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様式３

# 論　文　内　容　の　要　旨

| 氏　名　（　陳　智瑨　Zhijin Chen　） | |
|---|---|
| 論文題名 | Determination of Single Molecule Rectifying Direction of Perpendicularly Connected Porphyrin-imide and Data Analysis by Machine Learning<br>（直交型ポルフィリン・イミドの単分子整流方向の決定と機械学習によるデータ解析） |

論文内容の要旨

Over the past decades, electronic components are made smaller and smaller. Further minimization is difficult due to physical limitation of materials and manufacturing process. On the other hand, organic molecules can be designed and synthesized at atomic-precision. The establishment of break junction (BJ) methods made measurement of electronic properties of single molecule possible. Under this background, organic molecules are expected to become alternatives of conventional electronics.

Among the electronic components, rectifiers, i.e. diodes, are one of the most basic and important components that conducts in only one direction. The first theoretical molecular rectifiers were proposed by Aviram and Ratner in 1974, which contains an electron rich part (donor) and an electron poor part (acceptor). Since then, many molecular rectifiers are proposed, including perpendicularly connected porphyrin-imide molecule which has localized molecular orbitals due to its spatial structure. Although the single molecule rectifying behavior of porphyrin-imide was confirmed by mechanically controllable break junction (MCBJ), the experimental rectifying direction of electrons kept unknown due to the limitation of molecular structure

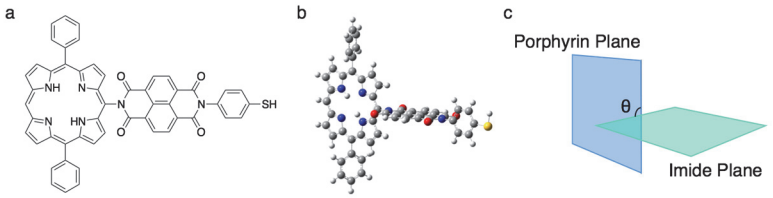


Figure 1 (a) Porphyrin-imide molecule researched in this thesis (**Por-Im-SH**). (b) Ball-stick model of porphyrin-imide. (c) Dihedral angle between porphyrin plane and naphthalenediimide plane.

This thesis focuses on determining the rectifying direction of perpendicularly connected porphyrin-imide molecule (Figure 1). Determination of the rectifying direction of porphyrin-imide is a key step to resolve the rectifying mechanism of porphyrin-imide.

Chapter 2 introduces experimental details of the thesis. In addition to synthesis and theoretical calculation, measurement technique and data analysis technique used in this thesis are described in detail. In order to keep the molecular orientation of porphyrin-imide during measurement, the blinking method was used to detect molecular junctions. A measurement system was set up on base of a scanning tunneling microscope (STM). The system is capable of automatic single molecular junction detection and *I-V* curve measurement. Moreover, an unsupervised clustering program using K-means algorithm was developed to help analyze the data from break junction measurements and *I-V* measurement. This program helps to reduce workload of processing

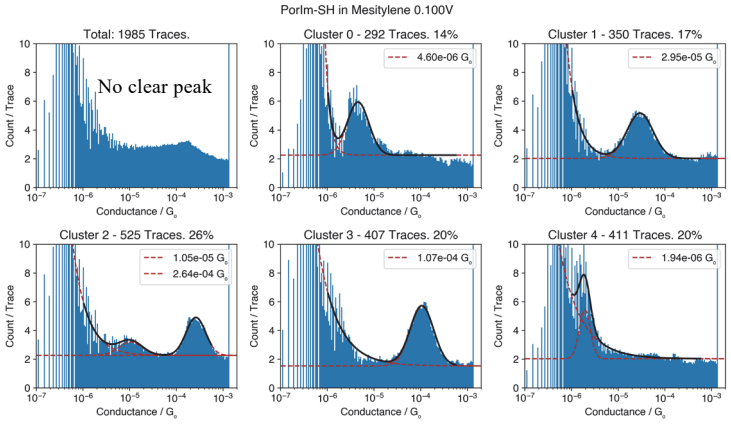


Figure 2 Histograms of raw break junction data showing no clear conductance peak (top left) and result clusters that showing clear conductance peaks.

and selecting the huge amount of data produced from single molecular measurements as well as cognitive bias introduced in manual selection. The clustering program is found to be useful in multiple cases including break junction data and *I-V* data (Figure 2).

Chapter 3 introduces molecular design and synthetic schemes of porphyrin-imide molecules. To accomplish the target to control molecular orientation during measurement, porphyrin-imide with asymmetrically protected thiol anchoring groups and porphyrin-imide with asymmetric anchoring groups were designed and synthesized. Porphyrin-imide utilizing porphyrin ring and thiol group as anchoring groups was chosen for theoretical study and measurement (Figure 1a).

Chapter 4 introduces theoretical studies of porphyrin-imide include density function theory (DFT) to study the possible anchoring conformations of porphyrin-imide between gold electrodes. The conductance of porphyrin-imide at zero bias was calculated by Non-Equilibrium Green Function (NEGF).

Chapter 5 introduces measurement of **Por-Im-SH** using STM break junction (STM-BJ) and blinking methods. Collected data were processed with unsupervised clustering to help analysis. Both STM-BJ and blinking method showed **Por-Im-SH** has conductance values of three different values, $G_H$, $G_M$, and $G_L$, corresponding to three different junction conformations, and they show different *I-V* shapes (Figure 3). When **Por-Im-SH** is attached to STM substrate, the current is higher at negative bias, and when **Por-Im-SH** is attached to STM tip, the current is higher at positive bias. This proves that the rectifying direction is in the direction of from imide part (acceptor) to porphyrin part (donor) (Figure 4), which is the same direction as theoretical NEGF calculation (Figure 5).

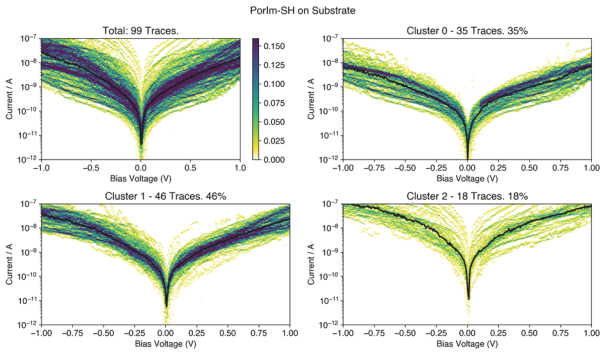


Figure 3 2D histograms of raw *I-V* curves (top left) and clustered result (rest). The clustered results show different *I-V* shapes, indicating multiple possible junction conformation.

The result of this results provided important information on rectifying behavior of porphyrin-imide molecules to reveal the rectifying mechanism. These results cannot be obtained without help of the new set up measuring system and unsupervised clustering. Further study about rectifying mechanism is under investigation.

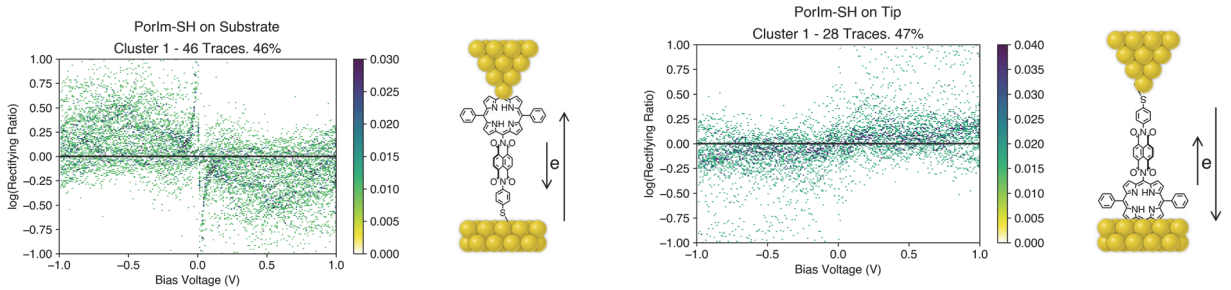


Figure 4 2D histograms of rectifying ratio of **Por-Im-SH** show opposite shape when **Por-Im-SH** is attached to either substrate or tip.

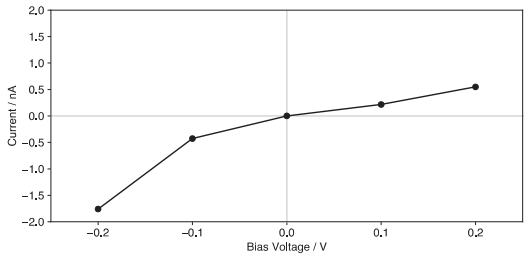


Figure 5 Calculated *I-V* of **Por-Im-SH** curve by NEGF. Bias voltage is defined as the voltage on imide side of the molecule.

様式 7

# 論文審査の結果の要旨及び担当者

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|---|---|

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## 論文審査の結果の要旨

単一分子整流子は、Aviram-Ratner（AR）が 1974 年に単一分子電子素子の可能性を最初に示した時に提案した能動電子素子である。2009 年に実験的に単一分子整流子が機能することが示されたが、その機構は AR が提案したものとは異なっており、またその整流の方向も当初の提案とは逆方向であった。AR の提案の特徴は、分子がドナー部分とアクセプター部分に分かれており、それぞれの分子軌道のレベルの差が整流性の原因となるとするものであったが、実際にそのような機構が機能するとの実験的に明確な証拠はいまだに無かった。

陳氏は、この問題に取り組むため、

（1） ドナー部（ポルフィリン）とアクセプター部（イミド）が直接結合しながら、垂直に交わらせることで二つの部分が共鳴せず独立した軌道を持つ分子を合成した。これにより、電気的な抵抗を最低限にしながらドナー部とアクセプター部の分子軌道の重なりを無くすることに成功した。

（2） 単一分子電気特性を計測するためによく使われている従来のブレークジャンクション法では、電極金属表面の乱れが大きく、測定中に分子が逆転する可能性があった。これを防ぐために金属表面の乱れが小さくなるブリンキング法を用いた実験を行うのに必要な装置の改造と自動測定プログラムを開発した。

（3） 金属との接合部分となるポルフィリン部位は複数の金属-分子接合コンフォメーションが可能であり、そのためと思われる複数の伝導ピークが見られた。それらを客観的に分類するために機械学習によるデータ解析を行い、明確な単分子電導度を求め、それぞれの電圧-電流特性を得ることに成功した。

（4） これらの実験により、主要な金属-分子接合コンフォメーションにおいては、電子がアクセプター側から入る方が伝導度が高くなる単一分子整流性が見られることを明らかにした。これは、AR の提案した電導機構と一致する整流方向である。

（5） ドナー・アクセプター・パイ電子系の３要素モデルを使い、非平衡グリーン関数法を用いた電圧依存の伝導度を計算し、伝導度、整流比とも実験と良い一致をすることを示した。

これらにより、分子軌道レベルの制御による非対称伝導性の設計が可能であることを、最初の提案から４０数年ぶりに実験的にあきらかにすることに成功した。この成果はナノ物性の科学として重要なものであり、本論文は博士（理学）の学位論文として十分価値のあるものと認める。