Abstract of Thesis

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Title	Study on the Properties of Organic Molecule / Nano-Carbon Conjugates （有機分子／ナノカーボン複合体の物性研究）

Abstract of Thesis

This proposal is to study properties of the "chiral" SWNTs decorated with functional molecules to enhance the functionalities. My research is on, self-organization of porphyrin derivatives on a carbon material surface. As the carbon material, I'm using graphite (HOPG) and single-walled carbon nanotubes (SWNT).

In our group in the past studies, the molecular electrical characteristics of the SWNT adsorbed to the surface had become clear[1,2]. Also, that self-organized structure of organic molecules on HOPG are significantly different at the slight differences in the molecular structure have also been revealed[3]. Together these two past findings, it is expected that there is a possibility that self-assembled structure of the organic molecules on SWNT greatly affects the physical properties of organic molecules / SWNT complex. As basic experiment to demonstrate this hypothesis, by performing the current experiments with a view to clarify the relationship of the self-assembled structure of the same organic molecules in a self-organized structure and the SWNT organic molecules on HOPG there. If the lattice structure of the underlying carbon in SWNT is greatly affects the self-assembled structure of the organic molecules on the surface, and self-organization of organic molecules on the SWNT which is inverted optically, different optical symmetry of the self-organizing structures is supposed can be formed, and is intended to observe it with a scanning tunneling microscope (STM)

This work has been dedicated to study some properties of organic molecule / nano-carbon conjugates for instance investigating and distinguishing the handedness chirality of SWNT using scanning tunnelling microscopic imaging (for the first time) via the supramolecular structures of some porphyrins and metal porphyrins on the tube surface, as well as more understanding the mechanisms by which such kind of these supramolecular structures can be formed on both the flat and curved nanocarbon materials surfaces. Here are the outputs of our study:

1. We succeed to investigate the handedness chirality of single-walled carbon nanotubes (SWNT) by using STM imaging technique and DFT calculations for the first time. This is can be achieved using the supramolecular chemistry of some porphyrin derivatives i.e. 5,15-bisdodecylporphyrin (C12P) on the tube surface. Surprisingly, by using two different types of chiral SWNTs (right handed ***P*** or plus SWNT and left handed ***M*** or minus SWNT); two opposite supramolecular structures have been observed showing the marvelous effect of SWNT handedness chirality on the alignment of organic molecules on its surfaces. Based

on our results, it has been found that alkyl chain substituted porphyrins can form a well-ordered supramolecular structure on the basal plane of SWNT surfaces that minutely maintains the Grozsek geometry with a little bit deviation. This vital finding explicate that SWNTs handedness chirality plays a crucial role for the molecular orientation of organic molecules on its surface.

2. The supramolecular structures of different central metal porphyrins i.e. ZnPor, NiPor and CoPor were successfully observed on SWNT (HiPCO raw) surface by using STM imaging technique and further characterized via HR-TEM and UV - Visible spectroscopy, with the purpose for identifying the effect of metalation on the supramolecular structures of porphyrins on SWNT surface. All the metal porphyrins can be adsorbed effectively on the tube surface leading to well-ordered supramolecular structures (especially in the cases of NiPor and ZnPor) on SWNT surface, as well as strong debundling effect (especially in CoPor case) for the nanotubes. Among the three metal porphyrins; NiPor produced the best STM resolution images. From an energetic point of view, DFT results displayed that the stability of these metal porphyrins complexes with the following order Ni < Zn < Co, additionally all the metal porphyrins complexes took chips shaped like structure or saddle structure with almost the same intermolecular contact distance between the porphyrin and SWNT surface which equal around 3 Å. Consequently by changing the central metal incorporated inside the porphyrin ring; different supramolecular structures can be observed on SWNT surface, which displaying the marvelous effect of different metal centers on the supramolecular structure of porphyrins on SWNT surface.

3. Successfully we confirmed the identification of SWNT handedness chirality using metalized porphyrin indicating that even though by changing the molecular structure i.e. insertion a central metals to the porphyrin ring; the handedness chirality of SWNT still can be recognized using the supramolecular structures of these organic molecules formed on the tube surface. Interestingly two opposite supramolecular structures of Ni-C12P molecules have been observed on SWNT surface, by using a mixture of two different types of chiral SWNTs (right handed P or plus SWNT and left handed M or minus SWNT), displaying the marvelous effect of SWNT handedness chirality on the alignment of organic molecules on its surfaces. In addition, surprisingly some novel supramolecular structures of Ni-C12P have been accidently observed on SWNT surface.

Ultimately, as a whole conclusion, by the aid of this study and these vital findings, hopefully it will be obvious to identify directly the absolute handedness chirality of the SWNTs, and being as key point for further understanding and building a new supramolecular architectures on curved nanocarbon surfaces, as well as can be used for designing and fabricating novel molecular architectonics of porphyrin / SWNTs based devices.

References

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様式 7

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

単層カーボンナノチューブ(SWNT)の構造を表す方法として(m,n)指数が用いられる。この指数は、可視～近赤外吸収スペクトル、近赤外発光スペクトル、ラマンスペクトルなどの結果を組み合わせる事で実験的に決められている。(m,n)により、ヘリシティ(helicity)が現れる構造も有り、ヘリシティを区別するためにP, Mという記号が用いられている。最近では、キラルな有機化合物を用いる事で、P, Mを分離することも可能になっているが、その絶対立体構造はまだ確定できておらず重要な課題になっている。候補者は、ヘリカルな単層カーボンナノチューブに電流を流したときの磁性に興味を持ってこの課題に取り組み、この研究の基礎となる絶対立体構造の決定を目指した研究を行った。

直接SWNTの原子構造を観察することは困難であるため、その上に有機分子の超構造を作成し、その超構造から下地の原子構造を推測するという手法をとった。SWNTのキラリティ(m,n)やP, Mにより、その上に出来る超構造体がどのように支配されるかの研究は、以前には全く報告が無い。

ほぼ純粋な(6,5)Pと(6,5)MのSWNTと予想されている物を用いて、長鎖アルキル基を導入したフリーベース・ポルフィリンとの複合体を形成し、その走査プローブ顕微鏡像を計測したところ、PとMで逆のヘリシティを持つ超構造の観察に成功した。次に、SWNT上の超構造の決定を目指して、同じポルフィリンを用いて、平面構造を持つ Highly Oriented Pyrolytic Graphite (HOPG)上で超構造を作成し、下地の炭素原子と超構造の関係を調べた。一般に、長鎖はHOPG上でGroszekモデルと呼ばれる構造に並ぶ事が多いことが知られているが、その構造からは約5°ずれていることがわかった。

また、DFT計算により、無置換ポルフィリンの(6,5)SWNT上での安定構造を求めたところ、SWNTの炭素格子からポルフィリンの対称軸が少しずれた構造になる事がわかった。更に、ポルフィリンの中心金属が、亜鉛、ニッケル、コバルトの化合物についても、SWNT上での超構造の観察、およびDFT計算を行った。計算結果からは、コバルト＞亜鉛＞ニッケルの順で安定な複合体を作るとの結果が得られた。STMによる複合体の観察では、ニッケルが最もはっきりした超構造を作った。これは、明確な超構造を作るために適切な相互作用の大きさがある事を示唆していることと思われる。上記のSTM像やDFT計算の結果を総合して、(6,5)SWNT上の長鎖ポルフィリン分子の超構造を提案し、当初の予備的なP, Mの同定と矛盾しないことを明らかにした。

有機分子の超構造が、SWNT のヘリシティに依存することを発見したのは、今回の実験が初めてで有り、大変重要な成果と考えられる。また、少ないサンプル量、大変大きな系の計算の困難さなど、様々な実験的制約の中で興味深い結果を引き出しており、また研究の背景となる知識もよく勉強していることから、研究者としての優れた資質をうかがい知ることができる。

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。