

氏 名 三宅 雄介

学位（専攻分野） 博士（理学）

学 位 記 番 号 総研大甲第 1221 号

学位授与の日付 平成 2 1 年 3 月 2 4 日

学位授与の要件 物理科学研究科 構造分子科学専攻
学位規則第 6 条第 1 項該当

学 位 論 文 題 目 Analysis of Versatile Self-assembled Two Dimensional
Structures of N, N'-bis (alkyl) Naphthalene-diimide on
Graphite Using Scanning Tunneling Microscopy and
Computer Simulation

論文審査委員	主	査	教授	加藤 晃一
			准教授	永田 央
			教授	横山 利彦
			准教授	櫻井 英博
			教授	埴田 博一（大阪大学）
			教授	小川 琢治（大阪大学）

1. Introduction

Construction of well ordered surface structures with functional molecular building blocks have attracted much attentions because of their potential applications for novel functional materials. In recent years, surface modification using self-assembly of organic molecules has been significantly advanced by scanning tunneling microscopy (STM) in ultra-high-vacuum (UHV)^{1, 2} or under ambient conditions.^{3, 4, 5, 6, 7, 8} Especially, *in situ* STM at the solid-liquid interface³ is a powerful and useful technique to characterize local surface structure, electronic state and surface dynamics of materials composed by organic molecules with submolecular resolution. Numbers of self-assembled structures on surfaces have been observed using *in situ* STM at the solid-liquid interface.^{3, 4, 5, 6, 7, 8} However, few report focused on influence of intermolecular and/or molecular-surface interactions of the component molecules systematically for the stable structures formed at the solid-liquid interface. I have investigated systematically the effects of the molecular structure on self-organized structure of porphyrin and naphthalenediimide, and their surface dynamics to explore new surface modification method based on self-assembled structures.

2. Investigation of Vanadyl and Cobalt(II) Octaethylporphyrin Self-Assembled Monolayer Arrays on Highly Oriented Pyrolytic Graphite (HOPG) by STM

Porphyrin and related compounds not only play an important role in photosynthesis, biochemistry and catalysis in nature, but are also important candidates for building blocks of future molecular devices.⁹ These compounds also have attracted significant attentions in the fields of life science, material science and physics because of their unique electronic structures, spectroscopic properties based on the large conjugated π -electron system and existence of metal coordination sites. Fundamental characterization of porphyrin metallate self-assembled structures by STM will contribute significantly to future applications of molecular devices. Two-dimensional crystals of [2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine] vanadium(IV)oxide and cobalt(II) (VOOEP and CoOEP, respectively) at the interface of 1-tetradecene and HOPG surface were studied by STM. The lattice parameters were determined for VOOEP ($a = 1.61 \pm 0.1$ nm, $b = 1.46 \pm 0.05$ nm, $\Gamma = 61 \pm 3^\circ$) and CoOEP ($a = 1.48 \pm 0.08$ nm, $b = 1.42 \pm 0.07$ nm, $\Gamma = 62.0 \pm 4^\circ$), which were calibrated using the HOPG lattice as the reference. High-resolution STM showed different type of the images for these two porphyrin molecules. The STM image of VOOEP was a square shape with four fold bright spots probably corresponding to the π -system of the porphyrin ring, and that of CoOEP showed a bright spot at the center metal site.

3. Effect of Alkyl Chain Length to the Two-Dimensional Structure and STS Studies of N, N'-bis(alkyl)naphthalenediimide on HOPG

Long alkyl chains are widely utilized as "anchor" groups for immobilizing organic molecules on graphite surface under ambient conditions in STM measurements. However, few report focused on effects of the alkyl chain length to self-assembled structures on HOPG systematically. STM investigations of self assembled structures of N,N'-bis(alkyl)naphthalenediimide (NDI) with a series alkyl chains ranging from propyl to octadecyl were carried out at 1-tetradecene/HOPG interface. NDI derivatives were prepared by the usual condensation reactions. Each NDI derivatives is abbreviated as CX-NDI (X is the corresponding carbon number of alkyl chains). The self-assembled structure of them on HOPG showed strong dependence on the alkyl chain length. I classified them into six types; (1) linear arrays with row lattice structure was observed in C3-NDI and C4-NDI, (2) chiral windmill structure in C4 and C5-NDI, (3) honeycomb structure in C6~C9-NDI, (4) chiral honeycomb structure in C10 and C12-NDI, (5) pseudo honeycomb structure containing super lattice in C11-NDI, (6) typical alkyl lamellar structure in C13~C18-NDI. In the self-assembled structure of C4, C5, C10, C11 and C12-NDI, meta-stable state structures were also observed. Molecular dynamics (MD) simulation for C3, C4, C9 and C18 are well coincident with the STM observations. Results of STM, MD simulation and X-ray single crystallography of C4-NDI clearly suggest that CH / O hydrogen bonding interaction is the critical driving force for the self-assembling.

4. Surface Dynamics and Nano-Size-Manipulation on Self-Assembled N,N'-bis(alkyl)naphthalenediimide on Graphite

During the STM observation of the self-assembled structure of NDI, thermally meta-stable states were found. I investigated dependence of the self-assembled structure of C11-NDI on temperature. A distort honeycomb structure was observed as a meta-stable state of C11-NDI, which converted to the thermally stable structure containing super lattice upon heating. The dynamic transition of the former structure to the latter was also observed.

5. Conclusion

I have investigated self-assembled structures of porphyrin and NDI derivatives in order to explore new self-assembled method and phenomena of surface dynamics. Self-assembled structures of two metallo octaethylporphyrins, VOOEP and CoOEP, were structurally characterized using STM. High-resolution STM images reflecting difference of the central metal were obtained.

Self assembled structures of NDI with a series of alkyl chain length ranging from propyl to octadecyl (excluding heptadecyl) were characterized using STM at 1-tetradecene / HOPG interface. Structural transition induced by the difference of

alkyl chain length was observed on self-assembled 2D structures of NDI derivatives. Competition of inter-molecular CH/O type hydrogen bonding interaction and intermolecular alkyl-alkyl interaction lead to complex self-assembled structures on HOPG. Thermal effects to the self-assembled structures were also investigated. Direct observation of a local structural transition was succeeded on C11-NDI self-assembled structure.

These surface studies described above will open a new method for self-assembled and solution-processed nano-fabrication.

論文の審査結果の要旨

有機分子が自己組織的に特定のナノ構造を形成し、そのナノ構造体の形状が機能に大きく影響することは良く知られている。しかし、こうした有機分子の自己組織化の研究はまだ黎明段階にあり、分子構造と自己組織体の構造の関連を予測することは困難である。高配向熱分解黒鉛(HOPG)上での有機分子の2次元自己組織化構造は古くから研究されており、規則構造の形成において長鎖のアルキル基が重要であることが経験的に知られていた。Groszekらは、1970年にHOPG上での長鎖アルカンの2次元自己組織化構造は、アルキル基のメチレン炭素がグラファイトの炭素原子の間に位置する構造になっていることを見いだした。それ以降アルキル基は有機分子がHOPG上で2次元自己組織化構造を作る際のアンカーとして働くとみられてきた。2000年頃になり、多種の有機分子のHOPG上での2次元自己組織化構造が多数報告されるようになり、長鎖アルキル基を持つ有機分子でも必ずしもGroszekモデルに従わないものがあることが見いだされてきた。

申請者は、典型的なドナー分子、アクセプター分子としてポルフィリンとナフタレンジイミド類に注目し、それらのHOPG上での2次元自己組織化構造を固液界面走査トンネル顕微鏡(STM)を用いて研究した。特にナフタレンジイミドについて、系統的にアルキル基の長さを変え、それらが多様な2次元自己組織化構造を形成することを見いだした。STMにより得られた画像から、それらがどのような分子配列によるものかを決定することは容易ではないが、申請者は分子動力学(MD)計算の助けを得て、観測されたSTM像の単位格子と良い一致を示す分子モデルを決定した。

それらの分子モデルを分析することで以下のことを明らかにした。

1. 炭素鎖が14以上のナフタレンジイミドにおいては、Groszekモデルに従う構造をとる。
2. 炭素鎖が13以下のナフタレンジイミドにおいては、ナフタレンジイミド同士の水素結合により形成される二量体(3種類)、三量体、六量体、八量体を構成要素とした構造を作る。

すなわち炭素鎖が13以下の分子においては、ナフタレンジイミド間およびナフタレンジイミドとHOPG基板の相互作用が構造を支配し、14以上ではアルキル基とHOPG基板の相互作用が構造を支配している。

このように、アルキル基の長さを変えるだけで多様な自己組織化構造が形成されることは、非常に興味深い。ナフタレンジイミドは、典型的な有機n型半導体として良く用いられており、その自己組織化構造が電子機能に大きく影響することが最近わかり始めている。こうした自己組織化構造の制御の観点でも申請者の基礎的研究は重要であり、博士(理学)の学位論文として十分であると判断した。