Chemical contact promising for coherent transport through tape-porphyrin molecular bridges

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In this paper we investigated the coherent electronic transport properties of molecular bridges where the tape-shaped oligoporphyrin molecular wires, called as the tape-porphyrins, are bridged between the two gold electrodes by thiolate (S-Au) bonds. In particular, we focused on effects of the chemical contact at molecule/electrode interfaces on the transmission spectra. Namely, we studied the dependence of the transmission spectra on the atomic sites where S-Au bonds are connected to the tape-porphyrin molecule, their dependence on the additional spacing functional group between the tape-porphyrin molecular edge and the S-Au bonds. When the S-Au bonds are connected to the meso atomic sites of the tape-porphyrin molecule, several resonant peaks with large amplitudes are observed around the Fermi level, which indicates that the assumed molecular bridge is conducting even at lower bias voltages. As long as they are connected to the meso sites, the transmission peaks do not change their amplitudes significantly, even if the phenyl ring is inserted between the S-Au bond and the tape-porphyrin. However, if the bulky substituents are additionally introduced at the β atomic sites, the steric rotation of the phenyl ring is considered to dramatically suppress the transmission through the molecular bridge. [DOI: 10.1380/ejssnt.2003.45]

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I. INTRODUCTION

Among various molecular wires synthesized so far [1–4], tape-shaped oligoporphyrin molecules have attracted much attention due to their extremely small HOMO-LUMO energy gaps [5–7]. For example, the gap was measured to be about 250 meV for the hexamer molecule in the scanning tunneling spectroscopy (STS) [8]. The building block of these molecules is a porphyrin ring, usually called as a macrocycle, which is fully conjugated by three C-C bonds, i.e., meso-meso-, β-β-, β-β- bonds. They have been found to assume planar structures and be stable in air. Thus the tape-shaped porphyrins, which we call the tape-porphyrins, are expected as candidates of conducting molecular wires. These considerations have been confirmed in our previous works where the coherent transport properties were studied by theoretical simulations, assuming close contact with wide area at the molecule/electrode interfaces [6, 7].

From synthetic viewpoints, however, such an ideal contact formation seems to be hardly realized. Rather, it is easier to make a contact using a selective chemical bonding such as a thiolate (S-Au) bond. As the tape-porphyrin molecular wires do not have sulfur atoms in their original forms, the thiol (S-H) bonds should be introduced at both ends of the molecules by a synthetic approach. Note here that when an S-H bond comes close to and reacts with an Au atom on the electrode, the H atom is removed and then an S-Au bond is formed. But, there remain several problems to be solved, i.e., the suitable atomic sites where S-H bonds should be connected, the effects of the additional spacing functional group between the tape-porphyrin and the S-H bonds, and so on. In the present work, therefore, we will attempt to clarify how these factors affect the quantum transport properties of the tape-porphyrin molecular bridges.

II. MODEL AND METHOD

To investigate the electronic transport properties, the left and right gold electrodes are assumed to extend semi-ininitely along a certain one-dimensional direction. The shape of both electrodes is assumed to be a rod-like structure whose diameter is about 10 Å. The interatomic distance in each electrode is set to 2,88 Å which is the nearest neighbor distance of the gold crystal at the fcc phase. The tape-porphyrin molecules are assumed to bridge the two

FIG. 1: Structures of molecular bridges where tape-porphyrin molecular wires are bridged between left and right gold electrodes (shaded). The mercapto-vinyl groups are assumed to be connected to the molecule at the (A) meso and (B,C) β atomic sites.

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FIG. 2: Transmission spectra of molecular bridges A, B, and C defined in Fig. 1. The origin of the energy is set to the Fermi level of the gold electrode.

electrodes by some functional groups which contain S-Au bonds. At the center site of each macrocycle the hydrogen atoms are assumed to be coordinated; namely, the free-base tape-porphyrins are considered in this work.

The electronic states and the charge distributions of these molecular bridge systems are obtained with the self-consistent tight-binding model based on the density-functional theory [9, 10]. In the past this model has been successfully applied not only to inorganic materials such as GaAs [11] but also to organic materials such as porphyrin molecules [6, 7, 12] and DNA molecules [13, 14]. It has been also applied in researches on clusters interacting with silicon surfaces [15–18].

In addition, in order to treat the infinite size of the modeled systems, we adopt the extended-molecule approach [20, 21]. In this theoretical approach the system is divided into three parts, i.e., the left electrode, the scattering region, and the right electrode. Here the molecules and a fraction of the electrodes are considered as the scattering region. In our case the molecules and 34 Au edge atoms on both electrodes are included in the scattering region. Accordingly, the Hamiltonian matrix $H$ and the overlap matrix $S$ are divided into $3 \times 3$ sections. The matrix elements which correspond to the intra-electrode interactions and the electrode-scattering region couplings are included in the matrix elements of the scattering region as the electrode Green's functions and the self-energy terms, respectively [22]. Once the charge distribution is converged, the transmission spectrum is quantitatively evaluated by the Landauer formula [20]. The details of the formalism denoted above is discussed elsewhere [23].

In the followings, first, we will present the dependence of the transmission spectra on the atomic sites where S-Au bonds are connected. Then we will explore effects of additional spacing functional groups between the tape-porphyrin and the S-Au bonds.

III. RESULTS

A. Meso- or $\beta$-substitution

Figure 1 illustrates the molecular bridge structures where the tape-porphyrins are bridged between the left and right gold electrodes, shown by the shaded regions, through two thiolate-containing functional groups, called...
as the mercapto-vinyl groups. We assume the octamer tape-porphyrin molecules, which indicates that the number $n$ in the figure is 6. In the type-A structure, these functional groups are connected to meso sites of the tape-porphyrin molecule, while in the type-B and C structures, they are connected to the $\beta$ sites. The difference between the latter two cases is whether the relative locations of the two thiolate bonds are parallel to the tape-porphyrin wire or not.

The structures of these edge-substituted tape-porphyrin molecular wires are prepared as follows. First, the repeating unit of the isolated tape-porphyrin wires is determined from the structure of a di-porphyrin molecule which is optimized by an ab-initio calculation, using the B3LYP exchange-correlation functional [24, 25] and the LANL2DZ bases. Namely, it is obtained from the central half of this dimer molecule. By linking this building unit, the longer molecular wires can be achieved. Next the structures of the remaining parts of the fabricated wire, which include the end halves of the tape-porphyrin and the attached mercapto-vinyl groups, are determined from the optimized structure of the mono-porphyrin molecule, one of whose atomic sites is meso- or $\beta$-substituted with the mercapto-vinyl group. Combing these two kinds of components, the structure of the thiol-containing tape-porphyrin of arbitrary length is obtained. Further geometrical optimizations of these longer molecules are not performed due to the limitation of computational resources. Finally, the end H atoms bonded to S atoms are replaced by the Au atoms on the electrodes.

Figure 2 shows the transmission spectra for these three types of molecular bridges. The origin of the energy is set to the Fermi level of the gold electrode. In each plot the resonant peak just below the Fermi level corresponds to the HOMO of the octamer tape-porphyrin molecule. The first resonant peak seen above the Fermi level corresponds to the LUMO of the molecule. In a similar way, the other peaks are attributed to the other molecular energy levels. The broadened peaks around $E=-0.50$ eV seen in the type-B and C structures indicate that the mercapto-vinyl group connected to the $\beta$ atomic site couples well with the tape-porphyrin wavefunctions at this energy range. The most striking in Fig. 2 is the point that in the type-A structure the resonant peaks with large amplitudes are observed just below and above the Fermi level. Besides, at the Fermi level, the conductance $G(E_F)$ takes as large a value as 0.04 $G_0$, where $G_0$ is a quantum conductance. In the other structures, in contrast, $G(E_F)$ are found to take much smaller values. Therefore, we can conclude that as long as the tape-porphyrin is coupled to the electrodes through the meso atomic sites, the molecular bridge can be conducting even at lower bias voltages.

Finally, we briefly comment on the origin of the different transmission amplitudes between the above three cases. A porphyrin macrocycle is composed of four pyrrole subunits; two pyrrole subunits have hydrogen atoms at the N atom sites, while the other two pyrrole subunits do not. Thus the $\beta$ sites of the macrocycle are not identical in the case of free-base porphyrins. Here, we refer to the $\beta$ site of the former as $\beta_1$ site, and that of the latter as $\beta_2$ site. Around the Fermi level, the electron density is found to be large in the order of the meso, $\beta_1$, $\beta_2$ sites. Thus, the transmission spectra in the type-A structure, where the mercapto-vinyl groups are connected to the meso sites, have the largest amplitudes. In the type-C structure these functional groups are connected to the $\beta_1$ sites at both ends, while in the type-B structure they are connected to the $\beta_1$ (left) and $\beta_2$ (right) sites. Therefore, the transmission amplitudes in the former are slightly larger than those in the latter (see Fig.2).

FIG. 3: Structures of molecular bridges where tape-porphyrin molecular wires are bridged between left and right gold electrodes (shaded). (D) The mercapto-phenyl, (E) mercapto-phenylene-vinyl, and (F) mercapto-phenylene-ethynyl groups are assumed to be connected to the molecule at the meso atomic sites.
FIG. 4: Transmission spectra of molecular bridges D, E, and F defined in Fig. 3. The origin of the energy is set to the Fermi level of the gold electrode.

B. insertion of phenyl group

In the above discussion, the mercapto-vinyl groups are assumed to lie between the electrodes and tape-porphyrin molecule. But, in research field of monomer porphyrin molecules, the phenyl group is the representative of the substituents. Thus, from the synthetic viewpoint of tape-porphyrin molecular bridges, it seems significant to clarify effects of the phenyl groups on the transmission spectra. Therefore, in the followings, we will present the transmission spectra in the case the phenyl groups are spaced between the thiolate and tape-porphyrin molecules. Hereafter these substituent functional groups are assumed to be connected to the meso sites of the tape-porphyrin molecular wire.

Figure 3 illustrates the molecular bridge structures where the tape-porphyrins are linked to the left and right electrodes by the (D) mercapto-phenyl and (E) mercapto-phenylene-vinyl, (F) mercapto-phenylene-ethyl groups. In the last two cases the vinyl and ethynyl groups are inserted between the phenyl group and the tape-porphyrin molecules, respectively. The structures of these modified wires are prepared from the ab-initio (B3LYP/LANL2DZ) calculations in a similar manner to those mentioned previously.

Figure 4 shows the transmission spectra for these three types of molecular bridges. Again in each plot the origin of the energy is set to the Fermi level of the gold electrode. The heights and widths of the resonant transmission peaks observed in the type-D structure are found to be slightly smaller than those observed in the other two structures, in spite of the shorter inter-electrode distance.

Such reduced transmission probabilities have a close relationship with the dihedral angle \( \theta \) between the phenyl ring and the tape-porphyrin molecular plane. Note that as the long-range electron transport is carried by the \( \pi \)-electron, the transmission is highly affected by the overlap of the above two \( \pi \)-orbitals, namely, by the dihedral angle \( \theta \). In the type-D structure, the value of \( \theta \) is about 63°, which is caused by the steric repulsion between the phenyl ring and the hydrogen atoms on the \( \beta \) sites of the tape-porphyrin molecular wire. As the distance between the phenyl ring and the molecular wire increases, the angle \( \theta \) decreases, i.e., about 43° and 0° in the type-E and type-F structures, respectively. Especially in the latter case, the phenyl ring is parallel to the molecular plane of the tape-porphyrin.

Here, the reduction of the conductance may seem to be rather small compared to the large change in the value of \( \theta \). However, a similar feature has been reported in the theoretical study of transmission through the bi-phenyl molecule [26]. In their research, the transmission probabilities are found to drop abruptly at \( \theta > 60^\circ \). Especially, in the extreme case of \( \theta = 90^\circ \), the transmission is possible only by the tunneling mechanism. Also in our case, the transmission spectra show almost negligible values at \( \theta = 90^\circ \), i.e., \( G(E)/G_0 \) at the HOMO resonant level is limited to at most \( 10^{-4} \) irrespective of the molecular bridge structure.
Thus we can conclude that even if the phenyl ring is inserted between the S-Au bond and the molecule, the transmission feature around the Fermi level does not change significantly over the variety of the functional groups in consideration. However, if the bulky substituents are additionally introduced at the β atomic sites, the dihedral angle between the phenyl ring and the tape-porphyrin molecular plane would be close to 90°, and the transmission through the molecular bridge is expected to be suppressed dramatically.

IV. SUMMARY

To summarize, we investigated the coherent electronic transport properties of the molecular bridges where the tape-porphyrin molecules are bridged between the two gold electrodes by thiolate (S-Au) bonds. In particular, we studied the dependence of the transmission spectra on the atomic sites where S-Au bonds are connected to the tape-porphyrin molecule, and their dependence on the additional spacing functional group between the tape-porphyrin molecular edge and the S-Au bonds. When the S-Au bonds are connected to the meso atomic sites of the tape-porphyrin, several resonant peaks with large amplitudes are observed around the Fermi level, which indicates that the assumed molecular bridge is conducting even at lower bias voltages. As long as they are connected to the meso sites, the transmission peaks do not change their amplitudes significantly, even if the phenyl ring is inserted between the S-Au bond and the tape-porphyrin. However, if the bulky substituents are additionally introduced at the β atomic sites, the dihedral angle between the phenyl ring and the tape-porphyrin molecular plane would be close to 90°, and the transmission through the molecular bridge is considered to be dramatically suppressed.

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