Tight-Binding Calculation of Electrical Properties of a Single Molecule Connected to a Few Semi-Infinite Electrodes

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We have investigated current distribution in a porphin molecule connected to a few electrodes by tight-binding calculation. The phenomenon that the current in the molecule becomes larger than the incident one, which is predicted for two electrode systems of the same and several other molecules, was found to occur also in the three electrode case. Currents in all four pyrrole rings in the porphin are nearly the same in the case of the two electrodes regardless of electrode positions and incident electron energies. On the other hand, currents in two pyrrole rings are often much larger than those in the other two rings in the three electrode cases, including the case where the length of the third electrode is finite. We also found that the number of rings where current is larger than in the other rings is related to the electrode positions and incident electron energy.
Key words: porphin, porphyrin, tight-binding method, current distribution, electric current

1. INTRODUCTION

Since Aviram and Ratner proposed the concept of molecular diode [1], molecular devices have been attracted much attention because they have possibility of providing a way of device miniaturization of devices which is different from that of the silicon devices [2,3]. Moreover, owing to the progress of technology such as the development of scanning probe microscopes in the early 1980s, it becomes possible these days to measure electrical properties of single molecules experimentally [4-7]. For example, Cui *et al.* reported that current-voltage curves measured by an AFM tip on a alkane thiol adlayer are quantized as integer multiples of one fundamental curve. This suggests that a single molecule is involved in electrical transport in the case of the fundamental curve [6]. Further, these situations have stimulated theoretical calculations on the electrical properties of single molecules [8,9], and several interesting results have been reported. For instance, Nakanishi *et al.* found that currents larger than the incident one appear in a C_{60} molecule between semi-infinite carbon electrodes [9].

As molecules suitable for single molecular devices, porphyrins, which are derivatives of porphin molecule, are promising, because they are expected to have relatively high conductivity owing to their π-conjugated states and controllable aggregation is possible [10-13]. Several interesting porphyrins, which may be useful in realizing single molecular devices, are synthesized such as porphyrin oligomers up to 128-mer [11] and a mandala-patterned bandana-shaped porphyrin [12]. However, electrical properties of single or a few porphyrins connected to electrodes have not been clarified yet. Very recently, several theoretical studies have been reported concerning electrical properties of molecules in the porphyrin family. Tagami and his collaborators examined porphyrin wires [14-16], and found an interesting phenomenon about magnetic moment induced in the molecule. We examined porphin molecule, and found that current directions on two paths which connect the electrodes are opposite in certain electron energies and positions of electrodes [17]. However, all of these theoretical studies treated porphyrins connected to two electrodes. Considering the fact that the many electrical devices at present, like MOS FET, are based on three electrode systems, it would be interesting and important to investigate electrical properties of porphyrins connected to three electrodes. Further, it is worth noting that even for other molecules, only a few theoretical calculations have been reported on the electrical properties of three electrodes systems.

In this paper, we present the results of our tight-binding calculations on the electrical properties of a porphin molecule connected to electrodes, including three electrode systems. We show that distinct difference is seen in the current distribution in a porphin between two and three electrode systems.

2. MODEL AND METHOD

As in our previous study [17], we adopted tight-binding method within the Hückel approximation and semi-infinite electrodes represented by one-dimensional C atomic chains for simplicity. Parameters used in the calculation were taken from the literature [18]. Though current could depend upon the choice of electrodes, we can expect to see important qualitative features by this simple model, such as the change of current distribution by positions and the number of electrodes. We considered the case where an electron is injected from an electrode (source), and partially transmitted to the other electrodes (drain). The wave functions in the semi-infinite electrodes can be obtained easily. After obtaining them, wave functions in the whole region for a given energy of an incident electron can be obtained by solving a closed set of simultaneous

linear equations for coefficients of atomic orbitals in the molecule together with transmission and reflection coefficients. Once the total wave functions are obtained, electric current between an atom and adjacent atom can be calculated.

3. RESULTS

3.1 Two electrode system

Though we have already reported the electrical properties in two electrode system [17], we summarize them here to make comparison with those in three electrode systems easy, showing an example which is not presented in the previous paper [17]. Figure 1 shows the calculated current distribution in the porphin in an example of the two electrode systems. In this case, the source and drain electrodes are attached to β and meso positions, respectively. Here, the definitions of β and meso positions are given in the inset in Fig. 1, together with that of another symmetrically independent position, α. Incident electron energy E is set to be -1.5654 eV. It is noted that four decimal digits is needed to specify energies, because sharp resonance occurs in some cases.

From this figure, first we can see that the current in the porphin molecule is larger than the incident one. For example, currents through the carbon atoms bridging two pyrrole rings are about 10 times larger than incident one. Such large currents were predicted previously in other molecules [9].

A more interesting feature seen in Fig. 1 is opposite current direction in the two paths connecting the source and drain electrodes. Except for branches within the pyrrole rings, two paths always exist in this molecule. In the case of the example shown in Fig. 1, the current direction of the shorter path, which includes the path having the definition of I_1, is opposite to the direction in the longer path and in the source electrode.

In Fig. 2, we show the energy dependence of I_1/I_t for the cases where the electrode positions are the same as those shown in Fig. 1. Keeping in minds that the current directions along the two paths are the same for $0 < I_1/I_t < 1$ and opposite for $I_1/I_t < 0$ and $I_1/I_t > 1$, we can say that the current directions become opposite for considerable fraction of the energy range corresponding to the energy band of the one-dimensional electrodes. These features are also seen in another example presented in our previous paper [17], and thus considered as the common
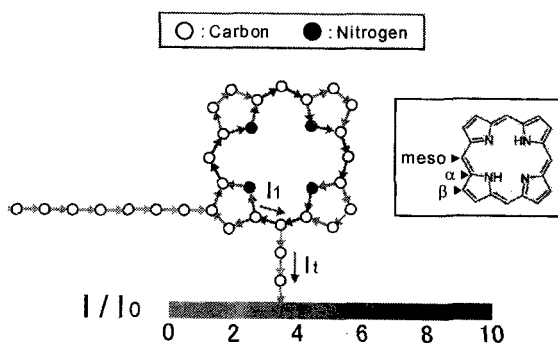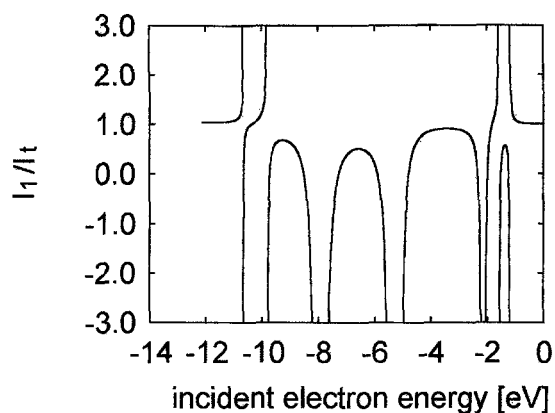

Fig. 2. Energy dependence of I_1/I_t. Here, I_1 is the current at the position indicated in the figure, and I_t is the total current between the two electrodes. The electrode positions are the same as those in Fig. 1.

feature of two electrode systems of the porphin.

Though we did not clearly mention in Ref. 17, another interesting feature is seen in Fig. 1: the currents in the four pyrrole rings are nearly the same. Examining various cases of electrode positions and incident energies, we found that the currents in the four pyrrole rings are nearly the same in most cases where current larger than the incident one appears in the porphin.

3.2 Three electrode systems

First, we show current distribution in the porphin connected to three electrodes in Fig. 3. Here, E was set to be -9.7880 eV. We found again that the currents in the porphin are larger than the incident one: currents in two pyrrole rings where electrodes are connected are about 7 times larger than the incident one. On the other hand, we can also see a feature that is not seen in the case of the two electrode systems in Fig. 3: large currents appear only in two of the four pyrrole rings, and thus we can say the current distribution in this case is much less uniform than in the two electrode systems.

Next, we examined whether the above non-uniform current distribution is a common feature of three electrode systems or not. Figure 4 shows average currents in respective pyrrole rings for various cases of electrode positions. Though we have examined all the

Fig. 1. Calculated current distribution in the porphin molecule in an example of two electrode systems. Inset shows the definitions of α, β and meso positions.
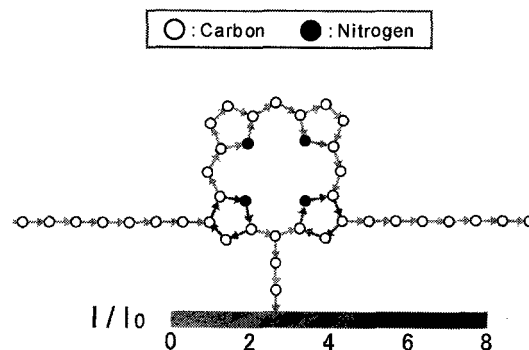

Fig. 3. Calculated current distribution in the porphin in an example of three electrode systems.
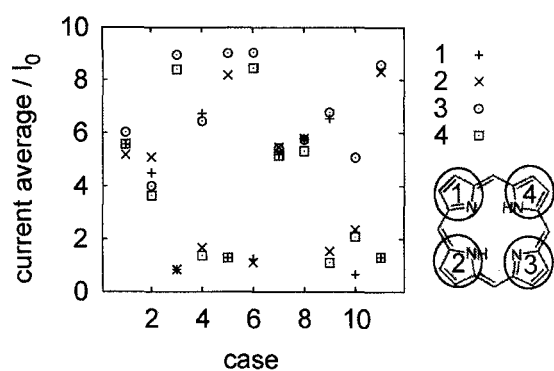
Fig. 4. Average currents in respective pyrrole rings. Each case corresponds to a certain combination of electrode positions. Incident energies are adjusted to give maximum currents for respective cases. Only cases where one of I/I_0 is more than 5 are plotted.

possible combinations of electrode positions, only cases where currents larger than the incident one appear are shown in Fig. 4. We can see that there are many cases where large currents appear in only two pyrrole rings. On the other hand, we also notice several cases where currents in all the four pyrrole rings are nearly the same, together with an exceptional case where current in only one pyrrole ring is larger then those in the other pyrrole rings. Therefore, we can classify the all cases into three types by the relative current distribution among the four rings.

By examining all the cases shown in Fig. 4 closely, we found a correlation between the above three types and the two factors, electrode positions and the incident electron energy which gives maximum current for the given electrode positions, though a few exception exists. Namely, in the cases where currents in two pyrrole rings are much larger than in the other rings, electrodes are attached to meso or β positions and the incident electron energy is ~ -9.790 eV. On the other hand, at least one electrode are attached to α position and incident electron energy is ~ -1.563 eV in the cases where currents in four pyrrole rings are nearly the same or large current appears only in one pyrrole ring.

To get an insight on the above correlation, we have examined transmission rates of incident electrons in a simple system shown in the inset in Fig. 5. The system is
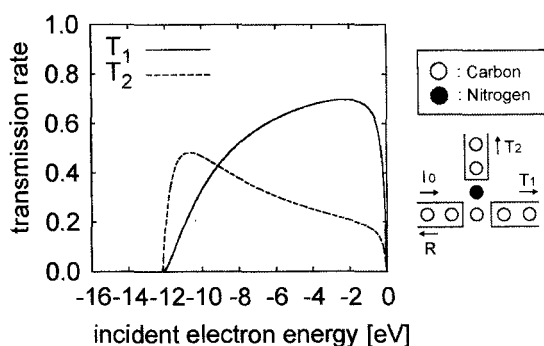
a junction of three semi-infinite C chains, and only a C atom next to the junction point is replaced by a N atom. The figure shows that when E is ~ -1.563 eV, the transmission rate for the path including the N atom is much smaller than the other path. On the other hand, when E is ~ -9.790 eV, the transmission rates for the two paths are nearly the same. This feature may be a clue to understand the above correlation as follows. In E ~ -1.563 eV, we can neglect the branching in the pyrrole rings in a rough approximation, while the branching is essential in E ~ -9.790 eV. In the cases where many branches exist, electrons interfere complicatedly, and this interference is considered to often make the current distribution less uniform. On the other hand, when there is no branching in a molecule, the current distribution tends to be more uniform because of the current conservation. This idea is partially supported by the current distributions in the cases shown in fig. 4: we found that the difference in the currents between the N atom and C atom sides in the pyrrole rings is small in many cases where E giving the maximum current is ~ -9.790 eV, while currents in the C atom side are much larger in all the cases where E giving the maximum current is ~ -1.563 eV. We, however, recognize that the origin of the correlation between the type and two factors, incident energy and electrode positions, has not been clarified sufficiently yet by the above explanation. In particular, we can give plausible explanation for neither the reason why large current appears in only one ring in a case nor the origin of the correlation between the type and electrode positions. Clarifying these points remains as the future task.

Finally, we have also examined the cases where the length of the third electrode is finite. In Fig. 6, we show the average currents in the lower two pyrrole rings and the upper two ones as a function of the length of the third electrode. The incident energy is set to be -9.7880 eV. As can be seen in this figure, the average currents oscillate periodically as the number of atoms in third electrode increases. This can be understood from the interference of electron waves in the electrode. A notable feature seen in Fig. 6 is that the average current in the upper pyrrole rings are larger than that in the lower ones in most cases, and thus the current distribution is non-uniform. This suggests that the

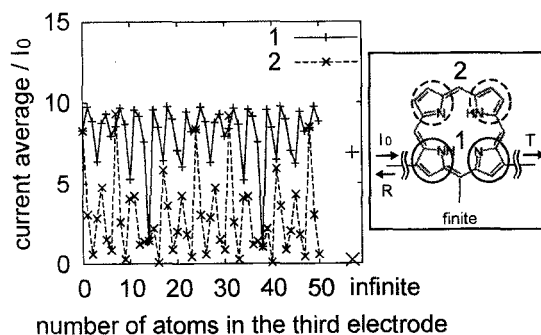Fig. 5. Calculated transmission rates for the system shown in the right inset.

Fig. 6. Average currents in the lower two pyrrole rings (denoted by 1) and the upper two ones (2) in the cases where the length of the third electrode is finite. The incident energy is set to be -9.7880 eV.

uniform current distribution seen in the two electrode systems may be not the general feature applicable to wide range of molecules, but peculiar to the porphin or molecules having high symmetry like porphin.

4. SUMMARY

We have calculated electrical properties of a porphin molecule connected to a few electrodes by tight-binding method. The phenomenon that the current in the molecule becomes larger than the incident one, which is predicted for two electrode systems of the same and several other molecules, was found to occur also in the three electrode case. Currents in all four pyrrole rings in the porphin are nearly the same in the case of the two electrodes regardless of electrode positions and incident electron energies. On the other hand, currents in two pyrrole rings are often much larger than those in the other two rings in the three electrode cases, including the case where the length of the third electrode is finite. We also found a correlation between the number of rings where current is larger than in the other rings and two factors, namely the electrode positions and incident electron energy.

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