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Electronic transport properties of free-base tape-porphyrin molecular wires studied by self-consistent tight-binding calculations

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We investigated by theoretical calculations the electronic states and the transport properties of one of the oligoporphyrin molecular wires, the free-base tape-porphyrins. Inside these molecules the adjacent building blocks, referred to as porphyrin macrocycles, are linked by three conjugating C-C bonds aligned in parallel. We found that the origin of the extremely small highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps of these molecules is the strong coupling between the unoccupied π orbitals of each macrocycle. Then we considered the molecular bridges where these porphyrin molecules are bridged between the aluminum electrodes. We found that the conductances have large values and that the current increases nearly in proportion to the applied bias. These features are explained by the strong hybridization of the HOMO with the electrode wave functions and by the wide bandwidth of the tape porphyrins. Finally we studied the current distribution inside the tape-porphyrin wire. The current is found to flow in an anisotropic way, i.e., it seems to flow along the spatial distribution of the HOMO of the tape porphyrins, reflecting the strong hybridization of the HOMO with the electrode wave functions.

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I. INTRODUCTION

Since the proposal of molecular electronic devices[1] plenty of organic functional molecules have been synthesized.[2] Accompanied with this, recent advances in the fabrication technique of substrates, including metal nanoelectrodes, would make it possible to realize molecular electronic devices. Among various types of functional molecules, the molecular wires have been extensively investigated. In most cases they are oligomers of some building blocks such as thiophene, ethynylene, and so on. The porphyrin is one of the building blocks from which several types of differently conjugated porphyrin molecular wires have been prepared.[3–6] In particular, the tape porphyrins, where the adjacent building blocks, referred to as porphyrin macrocycles, are linked by three conjugating C-C bonds aligned in parallel,[6] have attracted much attentions because of their extremely small HOMO-LUMO energy gaps. Here the HOMO and LUMO denote the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. Hereafter we use these abbreviated terms. For example, the gap was measured to be about 250 meV for the hexamer molecule in the scanning tunneling spectroscopy (STS).[7] In addition, the tape porphyrins were found to have rigid planar structures and be stable in air. Therefore the tape-porphyrin molecules are expected to be useful as good conducting molecular wires. However, the detailed current-voltage characteristics through these molecules have not been examined either from experimental or from theoretical studies.

Our aim in this work is to predict theoretically the transport properties of free-base tape-porphyrin molecules in which the hydrogen atoms are coordinated at the cation sites. For this purpose we considered the molecular bridges in which both edges of the tape-porphyrin molecules have close contact to the metal electrodes. The left/right electrodes are assumed to extend semi-infinitely along the molecular elongation axis. The electronic states and the charge distributions of these systems are solved under the self-consistent tight-binding model based on the density-functional theory.[8,9] In the past this model has been successfully applied to not only inorganic materials such as GaAs (Ref. 10) but also organic materials such as DNA molecules and porphyrin molecular stacks.[11,12] It has been also applied in researches on cluster/silicon surface interactions.[13–16] The Hamiltonian and the overlap matrices are described by the minimal basis sets, i.e., $2s$ and $2p$ orbitals for carbon and nitrogen atoms, $1s$ orbitals for hydrogen atoms, $3s$ and $3p$ orbitals for aluminum atoms. The on-site levels of all the atomic species in consideration, the two-center hopping integrals, and the overlap integrals between them at arbitrary interatomic distances are obtained from the norm-conserving atomic pseudopotentials and the corresponding pseudo-wave-functions in a similar way to that reported in Ref. 9.

To investigate the electronic states and the transport properties of these infinite systems, we assume the extended-molecule approach where the molecules and a fraction of the electrodes are treated as the scattering region; namely, the infinite system is divided into three parts, the left electrode, the extended molecule, and the right electrode. Accordingly, the Hamiltonian matrix and the overlap matrix are divided into 3×3 sections. The matrix elements that correspond to the intraelectrode 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. It means that the electrode-scattering region coupling is not treated as a small perturbation as in the case where the tunneling Hamiltonian is considered. Thus, in this theoretical treatment, the electronic transport can be handled not only in the tunneling regime but also in the ballistic regime. This kind of approach has been adopted in calculating the conductances of the Al-C_{60}-Al system,[17] Au-$C_4H_4S_2$-Au system,[18] nanotube junctions,[19] and so on.

Under the bias voltage V, the charge densities of the left/right electrodes are assumed to remain unchanged, but are assumed to suffer the lower/upper shift of the chemical potentials by eV/2. Inside the extended molecule, the charge distribution is solved in a self-consistent manner using the Keldysh Green's functions.[20,21] Note that the Hartree potentials inside the extended molecule are determined in a self-consistent process, and are *not* assumed to drop linearly along the wire. Once the charge distribution is converged, the current is evaluated quantitatively by the Landauer formula.[20,22]

The distinctive points in our formalism are the following.

(1) As the charge transfer at the molecule/electrode interfaces is taken into account through the self-consistent process, the level-shift inside the molecule is realized automatically, whose effects are neglected in the extended Hückel-type calculations.[23,24]

(2) Since the atoms in the electrodes are considered individually, the electrode-molecule interactions are described in a more realistic manner than by the jellium models[25] or with the cluster approximations.[26]

(3) Larger molecules can be treated in the simulations than in the first-principles calculations by evaluating the Hartree potential approximately.

In this work we confirmed the small HOMO-LUMO energy gaps of the free-base tape-porphyrin molecules. For example, it is about 360 meV for the hexamer molecule, which agrees well with the value obtained in a first-principles calculation and the value obtained in the STS measurement. This feature is found to be caused by the strong coupling between the unoccupied π orbitals of each macrocycle. Then we considered the molecular bridges where these porphyrin molecules are bridged between the aluminum electrodes. We found that the conductances have large values and that their decay against the molecular length is slow. The former feature is due to the close contact at the electrode/molecule interfaces, especially the strong hybridization of the HOMO with the electrode wave functions. The latter feature is explained by the extremely small HOMO-LUMO energy gaps of the tape-porphyrin molecules.

When the bias is applied between the electrodes, the current is found to increase nearly in proportion to the bias, with no threshold. The origin of this highly conductive feature is the large conductances at the equilibrium and the strong coupling between the adjacent macrocycles, i.e., the wide bandwidth of the tape porphyrins. Finally we discuss the current distribution inside the tape-porphyrin wire. The current is found to flow in an anisotropic way, i.e., it seems to flow along the spatial distribution of the HOMO of the tape porphyrins. This is because the electronic states around the Fermi level are dominantly composed of the HOMO states that are extremely broadened by the strong hybridization with the electrode wave functions.

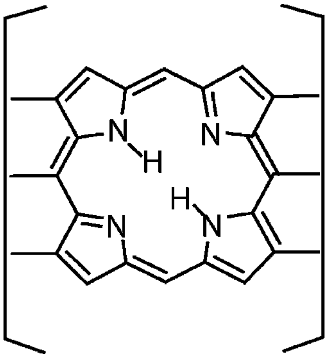

FIG. 1. Building block of free-base tape-porphyrin molecules.

The rest of the paper is as follows. In Sec. II the computational methods are described. In Sec. III the electronic states and the transport properties of the tape porphyrins are discussed. In Sec. IV the paper is summarized.

II. METHOD

The building block of the tape-porphyrin molecules is illustrated in Fig. 1. In this work we assume that the hydrogen molecules are coordinated at the center sites, i.e., we consider the free-base tape-porphyrin molecules. The atomic coordinates of these molecules are prepared in the following way. First, the optimized structure of the diporphyrin molecule is obtained by *ab initio* calculations using the B3LYP exchange-correlation functional[27,28] with the LANL2DZ bases. Then the Nmer tape porphyrin is generated by repeating the central half of the dimer structure by $N-1$ times with each edge terminated by a half of the macrocycle. Here the word "macrocycle" is used as a synonym of the monomer porphyrin. The number of atoms in the Nmer molecule is $32N+6$. The geometrical optimizations of these longer oligomers are not performed due to the limitation of computational resources.

These molecular wires are assumed to bridge the left and the right electrodes as illustrated in Fig. 2, so that only a half

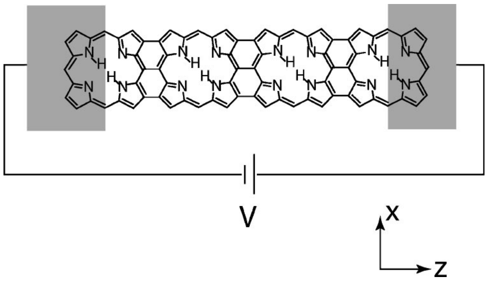

FIG. 2. Molecular-bridge structure when the tetramer tape porphyrin is used. The shaded regions are the Al(001) electrodes of four layers thickness. The periodic boundary condition is applied along the x axis. Parts of the electrodes, namely, 48 Al atoms on both edges of the electrodes are included in the extended molecules.

of the macrocycle "contacts" to each electrode (shaded region). A similar contact formation has been challenged by Langlais *et al.* experimentally.[29] The electrodes are modeled as ideal Al(001) films of four layers thickness and are assumed to continue semi-infinitely along the molecular elongation axis, i.e., the z axis. As the electrodes are assumed to be cut perpendicularly to the Al(001) surfaces at their edges, the Al(110) and Al$(\overline{11}0)$ surfaces appear there. The interatomic distance between Al atoms is kept 2.86 Å, which is the bond length in the crystalline structure. The molecules are located so that their planes are in parallel to the electrode surfaces, and their height is fixed to be 2.2 Å, which is close to the sum of the atomic radius of the aluminum and nitrogen atoms. The periodic boundary condition is applied along the x axis; namely, the molecules are aligned in parallel with the spacing of 17.16 Å, and the nearest distance between them is larger than 8 Å.

The electronic states and the charge distributions of these systems are solved under the self-consistent tight-binding model based on the density-functional theory.[8,9] In the past this model has been successfully applied to not only inorganic materials such as GaAs (Ref. 10) but also organic materials such as DNA molecules and porphyrin molecular stacks.[11,12] It has been also applied in researches on cluster/surface interactions.[13–16] The Hamiltonian and the overlap matrices are described by the minimal basis sets, i.e., $2s$ and $2p$ orbitals for carbon and nitrogen atoms, $1s$ orbital for hydrogen atoms, $3s$ and $3p$ orbitals for aluminum atoms. The on-site levels of all the atomic species in consideration, the two-center hopping integrals, and the overlap integrals between them at arbitrary interatomic distances are obtained from the norm-conserving atomic pseudopotentials and the corresponding pseudo-wave-functions in a similar way to that reported in Ref. 9.

To investigate the electronic states and the transport properties of these infinite systems, we assume the extended-molecule approach where the molecules and a fraction of the electrodes are treated as the scattering region; namely, the infinite system is divided into three parts, the left electrode, the extended molecule, and the right electrode. The porphyrin wires and 48 Al atoms, i.e., 4 atom planes (5.72 Å) counted from the edges, on both electrodes are treated as the extended molecules. (The boundaries between the electrodes and the extended molecules are parallel to the electrode edge surfaces.) Thus the number of atoms inside the scattering region is $32N+102$ in the case of Nmer tape porphyrin. Accordingly, the Hamiltonian matrix and the overlap matrix are divided into 3×3 sections. The matrix elements that correspond to the intraelectrode 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. It means that the electrode-*scattering region* coupling is not treated as a small perturbation as in the case where the tunneling Hamiltonian is considered. Thus, in this theoretical treatment, the electronic transport can be handled not only in the tunneling regime but also in the ballistic regime. This kind of approach has been adopted in calculating the conductances of the Al-C_{60}-Al system,[17] Au-$C_4H_4S_2$-Au system,[18] nanotube junctions,[19] and so on.

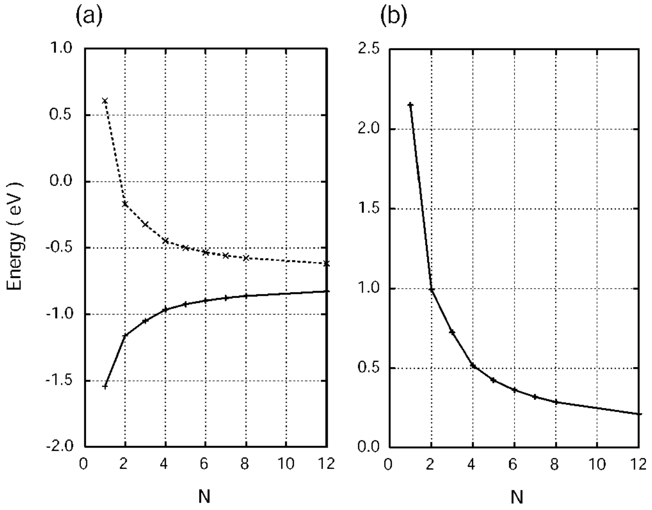

FIG. 3. (a) HOMO and LUMO energy levels plotted against the molecular length N. The solid and dotted lines correspond to HOMO and LUMO levels, respectively. (b) HOMO-LUMO energy gaps.

Under the bias voltage V, the charge densities of the left/right electrodes are assumed to remain unchanged, but are assumed to suffer the lower/upper shift of the chemical potentials by eV/2. Inside the extended molecule, the charge distribution is solved in a self-consistent manner using the Keldysh Green's functions.[20,21] Note that the Hartree potentials inside the extended molecule are determined in a self-consistent process, and are *not* assumed to drop linearly along the wire. Once the charge distribution is converged, the current is evaluated quantitatively by the Landauer formula.[20,22]

III. RESULTS

First the electronic states of the isolated tape-porphyrin molecules will be presented. Next the transport properties through these molecules will be discussed.

A. Electronic states of molecules

Figure 3(a) illustrates the energy levels of the HOMO and LUMO plotted against the molecular length N, which varies from 1 to 12.[30] Here the HOMO of these oligomers is derived from the HOMO (b_{1u}) of each macrocycle (building unit) and the LUMO is derived from the mixture of LUMO (b_{3g}) and LUMO+1 (b_{2g}) of the macrocycle. The word "LUMO+1" means the electronic state of the second lowest unoccupied molecular orbital. As the molecular length is increased, the HOMO and the LUMO levels shift upward and downward, respectively, but the change in the LUMO energies seems more rapid. It indicates that the strength of the $(b_{3g}+b_{2g})$-$(b_{3g}+b_{2g})$ interaction between the adjacent two macrocycles is stronger than that of the b_{1u}-b_{1u} interaction. This difference in the coupling strength is caused by the phase difference of the two interactions, i.e., the latter interaction that produces the HOMO of the molecule has nodes at the boundaries of the adjacent two macrocycles while the former interaction does not. The existence of nodes makes the intermacrocycle interaction weaker.

The corresponding HOMO-LUMO gap energies decreases in a monotonic manner as plotted in Fig. 3(b). For example, the gap value of the hexamer ($N=6$) molecule is calculated to be as small as 360 meV. A similar value has been obtained in a first-principles calculation where the gap of the zinc-porphyrin hexamer is estimated to be 350 meV. Note here that replacing hydrogen atoms with zinc atoms does not affect the HOMO-LUMO gap, because the zinc atomic levels are apart from the Fermi level, as pointed out by Yamaguchi.[31] In fact, in our tight-binding model, the gap value of the zinc-porphyrin hexamer is found to be 350 meV. These values are comparable to the HOMO-LUMO gap obtained in the STS measurement of the zinc-porphyrin hexamer, 250 meV.[7] It assures the reliability of our computational method. The small HOMO-LUMO energy gaps as seen in Fig. 3(b) are caused by the strong coupling between the adjacent macrocycles, especially by the ($b_{3g}+b_{2g}$)-($b_{3g}+b_{2g}$) coupling as described above. This is an outstanding effect of formation of three conjugating bonds between the macrocycles in parallel (see Fig. 1).

Finally we comment on the gap values at $N>12$. In most of the polymer molecules, the HOMO-LUMO gap energies are known to reach limiting values as the molecular length is increased. In the case of free-base tape porphyrins, this value is calculated to be as small as several tens of meV, which is estimated in the band structure of one-dimensional tape-porphyrin crystal. This result is supported by the first-principles calculation,[31] where the gap is found to be less than 100 meV; namely, the crystalline tape porphyrin is a nearly gapless semiconductor.

B. Large conductances

The zero-bias conductances $G(E_F)$ of different molecular lengths are plotted as the cross marks in Fig. 4. At $N<4$ the conductances are found to be enhanced. This is caused by the direct overlap of the metal electrode wave functions that penetrate into the molecule from the left and the right interfaces. As the molecule becomes longer than this invasion length, the enhancement in the conductance disappears. The slow decay of $G(E_F)$ at $N>4$ is specific to the tape-porphyrin molecules and is considered to be caused by the extremely small HOMO-LUMO gaps. In addition, $G(E_F)$ seems to decay exponentially as

$$G(E_F)=G_m e^{-\beta L}, \tag{1}$$

where $G_m=1.082G_0$, $\beta=0.0095$ Å^{-1}, and $L=(N-1)a$ is the interelectrode distance, and a is the length of the unit structure of tape porphyrins, 8.6 Å. This decaying function is drawn as the solid curve in Fig. 4. The value of β^{-1} is considered to be some characteristic length of these tape-porphyrin molecular bridges. But the large values of $G(E_F)$ indicate that the transport mechanism is close to the resonant regime rather than the tunneling regime. In addition, comparison of β among various types of wires has a significance for the transport in the tunneling regime.[24] Thus the meaning of this small value of β should be clarified in further studies.

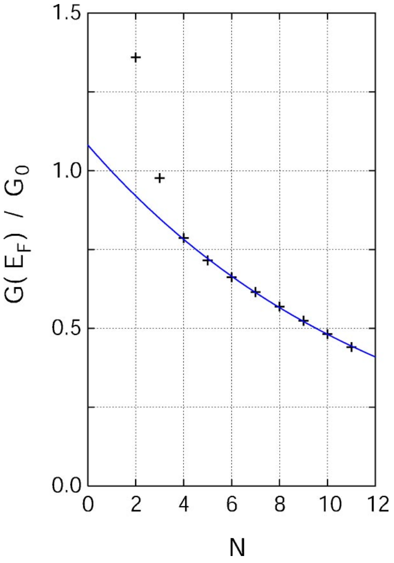

FIG. 4. Relation between zero-bias conductance $G(E_F)$ and molecular length N. The cross marks denote the values obtained in the calculations. The solid curve corresponds to the exponential decaying function of $G(E_F)=G_m\exp(-\beta L)$ (see text).

Then why the conductances are so large? It indicates that the contact resistance at the metal/molecule interfaces is small. To investigate the origin of the small contact resistance, we calculated the local density of states (LDOS) on the molecule. Figure 5(a) shows the spectrum of the LDOS in the case of the tetramer tape-porphyrin molecule. Here the "LDOS on the molecule" is obtained by summing up the LDOS calculated on each atom site over the atoms that comprise the molecule. Thus it may be viewed as the density of states projected onto the molecule. The horizontal axis denotes the energy of an electron incident from the electrode,

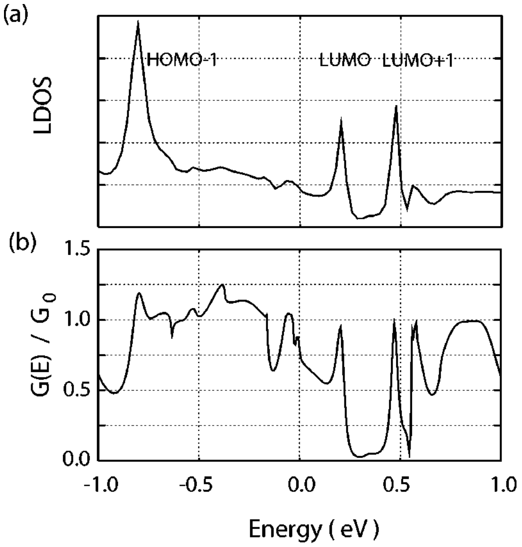

FIG. 5. (a) Local density of states projected on the molecule. (b) Conductance of the molecular bridge. The tetramer tape-porphyrin molecule is used. The Fermi level is set to 0 eV.

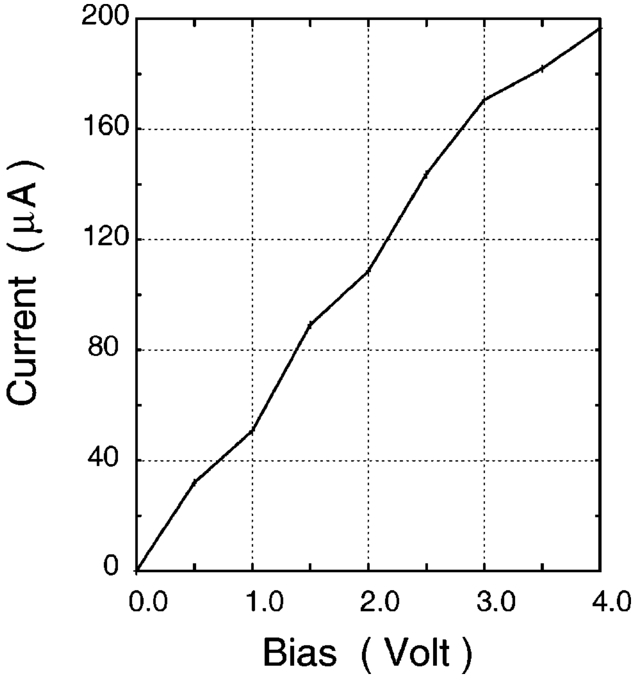

FIG. 6. Current-voltage curves of the molecular bridge in the case of tetramer tape-porphyrin molecule.

which is calibrated to the Fermi energy level. The three sharp peaks around -0.80, 0.20, 0.47 eV correspond to the HOMO-1, LUMO, LUMO$+1$ levels, respectively. The word "HOMO-1" means the electronic state of the second highest occupied molecular orbital. The HOMO-derived peak is highly broadened and is not clearly seen, which indicates the strong hybridization of the HOMO with the metal electrode wave functions. Due to this hybridization, the LDOS around the Fermi level has finite values and changes smoothly. Correspondingly, the conductances around the Fermi level has large values, as illustrated in Fig. 5(b). Thus the strong hybridization of the HOMO with the electrode wave functions is considered to reduce the contact resistance at the interfaces.

Figure 5(a) also shows that the LUMO peak is above the Fermi level, although the LUMO energy of the isolated tetramer tape porphyrin is below the Fermi level by 0.36 eV. It means that the "level shift" or "level tuning" occurs at the electrode/molecule interface. This effect is accompanied with the net charge transfer from the electrodes to the molecule, $-0.74e$, which occurs locally around the contact region.

C. *I-V* curves

Then how much current flows when the bias is applied between the electrodes? As an illustrated example, we present in Fig. 6 the current-voltage (I-V) curve through the tetramer tape-porphyrin wire. It shows that the molecular bridges become a highly conducting device; namely, no threshold bias is found and the current increases almost linearly against the applied bias. The former is expected from the large value of zero-bias conductance $G(E_F)$ as denoted above. The latter is explained by the strong coupling between the adjacent macrocycles as described in the precedings section, or in other words, the wide bandwidth of the tape porphyrins. If the intermacrocycle interactions were too weak, the electronic localization would occur when the bias is applied,[32] which would suppress the conduction through the tape porphyrin.

Here it may seem that too much current flows through the tape-porphyrin molecules, e.g., when the bias is set to 2.0 V, the current flows by about 108 μA. But current of similar strength has been reported in calculations of the other molecular nanodevices, where similar but more accurate computational methods were adopted.[17] Thus our results on the tape-porphyrin molecular bridges are considered to be reasonable. Of course, whether or not such high current is observed experimentally depends on the fabrication and the measurement conditions; namely, if the contact resistance becomes large for some reasons, e.g., the distortion of the molecules at the interfaces, the current may be weaker than in our simulation. In addition, in the finite temperature, the effects on phonon scattering would reduce the current.

Then how does the current flow inside the molecules? Figure 7 shows the current flow projected on the chemical bonds when the bias is set to 2.0 V. Again the calculations were done for the tetramer tape-porphyrin wire. For clarity, only the central two macrocycles of the tetramer molecule are illustrated. Notice that in this figure the hydrogen atoms are coordinated at the lower left and the upper right sites in the porphyrin rings (compare to Fig. 2). The direction and darkness of an arrow denote the path and the strength of the

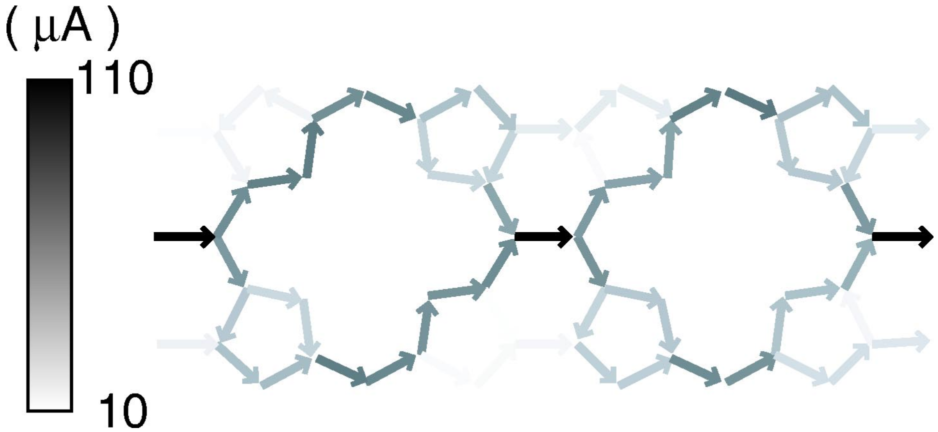

FIG. 7. Current flow inside tetramer tape-porphyrin molecule. The central two macrocycles are drawn for clarity. The current through the central C-C bond is about 108 μA.

current through the bond, respectively. Between the macrocycles, the current is found to flow dominantly along the central C-C bond, which is represented as the darkest arrows. Once the current enters a macrocycle, it splits upward and downward. Each component passes through the inner bonds of the macrocycle except around the N-H bond where some of the current is found to detour. The two components join at the edge of the macrocycle and go to the adjacent macrocycle along the central C-C bond. Here it is worth saying that the shape of this anisotropic path is very similar to the shape of the HOMO of the tape porphyrin. This point is understood as follows. As mentioned in the preceding section, the HOMO strongly hybridizes with the electrode wave functions, which brings about the highly broadened spectra in the conductance [see Fig. 5(b)]. In contrast, the LUMO and the LUMO+1 levels only produce the narrow peaks in the spectra. Thus the HOMO contributes to the current much more than the LUMO and LUMO+1 levels do. Therefore the current seems to flow along the spatial distribution of the HOMO.

IV. SUMMARY

In this work we investigated by theoretical calculations the electronic states and the transport properties of free-base tape porphyrins, where the adjacent building blocks, referred to as porphyrin macrocycles, are linked by three conjugating C-C bonds aligned in parallel. We confirmed the small HOMO-LUMO energy gaps of the tape-porphyrin molecules. For example, it is about 360 meV for the hexamer molecule, which agrees well with the value obtained in a first-principles calculation and the value obtained in the STS measurement. This feature is found to be caused by the the strong coupling between the unoccupied π orbitals of each macrocycle. Then we considered the molecular bridges where these porphyrin molecules are bridged between the aluminum electrodes. We found that the conductances have large values and that their decay against the molecular length is slow. The former feature is due to the close contact at the electrode/molecule interfaces, especially the strong hybridization of the HOMO with the electrode wave functions. The latter feature is explained by the extremely small HOMO-LUMO energy gaps of the tape-porphyrin molecules.

When the bias is applied between the electrodes, the current is found to increase nearly in proportion to the bias, with no threshold. The origin of this highly conductive feature is the large conductances at the equilibrium and the strong coupling between the adjacent macrocycles, in other words, the wide bandwidth of the tape porphyrins. Finally we discussed the current distribution inside the tape-porphyrin wire. The current is found to flow in an anisotropic way, i.e., it seems to flow along the spatial distribution of the HOMO of the tape porphyrins. This is because the electronic states around the Fermi level are dominantly composed of the HOMO states that are extremely broadened by the strong hybridization with the electrode wave functions.

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