



## Molecular and Electronic Structure of Some Symmetrically *meso*-Substituted Hg(II)-Porphyrin Complexes

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A theoretical study on the effect of substituent group on the molecular and electronic structure of some *meso*-substituted Hg(II)-porphyrin complexes using DFT-B3LYP/LanL2DZ method had been performed. The calculation result showed that the molecular structure of the complexes and density of states abundance of virtual orbital is independent of the substituent group effect. The band gap energy and density of states abundance of occupied orbital however is decrease for the complexes with electron donating group.

**Keywords:** Mercury(II), Porphyrin, Hg(II)-porphyrin, Molecular structure, Semiconductor.

### INTRODUCTION

Porphyrin and its derivatives are known for their role in organism as part of enzymes, vitamins and even red blood cells. On the other side, porphyrin and its derivatives were also known for their unique photoreactivity [1,2] and narrow band gap for semiconductor applications. Some of porphyrin derivatives in the form of metalloporphyrin complexes has been proven to have the properties of a semiconductor materials such as Pt(II)-porphyrin, Fe(II)-porphyrin, Mg(II)-porphyrin and zinc group-porphyrin complexes [3-8].

Metalloporphyrin complexes performance as semiconducting materials is determined by the central ion of the complexes and the functional group that is substituted on the porphyrin ring [5,9]. We have previously discussed how those factors help us to design a better metalloporphyrin semiconductor by looking into the electronic structures of some *meso*-substituted M(II)-porphyrin (M = Pt, Cd, Hg) [9]. In this paper we will further discussed the both electronic and molecular structure and properties of some *meso*-substituted Hg(II)-porphyrin.

### EXPERIMENTAL

*meso*-Substituted Hg(II)-porphyrin complexes molecular model were used. There are 10 complexes coded as HgP-R where -R are -CH<sub>3</sub>, -CHO, -COOH, -F, -I, -NH<sub>2</sub>, -NO<sub>2</sub>, -OH and Ph (phenyl group) and non-substituted Hg(II)-porphyrin complex (HgP-H) were used as standard.

All calculation were performed on High Performance Computer on Direktorat Sistem dan Sumber Daya Informasi,

Universitas Gadjah Mada (DSSDI UGM) and Austrian-Indonesian Centre (AIC) for Computational Chemistry using Gaussian 09 package software [10] and GaussSum 2.2.5 [11].

**Geometry optimization:** Geometry optimization was performed using density functional theory (DFT) calculation using Becke's 3 parameters with Lee, Yang and Parr exchange-correlation function (B3LYP) [12-15] and Hay and Wadt LanL2DZ basis set on Gaussian 09 package software.

**Density of states:** Density of states calculation were performed using Landau algorithm on GaussSum 2.2.5 software (E = -10 – 0 eV).

### RESULTS AND DISCUSSION

**Calculation methods validation:** Validation of calculation method that were performed need to be done in order to justifies the accuracy of the method. The validity of the method were tested by comparing the calculation result with experimental result. In this research we compared the molecular structure of *meso*-(tetra-*p*-cyanophenyl)porphyrinatomercury(II) (Hg-TPPC) core from single crystal XRD measurement [16] with the DFT/B3LYP/LanL2DZ calculation result.

By comparing both result we can see that the average relative deviation of the calculation result is less than 2.5 % which mean that the DFT/B3LYP/LanL2DZ calculation is valid method to calculate the molecular structure of HgP-R.

**Molecular structure of HgP-R:** Porphyrin is an aromatic molecule, therefore both its molecular and dianionic structure are planar with D<sub>2h</sub> and D<sub>4h</sub> symmetry. Substituted metallo-

TABLE-1  
STRUCTURAL PARAMETERS OF HgP-R CORE

R	Bond length (Å)				Bond angle (°)					
	Hg-N <sub>1</sub>	Hg-N <sub>2</sub>	Hg-N <sub>3</sub>	Hg-N <sub>4</sub>	N <sub>1</sub> -Hg-N <sub>2</sub>	N <sub>1</sub> -Hg-N <sub>3</sub>	N <sub>1</sub> -Hg-N <sub>4</sub>	N <sub>2</sub> -Hg-N <sub>3</sub>	N <sub>2</sub> -Hg-N <sub>4</sub>	N <sub>3</sub> -Hg-N <sub>4</sub>
CH <sub>3</sub>	2.239	2.239	2.239	2.239	86.790	152.607	86.686	86.889	152.643	86.796
CHO	2.241	2.241	2.241	2.241	87.213	154.536	87.213	87.205	154.503	87.219
COOH	2.234	2.234	2.234	2.234	87.239	154.673	87.253	87.253	154.681	87.239
F	2.250	2.250	2.250	2.250	86.042	149.542	86.041	86.049	149.537	86.040
H	2.241	2.241	2.241	2.241	86.789	152.612	86.775	86.807	152.605	86.774
I	2.238	2.239	2.239	2.239	87.098	153.839	87.047	87.021	153.760	87.056
NH <sub>2</sub>	2.246	2.246	2.247	2.246	86.624	151.695	86.565	86.569	151.848	86.606
NO <sub>2</sub>	2.248	2.245	2.245	2.246	86.517	151.621	86.548	86.713	151.886	86.548
OH	2.241	2.251	2.245	2.248	86.477	149.625	85.999	86.710	151.791	86.175
Ph	2.242	2.224	2.242	2.224	87.429	151.543	87.447	87.442	159.058	87.491

porphyrin complexes structure however is dependent on the central ion and their substituent group. It had been showed that substituted Ni(II)-porphyrin complexes exhibit a negatively curved structure (hyperbolic) with nearly perfect D<sub>2d</sub> symmetry with the amount of curvature that varies according to the substituent group [8]. Hg(II)-porphyrin complexes however exhibit a structure with positive curvature (elliptic) with nearly perfect C<sub>4v</sub> symmetry.

Unlike Ni(II)-porphyrin, HgP-R curvature is independent of the substituent group. This effect is due the large size of Hg(II) ion, making the steric effect of the central ion become the dominant factor in determining the molecular structure over the substituent effect, therefore making the core structure of all the complexes nearly identical (Table-1).

**Electronic structure:** In order to discuss the effect of the different substituent group to the electronic structure of HgP-R, ones first have to realize that the electronic structure is a function of electronic density which mean that the substituent effect on the electronic structure will be more conclusive than to the molecular structure.

**Band gap and frontier orbitals energy:** Band gap energy is a parameter that determine the minimal energy requirement an electron needed to be excited from occupied orbitals to the virtual unoccupied orbitals. In molecular semiconductor, the band gap can be approximated by Kohn-Sham band gap that defined by the energy difference between the frontier orbitals (HOMO and LUMO).

The energy of the frontier orbitals and band gap of HgP-Rs are given in Table-2. Previous study [9] showed that electron withdrawing group tend decrease the orbitals energy, but increase the gap. This effect is due to the effect of the electron density shift on the stability of the orbital is bigger on the occupied orbital than the virtual orbitals, thus decrease the orbital energy, but increase the gap between the orbitals.

This effect however is not a linear effect because the strength of a group in shifting electron density is not the only factor. This violation of the electron density band gap relation is exhibited by HgP-CHO and HgP-CH<sub>3</sub>.

**Density of states (DOS):** Density of states is the measure of numbers of allowed states per unit volume in any given energy level. In semiconductor science, the density of states is the measure of the probability density of an electron recombine with hole after being excited from an occupied orbital to the virtual orbital. Higher DOS abundance near and below Fermi

TABLE-2  
FRONTIERS ORBITALS AND BAND  
GAP ENERGY OF HgP-R [Ref. 9]

R	E <sub>LUMO</sub> (eV)	E <sub>HOMO</sub> (eV)	E <sub>g</sub> (eV)
CH <sub>3</sub>	-2.32	-4.87	2.55
CHO	-4.01	-6.47	2.46
COOH	-3.43	-6.13	2.70
F	-3.14	-5.76	2.62
H	-2.49	-5.34	2.85
I	-3.14	-5.67	2.54
NH <sub>2</sub>	-1.67	-3.46	1.79
NO <sub>2</sub>	-4.53	-7.13	2.60
OH	-2.51	-4.67	2.16
C <sub>6</sub> H <sub>5</sub>	-2.47	-5.01	2.53

level energy mean that the probability of electron-hole recombination is high.

Table-3 showed DOS abundance of virtual orbital is relatively independent of the substituent group, while the DOS abundance of the occupied orbital is significantly affected by the different substituent group. Complexes with electron donating group tend to have lower abundance on occupied orbital because the group shift the electron density toward the porphyrin ring and centre of the complexes, occupying the allowed states, thus decrease the number of available state in any given energy level and decrease the DOS abundance. The same thing is also causing DOS abundance of virtual orbital not affected by the substituent group on the complexes because virtual orbital is unoccupied by the electron, therefore, the number of available state are independent of the substituent group.

TABLE-3  
DENSITY OF STATES OF THE FRONTIER ORBITALS OF HgP-R

R	DOS abundances (states eV <sup>-1</sup> nm <sup>-1</sup> )	
	HOMO	LUMO
CH <sub>3</sub>	0.99970	1.99343
CHO	1.20392	1.99714
COOH	1.46417	1.99833
F	0.99997	1.99945
H	1.18704	1.99232
I	0.82106	1.99861
NH <sub>2</sub>	0.99602	1.99672
NO <sub>2</sub>	1.57133	1.99816
OH	0.99786	1.75786
C <sub>6</sub> H <sub>5</sub>	1.00059	1.99658

## Conclusions

We have used DFT/B3LYP/LanL2DZ calculation to investigate the effect of different substituent groups on the electronic and molecular structure of HgP-R. The calculation result showed that the core molecular structure of the complexes are independent of substituent group due to the steric effect of the Hg(II) ion.

The electronic structure of the occupied orbitals on the other hand is significantly affected by the different substituent group because of its dependency on the electron density. Complexes with electron withdrawing group will have lower orbital energy due to the orbital stabilization, but higher band gap energy because of the stabilization affect the occupied orbital more than the virtual orbital. Density of states abundance exhibit similar characteristic where the DOS abundance of virtual orbital is not affected by the substituent group while the occupied orbitals DOS abundance will decrease on complexes with electron donating group due to the high electron density on the centre of the molecule.

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