Probing Potential-Tuned Resonant Tunneling through Redox Molecules with Scanning Tunneling Microscopy

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We have studied electron transfer through redox molecules adsorbed on a conductive substrate with scanning tunneling microscopy (STM) in aqueous solution. By adjusting the substrate potential, the Fermi levels of the substrate and tip can be easily shifted relative to the energy levels of the molecules. Aligning the Fermi levels to an energy level, a nearly tenfold increase in the tunneling current that flows between the substrate and the STM tip via the molecules, due to resonant tunneling is observed. This experiment also shows that structurally similar molecules may be identified with STM based on their different redox properties. [S0031-9007(96)00248-7]

The rapid progress in electronics over the last several decades relies critically on miniaturization which has been realized by carving smaller and smaller features on semiconductor chips. Another approach towards ultimate miniaturization that has attracted much interest is to build a circuit with single molecules [1]. These two approaches begin to overlap as semiconductor devices shrink towards the nanometer scale. On such a small scale, the discrete nature of charge and energy becomes important, and devices such as quantum dots begin to exhibit atomic or molecular properties [2]. An important task in developing molecular devices is to understand electron transfer between molecules and electrodes [1]. Using a scanning tunneling microscope, Joachim *et al.* [3] have recently studied electron tunneling through single C_{60} molecules in ultrahigh vacuum as a function of tip displacement. In this work, we attach redox molecules to a conductive substrate in aqueous solution and study the electron transfer through the molecules between the substrate and a scanning tunneling microscopy (STM) tip [Fig. 1(a)]. In contrast to fabricated quantum dot systems, the discrete nature of charge and energy in the present system is important even at room temperature because of the small size and the large separation between the energy levels of the molecules. Another distinctive feature of the present system is that the substrate and tip Fermi levels can be flexibly adjusted relative to the molecular orbitals by controlling the substrate potential vs a reference electrode inserted in the solution (Fig. 1). By tuning the substrate Fermi level to an unoccupied molecular orbital, we have observed a nearly tenfold increase in the tunneling current due to a resonant enhancement.

Studying electron transfer reactions of molecules in aqueous solution is of great importance also because of its central role in a variety of processes ranging from electrodeposition in electrochemistry to photosynthesis in biology [5]. To date, experimental information about the phenomenon has been provided primarily by spectroscopic and electrochemical techniques that measure various quantities averaged over a large number of molecules. The present work demonstrates a method for following the electron transfer reactions of individual molecules which may, therefore, provide new information (e.g., the dependence of electron transfer on the adsorption sites of the redox molecules) that is buried in the statistical averaging of conventional techniques.

The possibility of studying electron transfer of redox molecules in aqueous solution with STM was first proposed by Schmickler *et al.* [6] by performing tunneling
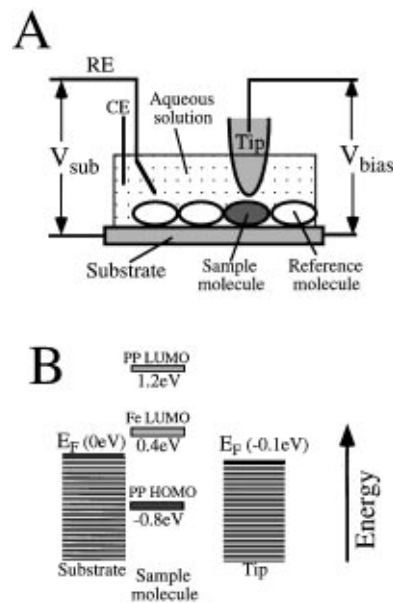

FIG. 1. (A) Schematic of a sample molecule coadsorbed with reference molecules on a substrate as probed by an STM tip. RE and CE represent the reference and counter electrodes, respectively. V_{sub} and V_{bias} are the substrate potential (with respect to the reference electrode) and the tip-substrate bias voltage, respectively, which are controlled independently by a bipotentiostat. (B) Energy diagram of Fe(III)-protoporphyrin IX in relation to the Fermi levels of the substrate and tip (Ref. [4]). PP LUMO and PP HOMO are the lowest unoccupied and highest occupied molecular orbitals of protoporphyrin IX, respectively, and Fe LUMO is the LUMO of Fe(III) in Fe(III)-protoporphyrin IX. Note that the addition of Fe(III) in protoporphyrin IX causes little change in the PP LUMO and PP HOMO.

spectroscopy. Although tunneling spectroscopy has been successfully used to obtain local electronic information of various samples in ultrahigh vacuum [7], the method is difficult to apply to molecules in aqueous solution due to a polarization current induced by the sweeping of the tip-substrate bias voltage. In the present work, we coadsorb a sample species with a reference species on a substrate and study the tunneling via the sample molecule, in relation to that via the reference molecules, as a function of the substrate potential with a small *fixed* tip-substrate bias voltage. The reference species is chosen so that the energy levels of its molecular orbitals are far away from the substrate and tip Fermi levels, therefore the tunneling current via it is not sensitive to the substrate potential. This approach does not have the problem of polarization current because no rapid sweeping of the tip-substrate bias is involved. It also reduces errors due to possible changes in the tip states during the measurement because the tunneling current via the sample molecules is measured in relation to that via the reference molecules.

The STM experiment was performed on a Pico-STM system (Molecular Imaging Co.) controlled by a Nanoscope III controller (Digital Instruments Inc.) with a home-made solution cell. The system can be operated at a tunneling current as small as 1 pA and has a typical drift of ~ 0.1 Å/s. STM tips were etched electrochemically from $Pt_{0.8}Ir_{0.2}$ and W wires which were then coated with apiezon wax [8]. The etching conditions were optimized to achieve a desirable tip profile for the coating. Although the tips were not the sharpest, they had a very small leakage current (<1 pA) over a broad potential range. In order to minimize the mechanical disturbance of the scanning tip on the molecules, the tunneling current was set to 30 pA or less with a tip-substrate bias of 0.1 V. Highly oriented pyrolytic graphite (Union Carbide) was used as the substrate on which the molecules are absorbed. In order to control the substrate potential, Pt wire was used as a counter electrode, and Ag wire was used as a quasireference electrode which was calibrated against a saturated calomel electrode (SCE). Potentials in this paper will be quoted vs the SCE. All the measurements were performed in a N_2 chamber.

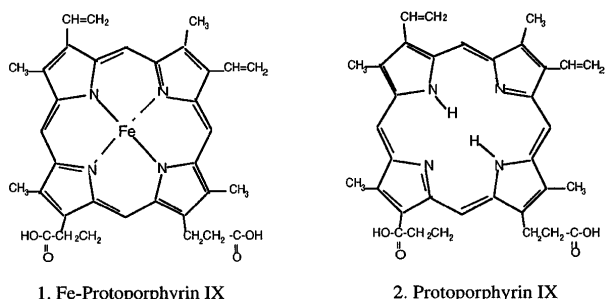Fe(III)-protoporphyrin IX [FePP, Fig. 2(left)] was studied in this experiment [9]. The molecule undergoes a reversible electron transfer reaction at -0.48 V in which Fe(III) is reversibly reduced to Fe(II) [Fig. 3(H)]. This occurs when the substrate Fermi level begins to align to the lowest unoccupied molecular orbital (LUMO) in Fe(III) as the substrate potential is adjusted to the reaction potential (-0.48 V). This electron transfer reaction has been intensively studied because FePP is the prosthetic groups of many important proteins such as hemoglobin and cytochrome c, and the electron transfer reaction is of direct relevance to the biological functions of these proteins [10]. Protoporphyrin IX [PP, Fig. 2(right)] was chosen as the reference species because it does not have a metal ion that provides an unoccupied orbital in the highest occupied molecular orbital (HOMO) and LUMO gap [see Fig. 1(B)] and it is structurally similar to FePP. FePP and PP were coadsorbed onto the graphite substrate by exposing the substrate to a solution containing them. By
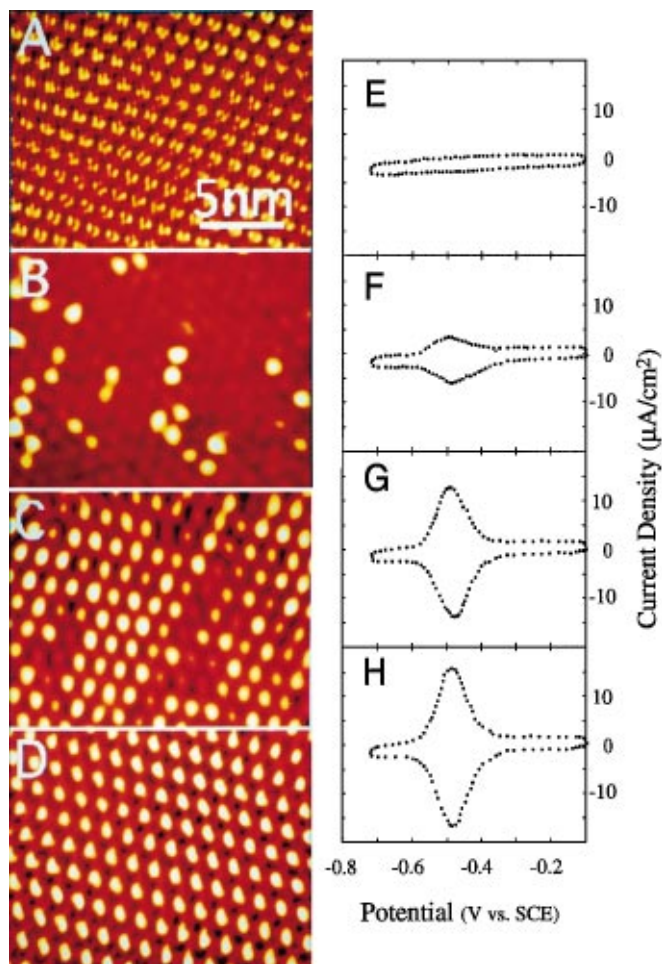
FIG. 2. Sample (left) and reference molecules (right) studied in this experiment.

FIG. 3 (color). STM images of FePP/PP adsorbed on a graphite substrate from $0.05M$ $Na_2B_4O_7$ solutions containing FePP and PP at the ratio of 0:1 (A), 1:4 (B), 4:1 (C), and 1:0 (D). The images were taken with a substrate potential of -0.41 V, a tunneling current of 30 pA, and a tip-substrate bias of -0.1 V. High frequency noise has been removed from the images. (E)–(H) are the corresponding cyclic voltammograms obtained with a sweeping rate of 0.2 V/sec.

controlling the ratio of PP to FePP in the solution, various amounts of FePP on the substrate can be easily obtained.

Figures 3(A) and 3(D) are STM images of PP and FePP in $0.05M$ $Na_2B_4O_7$, respectively. As we have shown in a previous work [11], PP and FePP lie flat on the substrate and self-assemble into identical two-dimensional lattices with $a = 13.4 \pm 0.2$ Å, $b = 12.2 \pm 02$ Å, and $\gamma = 68 \pm 2°$. Figures 3(B) and 3(C) are STM images of FePP coadsorbed with PP from $0.05M$ $Na_2B_4O_7$ solutions with a FePP to PP ratio of 1:4 and 4:1, respectively. The FePP molecules in the images are revealed as bright spots for reasons that will be discussed. From the images, we have determined the FePP to PP ratios on the substrate to be 1:3.4 and 4.5:1 which agree approximately with the FePP to PP ratios in the solutions. The amount of FePP has also been determined by integrating the cyclic voltammograms [Figs. 3(E)–3(H)] which further confirm the results estimated from the STM images. Note that all the images in Figs. 3(A)–3(D) were obtained with the substrate potential held at -0.41 V, close to the electron transfer reaction potential of FePP. We have imaged the molecules with the substrate held far away from the reaction potential and found that FePP and PP are hardly distinguishable because they are nearly structurally identical. The reason that FePP appears much "higher" (brighter) than PP near the reaction potential is due to resonant tunneling as the substrate Fermi level is aligned to the LUMO of FePP. This observation shows that structurally similar molecules adsorbed on a substrate in solution may be identified with STM based on their different electron transfer properties. Identifying absorbed atoms with STM based on measuring atomic resonance as a function of substrate-tip bias voltage has been demonstrated in ultrahigh vacuum [12]. In the present experiment, the electron tunneling is tuned into resonance by adjusting the substrate potential towards the electron transfer reaction potential rather than by varying the tip-substrate bias voltage.

We have measured the apparent height of individual FePP molecules relative to that of PP as a function of the substrate potential. When the potential is far away from the electron transfer reaction potential, there is little difference in the apparent heights of FePP and PP [Fig. 4(A)]. Adjusting the potential towards the reaction potential, the apparent height of FePP increases drastically [Figs. 4(B) and 4(C)]. Further change in the potential results in a decrease in the apparent height of FePP [Figs. 4(D) and 4(E)]. Cross sections along the path indicated in Fig. 4(A) are plotted in Figs. 4(F)–4(J) which show that the apparent height of FePP can increase by up to ~2.2 Å. If assuming a decay length of 1 Å in the tunneling current [13], the 2.2 Å apparent height difference corresponds to an increase in the tunneling current by nearly 1 order of magnitude. The measured apparent height vs the substrate potential is plotted in Fig. 5 which shows a clear maximum. This result is not due to a potential induced change in the tip states because FePP was measured relative to PP whose apparent height does not change over the same potential
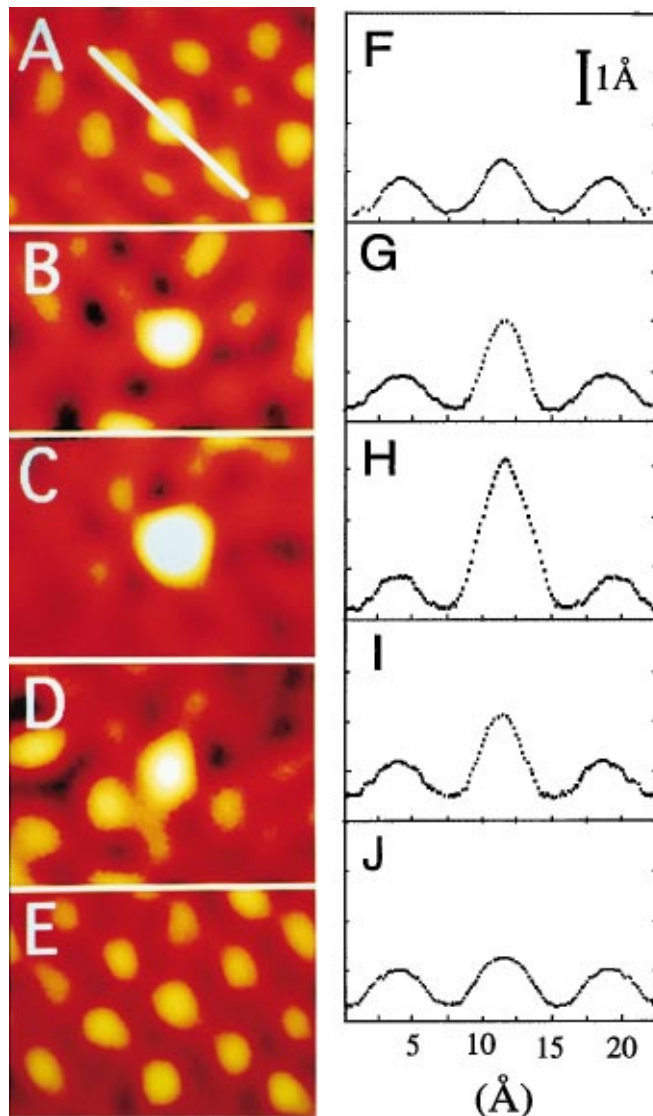

FIG. 4 (color). STM image of an FePP molecule embedded in an ordered array of PP molecules when the substrate was held at -0.15 (A), -0.30 (B), -0.42 (C), -0.55 (D), and -0.65 V (E), respectively. (F)–(J) are the corresponding plots of the cross sections along the white line indicated in (A). The data were symmetrized with respect to the center.

range. This is further confirmed by the fact that the results obtained by both W (filled circles) and $Pt_{0.8}$-$Ir_{0.2}$ (open circles) tips are essentially the same.

The sharpness of the resonant tunneling is related to the width of the Fe(III) LUMO which is broadened by the interactions of the redox center, Fe(III), with the surrounding solvent molecules [5,14] and with the substrate [15]. The redox center-solvent molecule interaction induced broadening arises from the fluctuation of the polar molecules that constantly shifts the energy level of the redox center via changing the potential experienced by the electrons in the redox center. This effect is known as a key in the electron transfer reactions in solution, and the effective width (full width at half maximum) is given by a simple expression, $4\sqrt{\lambda k_B T \ln 2}$ [14,16], where k_B is the Boltzman constant
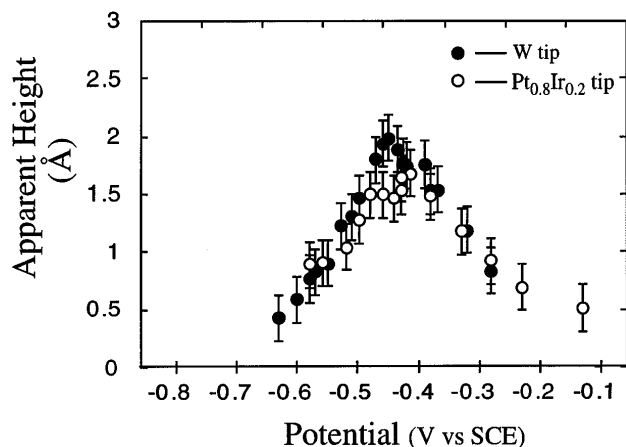
FIG. 5. Apparent height of FePP relative to PP as a function of the substrate potential. The data obtained with the $Pt_{0.8}$-$Ir_{0.2}$ tip and with the W tip are represented by open circles and filled circles, respectively.

and T is the temperature. The λ (reorganization energy [14,16]) in the expression is of the order of 1 eV according to the Marcus continuum dielectric model [16]. Using 1 eV for λ, the broadening in the LUMO due to the interaction of the redox center with the surrounding solvent is about $\sim$0.5 eV. This value is somewhat greater than the observed width ($\sim$0.3 eV) of the resonant tunneling, which is probably because the redox center, Fe(III), in FePP is partially isolated from the solvent when adsorbed on the substrate with an STM tip placed over the top of the molecule. The adsorbate-substrate interaction induced broadening is also well studied and believed to play an important role in the STM of adsorbed species [17]. For simple adatoms chemisorbed on metal surfaces, both theories and experiments have found that the broadening is $\sim$1 eV for s states and a few tenths of 1 eV for more localized d states [Fe(III) LUMO] [12,18]. So neither the solvent nor the substrate effects can be ruled out as the broadening mechanism in the resonant tunneling. Future experiments that may help us to separate the two effects would be to control the adsorbate-substrate distance by modifying the side groups of the molecules and to study solvent effect in the resonant tunneling.

In summary, we have shown that electron tunneling through redox molecules between an electrode and an STM tip can be tuned into and out of resonance by adjusting the electrode potential, and structurally similar FePP and PP molecules can be identified with STM based on their different redox properties. In terms of studying electron transfer reactions, the present method can be used to follow the reactions of individual molecules in aqueous solution.

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