding π orbital) and the HOMO of these complexes should be taken into account for the bond breaking of O_2. While a high spin population is mainly located on the Fe atom, the HOMO is distributed over the porphyrin ring. Considering the spin population and Mulliken charge distribution on these complexes, the mechanism of interaction between O_2 and the complex must be very complicated.

8. The calculations involving the complex of FeP

Considering the unexpected results concerning the Mulliken charges obtained with PM3. We also performed PM3 and ZINDO/1 calculation for the complex FeP to make a comparison with the results reported in the literature [16]. The PM3 calculations provided saddle geometries for three diferent spin states ($S = 0$, 1, 2) of FeP, and ZINDO/1 gave planar structures with a D_{4h} symmetry for them. The spin state does not greatly affect the Fe–N bond length which is about 1.88 Å as obtained by PM3 and 2.04 Å by ZINDO/1. PM3 gave Mulliken charges of the order of −0.44 on Fe atoms and 0.43 on N atoms. ZINDO/1 gave −0.031, −0.166, 0.004 on Fe atoms and −0.173, −0.071, −0.183 on N atoms for spin states of $S = 0$, 1 and 2, respectively. Apparently both PM3 and ZINDO/1 tended to give negtive Mulliken charge on the Fe atom.

9. Conclusion

Molecular modeling shows that the high electronic density on Fe of porphyrin is essential for these complexes possessing ability to activate the molecular oxygen. The catalytic turnovers of the iron tetraphenylporphyrin chloride and its derivatives greatly depend on the electronic density on Fe atom and the values of E_{HOMO}. Because the SOMO of O_2 is very low, a lower HOMO of the complex is favored for the activation of the molecular oxygen. The paddle geometry seems to be also important to maintain a high turnover for the complexes. A low HOMO and high electron density on the Fe atom are all propitious to improving the catalytic activity of the complexes. Iron centered radical is the common characteristic feature of these complexes. Although electrons are transferred from the porphyrin ring to the Fe atom, spin population on the porphyrin ring indicates the unpaired spin electron transfer to porphyrin ring from the Fe atom. Halogenation of complexes causes the Fe atom to attract more electrons from the porphyrin ring which is beneficial for higher catalytic activity to activate oxygen oxidation of alkanes. The trend of the change of Mulliken charges obtained in the present study seems convincing rather than their absolute values. The PM3 method has been proved useful in

the studies of porphyrin derivatives and chemometric QSAR studies are promising for practical design of catalysts involving porphyrin compounds.

Acknowledgements

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