論　文　内　容　要　旨

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学位論文の 題　　目	Electronic and spin properties of single molecule; characterization and manipulation by STM (単一分子の電子・スピン状態；STM による解析と操作)		

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[Introduction]　The application of the freedom of spin and charge of an electron to the quantum process of information is called ‘spintronics’. Single-molecule magnets (SMMs) are a unique class of compounds which show super-paramagnetic behavior at the single molecule level. They attracted much attention as materials for molecular spintronics devices, because we can control the spin distribution and the energy barrier for the magnetic relaxation. In the last two decades, variety of complexes with slow magnetic relaxation have been reported including phthalocyanine (Pc) multi-decker compound that shows a single molecule magnet (SMM) properties. The Pc based Tb(III) double-decker complex (TbPc2) shows a high blocking temperature, below which the magnetic relaxation becomes slow. Moreover, the magnetic relaxation behavior of the double-decker

complex is sensitive to the coordination and the surrounding conditions, which can be tuned using its flexible structure. It is possible to control their magnetic properties by changing the spin distribution via molecule synthesis or the molecule adsorption configuration control in films by using techniques such as a redox reaction or pulse current application from a STM tip. Also we investigated spin states of stable neutral pure-organic radical molecules of 1,3,5-triphenyl-6-oxoverdazyl (TOV) and 1,3,5-triphenyl-6-thioxoverdazly (TTV). Such properties are useful for the applications like as a quantum computing and a spintronics device.

[Experiment] Au mica is used for the substrate, which was prepared with a standard Ar+ sputtering and annealing process in ultra-high vacuum (UHV). The degassing of molecule is performed carefully by heating a container of Ta boat for several hours prior to evaporation. STM measurements are done in UHV chambers at 4.7K. STS dI/dV curve is obtained by using a lock-in amplifier.

[Results and Discussion] We investigated the phthalocyaninato (Pc) based Tb(III) double-decker complex (TbPc2) molecular adsorbed on Au (111) surface by using scanning tunneling microscope (STM) and detect the TbPc2 molecular spin with an atomic scale resolution by observing Kondo state. The detection of Kondo feature with scanning tunneling spectroscopy (STS) has been studied mainly for the metal atoms adsorbed on the surface. Also we control the molecular spin and switch spin "on/off" by molecular adsorption structure manipulation and alkali metal Cs doping.

Figure 1a shows the STM image of TbPc2 film on Au (111) surface. There are two types of the bonding configuration of the TbPc2 molecule, which are marked with 'B' and 'D'. Kondo feature is obtained only on the B molecule lobe and not center position, see Fig. 1b. The Kondo effect is only obtained on molecule lobe position, this demonstrates that the Kondo resonance is originated from TbPc2 molecule ligand unpaired π spin. 1)

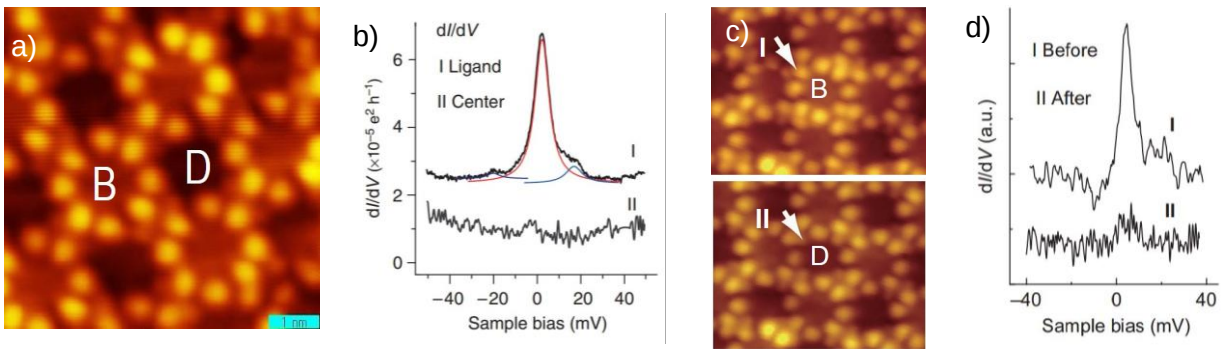

Fig. 1 (a) $TbPc_2$ film STM image. There are two types configurations marked with B and D; (b) shows Kondo STS on B type molecule lobe and center; (c) $TbPc_2$ molecule manipulation by applying current pulse and change molecule form B to D; (d) Kondo STS on the molecule before (I) and after (II) current pulse applied.

Next we control TbPc2 magnetic properties by changing the molecule configuration by using pulse current application from a STM tip. We change TbPc2 molecule form B to D in Fig. 1c. We obtain the Kondo STS on the molecule before (I) and after (II) changing. We find the Kondo feature is disappeared after manipulation, see Fig. 1d. Since the Kondo resonance is originated from the unpaired π orbital of the Pc ligand, we can switch spin on/off by changing the molecule's structure that can be realized by the pulse current application. The DFT calculation shows the unpaired π spin in Pc ligand SOMO become doubly occupied and unpaired π spin is paired by an electron transferred from Au surface when the molecule configuration is changed into the D state. 1)

Figure 2a shows the model of single TOV molecule. STM is able to confirm that the TOV adsorption structure is formed of monomer, dimer and hexamer on Au (111) surface. Also there are two types' configuration of TOV molecule, which are marked with 'A' and 'B' in TOV dimmer shown in Fig. 2b. Kondo feature was obtained only on the type B molecule and not on type A molecule, see Fig. 2c. The DFT calculation suggested that attachment of H atom to the O atom to form OH bond can make a bright spot in type A molecule (Fig. 2d). An electron transfer from the H atom to the unpaired π electron makes the unpaired π electron paired, which results in the disappearance of Kondo peak in type A. In this field, we first successfully detected the spin as Kondo resonance in pure-organic radical molecule at the atomic scale resolution by STM. 2)

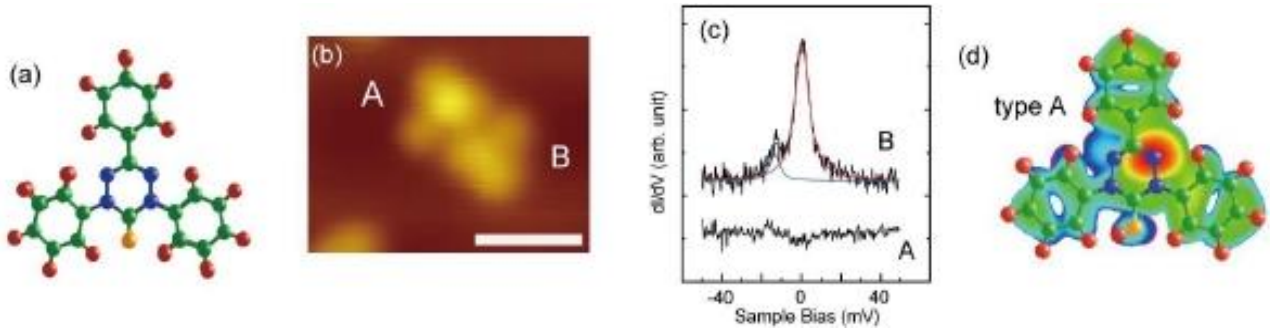

Fig. 2 (a) Model of TOV molecule. (b) STM image of TOV molecules; Size:2.0nm×2.0nm; Setpoint:0.1nA,-0.8V. (c) Kondo resonance observed on type B molecule. (d) Simulation image of type A molecule which formed "OH" bond by VASP calculation.

Reference:
1) Komeda Tadahiro, Liu Jie *et al.*, *NATURE COMMUNICATIONS*,2011,**2**, 217
2) Liu Jie, Komeda Tadahiro *et al.*, *J. Am. Chem.* Soc., 2013,**2**,135

論文審査の結果の要旨

分子の持つシャープな電子状態やスピン状態、あるいは構造とそれらの状態が密接に連動する性質などが電子材料等への応用を念頭に入れて注目されている。スピンは言うまでもなく化学の根幹をなす自由度であり、スピンの分析は化学分析の中で欠くことのできない要素である。電子や核のスピンの検出に ESR や NMR の測定技術が広く使われるが、これらの検出手法はマクロな試料の平均情報を与えるものであり、原子スケールでのスピン情報検出には多くの開発努力がなされている。

本論文においては、スピンを原子レベルで検知する手法として、走査トンネル顕微鏡のトンネル電子を分光することで近藤ピークを検出しスピンの情報を得る手法を開発しようとしている。対象として、単分子磁石や有機のみで形成される磁性分子を用いている。単分子磁石（SMM）は単一分子で磁石の性質を示す分子であり、基本単位のスピンが、いったんある方向を向いた場合に、逆の方向にスピンが向くまでの時間（緩和時間）が他の分子に比べて長く、緩和時間内ではその磁石としての特性を保持でき、SMM は大きな可能性を持った磁性を用いた電子材料になると考えられている。また、有機ラジカル分子における磁性は、金属原子が形成するスピンとは異なった非局在化された電子のスピンによるものであり、基礎化学的な興味とともに、ラベリング等での応用にも直結している。

構成として（１）SMM に関して、2 層のフタロシアニン（Pc）を配位子とするテルビウム錯体（bis(phthalocyaninato)terbium(III) complex（TbPc2)、TbPcNPc 分子ならびに２層ポルフィリン錯体における、近藤ピークの検出によるスピン情報の取得、（２）トンネル電子を単一分子に注入することで原子単位での分子の構造変化を引き起こし、それによるスピン状態変化の観察、（３）有機ラジカル分子 triphenyl-6-oxoverdazyl（TOV)分子についての近藤ピークの検出とスピン空間分布検知、からなる。

いずれの内容も世界に先駆けた化学的知見を得ている。また、これらの実験は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、Liu Jie 提出の博士論文は、博士(理学)の学位論文として合格と認める。