Molecular orbital analysis of frontier orbitals for molecular electronics:
a case study of unimolecular rectifier and photovoltaic cell

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Abstract
Recently, unimolecular devices have attracted significant attention as a ‘post-silicon technology’ to enable the fabrication of future nanoscale electronic devices. In this paper, we describe a candidate molecule for a rectifier function using porphyrin polymer and a photovoltaic cell using fullerene-based supramolecule. We have investigated the geometric and electronic structure of these organic molecules using an ab initio quantum mechanical calculation. These results for the porphyrin polymers show that the localization of the unoccupied orbital state on the acceptor moiety mostly depends on their structures. The calculated results for the electronic structure of a naphthalocyanine–fullerene supramolecule manifest that the HOMO’s were localized on the donor sub-unit and the LUMO’s were localized on the acceptor sub-unit.

Keywords: Molecular device; Molecular rectifier; Nanotechnology; Nanoelectronics; First-principles calculations; Photovoltaic cell

1. Introduction
For many years, progress in microelectronics has been associated with the reduction of the minimum feature size of integrated circuits. However, this trend, described by Moore’s law, seems to be ending due to process and physical limitations. The minimum device feature size is now approaching dimensions comparable with atomic and molecular sizes. In other words, ‘silicon technology’ has an intrinsic limitation in the near feature. To overcome this situation, the field of molecular electronics has attracted much attention as a ‘post-silicon technology.’ A quarter of a century ago, Aviram and Ratner \cite{1} first demonstrated how an organic molecule could function as a molecular device. Recently, this work has been further supported by a number of experimental results \cite{2–6} and several theoretical studies have been published \cite{7–13}. Nevertheless, the question regarding the properties of a relatively simple molecule and molecular systems remains unsettled, because the lack of suitable and effective technologies for measuring the conductance properties of an individual molecule, for example, the manipulation of a unimolecule and establishment of an electrical contacts.

Computer simulation a is useful tool in the field of molecular electronics, as the stable and electrical structures of a unimolecule are unknown and cannot be studied in detail by experiment. Our Institute has covered a wide range of molecular systems which have potential application in molecular electronics using first-principles calculations with a collaboration of experimental groups; molecular rectifiers \cite{14–16}, molecular enamel wires (covered wires) \cite{17–19}, molecular switches \cite{20}, molecular resonant tunneling diodes \cite{21,22}, molecular logic \cite{23}, connection between polymers and metal electrodes \cite{24,25}, Sb line on Si(001) \cite{26}, electronic transport though small molecules \cite{27–29}, bent carbon nanotubes \cite{30}, etc. In this paper, we present out recent investigations related to molecular electronics, using ab initio methods. All the calculations were performed using the \textsc{gaussian98} program \cite{31}.
2. Recent research activities

2.1. Molecular rectification using a porphyrin chain

The main challenge in the molecular electronics is to establish that single molecules or a finite number of self-assembled molecules can perform all the basic functions of conventional electronic components such as wires, diodes and transistors. The realization of a molecular device with a unimolecular rectifying function is one of the most important and fundamental requirements in nanotechnology. Aromatic molecules have π-conjugation systems through which electrons can flow easily. By substituting different functional groups on an aromatic system it is possible to increase or decrease the π-electron density and thereby creating acceptor (p-type) and donor (n-type) molecular subunits. Therefore, a rectifier could be built by combining these two molecular subunits between two electrodes, in which electrons can flow from cathode to the acceptor or from donor to the anode [14–16]. In this strategy to realize a rectifying function, HOMO and LUMO have to localize on a donor and an acceptor, respectively. Porphyrin possesses good electron-donating properties due to its large easily ionized π-electron system and a long molecular wire of fully conjugated porphyrin polymer has been reported by Tsuda and Osuka [32]. In this study, we propose that a rectifier diode can be created by combining two metal porphyrin molecules with different transition metal atoms. This porphyrin polymer would be a potential candidate for several applications: molecular wires in molecular electronics; materials for nonlinear optic devices; near-infrared (near-IR) dyes; spintronics devices, etc. In order to describe the electron transport through this polymer, we have analyzed the spatial distribution of the frontier orbitals (HOMO and LUMO), suggesting a strategy by which the rectifying properties of the porphyrin polymer can be understood.

Many configurations of porphyrin polymers have been already synthesized [32]. Fig. 1 indicates the different structures of porphyrin polymers investigated in this study. Fig. 1(a)–(c) are fully-, partially-, and non-conjugated free base porphyrin chains, respectively. These polymers have been chosen to permit the evaluation of the effect of the molecular structure on the localization of their frontier orbitals.

In this study, we investigate four porphyrin monomers, forming a metal-metal junction in a porphyrin polymer, inserting two transition metal porphyrins in the center of the polymer (see Fig. 2). Typical results of the orbital spatial distribution in a porphyrin polymer obtained by HF/6-311G are shown in Figs. 3–5 and Table 1. In Table 1, ‘No’ means that these molecules did not show the rectifying function. It is assumed that the unoccupied orbitals provide channels for electron conduction through the molecules. The difference in the energy of the lowest unoccupied levels between a donor and an acceptor was used to estimate a criterion (potential drop) of a rectifying function. The potential drop in a vacuum can be explained as the difference in the LUMO energies between the donor and acceptor molecules when they are widely separated \( \Delta E_{\text{LUMO}}(\infty) = E_{\text{LUMO}}(\text{donor}) - E_{\text{LUMO}}(\text{acceptor}) \) [14]. It is clearly seen from Fig. 3 that a full planar structure (fully conjugated) does not exhibit the rectification properties (except for the case of Cr–Cu in which the empty porphyrin plays donor function).

Fig. 1. Stable structure of (a) fully conjugated, (b) partially conjugated and (c) non-conjugated free base porphyrin chain at the HF/3-21G level.

Fig. 2. Four porphyrin monomers, arranged as a metal–metal junction in porphyrin chain.

Fig. 3. Orbital spatial orientation of the frontier orbital for the Zn–Fe pair in fully conjugated porphyrin chain. (a) HOMO, (b) LUMO, and (c) LUMO + 1.
Moreover, similar results are obtained for a partially conjugated chain. Fig. 4 clearly indicates that HOMO and LUMO are delocalized on a whole polymer. A rectifier is reported in the case of a D(donor)–p-A(acceptor) structure [33,34], even though, this porphyrin polymer does not exhibit the localized frontier orbital. However, a non-conjugated chain displays rectifying features (Cr–Cu and Zn–Fe). HOMO and LUMO + 5 for Cr–Cu in the non-conjugated polymer form the localized donor side (Cu porphyrin) and LUMO forms the localized acceptor side (Cr porphyrin). Consequently, these results together with previous reports [14–16] indicate that the geometry of spacer plays an important role in localizing the frontier orbitals.

2.2. Molecular photovoltaic cell

Conjugated polymers emerged in the mid-80s to early-90s and were 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 on conjugated polymers alone 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 [35,36]. Accordingly, photovoltaic elements based on conjugated polymer, have attracted much attention as a replacement for ‘silicon technology’ and offer the possibility of cheap, easily produced, photovoltaic energy from light. Naphthalocyanine and phthalocyanine possess good electron-donating properties due to their large easily ionized π-electron systems, whereas fullerene is good π-electron acceptor which can be bonded to other organic molecules. A naphthalocyanine–fullerene based supramolecular system is therefore a potential material for a photovoltaic cell due to its large and flexible absorption combined with electrical properties similar to those of an inorganic semiconductor.

Fig. 6 presents the chemical structure naphthalocyanine as a donor used in this study. These supramolecules have been reported in previous studies [37,38]. Many unimolecular
polymer–fullerene supramolecules have been synthesized for photovoltaic property [39]. These molecules have a σ-bond between the polymer and the fullerene to establish the localization of the frontier orbital. However, the above supramolecule have van der Waals bond instead of a σ-bond.

Fig. 7 shows the optimized structure of a naphthalocyanine–fullerene supramolecule using the HF/3-21G level.

This structure contains the Zn atom in the low spin state. The planar structure of the free base naphthalocyanine is retained with fullerene, whereas, a slight bending is observed in zinc naphthalocyanine. The zinc atom is

Fig. 7. Optimized structure of (a) a free base naphthalocyanine–fullerene supramolecule (H2-Nc + C60) and (b) a zinc naphthalocyanine–fullerene supramolecule (ZnNc + C60).

Fig. 8. Orbital spatial orientation of HOMO and LUMO + $K$ ($K = 0, 1, 2$) in phthalocyanine–fullerene supramolecule. (a) HOMO, (b) LUMO, (c) LUMO + 3.
protruding from plane of the naphthalocyanine molecule to the side of fullerene. The distance between the zinc atom and the nearest carbon atom in fullerene is 2.54 Å. The zinc atom is the bridge site between six-member ring of the absorbed fullerene. We can observe the charge transfer from the fullerene to zinc naphthalocyanine while there is no charge transfer to free-base naphthalocyanine.

To estimate the electron transport through this molecule, we have analyzed the spatial distribution of the frontier orbitals (HOMO and LUMO), providing a strategy by which the photovoltaic properties of the naphthalocyanine fullerene supramolecule can be understood. Fig. 8 indicates the spatial orientation for the molecular orbital spatial for the HOMO, LUMO, and LUMO + 3 energy levels of the naphthalocyanine fullerene complex. It is clearly seen from Fig. 8 that for naphthalocyanine fullerene supramolecule the LUMO is localized on the acceptor side, while the HOMO and LUMO + 3 is localized on the donor side.

Fig. 9(a) and (b) compares the five highest occupied and five lowest unoccupied orbital levels for the optimized structure of the free base naphthalocyanine, fullerene, and the naphthalocyanine fullerene supramolecule. It is interesting to note that the LUMO energy levels of the supramolecule compare well with the LUMO energy level of fullerene, and the HOMO energy levels of the supramolecule are close to the HOMO energy levels of the naphthalocyanine. It has been reported previously that the tendency for localization of the frontier orbitals of other donor fullerene (acceptor) supramolecular systems is similar [40,41].

3. Conclusions

The geometry and electronic structure of molecules selected as candidates for application in molecular devices have been calculated using an ab initio approach. The electron transport in these molecules has been analyzed, based on the spatial distribution of the frontier orbitals. The localization of the unoccupied orbital state on the acceptor moiety mostly depends on the structure of the porphyrin polymer. 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. Regardless of whether there is a mixed structure, the donor and acceptor structure still remains. The calculated results for the electronic structure of a naphthalocyanine fullerene supramolecule manifest that the HOMOs were localized on the donor sub-unit and the LUMOs were localized on the acceptor sub-unit. This research is continuing, and should be explored by employing more high accurate method and using a combinatorial approach.

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