

An Organic Molecule - Fullerene Mixture for a High Efficiency Photovoltaic Device: A Theoretical Study

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ABSTRACT

Many organic molecules such as phthalocyanine, porphyrin and naphthalocyanine possess good electron-donating properties due to their large easily ionized π -electron system, whereas fullerene is a good π -electron acceptor that can be readily connected with other organic molecules. Therefore, a compound consisting of an organic molecule connected to fullerene is a material that could potentially be used to fabricate a photovoltaic cell, due to its large and flexible absorption combined with electrical properties similar to those of an inorganic semiconductor. For this reason, many fullerene-based supramolecules have been proposed as potential organic photovoltaic devices, and their electrochemical and photo-electrochemical properties have been measured under light illumination. We investigated the geometric and electronic structure of an organic molecule - fullerene supramolecule using an *ab initio* quantum mechanical calculation. The results suggest that the LUMO state of this supramolecule localized on the fullerene and that the HOMO state is localized on the organic half of the molecule.

Keywords: phthalocyanine-fullerene supramolecule, molecular device, guest-host system, organic solar cell, photocurrent generation, simulation.

1 INTRODUCTION

Conjugated polymers emerged in the mid-eighties to early nineties, and were soon developed for a wide range of opto-electronic applications such as organic transistors, light emitting diodes and solar cells. The current general trend in research and development of photovoltaic elements is aimed at producing lower cost devices. Solar cells based solely on conjugated polymers have been disappointing because of their low quantum efficiencies. However, an encouraging breakthrough in the development of highly efficient materials has been achieved by mixing electron-donor type polymers with suitable electron acceptors [1,2]. Consequently, conjugated polymer-based photovoltaic elements have attracted much attention as a replacement for "silicone technology" and offer the possibility of cheap, easy to produce photovoltaic energy from light. The dual molecule approach, such as, using a conjugated

polymer/fullerene mixture, has been successful and is well documented [3-10]. This process mimics the early photo effects of natural photosynthesis [5-7].

Phthalocyanine has good electron-donating properties and fullerene is a good π -electron acceptor. Both of these molecules can be connected together [8]. In the present study, the genetics of the phthalocyanine-fullerene supramolecule were examined after optimization of the geometry. We explain in detail the numerical method that was used (Section II), along with the chemical structure and the results for various phthalocyanine-fullerene supramolecules (Section III).

2 MODEL AND NUMERICAL METHOD

The optimized geometries and energetics of all of the structural variables were obtained from first principles using the self-consistent Hartree-Fock (HF) method. All calculations were performed using the Gaussian98 program [11] along with HF theory and a suitable basis set. Because the supramolecules contain over 100 atoms, a smaller basis set was selected to save computation time. The molecular structure was energetically optimized to reach a stable structure using HF/3-21G level theory. After optimization, we investigated the localization of the frontier orbitals using a single point calculation. The spatial distribution of the frontier orbitals (HOMO and LUMO) provided a strategy by which the photovoltaic and electrochemical properties (such as charge separation) of the supramolecule could be understood.

3 RESULTS AND DISCUSSION

Figure 1 illustrates the chemical structure used in this study. These supramolecules have been reported in previous studies [8,9]. Many unimolecular polymer-fullerene supramolecules have been synthesized to examine their photovoltaic properties [5-7]. These molecules have a sigma bond between the polymer and the fullerene to realize the localization of the frontier orbital. However, the above supramolecule has van der Waals bonds instead of a sigma bond. In other words, these are only weak interactions.

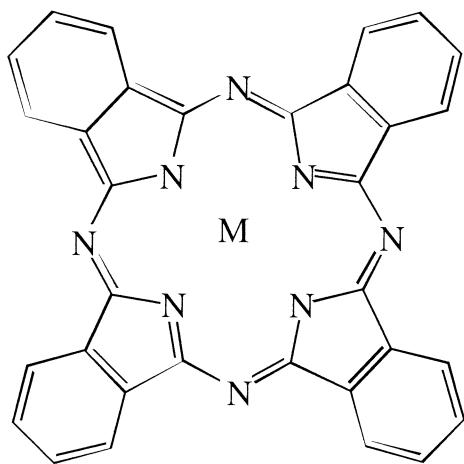


Figure 1: Chemical structure of phthalocyanine (M=2H, free base phthalocyanine, H₂-Pc; M=Zn, zinc phthalocyanine, Zn-Pc).

Figure 2 shows the optimized structure of a phthalocyanine-fullerene supramolecule using the HF/3-21G level. This structure is the low spin case of a zinc atom, which is more favorable than the high spin state. The planar structure of the free base phthalocyanine is retained with fullerene, whereas, a slight bending is observed with zinc phthalocyanine. The zinc atom protrudes from the plane of the phthalocyanine molecule towards the side of the fullerene. The distance between the zinc atom and the nearest carbon atom in fullerene is 2.54 Å. The zinc atom is the bridging site between the six-membered ring of the absorbed fullerene. We can see charge transfer from the fullerene to the zinc phthalocyanine, while there is no charge transfer to the free base phthalocyanine.

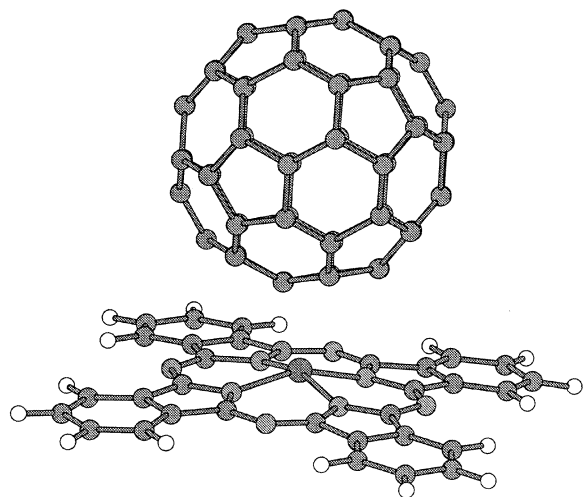
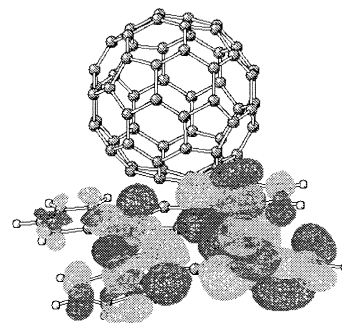


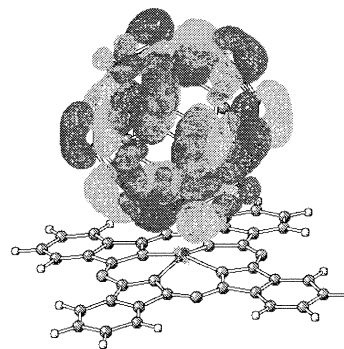
Figure 2: Optimized structure of zinc phthalocyanine-fullerene supramolecule (Zn-Pc + C₆₀).

To estimate the electron transport through this molecule, we have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), providing a strategy by which the photovoltaic properties of the phthalocyanine - fullerene supramolecule can be understood. Figure 3 shows the HOMO and LUMO+K (K=0, 1, 2, 3,...) distributions of this supramolecule. From Fig. 3, it is clear that for the phthalocyanine - fullerene supramolecule, the LUMO is localized on the acceptor, while the HOMO state is localized on the phthalocyanine half of the molecule.

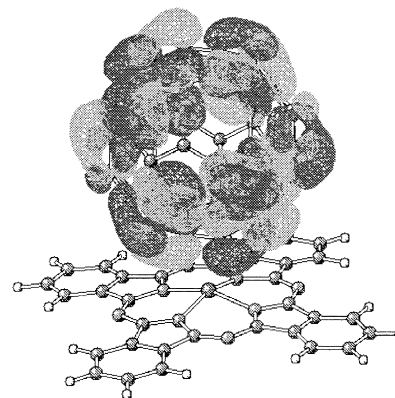
(a)



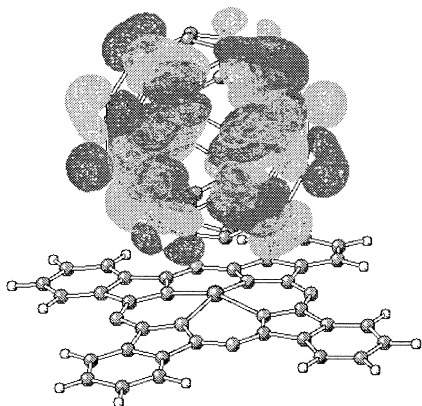
(b)



(c)



(d)



(e)

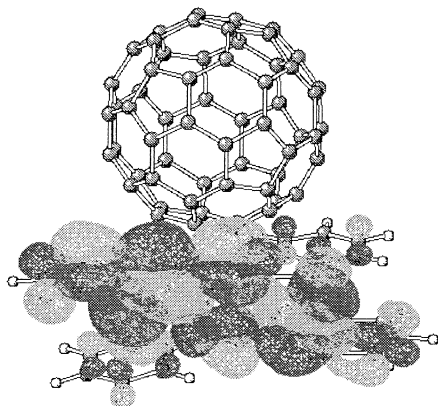


Figure 3: Orbital spatial orientation of HOMO and LUMO+K (K=0, 1, 2) for phthalocyanine - fullerene supramolecule. (a) HOMO, (b) LUMO, (c) LUMO+1, (d) LUMO+2, and (e) LUMO+3.

Figures 4 (a) and (b) compare the five highest occupied (HOMO) and five lowest unoccupied (LUMO) orbital levels for the optimized structure of the free base phthalocyanine, the fullerene and the phthalocyanine-fullerene supramolecule. It is interesting to note that while the LUMO energy levels of the supramolecule compare well with the LUMO energy level of the fullerene, the HOMO energy levels of the supramolecule are close to the HOMO energy levels of the phthalocyanine.

It has previously been reported that the tendency for localization of the frontier orbitals in other donor-fullerene(acceptor) supramolecular systems is the same [12, 13]. The main features and the difference in the energy levels are affected by the functional group on the donor and we can also see the same strategy in rectifier molecules with the same reported localization [14]. Finally, we made

calculations for other metal phthalocyanine and naphthalocyanine instead of zinc phthalocyanine. The same trend of localization of the frontier orbitals was observed [15].

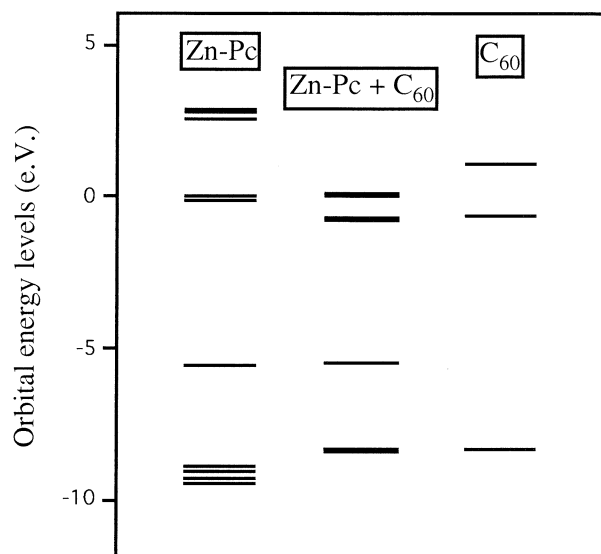


Figure 4: Comparison of the five highest occupied and five lowest unoccupied orbital levels. Pc, ZnPc-C₆₀ supramolecule, C₆₀.

From an application perspective, the polymer/fullerene mixture has attracted much attention as a potential candidate for organic solar cells due to its high efficiency [3,4]. Regardless of whether there is a mixed structure, we can summarize by saying that the donor and acceptor structure still remains.

4 CONCLUSIONS

The geometry and electronic structure of various phthalocyanine - fullerene supramolecules were computed using *ab-initio* calculations. The electron transport of the molecules was analyzed based on the spatial distribution of their frontier orbitals (HOMO and LUMO). It was found that the HOMO's were localized on the donor sub-unit and the LUMO's were localized on the acceptor sub-unit. The localization of the LUMO state on the donor moiety depended on the excess electrons and the acceptor group.

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