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学位論文題目 バナジウムフタロシアニン単層膜・多層膜の電子状態と磁気特性

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論文内容の要旨
Summary of thesis contents

Metal phthalocyanines (MPcs) and metal porphyrins (MPs) have attracted much attention as most promising materials to realize molecular devices and molecular spintronics, because MPcs and MPs can tailor their electronic and magnetic states by selecting the central metal ions. Whether we can control the wide range of functionalities of MPcs and MPs on substrate surfaces depends on our knowledge and techniques. It is of importance to reveal the interactions of MPcs and MPs with the substrate surfaces and the electronic states and magnetic properties at the interfaces. In addition, it is of interest from the fundamental science to elucidate the mechanism of appearance of their functionalities when they are put on extraordinary environments of surfaces. In this thesis, the author has set on the three subjects based on the viewpoints of molecular orientation, surface interactions, electronic structures and magnetic properties of complexes. The first is molecular orientation of pyramidal structured vanadyl phthalocyanine (VOPc) on Si(111)-(7×7) and Ag(111) surfaces. The interactions of VOPc with the substrate surfaces were investigated. The second is a magnetic interaction between the central V ion in VOPc and ferromagnetic metal surfaces. The last is the synthesis of vanadium phthalocyanine (VPc) and its electronic and magnetic states.

Preparations and measurements of the samples were performed under an ultrahigh vacuum (UHV) condition. Mainly three kinds of experimental methods, X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD) and X-ray photoelectron spectroscopy (XPS), were utilized to investigate element-selective chemical and spin states. XAS and XMCD measurements were carried out by using the XMCD system equipped with a superconducting magnet ($B = 7$ T) and a liquid He cryostat ($T = 3.8$ K) at the end station of Beamline 4B of UVSOR-III of the Institute for Molecular Science (IMS).

For the first topic, although molecular orientation and the effects of the work function of the substrate surfaces have been unveiled in previous reports, the interactions of adsorbed molecules with surfaces and the effects of the spin states of the central metals have not been understood well. Therefore, the author investigated molecular orientation and interactions of VOPc with Si and Ag surfaces. The results from XAS, XMCD and XPS measurements clarified that VOPc is adsorbed on the Si surface with an oxygen-down configuration, due to the strong interaction of the oxygen atom in VOPc with Si. It was also revealed that the chemical interaction between the framework of VOPc and Si is suppressed because of their large distance and the electron spin of the central V is maintained in VOPc on the Si surface as well as in a multilayer. On the other hand, it was found that VOPc is

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adsorbed on the Ag surface with an oxygen-up configuration. Furthermore, the site specific interaction of the framework of VOPc with the Ag surface was observed, although no interaction was observed between the central V and Ag and the spin of the central V was again maintained.

For the second topic, much effort has been devoted to understand the magnetic properties of MPcs and MPs on ferromagnetic surfaces. In the previous reports, ferromagnetic couplings between the central metals in the MPcs/MPs and the clean ferromagnetic surfaces have been elucidated, while antiferromagnetic couplings of the central metal atoms in MPs with the oxygen-adsorbed ferromagnetic surfaces are known. In this study, the magnetic interaction between VOPc and some ferromagnetic metal surfaces has been investigated to achieve an antiferromagnetic coupling of the central V with the ferromagnetic surfaces. The ferromagnetic surfaces were obtained by preparing Fe, Co and Ni ultrathin films on Cu(001). In the VOPc on the Fe system, it was found that the central V couples antiferromagnetically with the Fe surface. Similarly, antiferromagnetic interaction between the central V and Co was observed in the VOPc on the Co surface. In Contrast to these results, no effective magnetic coupling was detected in the VOPc on the Ni surface under a condition of a temperature of 5 K and an external magnetic field of 0 T, although the Ni film was fully magnetized. The existence of weak antiferromagnetic interaction between the central V and Ni was nevertheless expected, because the XMCD signal of the central V in VOPc on Ni at the field of 5 T was weakened in comparison to that on the Ag surface.

For the last topic, many MPcs have been synthesized since CuPc was discovered in 1927. In the 3d-transition-metal series, 3d-MPcs composed of a phthalocyanine ligand and a metal center have been synthesized for $M = \text{Ti, Cr-Zn}$, while the synthesis of ScPc and VPc have not been successful, because they are unstable under the atmospheric condition. The 3d orbitals in 3d-MPcs system split into four energy levels due to the ligand field effect. To systematically understand the electronic states of the central metal, the synthesis of the whole series of the 3d-MPcs is strongly required. In this study, VPc was synthesized for the first time on a substrate surface under the UHV condition. The author has investigated its electronic state and magnetic property. VPc was obtained by depositing metal free phthalocyanine (H_2Pc) and vanadium metal. From the results of angular dependence of V L edge XAS obtained using linearly polarized x-rays, it was found that the electronic ground state of VPc is mainly attributed to $(d_{xy})^2 (d_{xz}, d_{yz})^1 (d_z^2)^0 (d_{x^2-y^2})^0$ with the spin state of $S = 1/2$. In addition, the reduction of the XMCD signal of the central V was observed in multilayer, indicating that the VPc molecules are coupled antiferromagnetically with each other.

In summary, the author has investigated the electronic and magnetic structures

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of VOPc on the substrate surfaces. The results shows that the electronic structure of VOPc adsorbed on the surfaces is modified compared with that in multilayer due to the interaction with the surfaces. Furthermore, the author has succeeded in the synthesis of VPc and revealed its electronic state and magnetic property.

Summary of the results of the doctoral thesis screening

金属フタロシアニン(MPc)は、中心金属の種類に応じた多様な電子・スピン状態を利用した分子デバイスや分子スピントロニクスへの応用が期待されており、基板表面上での MPc の電子状態、磁気特性の評価と機能制御が重要となっている。基礎科学的には、基板表面という特異な環境に置かれた分子が示す物性の発現メカニズムを解明するという観点も重要である。本学位論文では、これまで報告のない大気中で不安定なバナジウムフタロシアニン(VPc)の合成とその薄膜の構造的・磁氣的性質を解析することを目的(第5章)とするとともに、大気中で安定なバナジルフタロシアニン(VOPc)薄膜の構造的・磁氣的性質の解析(第3章、第4章)をまとめている。論文の概要は以下の通りである。

第1章の序論に続き、第2章では実験や測定手法がまとめられている。試料の作製および測定はすべて超高真空下で行われ、主な測定手段は X 線吸収分光法(XAS)、X 線磁気円二色性(XMCD)、X 線光電子分光法(XPS)であり、元素選択的化学状態・スピン状態が調べられている。XAS および XMCD は分子科学研究所の放射光施設 UVSOR-III において、高磁場極低温装置を使用して行っている。

第3章では、ピラミッド型構造バナジルフタロシアニン(VOPc)の非磁性の Si(111)-(7 × 7)基板表面、Ag(111)基板表面との相互作用と分子配向について書かれている。その結果、Si 表面上では酸素とケイ素の強い相互作用で VOPc は酸素を下向きにして吸着し、Pc 骨格と Si 間の化学的な相互作用は抑制され、中心金属の V のスピンが保持される。一方、Ag(111)表面上では酸素を上向きにして吸着し、Pc 骨格と Ag 表面間にサイト特異的な強い相互作用が観測されたものの、中心金属の V のスピンについては保持されることが示されている。

第4章では、強磁性薄膜表面上の VOPc の V イオンと強磁性表面との磁氣的相互作用を検討している。Fe 薄膜上の VOPc では、中心 V と Fe 表面が反強磁性的に磁気カップリングしていることが示されている。このように常磁性分子と強磁性金属薄膜の相互作用で反強磁性相互作用が観測されたのは初めての報告である。同様に、Co 薄膜上でも相互作用は弱いものの中心 V と Co 表面との反強磁性的相互作用が観測された。一方、Ni 薄膜上の VOPc では常磁性的な挙動を示し、相互作用が非常に弱いことが示唆された。このように基板の強磁性金属の違いによる差異が鮮明に示された。

第5章では、大気下で不安定な VPc を超高真空下で初めて合成できたことが記されている。さらに電子状態および磁気特性についても検討され、VPc のスピン状態が $S = 1/2$ であることが示された。多層膜 VPc の試料では、中心 V の磁性が消失しており、隣接する VPc 間に反強磁性的相互作用が働いていると結論している。

以上の研究課題は出願者自身が独自に考えたものであり、不安定化合物 VPc の超高真空下での薄膜合成、常磁性 VPc, VOPc 分子と基板とのさまざまな相互作用に関して新しく有用な知見を得ており、高く評価できる。以上から、博士(理学)の学位を与えるのにふさわしい学位論文であると審査員全員一致で結論した。