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研究課題名（和文） Investigation of tautomerization in meso-dibenzoporphycene by intramolecular resolution atomic force microscopy and scanning tunnelling microscopy

研究課題名（英文） Investigation of tautomerization in meso-dibenzoporphycene by intramolecular resolution atomic force microscopy and scanning tunnelling microscopy

研究代表者

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研究成果の概要（和文）：我々は、銀、鉛および銅の基板の上に蒸着したメソジベンゾポルフィセン分子(mDBPc)を分子内分解能原子間力顕微鏡および走査型トンネル顕微鏡を用いて研究した。特に、上記表面に吸着したmDBPc分子に予測されるシスとトランス配置を明らかにし、その互変異性化反応に対する局所環境の影響を調べた。実験の結果、mDBPc分子の吸着エネルギーの複雑な様相が明らかになった。すなわち、一方の配置がもう一方に対して明らかに優勢なポテンシャル井戸を持っており、最も安定的な配置としてシスまたはトランス形を示す吸着位置は、分子内の不飽和窒素原子の相互作用を通じて、その基板の性質に依存していると考えられる。

研究成果の学術的意義や社会的意義
我々の研究結果には、金属表面および絶縁表面と相互作用している分子系の複雑な挙動の理解という意義がある。

研究成果の概要（英文）：In this project, we deposited meso-dibenzoporphycene (mDBPc) molecules on silver, lead and copper substrates and studied these systems with intra-molecular resolution atomic force microscopy and scanning tunneling microscopy using functionalized probes with a carbon monoxide molecule attached to the forefront part of the probe apex. We wanted to characterize the cis- and trans- configurations predicted for the mDBPc molecule upon adsorption on the above mentioned surfaces and study the influence of the local environment on the tautomerization reaction. Our experiments point towards a complex energy adsorption landscape of the mDBPc molecule where one of the configurations has a clear dominant energy potential well with respect to the other, and an adsorption position displaying the cis or trans form as the most stable adsorption configuration seems to depend on the nature of the substrate, through the interaction of the unsaturated nitrogen atoms of the molecule with it.

研究分野： 物理化学

キーワード： 走査プローブ顕微鏡

１．研究開始当初の背景

Tautomerization is a chemical reaction involving the migration of hydrogen atoms (i.e. protons) inside a molecule, and its characterization is of great interest in the field of surface chemistry. Tautomerization in phthalocyanine and porphycene molecules deposited on metallic surfaces has been previously studied using cryogenic temperature scanning tunneling microscopy (STM) [1-3]. Similarly, in this project we aimed at the characterization of the tautomerization reaction predicted for meso-dibenzoporphycene (mDBPc) by using scanning probe microscopy techniques. mDBPC is a porphycene derivative that has been recently synthetized for the first time at Osaka University's Prof. Takashi HAYASHI's group [4]. This molecule is not commercially available yet, and there are no studies on the adsorption and behavior of this molecule upon deposition on a surface. Since mDBPc may have potential application as a solar cell component as well as photosensitizers for photodynamic therapy, we wanted to study the adsorption of mDBPc on several surface, and elucidate whether the tautomerization reaction predicted for this molecule could also make of mDBPc a molecular switch.

２．研究の目的

By using intra-molecular resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM), we wanted to focus the study on clarifying the influence of the local environment (such as the conducting/insulating nature of the substrate, or the presence of nearby atoms and molecules) in the tautomerization process, and to try to characterize the differences expected for the "cis" and "trans" forms of the molecule. We also planned to try to induce the tautomerization reaction by using both the tunneling current and the probe-surface interaction force, and ultimately clarify the atomistic processes behind it.

３．研究の方法

In the first phase of the study we deposited the mDBPc over several metallic surfaces, including Cu(111), Cu(100), Ag(111), Au(111), and Pb(111) to explore the most suitable substrate to study the tautomerization reaction on individual molecules. On top of all these surfaces, it is possible to grow islands of sodium chloride (NaCl) insulating thin film, which would help us to clarify the influence of the substrate in the tautomerization reaction.

In our homemade experimental system, it is possible to evaporate atoms and molecules directly on the sample while it is kept below 16K. We deposited single mDBPc molecules on the above mentioned metallic surfaces, with and without small islands of NaCl thin film previously grown on them, and studied the molecule adsorption properties and stability at a minimum temperature of 4.8K, as well as the possibility of inducing the tautomerization reaction by both current injection and by increasing the probe-molecule interaction force. Furthermore, using atom manipulation techniques, we wanted to create artificial nano structures using mDBPc molecules and adsorbates that will allow us to investigate how the presence of nearby adsorbates influences the tautomerization.

A key element of on this project was to perform the characterization of the mDBPc molecules using intra-molecular resolution imaging using carbon monoxide functionalized probes, which provides AFM images that resemble the chemical structure of the molecule [5].

The clarification of the atomistic origin behind current-induced and force-induced tautomerization of the mDBPc molecule requires support from first-principles simulations.

４．研究成果

During the first phase of the project we deposited the mDBPc molecule on Ag(111), Pb(111), Cu(111) and Cu(100) metallic substrates. An example of mDBPc molecules deposited on the Cu(100) and NaCl/Cu(100) surface are depicted in Fig. 1. In contrast to the cases reported for phthalocyanine [1] and porphycene molecules [2], where cis and trans forms of the molecules were found after deposition on a metallic substrate, we have not observed a clear difference between the cis- and trans- configurations for the mDBPc molecule upon adsorption on the above mentioned metallic surfaces. These facts made us suspect that the molecule was loosing the hydrogen atoms that produce the tautomeraization reaction upon sublimation of the molecules from the evaporation cell, because the temperature for the molecular sublimation and the molecular decomposition are close.

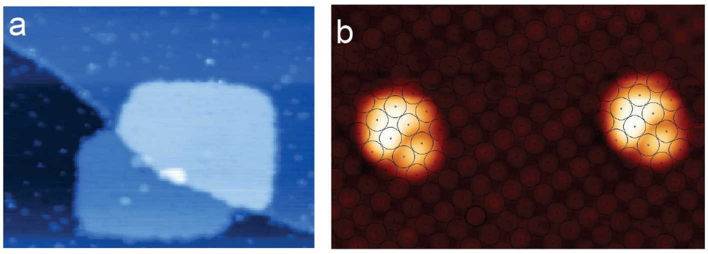

Figure 1: **(a)** Topographic STM image of an island of NaCl thin-film (bright square structure) grown on top of a Cu(100) substrate. The spots visible around the island are mDBPc molecules. **(b)** Topographic STM image showing the adsorption position of two mDBPc molecules deposited on top of a NaCl island while keeping the substrate cooled down with liquid helium.1

To verify this hypothesis, we performed AFM intramolecular resolution imaging with CO-functionalized probes. We co-deposited the mDBPc molecules and CO molecules on a Cu(100) substrate that was previously cooled down to 4.8K. Using vertical manipulation techniques, we were able to pick up a CO molecule from the substrate (Fig. 2a-d). The carbon atom of the CO molecule strongly binds to the outermost metal atom of the probe, and the oxygen atom protrudes from the probe apex producing a robust, stable, relatively inert, and flexible apex. This probe functionalization enables one to explore the repulsive part of strong inter-atomic short-range forces between the atoms and bonds of the mDBPc molecules and the CO, and produce AFM images that resemble the molecule structure [5], as it is shown in the lower panel of Fig.2.

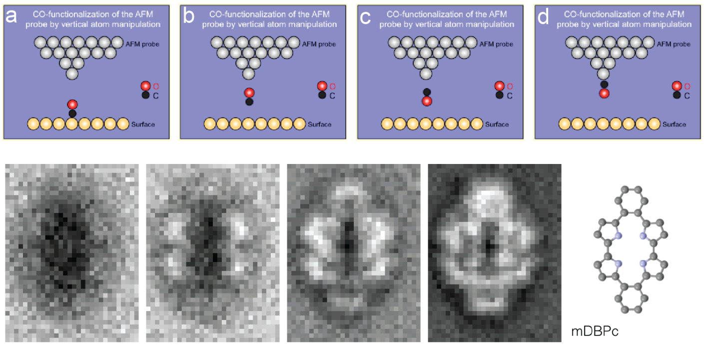

Figure 2: **(a)-(d)** Series of images representing the picking up of a CO molecule from the surface to functionalize the AFM probe. The adsorption of the CO molecule at the apex of the probe is performed by momentarily increasing the electric field between the probe and the surface by a applying a small bias pulse. The panels at the lower part of the figure present constant-height AFM images extracted from a three-dimensional force map measured over a mDBPc molecule deposited on the bare Cu(100) surface using a CO-functionalized AFM probe. The structure of the mDBPc molecule is shown on the right for comparison. The probe-surface separation is successively reduced from left to right.

In parallel, we asked a collaborator of us -who is an expert on first-principles calculations- to make simulations of the adsorption geometry of mDBPc molecules deposited on a Cu(100) and NaCl substrates. Our collaborators found that the differences between

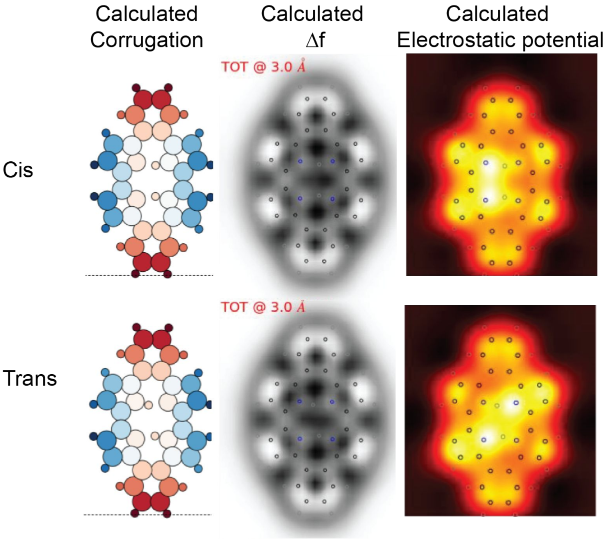

Figure 3: Initial output from first-principles calculations on the AFM signals to be expected from cis (upper panels) and a trans (lower panels) configurations of a mDBOc molecule. The calculated corrugation shows a slightly bending of the molecule upon adsorption on the surface with the red atoms in a closer position to the surface and the blue atoms slightly protruding from the plane of the molecule, with a height difference between them of approximately 1Å. The calculated frequency shift signal from the structural model reveals almost no difference between the cis and the trans configurations. The calculated short-range electrostatic potential is the only signal that offers an apparent difference between cis and trans configurations of the mDBOc molecule. It is quite remarkable the similarity of the calculated frequency shift images and the experimental image at the closest probe-surface separation shown in Fig. 2.

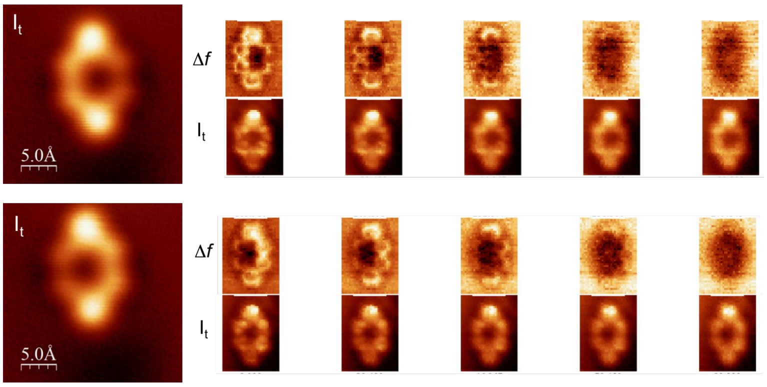

Figure 4: Images of a mDBPc molecule adsorbed on a bare Ag(111) surface acquired with a CO-functionalized probe. The images in the upper and lower part of the figure correspond to the same molecule. The series of small images on the right correspond to constant-height frequency shift (Δf) and STM (It) signals simultaneously acquired over each of the configurations of the molecule, with the probe approaching towards the surface from right to left.

the calculated AFM signal of cis- and trans-forms of the mDBPc molecule are indeed quite subtle, almost imperceptible. Additionally, they found that the major differences between cis and trans forms of the mDBPc molecule are in the short-range electrostatic potential (Fig. 3). Upon this prediction, we conducted Kelvin probe force microscopy experiments on the mDBPc molecules, however at the probe-surface separations we performed the experiments to prevent a strong contribution of the short-range forces, we were unable to discern between cis and trans configurations in the short-range contact potential difference. While in the calculations it is relatively easy to separate between the different signals that can be measured with atomic resolution AFM, experimentally it is sometimes tremendously difficult to access each of these force channels individually, without having a contribution from the other force channels. It is remarkable, the resemblance between the experimental frequency shift (Δf) signal at the closest probe-surface approach depicted in Fig. 2 with the calculated ones for the cis and trans configurations of the molecule shown in Fig. 3.

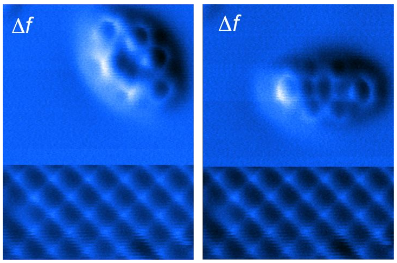

Figure 5: Constant-height AFM mages of the same mDBPc molecule adsorbed in two different configuration on top of a NaCl island grown on the Ag(111) surface. The images were acquired with a CO-functionalized probe, and the change in the adsorption configuration was induced by a voltage pulse. The lower part of the images was acquired at a closer probe-surface distance to reveal the NaCl atomic lattice. By extrapolation of the atomic lattice it is possible to determine the adsorption position of the molecule in each configuration.

Since no clear difference between cis and trans configurations of the mDBPc molecules were detected in experiments performed on the surfaces mentioned above, we decided to focus the study on the Ag(111) surface. We chose this substrate for several reasons: the first one is that we have developed a method to very efficiently regenerate the apex of the probe and make it atomically sharp; another reason is that on Ag(111) is relatively easily to pick up a CO molecule adsorbed on the surface to create a CO-functionalized AFM probe [5]; and finally, as mentioned above, it is also quite easy to grow relatively small islands of NaCl insulating thin film on this surface too.

Figures 4 and 5 show the appearance of the mDBPc molecules on the bare Ag(111) surface and on top of a NaCl island grown on a Ag(111) substrate, respectively. We have found remarkable differences between the molecules adsorbed on the Ag(111) surface and other metallic substrates. At variance with the Cu(100) case shown on Fig. 2, for instance, the mDBPc molecules on Ag(111) display a depression in the AFM signal along the molecular axis. This depression makes the molecule asymmetric (see Fig.4), and it resembles the cis-conformation of phthalocyanine deposited on Cu(111) [2]. On Ag(111), the mDBPc molecule adsorb with its long molecular axis aligned to the [111] planar direction. We have been able to induce the flipping of this asymmetric feature by setting an appropriate bias, however, the appearance of the molecule after the flipping is a mirror image of the previous configuration (Fig. 4). We have measured three-dimensional force maps on the molecule before and after the flipping. The presence of a still attractive force over the depression displayed along the axis of the molecule at a surface distance where the onset of the short-range repulsive interaction force is detected all over the rest of the molecule points towards this conformation being the cis-configuration of the molecule.

On the NaCl islands grown on a Ag(111) substrate, we have detected two adsorption positions for the mDBPc molecule, as depicted in Fig. 5. One configuration is asymmetric, parallel to the NaCl lattice, and its appearance resembles the molecules adsorbed on the Ag(111) bare surface. The other configuration is symmetric with the long axis of the molecule rotated 45 ° from the NaCl lattice. The appearance of the symmetric molecule looks similar to the one detected for Cu(100) (Fig. 1) and the calculated images displayed in Fig. 2. This symmetric configuration could correspond to the trans-form of the mDBPc. At variance with the asymmetric form, curves extracted from a three-dimensional force map measured on the latter configuration show the absence of a large attractive force over a specific area of the molecule, and a quite similar behavior of the short-range forces over equivalent probe-surface separation regimes over the resolved structures.

Our experiments point towards a complex energy adsorption landscape of the mDBPc molecule over different substrates where one of the configurations of the molecule has a clear dominant energy potential well with respect to the other. In contrast to the case of simpler porphycene molecules, an adsorption position displaying the cis or trans form as the most stable adsorption configuration seems to depend on the nature of the substrate, through the interaction of the unsaturated nitrogen atoms of the molecule with it. Currently, calculations are being performed to confirm the assignment of the configurations detected on Ag(111) and NaCl/Ag(111) surfaces to the cis and trans forms of the molecule, by the compassion of measured intramolecular resolution images and forces with computer-simulated AFM images of the most stable adsorption configuration obtained from first-principles calculations.

References:

[1] Liljeroth et al., Science 31, 2007, 1203
[2] Kumagai et al. Nature Chemistry 6, 2014, 41
[3] Ladenthin et al. ACS Nano 7, 2015, 7287
[4] Oohora et al., Angew. Chem. Int. Ed. 54, 2015, 6227–6230
[5] Gross et al. Science 325, 2009, 1110

５．主な発表論文等

〔雑誌論文〕（計１件）

Title: Pentacene/TiO2 Anatase Hybrid Interface Study by Scanning Probe Microscopy and First Principles Calculations
Authors: Milica Todorovic, Oleksandr Stetsovych, Cesar Moreno, Tomoko Shimizu, Oscar Custance, Ruben Perez.
Journal: ACS APPLIED MATERIALS & INTERFACES, Vol.10, Pg. 34718 to 34726, (2018)

Reviewed by referees.

６．研究組織