A fullerene molecular tip can detect localized and rectified electron tunneling within a single fullerene–porphyrin pair

Tomoaki Nishino, Takashi Ito*, and Yoshio Umezawa†

Department of Chemistry, School of Science, University of Tokyo, Bunkyo-Ku, Tokyo 113-0033, Japan

Edited by Royce W. Murray, University of North Carolina, Chapel Hill, NC, and approved March 9, 2005 (received for review November 15, 2004)

A fullerene molecular tip was used to detect electron tunneling from a single porphyrin molecule. Electron tunneling was found to occur locally from an electron-donating moiety of the porphyrin to the fullerene through charge-transfer interaction between them. In addition, electron tunneling within the single fullerene–porphyrin pair exhibited rectifying behavior in which electrons can be driven only at the direction from the porphyrin to the fullerene. It is demonstrated that localized electron tunneling enables us to spatially visualize the frontier orbital of the porphyrin involved in electron tunneling. In addition, rectification demonstrates that the fullerene–porphyrin pair constitutes a molecular rectifier. We believe that molecular tips bring insight into intermolecular electron transmission toward realization of molecular electronics as shown here.

molecular electronics | nanoscale | scanning tunneling microscopy

Electron transmission through single molecules is currently an interdisciplinary subject of substantial interest (1) because of molecular-scale electronic device research (2, 3). It is desired to measure the molecular conduction on a single molecule rather than on an ensemble of molecules to eliminate a cooperative transport (4) and avoid averaging out the conduction through the molecules in different conformations (5). Recently, there have been significant advances in knowledge of electron transmission through a single molecule (4). However, few works have been reported on electron transmission through a single molecule to an adjacent single molecule on a nanoscale.

Scanning tunneling microscopy (STM) has been an essential tool in nanosciences (6). We have studied the construction of molecular tips for STM. The molecular tip is prepared by chemical modification of an underlying metal tip, and the outermost single adsorbate probes electron tunneling to or from a sample molecule. Importantly, the tunneling current increases when sample and tip molecules form metal coordination or hydrogen-bond interactions that provide overlap of their electronic wave functions. The current increase is ascribed to facilitated tunneling through overlapped wave functions. We have demonstrated that this phenomenon can be used for selective observation of chemical species to overcome poor chemical selectivity in conventional STM (7–13). Because the overlap of electronic wave functions is important for the facilitation of electron tunneling, these results suggest that intermolecular electron tunneling can also be facilitated through a charge-transfer interaction as well as metal coordination and hydrogen-bond interactions.

Here, we report on the detection of intermolecular electron tunneling within a single fullerene–porphyrin molecular pair. Electron tunneling was found to occur locally from an electron-donating moiety of the porphyrin to the fullerene through charge-transfer interaction between them, but not in the opposite direction. It was shown that localized tunneling can be applied to visualize the frontier orbital of the porphyrin. Rectified tunneling indicates that the fullerene–porphyrin pair constitutes a molecular rectifier.

Materials and Methods

General. All reagents were of the highest grade available and used as received. Sarcosine and 1,2,4-trichlorobenzene were purchased from Wako Pure Chemicals (Osaka), and fullerene was from Tokyo Kasei. Deionized water purified with a Milli-Q water purification system (Millipore) was used throughout the experiments. STM observation was performed on a Nanoscope E (Digital Instruments, Santa Barbara, CA) at ambient temperature under air.

STM Tip Preparation. Small pieces of gold wire (0.25-mm diameter; 99.95%; Nilaco, Tokyo) were electrochemically etched in 3 M NaCl at ac 10 V. They were washed by sonicating in pure water and further dipping in piranha solution (7:3 concentrated H2SO4/H2O2; caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers), and finally washed thoroughly with pure water. Molecular tips possessing a fullerene moiety were used for STM observation of a free-base porphyrin and metallolporphyrins (Fig. 1a) on highly oriented pyrolytic graphite (HOPG). They were prepared from a fullerene derivative, N-methyl 2-(2-propyldithiophenyl)-fulleropyrrolidine (MPF; Fig. 1b), by self-assembly onto an underlying gold tip (Fig. 1c). For the formation of the self-assembled monolayer, MPF was dissolved in argon-saturated toluene at the typical concentration of 20 μM, and the gold tips were immersed in the solution overnight. The modified tips were successively rinsed with toluene and water before use.

STM Observation of Physisorbed Monolayers of the Porphyrin Derivatives. Cobalt(II) 5,15-bis-(4-octadecyloxyphenyl)porphyrin (CoPor) (Fig. 1a) was dissolved in 1,2,4-trichlorobenzene at a concentration of 0.5 mg/ml. Zinc(II) 5,15-bis-(4-octadecyloxyphenyl)porphyrin (ZnPor) and 5,15-bis(4-octadecyloxyphenyl)-porphyrin (FBPor) (Fig. 1a) were codissolved in 1,2,4-trichlorobenzene at a molar ratio of 1:3 and total concentration of 1.0 mg/ml. Either one of the solutions was applied onto a basal plane of a freshly cleaved surface of HOPG. Within minutes after the deposition of the solution, STM observations were performed at the solution/HOPG interface typically with a bias voltage of ~1.2 to ~1.5 V and a tunneling current of 0.3–0.5 nA. In the STM observations, a chemically selective change in image contrast (see below) was observed by using 50–60% of ~80 MPF tips that exhibited molecular resolution. The remainder of the

This paper was submitted directly (Track II) to the PNAS office.

Abbreviations: STM, scanning tunneling microscopy; HOPG, highly oriented pyrolytic graphite; MPF, N-methyl 2-(2-propyldithiophenyl)fulleropyrrolidine; CoPor, cobalt(II) 5,15-bis-(4-octadecyloxyphenyl)porphyrin; ZnPor, zinc(II) 5,15-bis(4-octadecyloxyphenyl)porphyrin; FBPor, 5,15-bis(4-octadecyloxyphenyl)porphyrin; I–V, current–voltage; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

*Present address: Department of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, KS 66506.

†To whom correspondence should be addressed. E-mail: umezawa@chem.s.u-tokyo.ac.jp.

© 2005 by The National Academy of Sciences of the USA
voltages of half-filled d orbitals 
interpreted as large tunneling probability associated with the protrusions are assigned to the central cobalt(II) ions, which is consistent with the polarity dependence in STM imaging. The negligible contrast when the sample was negatively biased. The contrast change did not depend on the magnitude of the bias voltage in the range of $-1.2$ to $-1.5$ V, where the porphyrin molecules were clearly observed. 

Interestingly, with sample-positive bias and the MPF tips, the selectively observed porphyrin rings disappeared and the STM images showed nothing but noisy streaks. The contrast change was restored upon reversing the polarity (Fig. 3a). To quantitatively examine polarity dependence, current–voltage ($I$–$V$) curves were measured in an argon atmosphere. When the $I$–$V$ curve was measured with the MPF tip at the porphyrin ring of the CoPor molecule a large current was observed at a negative bias voltage (Fig. 5), which is published as supporting information on the PNAS web site). In contrast, the current flow was negligible at positive bias. This asymmetric current flow is consistent with the polarity dependence in STM imaging. The asymmetry in $I$–$V$ characteristics is quantified with an asymmetry ratio ($R$), which is defined by $I(-V)/I(V)$ (15). At the bias voltages of $+1.2$ and $-1.2$ V, where the STM images in Fig. 3a were obtained, the asymmetry ratio was 12 for the $I$–$V$ curve of the porphyrin measured with the fullerene tip, indicating rectifying behavior within the fullerene–porphyrin pair. With gold tips, this polarity dependence was absent for the CoPor molecules (Fig. 6, which is published as supporting information on the PNAS web site) and a symmetric $I$–$V$ curve was observed at their porphyrin rings ($R = 0.9$, Fig. 5). The $C_{60}$ molecules, which lack functional moieties, also exhibited polarity-independent images (Fig. 7, which is published as supporting information on the PNAS web site) and a symmetric $I$–$V$ curve ($R = 1.1$, Fig. 5) despite the use of the fullerene molecular tips. These results clearly demonstrate that neither the porphyrin–substrate junction nor the fullerene–underlying tip junction is responsible for the rectification. 

Recent studies have shown that fullerenes form supramolecular complexes with porphyrins (16). It is widely suggested that charge transfer or $\pi$–$\pi$ interactions account for the supramolecular assembly (17–19). These studies indicate that the changes in image contrast observed with the MPF tips (Fig. 2b) are caused by the charge-transfer interaction concomitant with the overlapped $\pi$ orbitals between a fullerene moiety of the molecular tip and a pyrrole moiety of the CoPor. The charge-transfer interaction facilitates electron tunneling locally at the pyrrole moiety. We ascribed the bright appearance of the pyrrole moieties in Fig. 2b to the localized electron tunneling between

Fig. 1. Structures of sample and tip molecules. Chemical structures of the sample porphyrins (a) and fullerene derivative (b) used as a precursor to the molecular tip. SSPr stands for $\text{SS(CH}_2\text{)}_3\text{CH}_3$. (c) Schematic of the molecular tip. The atomic labels of the nitrogen atom of the pyrrole ring are omitted, and the sulfur atoms of the thiolate are represented by solid circles for simplicity.

Fig. 2. STM images of CoPor monolayers physisorbed onto HOPG. The insets schematically show the molecular arrangement in the images. White rings, blue circles, and bars represent pyrrole moieties, Co(II) ions, and alkyl chains, respectively. The cross-sectional profiles measured along with the lines in the STM images are presented under the images. Blue arrows in the images and cross-sectional profiles indicate the position of Co(II) ions. (a) An STM image observed with an unmodified gold tip. Bias voltage, $-1.30$ V (sample negative); tunneling current, 0.30 nA. (b) An STM image observed with the fullerene molecular tip. Bias voltage, $-1.25$ V; tunneling current 0.30 nA. (c) An energy diagram of cobalt(II) tetraphenylporphyrin (CoTPP) and fullerene ($C_{60}$). The energy values of the former were taken from ref. 14, and the energy values of the latter were taken from ref. 30. Both of them are relative to the vacuum level.
the porphyrin and fullerene tip. Porphyrins are one of the most used electron donors, and fullerenes possess facile electron acceptability (20). The charge-transfer interaction between the CoPor and fullerene tip thus involves the highest occupied molecular $\pi$ orbital ($\pi$ HOMO) of CoPor and lowest unoccupied molecular orbital (LUMO) of the fullerene tip. The former and the latter are high and low in energy, respectively, and this energy relation should allow electrons to flow only in one direction with a finite applied voltage (Fig. 2c). The observed polarity dependence thus indicates that the facilitated electron tunneling at pyrrole moieties of CoPor involves the charge-transfer interaction with the fullerene moiety of the tip molecules. Halas and coworkers (21) reported that a physisorbed fullerene tip is able to observe electron-scattering patterns around graphite defects of a graphite surface, and they ascribed it to the electronic configuration of the fullerene tip that energetically matches scattered electrons. They demonstrated another ability of fullerene tips, which cannot be recognized with metal tips, although their tip preparation and imaging mechanism is different from those of our fullerene tips.

Rectified electron tunneling is a noteworthy aspect from a viewpoint of molecular devices. Rectification was reported in a hybrid molecular electronic device where copper phthalocyanine (CuPc) molecules were chemically attached to an oxidized HOPG surface (15). This rectification was explained by resonant tunneling through the peak in the density of states of HOPG/CuPc originated by the molecular adsorption. Although this system exhibited a strong rectifying effect, construction of the rectifiers without any bulk materials, such as HOPG, has been required for a molecular-scale electronic device. In the present study, the electron-deficient fullerene and electron-rich porphyrin faced to and interacted with each other (Fig. 3b), and such appropriately coupled acceptor–donor pairs have been theoretically predicted to possess rectifier properties (22). Rectification behavior was indeed observed in the polarity dependence of the STM images and the $I$–$V$ curve (Figs. 3a and 5; see above), which verifies the molecular diode by the acceptor–donor configuration. The rectified current in the fullerene–porphyrin pair began to flow at around $-0.5$ V, where the $\pi$ HOMO of the porphyrin and LUMO of the fullerene are expected to energetically align with each other. It is known that upon the adsorption onto a gold surface, the fullerene LUMO broadens and shifts down in energy by $\sim1.4$ eV (23). This shift may cause a decrease in the energy difference between the frontier orbitals of the fullerene and porphyrin, $\Delta E$ (1.7 eV, Fig. 2c). The turn-on voltage of the asymmetric current ($-0.5$ V, Fig. 5) agrees with the energy difference decreased by the adsorption. Also in STM imaging, the contrast change as observed in Fig. 2b should be affected depending on whether the bias voltage is below or above the turn-on voltage. However, we could not confirm this bias dependence, because the voltage range where the clear molecular images of the porphyrins were observed (from $-1.2$ V to $-1.5$ V, see above) was well above the threshold. The fullerene–porphyrin rectifier exhibited the asymmetry ratio of 12 (see above). This value is comparable with that observed in the HOPG/CuPc hybrid molecular rectifier where an asymmetry ratio of 10 was observed, although the ratio occasionally reached a value as high as 40 (15). A stronger rectification would be attained by the use of an acceptor–donor pair that has a smaller gap between the donor HOMO and acceptor LUMO (24).

Fig. 3. Polarity dependence in STM observation of CoPor. (a) STM images of CoPor monolayers physisorbed onto HOPG observed with MPF tips and different bias voltage ($V_b$). These images were successively observed with the same tip and the same sample region. Tunneling currents were 0.3 nA (Left and Center) and 0.35 nA (Right). Total z-scale ranges were 0.25 nm (Left), 0.5 nm (Center), and 0.35 nm (Right). The insets schematically show the molecular arrangement in the images. White rings, blue circles, and bars represent pyrrole moieties, Co(II) ions, and alkyl chains, respectively. (b) Schematic illustration of the electron flow between a porphyrin (orange) and fullerene-derivative tip (green). All of the atomic labels were omitted for simplicity in the chemical structures of the tip and sample molecules.
It is known that a tip terminated with multiple protrusions exhibits strongly distorted images (25). We checked the STM image obtained with the molecular tip in each experiment, and the scanning tunneling spectroscopy measurements were performed only when molecular resolution was clearly observed. Although fullerene moieties were closely packed on the surface of the MPF self-assembled monolayer (see Supporting Text and Fig. 8, which are published as supporting information on the PNAS web site), the clear resolution indicates that a single fullerene existed at an apex of the molecular tip. Because the apex is a predominant path for tunneling electrons, the molecular tip enables us to measure electron tunneling between a single fullerene and an adjacent single porphyrin (Fig. 3b). We conclude that the molecular tip revealed rectified electron tunneling within a single fullerene–porphyrin pair through the charge-transfer interaction. It has been reported that a fullerene molecular tip can construct a negative differential-resistance device involving two fullerene molecules. A fullerene molecule on a sample surface was picked up in situ onto a metal tip by physiosorption, and scanning tunneling spectroscopy measurement was performed between the fullerene on the tip and one remaining on the substrate (26). In the present study, we used robust chemisorption of the fullerene-terminated unsymmetrical disulfide (Fig. 1b; see also Supporting Text), because it has been reported that such organosulfur compounds chemisorb onto gold surfaces to form self-assembled monolayers that expose well packed fullerene moieties (27, 28). This ex situ preparation scheme enables the fullerene tips to measure electron tunneling to or from a molecule other than a fullerene.

Next, we observed a mixed monolayer of ZnPor and FBPor. Fig. 4a and b shows STM images of the monolayer observed with gold and MPF tips, respectively. The sample solution contains well packed fullerene moieties (27, 28). This fact presumably accounts for the depressed appearance of the centers of ZnPor (14). In addition, all of the porphyrin rings were observed as equally bright protrusions in Fig. 4a, and as a result the two species that should coexist on the surface cannot be discriminated from each other. In contrast to the findings shown in Fig. 4a, one porphyrin ring was observed to be much brighter than the other one in Fig. 4b. A wider image obtained with a MPF tip (75 nm × 75 nm, data not shown) showed 108 and 326 molecules having the brighter and dimmer rings, respectively. Their ratio (108:326 = 1:3.0) is in an exact agreement with the molar ratio of ZnPor to FBPor in the sample solution. This result suggests that the brighter and dimmer porphyrin rings in Fig. 4b correspond to those of ZnPor and FBPor, respectively (11).

The difference in image contrast of FBPor and ZnPor in Fig. 4b is ascribed to the differing extent of the charge-transfer interactions of the two kinds of porphyrins with the fullerene tip. The difference in the extent of the charge-transfer interaction is evident by considering the difference in energy between \( \pi \) HOMOs of FBPor and ZnPor. The \( \pi \) HOMO energy of zinc(II) tetraphenylporphyrin is reported to be 0.3 eV above that of the free-base derivative (14). The zinc(II) derivative is thus expected to have favorable charge-transfer interaction with the fullerene compared to the free-base derivative (29), because the \( \pi \) HOMO of the former is energetically closer to the LUMO of a fullerene than the latter (Fig. 4c). The favorable charge-transfer interaction between the fullerene and ZnPor facilitates electron tunneling to a great extent compared with the interaction between the fullerene and FBPor, which results in the brighter appearance for ZnPor in Fig. 4b. These results demonstrate that the localized electron tunneling through charge-transfer interactions can be applied to spatially visualize frontier orbitals involved in the interaction.

In summary, it was revealed that a fullerene molecular tip can detect localized and rectified electron tunneling from a single porphyrin molecule to the fullerene through charge-transfer interaction. We found that localized electron tunneling enables us to spatially visualize the frontier orbital of the porphyrin involved in tunneling. And the rectification behavior in which electrons were driven only from the pyrrole moiety of the porphyrin to the fullerene demonstrated that the fullerene–porphyrin molecular pair constitutes a molecular rectifier.

We thank Prof. M. Tsukada, Dr. K. Tagami, and Dr. N. Ishikii for illuminating discussions and Dr. H. Isobe for useful advice on fullerene derivatization. This work was supported by grants from Japan Society for the Promotion of Science and a Sasakawa Scientific Research Grant from The Japan Science Society.