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# Theoretical Study of Gallium Phthalocyanine Dimer-Fullerene Complex for Photovoltaic Device

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## Abstract

Geometry and electronic structures of gallium phthalocyanine dimer and fullerene molecules were investigated by theoretical calculation. The highest occupied molecular orbital was localized on the donor site, and the lowest unoccupied molecular orbital were localized on accepter site. The present results indicate that high conversion efficiency would be expected when phthalocyanine dimers were used as solar cell materials.

## 1. Introduction

Organic thin film solar cells are promising alternatives for low cost renewable energy, large-area fabrication on light weight, flexible substrates at low temperatures by coating and printing methods. Therefore, the organic solar cells are attractive for next generation solar cells. Metal phthalocyanines (MPc), which have photovoltaic property, heat-resistance, light-stability, chemical stability, and high optical absorption at visible range, are used for oxidation catalysts, catalysts of fuel cells and solar cells. An efficiency of ~5% was achieved for organic solar cells by employing small molecules such as copper phthalocyanine and fullerenes [1-4]. When the nearest neighbor two phthalocyanines with substituent such as amino group and hydroxy group are connected by hydrogen bridged substituent, high photoconduction was observed [5]. However, few phthalocyanine dimers have been reported, and high photoconduction can be expected for the covalently-bridged phthalocyanine dimers.

The purpose of the present work is to investigate molecular orbital of gallium phthalocyanine (GaPc) dimer and fullerene which is a good electronic accepter, and to examine this structure as solar cell material.

## 2. Method of Calculations

First principle calculations of the electronic properties have been used to predict the geometry of molecular structures and vibration spectra for phthalocyanine [6].

The optimized geometries and energies of all the present structures were calculated by *ab-initio* molecular orbital calculations using Gaussian 03. A detailed analysis of ground states of the electronic structures is based on self-consistent solutions of the Kohn-Sham (KS) molecular orbital model on density functional theory (DFT) with hybrid B3LYP function [7]. The KS equation is defined as an Equation (1).

$$\left[ -\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r-r'|}dr' + \frac{\partial E_{xc}\left[\rho(r)\right]}{\partial \rho} + \gamma(r) \right]\varphi_i = \epsilon_i \varphi_i \quad (1)$$

Exchange-correlation potential of the third term in the (1) is defined as the functional derivative of $E_{XC}[\rho(r)]$ with respect to $\rho(r)$. The isolated molecular structures were optimized by the DF calculation using restricted Hartree-Fock (RHF) and hybrid B3LYP function based on the Becke exchange function and the Lee-Yang-Parr correlation function, with the KS orbital expanded to LANL2DZ and STO-3G*, 3-31G* and 6-31G* basis sets. Electronic densities and energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and electronic densities were investigated.

## 3. Results and Discussion

**Figure 1** is a structure of $\mu$-oxo-bridged gallium phthalocyanine dimer used in the present study. Two GaPc planes are parallel to one another, and the rotational de
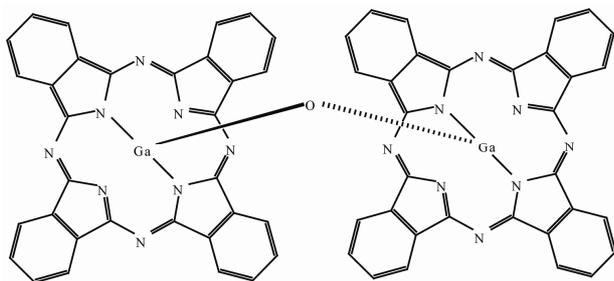
**Figure 1. Structure of *μ*-oxo-bridged gallium phthalocyanine dimer.**

grees are 41.35°. The plane distance between GaPc monomer is ~0.34 nm [8]. When the nearest neighbor two phthalocyanines is arranged with hydrogen bridged substituent, high photoconduction can be expected for the covalently-bridged phthalocyanine dimer.

**Figure 2** shows HOMO and LUMO energy levels of the GaPc dimer with $C_{60}$ after structural optimization using DFT/6-31G*. In **Figure 2**, electronic densities of

LUMO, LUMO+1, and LUMO+2 are localized for the fullerene side, while the HOMO is localized for the GaPc-dimer side, which suggests electron transfer between the GaPc dimer and fullerene. The similar localization of frontier orbital was previously reported for the other donor-fullerene supramolecular systems [9-11].

A schematic diagram of energy levels of GaPc dimer, $C_{60}$, and GaPc with $C_{60}$ is shown in **Figure 3**. The energy levels of the four highest occupied and four lowest unoccupied orbital levels are summarized in **Table 1**. It should be noted that the LUMO energy levels of the GaPc dimmer + $C_{60}$ are comparable to the LUMO energy levels of fullerene, and the HOMO energy levels of the GaPc dimer + $C_{60}$ are close to the HOMO energy levels of GaPc dimer. However, the symmetry of the GaPc dimer seems to be lowered because of decreasing of degeneracy, which would be due to the interaction with $C_{60}$.
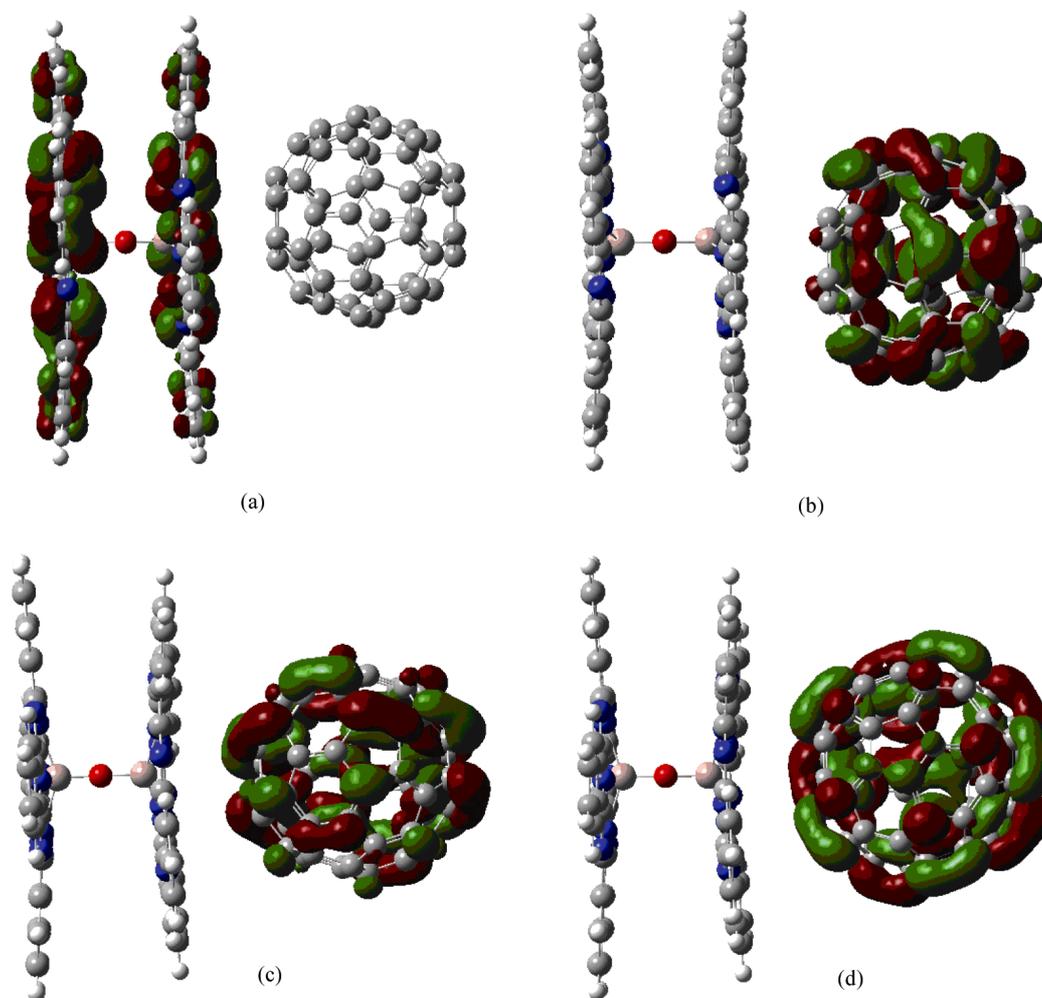
Electronic density of the GaPc dimer was widely dis-



(a)

(b)

(c)

(d)

**Figure 2. HOMO and LUMO energy levels of the GaPc dimer + $C_{60}$. (a) HOMO, (b) LUMO, (c) LUMO+1, and (d) LUMO+2.**
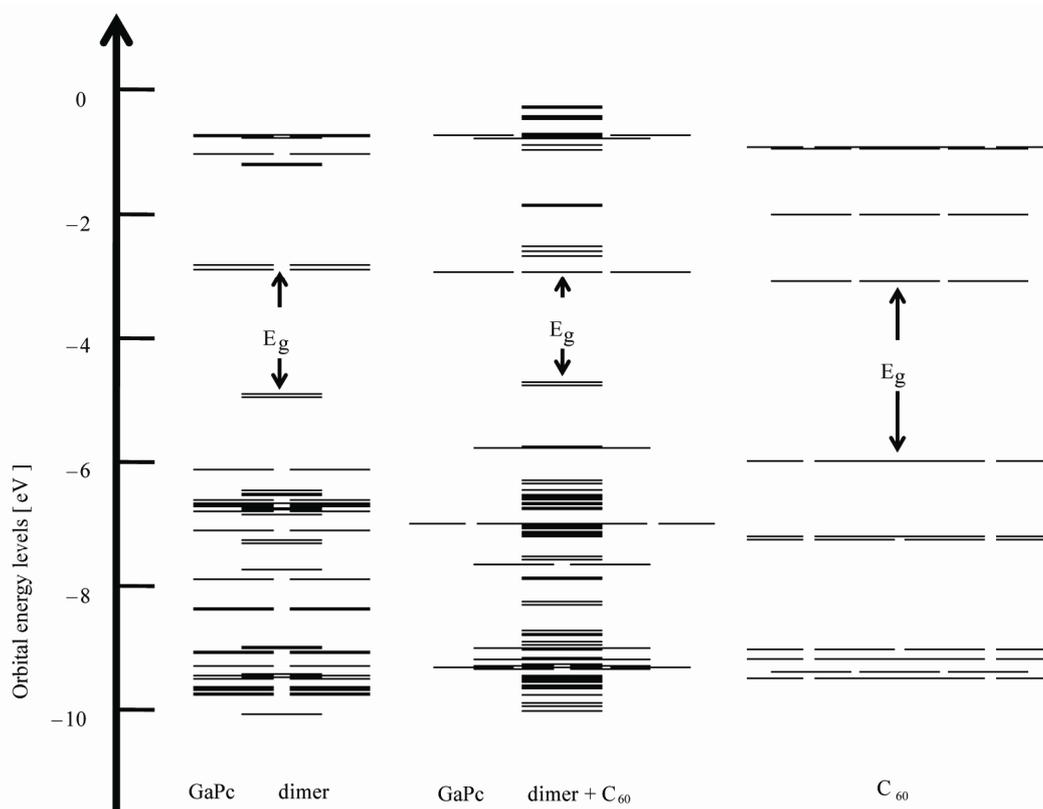
**Figure 3. Comparison of energy levels of GaPc dimer, $C_{60}$, and GaPc dimer with $C_{60}$.**

**Table 1. Comparison of the four highest occupied and four lowest unoccupied orbital levels.**

| States | GaPc dimer [eV] | GaPc dimer + $C_{60}$ [eV] | $C_{60}$ [eV] |
|---|---|---|---|
| LUMO+3 | −2.978 | −2.832 | −2.092 |
| LUMO+2 | −2.978 | −3.106 | −3.231 |
| LUMO+1 | −3.051 | −3.105 | −3.231 |
| LUMO | −3.051 | −3.103 | −3.231 |
| HOMO | −5.165 | −4.972 | −6.294 |
| HOMO−1 | −5.214 | −5.027 | −6.294 |
| HOMO−2 | −6.449 | −6.079 | −6.294 |
| HOMO−3 | −6.449 | −6.085 | −6.294 |

tributed around π orbital on the both aromatic rings as observed in **Figure 2(a)**. Energy levels of GaPc dimer at HOMO and LUMO were calculated to be −5.165 eV and −3.051 eV, as listed in **Table 1**. The energy level of GaPc dimer would indicate advantage of GaPc dimer for charge-transfer of the excited carriers to conduction band of $C_{60}$. The HOMO of GaPc dimer and the LUMO of $C_{60}$ is closely related with open circuit voltage ($V_{oc}$) of the solar cells, which is described by $V_{oc} = (1/e) (|E_{GaPc}HOMO| - |E_{C60}LUMO|) - 0.3$ (V), where e is the elementary change [12]. The value of 0.3 V is an empirical factor and this is enough for efficient charge separation [13,14]. The model of photovoltaic mechanism would be described by this equation, and the control of the energy levels is important for improving conversion efficiency. It is believed that the present GaPc dimer would be useful for the solar cells as previously reported fullerene-based supramolecules for high-performance photovoltaic devices [10], and excitation and charge transfer during light irradiation should be investigated further.

## 4. Conclusions

Geometry and electronic structure of phthalocyanine dimer-fullerene molecules were investigated by using *ab-initio* molecular orbital calculations, which indicated that the HOMOs were localized on the donor site and LUMOs were localized on accepter site. The present GaPc dimers would be expected as solar cell materials.

## 5. Acknowledgements

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# 6. References

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