称号及び氏名　博士（工学）　ブイ　タン　フク

学位授与の日付　平成25年9月30日

論　文　名　「Quantification of Electron Transfer through Noncovalent Interaction between Single Molecules
（単分子間における非共有結合を介した電子移動の定量評価）」

論文審査委員　主査　森　茂生
副査　高橋　雅英
副査　久本　秀明
副査　西野　智昭

論文要旨

Understanding electron transport at the single molecule level is of primary importance in utilizing a single molecule as an electronic component. Recently, there have been significant advances in the measurement of electron transport through a single molecule, and a large variety of molecules with unique electronic functions, e.g., wires, diodes, switches, and transistors, has been reported. Functional nanoelectronic devices can be realized by the controlled organization via self-assembly processes, where individual molecules are organized through noncovalent interactions between each other. These chemical interactions should allow not only the structural robustness of the molecular assemblies, but also a suitable electrical connection between the constituent molecules. Thus, the next challenge lies in measuring electron transfer between single molecules interacting with each other noncovalently. However, rather little is currently known about the electron transfer properties through the noncovalent interactions at the single-molecule interface, and even at the macroscopic scale.

In the present research, molecular tips of scanning tunneling microscopy (STM) were utilized to develop novel methodologies for quantification of electron transfer through noncovalent interaction between single molecules. The molecular tips have been used to overcome poor chemical selectivity of conventional STM. In addition to this advantage, these functionalized tips are also expected to provide a unique means of detecting intermolecular electron transfer given the fact that the electron tunneling takes place between a single molecule on the tip and another adjacent single molecule on a sample surface.

The present doctoral thesis consists of six chapters.

Chapter 1 is Introduction, which describes the background of the present research and related previous studies. The purpose and contents of the thesis are also provided.

Chapter 2 describes quantification of electron transfer through a hydrogen bond between single molecules. In this work, STM tips were modified with self-assembled monolayers of ω-carboxyl alkanethiol to prepare the molecular tips. A gold substrate was also modified with ω-carboxyl alkanethiol, and the molecular tip was brought into proximity with this sample surface. The electron transfer between the tip and sample molecules were measured while keeping the tip–sample distance constant by freezing the feedback loop of STM. The resulting current–time plot showed current jumps and consecutive plateaus. In the present measurement, the tip and sample molecules have carboxyl groups at their free ends, and the current jumps were attributed to hydrogen bond formation between these terminal carboxyl groups. The current increase brought on by the current jump, therefore, reflects electron transfer through the hydrogen bond interaction between the two single molecules. Surprisingly, the conductance of the hydrogen-bonded single molecules was found to be larger than that of the single molecule fully connected with covalent σ bonds. The first-principle calculations were carried out to qualitatively examine the origin of the superior conductivity of the hydrogen-bonded molecular junction. A prominent peak in the density of states projected onto the central region was found near the Fermi level for the hydrogen-bonded molecular junction while such a peak was absent for the covalently connected molecular junction. Because valence band structures affect the tunneling current through molecular junctions, the higher conductivity of the hydrogen-bonded junctions was attributed to the prominent peak in the projected density of states.

Chapter 3 concerns electron transfer through coordination bond interaction between single molecules. The ω-carboxyl alkanethiol was again used as tip and sample molecules to explore the effect of the metal coordination on the single-molecule conductance. Without a metal ion in the measurement solution, the molecular tip formed a hydrogen bond with the sample molecule through the carboxyl groups, and facile electron transfer took place as demonstrated in Chapter 2. In the presence of the metal ion, two kinds of electron transfer were detected. One of them was through the hydrogen bond between the carboxyl groups. Another electron transfer was attributed to electron transfer through a sandwich coordination molecular junction where the molecules on the tip and substrate coordinate with the metal ion. In Chapter 2, it was demonstrated that a hydrogen bond between single molecules can conduct electrons better than a covalent σ bond does. This chapter demonstrates that further facilitation of electron transfer occurs through metal-coordination bond interaction. These observations deepen our understanding of electron transfer between single molecules. Furthermore, the electron transfer induced by metal coordination was exploited in the construction of potential molecular switches activated by a single metal ion.

Chapter 4 deals with quantitative exploration of electron transfer from a single electron donor to a neighboring another single electron acceptor. Specifically, electron transfer in a single noncovalent porphyrin–fullerene dyad was measured by utilizing an STM tip functionalized with fullerene, prepared by chemical modification of the Au tip with a fullerene derivative. In the single-molecule conductance measurements, linking groups, such as thiols, which couple the sample with the electrodes, are mandatory and currently the subject of extensive research in the field of molecular electronics. Against this situation, this study introduced a novel method for electrical connection of a sample molecule to a Au substrate, i.e., ligation-mediated coupling. This protocol facilitates the detection of electron transfer without the use of a linking group and, thus, without chemical modification of the sample porphyrins. Combination of the fullerene molecular tip and ligation-mediated coupling enabled quantitative characterization of the conductance of the single fullerene–porphyrin assembly. It has been demonstrated that a porphyrin–fullerene pair exhibits a rectification property; this characteristic renders the molecular assembly particularly attractive in molecular electronics. Herein, the rectification was successfully quantified. The present study opens up a way for quantitatively exploring rich electronic properties of a supramolecule at the single-molecule level.

Chapter 5 demonstrates the application of the detection of intermolecular electron transfer to single-molecule sensing. Single-stranded DNA was utilized as a probe tip for single-molecule DNA detection. Hybridization occurred between the DNA tip and the target DNA adsorbed on the Au substrate during the conductance measurements so that the resulting double-stranded DNA bridges the gap between the Au tip and substrate. Subsequently electrons were transferred through the single DNA molecular junction. It was concluded that a DNA tip enables single-molecule DNA detection based on electron transport induced by the *in situ* hybridization during the current measurements. Furthermore, it was found that the presence of a single-base mismatch or methylated nucleobase in the DNA duplex results in significant decrease in the DNA conductance. These results demonstrate that the DNA tips offer a single-molecule sensitive, rapid, and low cost methodology for single-molecule genetic diagnosis through direct electrical detection.

Chapter 6 is Conclusion. This chapter summarizes the whole results in the doctoral thesis and provides their prospects.

審査結果の要旨

本論文は、化学相互作用を形成した単分子と単分子界面における電子移動の計測に関して、分子探針を用いた走査型トンネル顕微鏡（STM）に立脚し，単分子間における電子移動を計測する手法を開発し，様々な単分子界面において生起する電子移動の特性に関する研究成果をまとめたものであり、以下の成果を得ている。

⑴ 水素結合を介した電子移動の計測の提案を行った。種々の分子長からなるω-hydroxy alkanethiol（HS$(CH_2)_n$COOH；C_nCOOH）をAu STM探針，およびAu(111)基板に吸着させ、両者の距離を精密に制御し、分子レベルで互いに近接させることにより，探針上のC_nCOOH分子と基板上のC_nCOOH分子との間に生起する、水素結合を介した単分子間電子移動を計測することに成功した。

⑵ 配位結合を介した単分子間電子移動に関する研究を行い、2種類の電子移動が生じていることを見出し

た。ひとつは、水素結合を介した電子移動によるものであり、溶液中には金属イオンが存在するものの、これを含まない分子ジャンクションが形成されたためによるものである。他方の電子移動は、金属イオンが探針、および試料のカルボキシ基と配位結合を形成し、これを介して電子移動が生じたものであることが見出された。以上の測定により、分子ジャンクションに金属イオンを加え、配位結合を形成すると水素結合に比べさらにコンダクタンスが増加することを初めて明らかにした。さらに、このような現象を利用して、単分子の界面における電子移動を金属イオンにより制御できることを示した。

(3) 単分子間における電子移動計測をバイオセンシングへと展開した。8 mer の一本鎖 DNA を Au STM 探針に修飾し、DNA 探針を作製した。また、この DNA 探針と相補的な 8 mer の一本鎖 DNA を Au(111)基板に吸着させ、試料として用いた。これらを互い近接させ、電子移動を計測すると、探針、および基板上の DNA が二本鎖を形成し、これを介して電子移動が生じることが明らかになり、これによって DNA 単一分子の検出が可能であると結論づけた。また、DNA 探針、またはターゲット DNA にミスマッチやメチル化塩基が含まれている場合には電子移動により生じる電流値が大きく減少することを見出した。これにより DNA 単一分子のミスマッチ検出や DNA のメチル化を検出することによる癌の診断が単分子レベルにて実現できることが示唆された。

以上の諸成果は、分子探針を用いた走査型トンネル顕微鏡（STM）に立脚し，単分子間における電子移動を計測する手法を開発し、様々な単分子界面において生起する電子移動の特性を明らかにすることにより、新たな重要な知見を与えるとともに、学術的に大きく貢献するところである。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。学位論文審査会は、本論文の審査ならびに学力試験の結果から、博士（工学）の学位を授与することを適当と認める。