

## Interaction between Metalloporphyrins and Diazine Tautomers

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Received August 25, 2013, Accepted September 22, 2013

The interaction between metalloporphyrins and diazine tautomers was investigated using quantum chemistry method. The results showed that the metal atom in the metalloporphyrin was not coplanar with porphyrin ring, and zinc porphyrin has the most extent of its non-coplanar nature. The most stable complex in nine complexes was iron porphyrin. NBO analysis indicated that the interaction between the lone pair of electrons on the nitrogen atom and the unoccupied lone pair orbital of metal contributes significantly to the stability of the complexes. Through the conceptual DFT parameter and Fukui dual descriptor, the thermodynamic stability and reactivity of complexes were analyzed. The density difference function (DDF) analyses were performed to explore the rearrangement of electronic density after the coordination interaction. NICS calculation indicated that metalloporphyrin aromaticity was reduced after the coordination interaction, and aromaticity of diazine tautomer was increased along direction vector of the coordination interaction force.

**Key Words :** Metalloporphyrin, Coordination interaction, Density difference function (DDF), Fukui function, Aromaticity

### Introduction

Metalloporphyrins exist widely in the nature and organism, such as heme, chlorophyll and cytochrome.<sup>1</sup> Literature shows that metal porphyrin complexes play an important role in biomimetic catalysis, enzyme reactions, molecular imaging and other biological forefront topics.<sup>2-9</sup> Supramolecular chemistry is also the chemistry studying that two or more chemical species form a complex and ordered system with specific functions by intermolecular interaction.<sup>10</sup> Therefore the research of porphyrin supramolecular chemical can provide important clues to the study of the nature of life processes. The research of the interaction of nitrogen-containing hexatomic ring such as diazine (serving as an important constitutional unit of biomolecules like protein and nucleotide) with metal porphyrin has an important significance in understanding life processes and metabolic mechanisms. In this paper, taking metalloporphyrins as the hosts and diazine tautomers as the guests, DFT methods was used to calculate the metal porphyrins and their supramolecular complexes. Their electronic structure and reactivity were investigated by using NBO and Fukai dual descriptor respectively. Meantime, by using electron density difference map and independent chemical shifts, the electronic rearrangements and the aromaticity of complexes after coordination were calculated and analyzed.

### Computation Method

The geometrical configuration of metal porphyrin host and diazine guest are optimized by using the B3LYP/GEN level

in Gaussian 03<sup>11</sup> (LanL2DZ basis set for metal atoms and 6-311G\*\* basis set for other atoms). Complexes are constructed with optimized configurations, and supramolecular complexes are formed by metalloporphyrins and diazine tautomers by the ratio of 1:1, as shown in Figure 1. The initial model is constructed as follows:<sup>12</sup> (a) the guest molecules are perpendicular to the metal porphyrin in the axial plane; (b) the shortest space between the guest molecules and metal porphyrin molecules is 0.45 nm; (c) the distance between the center of host molecules and center of metal porphyrin is 0.65 nm. B3LYP/GEN method is used to optimize the geometry configuration of the complexes **1-9** without any symmetry restrictions. For divalent metal M (M = Fe, Cu, Zn) ions, because different spin states will produce different energy, we will take the divalent metal ions (2 *s* + 1) in the lowest energy state to calculate and the spin contamination value is smaller (*S*<sup>2</sup> < 10%). If the complex is viewed as a whole, *i.e.* electron movement in the orbit of supramolecular, the energy minima on potential energy surface can be found. The energy of complex deducted by the energy of the host and the guest is stabilization energy of the complex ( $\Delta E$ ). Stabilization energy of nine complexes is corrected using Boys-Bemardi.<sup>13</sup> The second-order perturbation stabilization energy ( $\Delta E^2$ ) is calculated by NBO program of 3.1 version in Gaussian 03.<sup>11</sup> On the basis of B3LYP/GEN optimized structure, GIAO method (gauge-including atomic orbital) is used to calculate nuclear independent chemical shift on the level of B3LYP/6-31++G\*\*. The density difference function (DDF) is defined as the difference between the electron density of the complex ( $\rho_0$ ) and the electron density ( $\rho_1$ ,  $\rho_2$ ) of isolated monomer composed of the complex

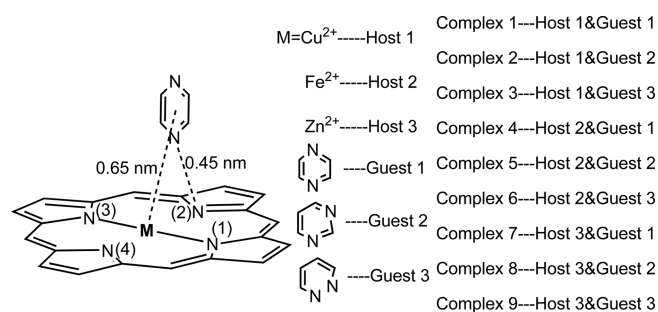


Figure 1. Host and guest initial configuration.

molecule in spatial grid points. The mathematical expression is  $\Delta\rho = \rho_0 - \rho_1 - \rho_2$ . According to electron density values obtained by calculation, Multiwfn software<sup>14</sup> is used to draw their electron density difference map in the optimized geometries.

## Results and Discussions

### Geometry Optimization and Stabilization Energy Analysis.

Table 1 shows the geometric parameters and interaction energies of three metal porphyrins and nine complex molecules by using density functional method. It has been shown that uncorrected stabilization energy ( $\Delta E$ ) of the nine complexes and BSSE corrected stabilization energy ( $\Delta E + \text{BSSE}$ ) are all negative, indicating that the formation of complex formed is stable configuration. Meanwhile, the energy difference between the stabilization energy ( $\Delta E$ ) and corrected stabilization energy ( $\Delta E + \text{BSSE}$ ) is between 2.7 kcal·mol<sup>-1</sup> and 4.2 kcal·mol<sup>-1</sup>, suggesting that it is necessary to make basis set superposition error (BSSE) correction to the stabilization energy of complex. From the corrected stabilization energy ( $\Delta E + \text{BSSE}$ ) values, the following can be obtained: iron porphyrin complex is stabler than zinc porphyrin complex; copper porphyrin has the minimum stability, which indicates that iron porphyrin is easier to induce diazine isomers in coordination-induction process.

The interaction in complexes formed by three diazine tautomers with three kinds of metal porphyrin gives priority to coordination interaction (as shown in Figure 2). It is noteworthy that the three complexes formed by zinc porphyrin not only have coordination interaction, but also have surrounding hydrogen bond interaction (surrounding hydrogen bond hereof refers to the hydrogen bond formed by the hydrogen atoms in diazine and the nitrogen atoms in zinc porphyrin), which is the same as the conclusion of magne-

Table 1. The geometric parameters and stabilization energy of complexes and hosts

| Complexes | $\angle \text{N}(2)\text{-N}(1)\text{-M-N}(4)/^\circ$ | $d_{\text{M-N}}/\text{nm}$ | $\Delta E/\text{kcal}\cdot\text{mol}^{-1}$ | $\Delta E+\text{BSSE}/\text{kcal}\cdot\text{mol}^{-1}$ |
|-----------|---|----------------------------|--|--|
| Host 1    | 179.9   | —                          | —  | —  |
| Host 2    | 179.9   | —                          | —  | —  |
| Host 3    | 179.9   | —                          | —  | —  |
| Complex 1 | 174.7   | 0.2598                     | -3.652                                     | -0.875   |
| Complex 2 | 174.5   | 0.2579                     | -3.779                                     | -1.037   |
| Complex 3 | 173.9   | 0.2573                     | -3.207                                     | -0.218   |
| Complex 4 | 171.0   | 0.1956                     | -30.928                                    | -27.211  |
| Complex 5 | 170.7   | 0.1971                     | -30.405                                    | -26.705  |
| Complex 6 | 170.7   | 0.1927                     | -32.103                                    | -27.914  |
| Complex 7 | 163.9   | 0.2312                     | -11.323                                    | -8.353   |
| Complex 8 | 163.4   | 0.2307                     | -11.451                                    | -8.504   |
| Complex 9 | 161.3   | 0.2308                     | -11.367                                    | -8.240   |

$d_{\text{M-N}}$ : coordinate bond distance; M: Cu, Fe, Zn;  $\Delta E$ : stabilization energy;  $\Delta E+\text{BSSE}$ : BSSE corrected stabilization energy

sium porphyrin complexes we previously studied.<sup>15</sup> When the dihedral angle values of  $\angle \text{N}(2)\text{-N}(1)\text{-M-N}(4)$  is compared, it is found that dihedral angle values of zinc porphyrin complexes is smaller than ones of iron porphyrin and copper porphyrin complexes. The reason for this phenomenon is perhaps due to the influence of surrounding hydrogen bond so that the dihedral angle of zinc porphyrin complex becomes smaller. As we all know, the bond length of chemical bonds is closely related to the stabilization energy of complexes. The main interaction in the nine complexes is coordination interaction. The shorter the length of the coordination bond is, the greater energy it has, and the greater stability of the complexes will have. Therefore, from the bond length of the coordination bond in Table 1, it can be seen that the three complexes formed by iron porphyrin have the greatest stability.

**NBO Analysis.** The formation process of complex can be understood from orbit interaction by Natural Bond Orbital (NBO).<sup>16</sup> The stability of the complex caused by orbit interaction can be described with second-order perturbation stabilization energy ( $\Delta E^2$ ), which can be obtained by the following formula:

$$\Delta E^2 = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i}$$

$q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are diagonal elements (orbital energies),  $F$  is the off-diagonal NBO Fock

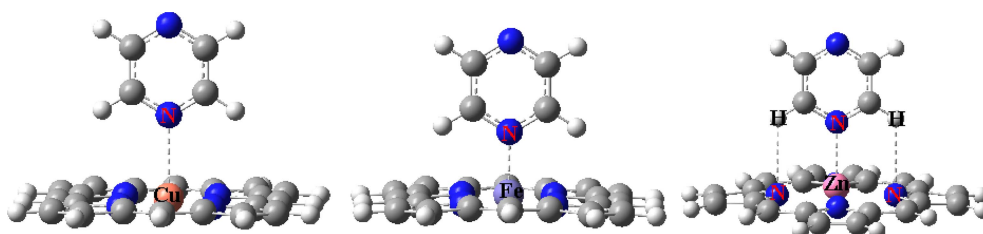


Figure 2. The optimized geometries of complexes.

**Table 2.** The magnitude of charge transfer and second-order perturbation stabilization energy of complexes 1-9

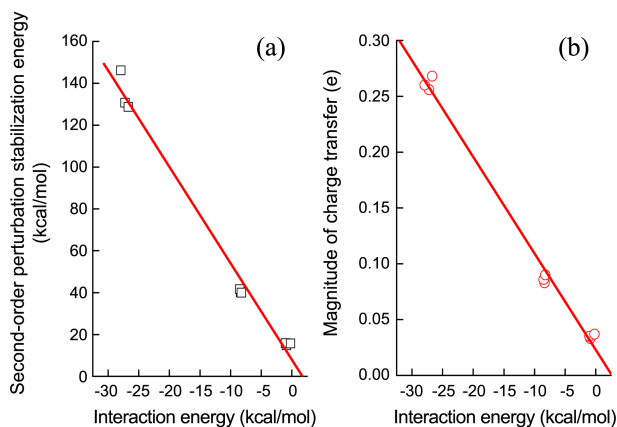
| Complexes | Donor NBOs  | Acceptor NBOs | $\Delta E^2/\text{kcal/mol}$ | $Q_{\text{CT}}/e$ |
|-----------|-------------|---------------|------------------------------|-------------------|
| Complex 1 | N lone pair | LP* Cu        | 14.83                        | 0.033             |
| Complex 2 | N lone pair | LP* Cu        | 15.84                        | 0.035             |
| Complex 3 | N lone pair | LP* Cu        | 15.66                        | 0.037             |
| Complex 4 | N lone pair | LP* Fe        | 130.78                       | 0.256             |
| Complex 5 | N lone pair | LP* Fe        | 128.74                       | 0.268             |
| Complex 6 | N lone pair | LP* Fe        | 146.19                       | 0.260             |
| Complex 7 | N lone pair | LP* Zn        | 40.19                        | 0.083             |
| Complex 8 | N lone pair | LP* Zn        | 41.68                        | 0.086             |
| Complex 9 | N lone pair | LP* Zn        | 39.94                        | 0.090             |

matrix element. Table 2 lists major second-order perturbation stabilization energy ( $\Delta E^2$ ) caused by coordination interaction in complex formed by diazine guest and metal porphyrin.

NBO analysis shows that in the coordination interaction of nine complexes, the main stabilizing factor is interaction between the nitrogen lone pair in the guest molecule and 1-center valence antibond lone pair of divalent metal ion, that is, lone pair (N)  $\rightarrow$  LP\* (M). Also, it has been found that the second-order perturbation stabilization energy of complexes is highly related with their interaction energies and the correlation coefficient is 0.994 (see Figure 3(a)). Based on these, the conclusion can be obtained that orbit interaction of lone pair (N)  $\rightarrow$  LP\* (M) has made great contributions to the stability of the complexes. When the complex is formed, the charge was transferred from one monomer to another monomer, which finally results in increase of the electron density of anti-bond orbit. There is a good linear relationship between charge-transfer amount ( $Q_{\text{CT}}$ ) and corrected stabilization energy, which the correlation coefficient ( $R$ ) is equal to 0.996, as shown in Figure 3(b). It has been shown that the charge-transfer amount of the three complexes formed by iron porphyrin is the biggest in nine complexes, and indicating that they have the strongest stability.

#### Conceptual DFT and Fukui Dual Descriptor Analysis.

Table 3 lists the conceptual DFT parameters of three hosts

**Figure 3.** The relationship between second-order perturbation stabilization energy, magnitude of charge transfer and stabilization energy.

and nine complexes obtained by using B3LYP/GEN method. Conceptual DFT parameters are widely used to study the reactivity of system.<sup>17</sup> It has been shown that the chemical potential is the highest in the transition state (*i.e.* hardness is the smallest), and is the lowest in steady state (*i.e.* hardness is the biggest).<sup>18</sup> The direction of the chemical reaction is to first generate product with greater hardness. In this paper, the activity of the ground state structure for the complex is studied by conceptual DFT parameters. In the Table 3,  $E_g$  is energy gap;  $\eta$  and  $\chi$  are called absolute hardness and absolute electronegativity, respectively. Moreover, the reactive sites of the complex are visually represented using Fukai dual descriptor ( $f^2(r)$ ) distribution map. Fukui dual descriptor, electrophilic Fukui function ( $f^-(r)$ ), and nucleophilic Fukui function ( $f^+(r)$ ) are respectively defined as:<sup>19</sup>

$$\begin{aligned} f^2(r) &= f^+(r) - f^-(r) \\ f^-(r) &= \rho(N) - \rho(N-1) \\ f^+(r) &= \rho(N+1) - \rho(N) \end{aligned}$$

in which the  $\rho(N)$ ,  $\rho(N+1)$  and  $\rho(N-1)$  represent the electron density of neutral molecules, anions and cations, respectively.

Data in Table 3 show that the energy of the highest occupied molecular orbital and the lowest unoccupied molecular orbital are all rising after complexes are formed. Compared with the host, the complexes formed by the copper porphyrin and zinc porphyrin have smaller energy gap, and complexes formed by iron porphyrin have larger energy gap. The smaller the energy gap is, the more electron is prone to transition, and the stronger the reactivity will be, so in the nine complexes, complexes formed by iron porphyrin are less active than the iron porphyrin itself and other complexes are more active than their hosts itself. Change of complex energy gap will also affect the electronic spectrum. The electronic spectrum will produce red shift when the energy gap becomes smaller, and do blue shift when the energy gap becomes larger. Therefore, the formation of complex changes the spectrum band of metal porphyrin host, consequently changes the signal transmission, and ultimately affects the induction conversion *in vivo*. The  $\eta$  value is used to measure the thermodynamic stability of complex. The higher the  $\eta$  value is, the stronger thermodynamic stability complex has. The  $\chi$  value (absolute electronegativity) may reflect the antioxidant ability. The higher the  $\chi$  value is, the harder the complex is oxidized.<sup>20</sup> The  $\chi$  and  $\eta$  values of complexes formed by iron porphyrin are higher than the ones of iron porphyrin host, indicating that the thermodynamic stability and the antioxidant ability of these complexes are superior to iron porphyrin host; while  $\eta$  and  $\chi$  values of complexes formed by copper porphyrin and zinc porphyrin are less than their hosts, indicating that the thermodynamic stability and oxidation resistance of the complexes are poorer. Taking above analysis, it can be obtained that after the coordination recognition, thermodynamic stability of iron porphyrin complexes increases and the reactivity decreases, while the two properties of the complexes formed by zinc porphyrin and copper porphyrin are just the opposite.

**Table 3.** Conceptual DFT parameters for complexes 1-9 and host

| Complexes | $E_{\text{HOMO}}/\text{eV}$ | $E_{\text{LUMO}}/\text{eV}$ | $I_{\text{p}}/\text{eV}$ | $E_{\text{A}}/\text{eV}$ | $E_{\text{g}}/\text{eV}$ | $\eta/\text{eV}$ | $\chi/\text{eV}$ |
|-----------|-----------------------------|-----------------------------|--------------------------|--------------------------|--------------------------|------------------|------------------|
| Host 1    | -5.476                      | -2.417                      | 5.476                    | 2.417                    | 3.059                    | 1.529            | 3.947            |
| Host 2    | -5.427                      | -2.887                      | 5.427                    | 2.887                    | 2.540                    | 1.270            | 4.157            |
| Host 3    | -5.435                      | -2.417                      | 5.435                    | 2.417                    | 3.017                    | 1.509            | 3.926            |
| Complex 1 | -5.372                      | -2.352                      | 5.372                    | 2.352                    | 3.019                    | 1.510            | 3.862            |
| Complex 2 | -5.332                      | -2.314                      | 5.332                    | 2.314                    | 3.017                    | 1.509            | 3.823            |
| Complex 3 | -5.147                      | -2.135                      | 5.147                    | 2.135                    | 3.012                    | 1.506            | 3.641            |
| Complex 4 | -5.345                      | -2.229                      | 5.345                    | 2.229                    | 3.116                    | 1.558            | 3.787            |
| Complex 5 | -5.290                      | -2.170                      | 5.290                    | 2.170                    | 3.120                    | 1.560            | 3.730            |
| Complex 6 | -5.103                      | -2.054                      | 5.103                    | 2.054                    | 3.049                    | 1.525            | 3.579            |
| Complex 7 | -5.198                      | -2.288                      | 5.198                    | 2.288                    | 2.910                    | 1.455            | 3.743            |
| Complex 8 | -5.153                      | -2.232                      | 5.153                    | 2.232                    | 2.921                    | 1.461            | 3.693            |
| Complex 9 | -4.968                      | -2.263                      | 4.968                    | 2.263                    | 2.706                    | 1.353            | 3.615            |

$E_{\text{g}}$ : energy gap defined as  $E_{\text{LUMO}}$  minus  $E_{\text{HOMO}}$ ;  $I_{\text{p}}$ : ionization potential defined as  $-E_{\text{HOMO}}$ ;  $E_{\text{A}}$ : electron affinity defined  $-E_{\text{LUMO}}$ ;  $\eta$ : absolute hardness defined as  $(I_{\text{p}} - E_{\text{A}})/2$ ;  $\chi$ : absolute electronegativity defined as  $(I_{\text{p}} + E_{\text{A}})/2$ .

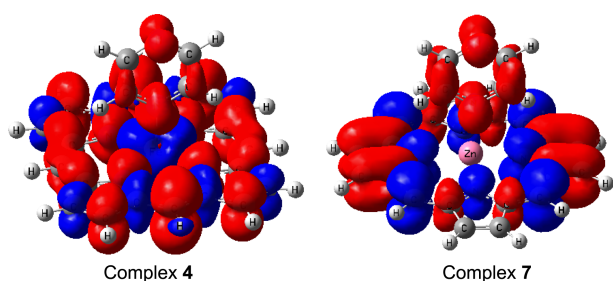
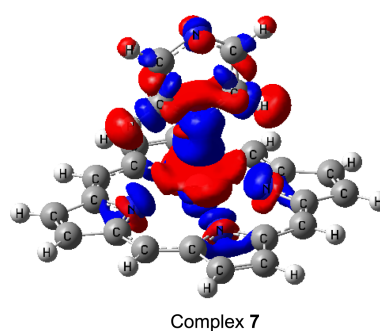
**Figure 4.** Dual descriptor distribution for complex 4 and complex 7.

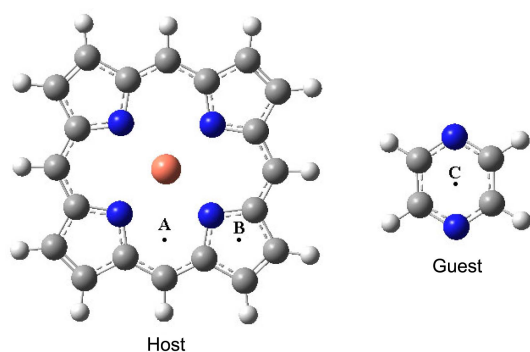
Figure 4 is the distribution map of Fukai dual descriptor for complexes 4 and 7, in which the blue region of  $f^2(r) > 0$  is the electrophilic active site, and red region of  $f^2(r) < 0$  has nucleophilic active site.<sup>21</sup> From Figure 4, the following conclusions can be deduced: (1) Different metal porphyrins have different effects on reactivity. There is electrophilic activity around the metal iron in complex 4 ( $f^2(r) > 0$ ), while the metal zinc in complex 7 has no electrophilic/nucleophilic activity. (2) Diazine molecule in complexes 4 and 7 has nucleophilic activity ( $f^2(r) < 0$ ), which shows that diazine molecules have nucleophilic reactivity after they form complexes with metal porphyrin.

**DDF Analysis.** The density difference function (DDF) methods can analyze electron density rearrangement in the process of intermolecular interaction. This method was applied to the halogen bond research in metal coordination complex by Zou,<sup>22</sup> which results were satisfactory. In this paper, the electron density difference visual diagram is used to analyze coordination bond interaction. Figure 5 shows the electron density difference map of complex 7, in which the red area is the part where the electron density is reduced ( $\Delta\rho < 0$ ) and the blue area represents the part where electron density ( $\Delta\rho > 0$ ) increases. It was apparent from Figure 5 that the electron density decreases at the top of zinc in complex 7, otherwise the electron density increases at the five nitrogen atoms around the zinc. Therefore, the effect of interaction is to reduce the electron density over the metal

**Figure 5.** The electronic density difference map of complex 7.

atoms, and the electron in guest molecule (pyrazine) is moved toward the metal atoms of electron density reduction in order to achieve the best results of coordination interaction. It has also been found that the effect of coordination interaction on electronic rearrangements of host molecular is mainly concentrated in the central metal place, and effect on electronic rearrangements of guest is in the entire molecule. The reason is perhaps that the provision of the lone electron pair by nitrogen atom of pyrazine molecule affects large  $\pi$  bond of pyrazine. It is noteworthy that in the complex 7, electron density around two hydrogen atoms in pyrazine molecule near the side of porphyrin is reduced. According to DDF analysis of the representative complex 7, we can conclude that coordination interaction makes the electron density over metal porphyrin central atom decrease and electron density of the surrounding five nitrogen atoms increase. In particular, electron density of nitrogen atom at the coordination interaction has the maximum increase.

**Aromaticity Analysis.** Literature shows that the aromaticity of porphine molecule is determined by tautomeric structures of aza[18]annulene.<sup>23</sup>  $^1\text{H}$  NMR spectral data also clearly reflects that porphine molecule has a good conjugated system and special aromaticity. Schleyer *et al.*<sup>24,25</sup> proposed that the absolute value of the magnetic shielding coefficient of ring center, namely, the nucleus independent chemical shifts (NICS) was used to study the molecular



**Figure 6.** The A, B, C shows the location by NICS calculation.

aromaticity. They pointed out that, if there is clear negative NICS value in the ring or cage, the induction ring current in the compound is present, that is to say, there is the aromaticity. In reverse, the compound with positive NICS value is anti-aromatic. In our previous study,<sup>15</sup> point A and B in the host compound were selected to calculate NICS values of magnesium porphyrin and heterocyclic complexes, which has obtained satisfactory results (see Figure 6). In this paper, in addition to calculate NICS values of A and B points in host, NICS value in guest molecule is also calculated to investigate the influence of coordination interaction on the guest molecule aromaticity. The Bq atom is put at A, B, and C points in Figure 6, respectively, which calculates NICS values with the B3LYP/6-31++G\*\* level (as shown in Table 4). It has been shown from Table 4 that NICS values of the host molecules and guest molecules at A, B and C points are all negative, indicating that the metal porphyrin molecule and diazine molecule have good aromaticity, and the aromaticity at point A is larger than that at point B in every metal porphyrin. Aromaticity of three isomers of guest (diazine) has little difference. The NICS values of the nine complexes at A, B and C points are all negative, indicating

the complexes also have aromaticity though the aromaticity has been changed after coordination interaction. It is worth noting that the degree of aromaticity changed is different. For example, aromaticity of copper porphyrin complex at point A slightly increases, but aromaticity of iron porphyrin and zinc porphyrin complexes significantly reduces, especially iron porphyrin. At point B, the aromaticity of the nine complexes are all reduced, in which NICS values of the three complexes formed by iron porphyrin have the most significant changes. At point C, the NICS values of the nine complexes are lower than that of diazine, indicating their aromaticities increases significantly. Therefore, the coordination interaction has great influence on the change of aromaticity in complexes, that is, after the coordination interaction, the aromaticity of the metal porphyrin decreases and that of guest diazine increases along direction vector of the coordination interaction force.

## Conclusions

Metalloporphyrin host can form stable complexes with diazine guest by axial coordination interaction. The interaction between metalloporphyrin and diazine causes that metal atom and porphyrin ring are not coplanar and the dihedral angle value becomes smaller. Wherein, the dihedral angle value in complexes formed by the zinc porphyrin is smaller than that of the complexes formed by iron porphyrin and copper porphyrin. The reason of this phenomenon could be the influence of the surrounding hydrogen-bond. The shorter the length of coordination bond is, the stabler the complexes are. It can be concluded that complexes formed by iron porphyrin have greatest stability. Natural bond orbital (NBO) analysis draws conclusion that interaction of the nitrogen lone pair in diazine and 1-center valence antibond lone pair of divalent metal ion in metal porphyrin, that is, lone pair (N)  $\rightarrow$  LP\* (M) has great contribution to the stability of complexes. Concept density functional index shows that after coordination interaction, the thermodynamic stability of iron porphyrin complexes is larger than host itself, and their reactivity is weaker, while the two properties of the complexes formed by zinc porphyrin and copper porphyrin are just the opposite. Fukui dual descriptor illustrates that different metal porphyrins have different effects on the reactivity of complexes, and the guest diazine molecule in complexes has nucleophilic reactivity. The density difference function analysis shows that the electron density over metal porphyrin central atom decreases and electron density of the surrounding five nitrogen atoms increases. Among them, the electron density of nitrogen atom at the coordination interaction increases mostly. The aromaticity analysis indicates that after the coordination interaction, the aromaticity of the metal porphyrin decreases and that of guest diazine increases along direction vector of the coordination interaction force.

**Acknowledgments.** Project supported by the Natural Science Foundation of Zhejiang province, China (No. LY12B07013; LY12C03009), the Public Technology

**Table 4.** NICS value for 3 hosts, 3 guests and 9 complexes

| Complexes | NICS   |        |        |
|-----------|--------|--------|--------|
|           | A      | B      | C      |
| Host 1    | -19.50 | -7.74  | —      |
| Host 2    | -80.65 | -33.77 | —      |
| Host 3    | -18.83 | -7.66  | —      |
| Guest 1   | —      | —      | -5.47  |
| Guest 2   | —      | —      | -5.54  |
| Guest 3   | —      | —      | -5.48  |
| Complex 1 | -21.50 | -6.73  | -9.85  |
| Complex 2 | -20.04 | -7.37  | -10.14 |
| Complex 3 | -19.34 | -6.41  | -9.71  |
| Complex 4 | -3.24  | -1.74  | -10.39 |
| Complex 5 | -3.09  | -1.58  | -11.52 |
| Complex 6 | -5.61  | -1.92  | -10.28 |
| Complex 7 | -16.51 | -7.12  | -10.43 |
| Complex 8 | -16.47 | -7.09  | -10.32 |
| Complex 9 | -16.50 | -7.56  | -9.96  |



Research Project (Analysis and Measurement) of Zhejiang Province (No. 2013C37098) and State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (No. KF2011-19). And the publication cost of this paper was supported by the Korean Chemical Society.

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