Quantum Chemical Study of the 1:1 Complex between Ferrocene and Zinc Porphyrin, a Building-Block of Charge-Transfer Molecular Materials

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The molecular and electronic structure of the 1:1 charge-transfer complex between ferrocene (Fc) and zinc porphyrin (ZnP) are investigated with the aid of dispersion-corrected density functional theory (DFT) calculations. Four stable configurations were obtained, two with the Fc molecule laying on the ZnP plane and the other two where Fc interacts with the porphyrin’s perimeter. The dipole moment vectors of these Fc/ZnP complexes indicate that they are stabilized by the transfer of electronic charge density from Fc to ZnP or vice versa.

[doi:10.2320/matertrans.MA201561]

(Received February 2, 2015; Accepted April 3, 2015; Published May 29, 2015)

Keywords: charge-transfer materials, quantum chemistry, ferrocene, molecular design

1. Introduction

The development of novel molecular materials with potential applications in the fields of electronics and photonics has attracted the attention of many research groups around the world. A straightforward approach for the synthesis of such materials is the co-crystallization of two compounds, A and B, to obtain a binary solid-state product. The formation of such a co-crystal is favored when molecules of A and B interact with each other via charge-transfer (CT) interactions or H-bonding to form a stable 1:1 complex (A:B). Notable examples of novel CT materials are those recently obtained from the co-crystallization of the football-shaped C60 fullerene molecule with either spherically-shaped metal clusters or planar molecules like Co(III) tetraphenylporphyrin (CoTPP). Further, co-crystals containing planar aromatic molecules and spherical polyoxometalates have been experimentally characterized.

In this paper we computationally investigate the CT complex formed between ferrocene (Fc) and Zn(II) porphyrin (ZnP) which represents the building block of a potential CT molecular material. As shown in Fig. 1, ferrocene, Fe(C5H5)2, is a sandwich-type molecule with the ability to donate electrons upon oxidation of the iron center from Fe(II) to Fe(III) while ZnP can act as electron acceptor. Computational studies by Zwaans et al. indicated that ZnP possesses higher electron affinity with respect to other metal porphyrins such as those of cobalt (CoP), nickel (NiP), and copper (CuP). It must be noted, however, that in covalently-linked ZnP-fullerene dyads the CT takes place from the ZnP moiety to the fullerene cage owing to the high electron withdrawing ability of ZnP which possesses six low-lying empty orbitals where up to twelve electrons can be accommodated to yield the corresponding anions.

2. Computational Methods

All the density functional theory (DFT) calculations were performed with the Gaussian 09 software package. The dispersion-corrected oB97X-D functional of Head-Gordon and coworkers was employed in this study so as to account for the London-type dispersion interactions that operate between molecules. The Stuttgart-Dresden (SDD) basis set with effective-core potentials (ECP) for elements with Z > 21,13 was employed in combination with the above functional. Both the geometry optimizations and vibrational frequency calculations were performed with an ultrafine grid having 99 radial shells and 590 angular points per shell. The interaction energy between ZnP and Fc molecules was corrected for the basis-set superposition error (BSSE) using the method of Boys and Bernardi. BSSE arises from the overlap of basis sets employed to investigate the geometry and electronic structure of molecular complexes. The overall result is that the energy of the complex is further lowered by such orbital overlap and hence the computed binding energy overestimated.

3. Results and Discussions

The DFT-optimized geometries of four 1:1 complexes
(1–4) between Fc and ZnP are shown in Fig. 2. All the geometries are characterized by positive values of the normal modes of vibration thus indicating that they are local minima on the corresponding potential energy (hyper)surface. These complexes differ from each other in the positioning and orientation of the Fc molecule (in the eclipsed conformation, Fc-e) with respect to the molecular plane of ZnP. Complexes 1 and 2 have the Fc molecule positioned above the porphyrin plane, the former with the Cp-Fe-Cp axis oriented parallel to the porphyrin plane and the latter with the axis that is almost normal to the porphyrin plane. The other two complexes, 3 and 4, on the other hand, have the Fc molecule interacting with the porphyrin’s edge made of CH bonds that are oriented outwardly with respect to the metal center.

The Fe-Zn distance (in Å), BSSE-corrected relative energy ($\Delta E_r$, in kcal/mol), BSSE-corrected binding energy with respect to the eclipsed (Fc-e) and staggered (Fc-s) ferrocene conformers ($E_b$(Fc-e) and $E_b$(Fc-s) in kcal/mol), dipole moment ($\mu$, in Debye), and Mulliken atom charges ($q_{Fe}$ and $q_{Zn}$ in atomic units) of the four Fc:ZnP complexes investigated in this study.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Fc*</th>
<th>$d_{Fe-Zn}$</th>
<th>$\Delta E_r$</th>
<th>$E_b$(Fc-e)</th>
<th>$E_b$(Fc-s)</th>
<th>$\mu$</th>
<th>$q_{Fe}$</th>
<th>$q_{Zn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>4.286</td>
<td>12.03</td>
<td>12.62</td>
<td>0.45</td>
<td>-1.74</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>V</td>
<td>4.743</td>
<td>10.95</td>
<td>11.54</td>
<td>0.63</td>
<td>-2.08</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>E</td>
<td>7.516</td>
<td>5.68</td>
<td>6.26</td>
<td>0.03</td>
<td>-1.83</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>8.608</td>
<td>3.45</td>
<td>4.04</td>
<td>0.42</td>
<td>-1.76</td>
<td>0.83</td>
<td></td>
</tr>
</tbody>
</table>

*H = horizontal; V = vertical; E = edge; C = corner.

Table 1 Orientation or position of Fc with respect to the ZnP plane, Fe-Zn distance ($d_{Fe-Zn}$ in Å), BSSE-corrected relative energy ($\Delta E_r$ in kcal/mol), BSSE-corrected binding energy with respect to the eclipsed (Fc-e) and staggered (Fc-s) ferrocene conformers ($E_b$(Fc-e) and $E_b$(Fc-s) in kcal/mol), dipole moment ($\mu$, in Debye), and Mulliken atom charges ($q_{Fe}$ and $q_{Zn}$ in atomic units) of the four Fc:ZnP complexes investigated in this study. Also reported in Table 1 is the magnitude of the electric dipole moment ($\mu$) of each Fc:ZnP complex along with the Mulliken charges of the two metal ions. We notice that the dipole moment of complex 3 where Fc interacts with one edge of the metal porphyrin (Fc-â:HC = 2.999 Å) is close to zero in magnitude thus indicating that the CT between Fc and ZnP is not effective for this particular orientation. The dipole moment with the largest magnitude is that of 2 ($\mu = 0.63$ D) where Fc is oriented perpendicularly with respect to the porphyrin plane while the dipole moments of 1 and 4 are slightly smaller in magnitude and close to 0.4 D. One must notice that the small dipoles of these four complexes are a consequence of the fact that both ZnP and Fc are non-polar molecules. The horizontal complex 1 is characterized by the shortest Fe-Zn distance (4.286 Å) which is likely to enhance CT effects. The magnitude of $\mu$ in 1, however, is slightly smaller than that of $\mu$ in 2 thus indicating that there is no clear correlation between $\mu$ and $E_b$. On the other hand, the Fe-Zn distance seems to correlate well with the computed binding energy: the shorter the metal-metal distance the stronger the interaction of Fc and ZnP within the complex (see Table 1).

As far as the Mulliken charges of the metal ions are concerned, we observe that Fe bears a negative charge whereas the charge on Zn is always positive. The different magnitude in the atom charges is a result of the CT effects that operate within each complex. However, when analyzing the atom charges one should bear in mind that the CT interaction is mediated by either one or both cyclopentadienyl (Cp) rings (formally each Cp ring bears a negative charge) which are equipped with six π-electrons. Taken together, the present results indicate that CT may occur either from Fc to ZnP or vice versa, depending upon the relative orientation of the two molecules within each complex.
4. Conclusions

In conclusion, our dispersion-corrected DFT calculations indicate that Fc and ZnP do interact with each other by forming (at least) four stable 1:1 complexes which are stabilized by CT interactions. The complexes (1 and 2) with the larger binding energy are those where the distance between the metal centers is smaller. It is expected that the co-crystal obtained from the crystallization of Fc and ZnP in a suitable solvent (e.g. benzene or toluene) may display the intermolecular interactions observed in the above complexes.

Acknowledgments

F.P. thanks the Department of Applied Chemistry of the Graduate School of Engineering (Tohoku University) for financial support.

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10) Gaussian 09, Revision C.01, M. J. Frisch et al., (Gaussian, Inc., Wallingford CT, 2009).