ARTICLE DFT Study of Iron Tetraphenylporphyrin Chloride and Iron Pentafluorophenylporphyrin Chloride

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The geometry optimizations and the single point energy calculations of iron tetraphenylporphyrin chloride Fe(TPP)Cl and iron tetraphenylporphyrin chloride (Fe(TPP)Cl), iron pentafluorophenylporphyrin chloride $(Fe(TPPF_{20})Cl)$ were carried out by using the Density Functional Theory (DFT) UB3LYP with STO-3G* and 6-31G* basis sets, respectively. The electronic properties and the structures of high-lying molecular orbitals were analyzed in detail. The results show that partial spin is transferred from the Fe atom to the porphyrin ring and some electron with the spin opposite to the unpaired electron on the Fe atom is transferred from the porphyrin ring to the Fe atom. The π - and σ -type bonding between the Fe atom and the porphyrin ring cause the transfer. The fluorination enhances the electron transfer and the chemical stability of the complex. The high stability is important for the complex surface is also discussed based on the symmetry of the molecular orbitals.

Key words: Iron porphyrin, DFT, Molecular orbital, Activation mechanism of molecular oxygen

I. INTRODUCTION

Proteins, such as hemoglobin, myoglobin, cytochrome P450, and peroxidase *etc.* have iron-porphyrin in their structures, which is treated as their active sites. They are known to be very important for the transfer of oxygen, carbon dioxide, and electrons during redox reactions in organisms. The active site of cytochrome-P450 is the heme-protoporphyrin which can combine with an oxygen molecule. Because iron-porphyrin were used to model the catalysis of cytochrome-P450 in life process, they are constantly introduced as catalysts in the selective oxidation of alkanes with molecular oxygen to produce alcohol or carbonyl compounds [1]. Many works have shown that the halogenated metalloporphyrin complexes are very efficient catalysts for the direct reaction of alkanes with molecular oxygen under very mild conditions [2-4]. The iron pentafluorophenyl porphyrins, in particular, Fe(TPPF₂₀)Cl, $Fe(TPPF_{20}Br_8)Cl$ and $Fe(TPPF_{20})OH$ show very high catalytic activity as reported by Lyons et al. [5,6]. Their results showed the oxidation reaction of isobutane with oxygen molecule at 80 °C in benzene solutions with metallotetraphenylporphyrin complexes to produce tert-butyl alcohol is a predominant reaction with yields of 90%. The most important step in the catalysis mechanism is the step of the activation of the oxygen molecule by the iron-porphyrin complexes. Although some studies on the reaction mechanism have been reactivation mechanism are not yet very clear. Only some calculations of simplified four-coordinate iron(II) porphyrin complexes (Fe(P)) were reported based on the restricted geometry optimization [7-9]. Recently, the structures and electronic spectra of Fe²⁺ and Fe³⁺ porphyrin (Fe(P)) were calculated by using the INDO quantum chemical procedure in the ZINDO program [10]. In this work, iron tetraphenylporphyrin chloride Fe(TPP)Cl and iron pentafluorophenylporphyrin chloride Fe(TPPF₂₀)Cl with very high catalytic oxidation activity were calculated by using high level of quantum chemical theory to study the electronic structures and the catalysis mechanism of iron-porphyrin.

ported [1,5], the complex microstructure and oxygen

II. COMPUTATIONAL METHODS

Density Function Theory (DFT) has been greatly developed in recent years and proved to have a comparatively high level of theory, which is similar to MP2 method. So far, DFT method has been widely applied in high level of theory for large molecules systems [11-13]. The iron-porphyrin complexes studied in this work have very complicated structures containing about 78 atoms. So the geometry optimizations were performed using the unrestricted hybrid density functional UB3LYP method with STO-3G^{*}, and then the single point calculations were performed using UB3LYP method with 6-31G* basis set. For the five-coordinate iron(III) porphyrins, high electronic spin state was adopted to perform the calculation. Collman et al. [14] proved that the five-coordinate iron(III) porphyry Fe(TPP)X is in the high-spin state. Silva *et al.* [15] also

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found the resonant 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}(TPPBr₄)Cl [16]. At the same time, the C₄ point group was adopted to perform the geometry optimization. For simplicity, the H or F atoms in the phenyls were fixed on the same plane. All calculations were performed with the Gaussian-98 package [17].

III. RESULTS AND DISCUSSION

The main geometrical parameters of the complexes optimized by using UB3LYP/STO-3G* method are shown in Table I.

TABLE I The main geometry parameters of Fe(TPP)Cl and $Fe(TPPF_{20})Cl$ (see Scheme)

	Fe(TPP)Cl	$\rm Fe(TPPF_{20})Cl$
Bond length/Å		
Fe-N	2.0814	2.0824
Fe-Cl	1.9772	1.9752
C_1-N	1.4238	1.4234
$C_1 - C_2$	1.4630	1.4633
$C_2 - C_3$	1.3660	1.3655
C_4-C_0	1.5239	1.5200
$C_1 - C_0$	1.4194	1.4202
C_4-C_5	1.4182	1.4283
$C_5 - C_6$	1.4079	1.4371
C_6-C_7	1.4091	1.4344
C_7-C_8	1.4091	1.4345
$C_8 - C_9$	1.4078	1.4364
C_4-C_9	1.4182	1.4281
C-F		1.3724 - 1.3758
Bond angle/($^{\circ}$)		
$\angle \mathrm{Cl}\mathrm{-Fe-N}$	103.95	103.99
Dihedral angle/(°)		
$C_5 - C_4 - C_0 - C_1$	65.04	65.83



The results show their geometries are similar to each other. The porphyrin rings of the complexes slightly have a departure from a plane and are biased towards the Fe–Cl bond. The Fe atom is out of the plane formed by the 4 nitrogen atoms and locates about 0.5 Å above the plane. And the 4 phenyls are crossed by the porphyrin ring with a dihedral angle of 65° . Based on the bond lengths of the porphyrin rings, the geometries of the two complexes are a bit different. The difference of the C-C bond lengths for phenyls are more obvious. All of the Fe–N bond lengths are about 2.08 Å, which are similar to that (2.03 Å) in Fe(TPP)OH crystal structure. While, the lengths of C-C bonds in the porphyrin ring are close to that in Mn(TPP)Cl. The lengths of C–N bonds in the Fe(TPP)Cl complex are about 1.42 Å, which is consistent with the experimental value of 1.39 Å of Mn(TPP)Cl [18]. The results show the geometries obtained in this work accord well with the experimental values of the complexes.

The Mulliken atomic charges and spin densities of the two complexes obtained by using the UB3LYP DFT method with STO-3G^{*} and 6-31G^{*} basis sets are presented in Table II.

The data in Table II present some interesting information. At the first sight one notices that the Mulliken atomic charges and spin densities of Fe, Cl, N and C atoms on the porphyrin ring calculated by using the UB3LYP/STO-3G* method for the two complexes are almost the same respectively. The atomic charge difference on the Cl atom between the two complexes is just 0.0037 based on the results of the UB3LYP/STO-3G* method. The results obtained by $UB3LYP/6-31G^*$ are different from that by UB3LYP/STO-3G*. While the results obtained by using the UB3LYP/6-31G* method are not very notably different between the two complexes except the atomic charges of the C atoms on the phenyls owing to the H atoms is replaced by the F atoms on the phenyls. All of the atomic charges of carbon atoms on phenyls in $Fe(TPPF_{20})Cl$ are positive and are in the range of 0.311 to 0.263, while the atomic charges in Fe(TPP)Cl are negative and are in the range of -0.133 to -0.163. The atomic charge of the carbon atom C_4 connected with porphyrin ring is about -0.18 in Fe(TPPF₂₀)Cl and about 0.026 in Fe(TPP)Cl, respectively. These results indicate the Cl atom in $Fe(TPPF_{20})Cl$ obtained less electron density than in Fe(TPP)Cl, the carbon atom C_1 connected with the N atom lost more electron density, and the positive charge on the Fe atom is less than that in Fe(TPP)Cl by about 0.03. The atomic spin density on the Fe atom in $Fe(TPPF_{20})Cl$ is less than that in Fe(TPP)Cl by about 0.026. Considering the trends of changes for the atomic charges and spin densities on Cl atom from Fe(TPP)Cl to $Fe(TPPF_{20})Cl$, it can be found that the change of atomic charges and spin densities on the Fe atoms seems to be parallel to that on Cl atoms. That is to say, the replacement of H atoms on phenyls by F atoms leads

TABLE II T	'he Mulliken	atomic charges	and spin	densities	obtained by	UB3LYP	method ^a
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		STO-3G*		6-	-31G*
		Fe(TPP)Cl	$Fe(TPPF_{20})Cl$	Fe(TPP)Cl	$Fe(TPPF_{20})Cl$
Mulliken atomic	Fe	1.0016	1.0081	1.2961	1.2668
charges	Cl	-0.5737	-0.5699	-0.3264	-0.2974
	Ν	-0.2825	-0.2809	-0.7987	-0.7997
	C_1	0.0790	0.0825	0.3256	0.3362
	C_2, C_3	-0.0919	-0.0894	-0.1771	-0.1601
	C_0	-0.0055	-0.0044	-0.0622	0.0012
	C_4	0.0006	-0.0429	0.0261	-0.1797
Mulliken atomic	Fe	4.7402	4.7410	4.1821	4.1564
spin densities	Cl	0.1021	0.1031	0.3419	0.3665
	Ν	0.0263	0.0257	0.0884	0.0933
	C_1	0.0003	0.0002	-0.0017	-0.0043
	C_2, C_3	0.0009	0.0009	0.0043	0.0054
	C_{0}	0.0113	0.0110	0.0251	0.0233
	C_4	-0.0011	-0.0011	-0.0016	-0.0065

^a $C_5-C_4-C_0-C_1$ see Table I

TABLE III The natural population analysis for the Fe atom in Fe(TPP)Cl and Fe(TPPF₂₀)Cl^a.

Occupation	Fe(TPP)Cl	Fe(TPPF ₂₀)Cl
Total	$(3d_{xy})^{0.9978}(3d_{xz})^{1.1241}(3d_{yz})^{1.1241}(3d_{x^2-y^2})^{1.1241}(3d_{z^2})^{1.2751}$	$(3d_{xy})^{0.9976}(3d_{xz})^{1.1362}(3d_{yz})^{1.1362}(3d_{x^2-y^2})^{1.2158}(3d_{z^2})^{1.2687}$
a-spin	$(3d_{xy})^{0.9914}(3d_{xz})^{0.9947}(3d_{yz})^{0.9947}(3d_{x^2-y^2})^{0.9928}(3d_{z^2})^{0.9898}$	$(3d_{xy})^{0.9916}(3d_{xz})^{0.9950}(3d_{yz})^{0.9950}(3d_{x^2-y^2})^{0.9930}(3d_{z^2})^{0.9901}$
β -spin	$(3d_{xy})^{0.0064}(3d_{xz})^{0.1294}(3d_{yz})^{0.1294}(3d_{x^2-y^2})^{0.2143}(3d_{z^2})^{0.2853}$	$(3d_{xy})^{0.0060}(3d_{xz})^{0.1412}(3d_{yz})^{0.1412}(3d_{x^2-y^2})^{0.2228}(3d_{z^2})^{0.2786}$

^a Electron configuration : [core] $4s^{0.34}3d^{5.73}4p^{0.024}4d^{0.01}$.

to the electron transfer from Cl to Fe, and both of the positive charge and the spin density on Fe decrease, at the same time, the electronic density is decreased and the spin density is increased on the Cl atom.

The spin densities on the Cl, N and Fe atoms are remarkable, while those on other atoms are almost zero. The Mulliken atomic charges on the N, C_1 and Fe atoms obtained by using UB3LYP/6-31G^{*} are about -0.8, +0.326(0.336), and +1.3 respectively. The high spin state of Fe³⁺ has 5 unpaired spin-parallel electrons but its atomic spin density is just about 4.2. The remarkable spin densities on the Cl and N atoms clearly show that the spin density is transferred partly from the Fe atom to the Cl atom and the N atoms on porphyrin ring. The spin transfer may result from the unpaired electrons on the Fe atom transfer to the Cl and the N atoms or the electrons with opposite spin transfer from the porphyrin ring to the Fe atom. Considering the atomic charge on the Fe atom with a valence of +3 is only about +1.3 based on the latter, the electron population in the five 3d atomic orbitals of Fe is more than 5. The natural 3d atomic orbital occupancies and the electronic configuration of Fe obtained by uB3LYP/6-31G* for Fe(TPP)Cl and Fe(TPPF₂₀) as followed below strongly support these results.

The natural population analysis for the Fe atom in Fe(TPP)Cl and $Fe(TPPF_{20})Cl$ are shown in Table III. The α -spin electron occupancies in the five 3d orbitals are about 1 except the $3d_{xy}$ orbital, the β -spin electron occupancies in other four 3d orbitals namely $3d_{xz}$, $3d_{uz}$, $3d_{r^2u^2}$ and $3d_{z^2}$ are notable. Clearly some opposite spin electrons are transferred to the Fe atom and reduces the spin density on the Fe atom. The spin transfer and the Fe–P(porphyrin) π bonding in the ferrous-porphyrin complexes were suggested in literatures [16,19]. Based on their proton nuclear magnetic resonance spectra, and the shifts for pyrrole substituents reflected extensive π spin transfer, which originated solely from the porphyrin-iorn charge transfer. The Fe($3d_{z^2}, 3d_{xz}, 3d_{yz}$)-P π bonding is clear from the molecular orbital structures described in the following section. Based on this work, besides the mentioned π bonding, the Fe($3d_{x^2-y^2}$)-P and Fe($3d_{z^2}$)-Cl($3p_z$) σ type bonding also lead to the electrons and spin density transfer. The two σ bonding leads to the visible β -spin electron occupancies in $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of Fe. Because the symmetry of $3d_{xy}$ dose not match the group orbitals of porphyrin, there is no σ bonding between the $3d_{xy}$ orbital and the group orbitals of the four N atoms on the porphyrin ring and there is no β -spin electron transfers to $3d_{xy}$ of Fe atom.

The energies of the highest occupied molecular orbitals (HOMO) of Fe(TPP)Cl and Fe(TPPF₂₀) obtained by using UB3LYP/STO-3G* are -0.10460 and -0.11244 a.u., respectively. The corresponding values obtained by UB3LYP/6-31G* are -0.18338 and -0.21818 a.u., respectively. The results of two methods show that the HOMO energy of Fe(TPPF₂₀)Cl is lower than that of Fe(TPP)Cl, that is to say, the substitution of H atoms on phenyls by F atoms decreases the energy of HOMO. The HOMO energy may have an influence on the stability and the activity in O₂ catalytic activation of the complexes.

To analyze the property of the complexes, the six high-lying occupied α -spin orbitals are presented for the two complexes in Fig.1. It is notable that the corresponding orbitals of the two complexes are very similar to each other except the 5th and 6th HOMO α -spin orbitals, the two degenerate orbitals, which have slightly different plots between the two complexes.

The first HOMO is mainly composed of the $3d_{z^2}$ atomic orbital of Fe, the $3p_z$ atomic orbital of Cl atom and the p_z atomic orbital of N and C_0 atoms on porphyrin ring. It has a four-fold axis and is an antibonding in the Fe-Cl bond and a weak antibonding or nonbonding in the 4 Fe–N bonds. The second HOMO is only composed of the p_z atomic orbitals of C atoms on porphyrin ring and no component of Fe atomic orbitals. It also has a four-fold axis, and is π -bonding in all $C_1 - C_2$ bonds and antibonding in C_2-C_3 . The third HOMO is complicated, compared with the former two orbitals. It consists of the $3d_{x^2-y^2}$ atomic orbitals of Fe and has a two-fold axis, and is σ^* -type antibonding in the 4 Fe–N bonds. The 4th HOMO is composed of the $3d_{z^2}$ atomic orbitals of Fe, the $3p_z$ atomic orbitals of Cl and the p_z atomic orbitals of all the N and C atoms on porphyrin ring. It also has a four-fold axis, and is π^* -type antibonding in the 4 Fe–N bonds and σ -type weak bonding or nonbonding in the 4 Fe–Cl bonds, and is π -type bonding in all $N-C_1$ and C_2-C_3 bonds. The 5th degenerate orbitals and the 6th HOMO-s have same structure and can translate to each other by turning round the Fe-Cl bond by 90°. One of them contains the $3d_{xz}$ atomic orbitals of Fe and the $3p_x$ atomic orbitals of Cl and the p_z atomic orbitals on porphyrin, and the second contains the $3d_{uz}$ atomic orbitals of Fe and the $3p_u$ atomic orbitals of Cl and the p_z atomic orbitas on porphyrin. It is a π -type orbital with a two-fold axis, and is nonbonding or weak antibonding in the Fe–N bonds



FIG. 1 The structure of the high-lying occupied α spin molecular orbitals of Fe(TPP)Cl (A) and Fe(TPPF₂₀)Cl (B) obtained by B3LYP/6-31G* method.

and nonbonding or weak bonding in the Fe–Cl bond. It contains small component of the atomic orbitals of Fe and Cl. Except for the Fe and Cl atomic orbitals, the other components of atomic orbitals in the two complexes are very different. All the HOMO-s above show the π^* and σ^* types bonding interaction between the

Fe atom and the porphyrin ring, which results from the transfer of electrons and spin density.

The same characteristic of the two complexes is that the first HOMO contains the $3d_{z^2}$ atomic orbital of Fe, the second HOMO contains no Fe atomic orbital, the third HOMO contains the $3d_{x^2-y^2}$ atomic orbital of Fe, the 4th HOMO contains the $3d_{z^2}$ atomic orbital of Fe, and the 5th and 6th degenerate HOMO-s contain the $3d_{xz}$ or $3d_{yz}$ atomic orbital of Fe respectively. The unpaired electrons filled in the five 3d atomic orbitals of Fe atom made a contribution to the spin density in the complexes.

Based on the ligand field theory, the energies of the five 3d atomic orbitals of Fe atom will be split in the five-coordinated field formed by the 4 N atoms on porphyrin ring and the 5th coordinated Cl atom. Because the Cl atom is closer to the Fe atom than the four N atoms and has a bulkier electron cloud than the N atom. If the four N atoms are located on x and y coordinate axis and the Cl atom is located on z axes, the energy sequence of the five 3d orbitals of Fe should be split as below:

$$3d_{z^2} > 3d_{x^2-y^2} > 3d_{xz} = 3d_{yz} > 3d_{xy}$$
 of
 $3d_{z^2} > 3d_{x^2-y^2} > 3d_{xy} > 3d_{xz} = 3d_{yz}$

Based on the analysis of the high-lying orbitals the $3d_{xy}$ atomic orbital of the Fe atom dose not play a role in the six high-lying orbitals of the complexes. So one can conclude the energy sequence of the five 3d atomic orbitals is the first one. The mixture of them leads to the electronic density and spin density transfer by π - and σ -type bonding between the Fe atom and the porphyrin ring.

The single occupied π^* -type HOMO and σ^* -type LUMO of O₂ are presented in Fig.2.



FIG. 2 The single occupied degenerate HOMO $\pi *_{2p_x}$ or $\pi *_{2p_y}$, and LUMO $\sigma *_{2p_z}$ of O₂.

To activate O₂ or decrease the strength of O–O bond, there must be electrons transfer to the $\pi^*_{2p_x}$ or $\pi^*_{2p_y}$ or $\sigma^*_{2p_z}$ orbital in the molecule. The energies obtained by restricted B3LYP/6-31G* are -0.15386, -0.15386, and 0.12598 a.u. for $\pi^*_{2p_x}$ or $\pi^*_{2p_y}$ and $\sigma^*_{2p_z}$ respectively. Based on the symmetry of the high-lying orbitals of the complexes, the symmetries of the first and the 4th

HOMO containing the $3d_{z^2}$ orbital of the Fe atom are adapted to those of the $\sigma^*_{2\mathbf{p}_z}$ orbital of the O₂ molecule when the O_2 molecule approaches the Fe atom, respectively, with the O–O bond perpendicular to the surface of the complexes. And the symmetries of the 5th and 6th degenerate HOMO-s containing the $3d_{xz}$ or $3d_{yz}$ orbitals of the Fe atom are adapted to the single occupied $\pi^*_{2p_x}$ or $\pi^*_{2p_y}$ orbitals of the O₂ molecule respectively, when the O_2 molecule approaches the complexes with the O–O bond perpendicular to the surface of the complexes. Considering the very high energy of the LUMO $\sigma^*_{2\mathbf{p}_z}$ of the \mathbf{O}_2 molecule and the lower energies of the high-lying molecular orbitals of the complexes, the interaction between the $\sigma^*_{2\mathbf{p}_z}$ orbital and the molecular orbitals of the complexes should be very weak. The energy of the degenerate single occupied $\pi^*_{2p_x}$ or $\pi^*_{2p_y}$ orbital is about -0.24 a.u. and is closer to that of the 5th and 6th degenerate HOMO-s of the complexes. So their interactions will be very important for the activation of the O_2 molecule on the surface of the complexes. The third HOMO containing the $3d_{x^2-y^2}$ orbital of the Fe atom is not adapted to the orbitals of the O_2 molecule. The distances between the electron cloud of the $3d_{x^2-y^2}$ orbital and the O₂ orbitals are also larger than those between the $3d_{z^2}$ or $3d_{xz}$ or $3d_{yz}$ orbitals and the O_2 orbitals. The larger distance decreases the interaction between the orbitals of O_2 and the $3d_{x^2-y^2}$ orbital of the Fe atom on the complexes. In fact, the O_2 molecule can take another way to approach the Fe atom, namely one O atom is from above the Fe atom at a certain distance and the second O atom is at a site to keep the O-O-Fe bond with an angle of less than 180°. Based on the result of UB3LYP/STO-3G*, under this condition, the symmetry of one π^*_{2p} orbital of the O_2 atom is adapted to the symmetry of one of the 5th and 6th degenerate HOMO-s containing the $3d_{xz}$ or $3d_{yz}$ orbital of the Fe atom, and at the same time, the symmetry of the second π^*_{2p} orbital is adapted to the 4th HOMO containing the $3d_{z^2}$ orbital of the Fe atom as shown in Fig.3. This result agrees with the literature [20]. No matter what status the oxygen molecule adopts, the $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals of the O₂ molecule are all very important in oxygen activation over porphyrines in the interaction between the O_2 molecule and the iron porphyrine.

Based on the orbital structure, it is notable that there is not very big difference between Fe(TPP)Cland $Fe(TPPF_{20})Cl$. The property that the activity of $Fe(TPPF_{20})Cl$ in oxygen activation is much higher than that of Fe(TPP)Cl may be from its higher stability. The O radical or activated O₂ may attack the H atoms on phenyls of Fe(TPP)Cl and accordingly leads to the complex broken down and its activity decreased greatly. Based on the results, the fluorinated complex protects the complex well and leads to the energy of the HOMO lower and enhances its catalytic activity in the oxygen activation on the porphyrine surface. In fact,



FIG. 3 The interaction between the $\pi^*{}_{2p}$ of O_2 and the high-lying orbitals of iron porphyrines.

although the fluorination reduces the spin density and increases the electron density on the catalytic center Fe atom a little, it may make much contributes to its catalytic activity of the oxygen activation on the porphyrine surface.

IV. CONCLUSIONS

density functional theory UB3LYP/6-The 31G*//UB3LYP/STO-3G* can present good results for the studies of Fe(TPP)Cl and Fe(TPPF₂₀)Cl complexes. The molecular orbital parameters show that not only the π -type bonding of Fe-porphyrin but also the σ -type bonding in the complexes induces the electron density and spin density transfer between the Fe atom and the porphyrin ring. The calculations show that there are some electrons in opposite spin to the unpaired electrons in the 3d orbitals of the Fe atom transfer to the Fe atom from the porphyrin ring. The substitution of H atoms on the four phenyls by F atoms brings about more electron transfer to the Fe atom, the catalytic activation center, and decreases the energy of the HOMO in porphyrin and makes the complex more stabilized without observable changing of the characteristics of the high-lying molecular orbitals. The higher stability of $Fe(TPPF_{20})Cl$ than Fe(TPP)Clleads to its higher catalytic activity in the oxygen activation reaction than Fe(TPP)Cl. When the oxygen molecule approaches the Fe atom with the symmetry adapted, it is the single occupied degenerate orbitals $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ of the oxygen molecule that interact with the high-lying orbitals of the iron porphyrines.

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