Trapping a Charged Atom

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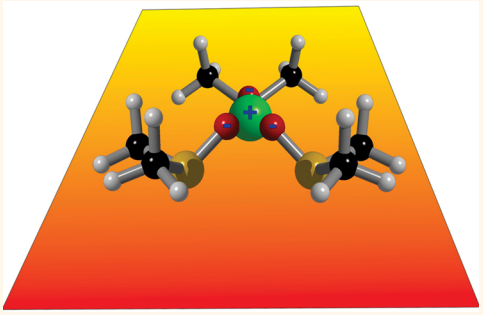
ABSTRACT Engineering of supramolecular assemblies on surfaces is an emerging field of research impacting chemistry, electronics, and biology. Among supramolecular assemblies, metal-containing structures provide rich properties and enable robust nanostructured designs. In this issue of *ACS Nano*, Feng *et al.* report that supramolecular assemblies can trap gold adatoms that maintain a charged state on a Au(111) surface. Such charged adatoms may offer additional degrees of freedom in designing novel supramolecular architectures for efficient catalysts, memory, and charge storage for medical applications.



Since prehistoric times, nearly all civilizations have considered gold to be divine and have associated it with religion and wealth. Its brilliance and natural beauty originate from its shining bright color. One of the reasons why gold continues to shine is due to its chemical inertness; gold is one of the least reactive metals. However, if the size of the gold is reduced to the nanoscale, it becomes reactive. Based on their reactivity, gold nanoparticles find many applications ranging from catalysts to medicine.[1,2] In this issue of *ACS Nano*, Feng *et al.*[3] report taking the properties of gold a step further: They show that individual gold atoms on gold surfaces can maintain net charge when they are trapped inside adsorbed molecular complexes.

Feng *et al.* discovered charged gold adatoms in a study of dimethyl sulfoxide (DMSO) on Au(111) surfaces. Discovered in 1867 by Alexander Saytzeff,[4] DMSO ($(CH_3)_2-SO$) is a polar molecule composed of two methyl groups linked *via* a sulfinyl group (S═O). It is a byproduct of the wood industry and is widely used as an aprotic solvent,[5] including in applications in electrochemistry and batteries.[6,7] In biology, DMSO is used as a cryoprotective agent, as a membrane penetration enhancer, and as a cell fusogen;[8,9] in medicine, it is a popular pain reliever in addition to its usage for hundreds of other ailments.[10,11] Although DMSO is widely studied,[12] it is considered to be one of the least understood pharmaceutical agents of our time.

In this issue of *ACS Nano*, Feng *et al.* report taking the properties of gold a step further: they show that individual gold atoms on gold surfaces can maintain net charge when they are trapped inside adsorbed molecular complexes.

In the current work,[3] the researchers deposited DMSO on atomically clean Au(111) surfaces under ultrahigh vacuum at substrate temperatures between 153 and 300 K. Then, they carried out a comprehensive study using X-ray photoelectron spectroscopy (XPS), near-edge X-ray adsorption spectroscopy (NEXAFS), low-temperature scanning tunneling microscopy (LTSTM), and molecular manipulation. They explain and complement their experimental findings with density functional theory (DFT) calculations. Their XPS data show that the molecule interacts with the Au(111) surface *via* its S and O atoms, while NEXAFS data reveal the tilting of the S═O bond outward from the surface plane. It is their STM study that leads to very interesting findings. The STM images unveil formation of molecular complexes composed of three to four

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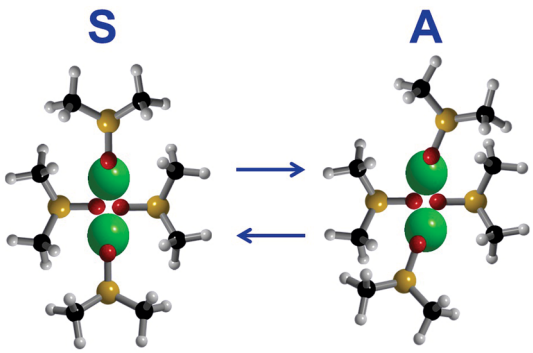

Figure 1. Schematic of scanning tunneling microscope probe-tip-induced reversible switching from a symmetric assembly (S) to an asymmetric assembly (A) on a Au(111) surface.

DMSO molecules, albeit a few isolated molecules can still coexist on the surface. They found five types of molecular complexes on Au(111): square, symmetric rectangle, asymmetric rectangle, chiral rectangle, and triangle. Except for the square, which was observed at surface temperatures below 233 K, the remaining four structures were mostly found at temperatures above 233 K.

Next, Feng *et al.* tested the stability of individual molecular complexes using STM manipulation. They found that the observed DMSO complexes were not only stable but also could be switched from one form to another reversibly. To date, STM manipulation has been mostly realized on conformation switching of individual molecules.[13] The reversible STM manipulation of molecular complexes here[3] (Figure 1) indicates that an electric field can also be used for the controlled switching of supramolecular assemblies. However, there was a puzzle in this finding. To form such DMSO complexes, the oxygen atoms of DMSO molecules need to be proximate. Because their net negative charges would repel each other, these complexes would not be expected to be stable. The STM manipulation experiments indicate stable DMSO complexes. Indeed, DFT calculations of a triangular complex came to the same conclusion: maintaining a triangular structure of the DMSO complex would have higher energy costs. To solve the puzzle, the researchers artificially added a gold atom at the middle of the triangular complex in their DFT calculations. This gold adatom, with net positive charge, coordinated the oxygen atoms of the three DMSO molecules and stabilized the complex. Similarly, stable complexes were found after adding two gold adatoms at the middle of symmetric, asymmetric, and chiral rectangular assemblies. The addition of gold adatoms to the DMSO complexes motivates further questions. (1) Where do these gold atoms originate? (2) How can gold adatoms maintain their charged state on Au(111) surfaces? (3) Why do the STM images not show the gold adatoms in the molecular complexes?

The first question is straightforward to answer. It is known that gold atoms from step edges and defects are mobile at the surface temperature of the current study, and they can easily join to link up the molecules.[14] In fact, a number of studies have already reported the formation of molecular complexes linked by gold adatoms on a Au(111) surface.[14,15] The most interesting question is the second one: how the gold adatom remains in a charged state on the Au(111) surface, which has free Shockley surface-state electrons to neutralize charges. Indeed, Feng *et al.*'s DFT calculation shows that a gold adatom on a Au(111) surface donates some charge to its nearest neighbor surface atoms, and as a result, charge depletion occurs in the adatom. For the triangular DMSO complex, even after withdrawing charge from oxygen, the gold adatom remains positively charged. The DMSO oxygen, on the other hand, has anionic character, and using the gold adatom as a binding post, it is anchored to form complexes. The charge rearrangement of gold adatoms inside the molecular complex effectively reduces the available states for electron tunneling. Such an effect has been observed in other cases. For instance, Shi and Lin[15] observed that the formation of two-dimensional Kagome lattices by porphyrin molecules on Au(111) surfaces can be explained only with gold adatoms linking them. Yet, they were not able to image these gold adatoms in STM images. Since STM images are related to the local density of states for tunneling, the absence of accessible states for tunneling makes the gold adatoms in the complexes invisible.

OUTLOOK AND FUTURE CHALLENGES

The formation of polar molecular complexes and the role of charged gold atoms trapped inside these complexes have several important aspects. By exploiting surface and interfacial properties, novel supramolecular assemblies are possible to tailor. Supramolecular engineering at surfaces has the potential to revolutionize the creation of nanostructures, with applications in electronics, spintronics, memory, charge storage, and molecular recognition.[16−18] The possibility of linking different types of polar molecules in single supramolecular assemblies would enable even richer functionality. Retaining the charged state of the gold adatom trapped inside each of the DMSO complexes means that it can be useful to add more molecules and perhaps even different types of polar molecules into the complexes. The manipulation experiments show that an entire supramolecular assembly can be reversely switched to different structures. If switching of multiple supramolecular assemblies can be performed at the same time in a controlled

manner, then this will impact potential applications such as chiral recognition. Moreover, the formation of DMSO molecular complexes on surfaces may have implications for biochemistry and medicine. Although DMSO is widely used for ailments, it is surrounded by many mysteries: some researchers have dubbed DMSO as a miracle medicine, while other have cautioned against its effects. The unpredictability of DMSO likely originates from the rich properties associated with its high polarity. Understanding how DMSO interacts with different surfaces, including with biological molecules, will enable researchers to use its full capabilities while avoiding undesired effects. With the use of robust experimental and theoretical tools, scientists now have the capability to push the limit of investigations to the ultimate level of individual atoms and single bonds. If this knowledge can be transformed to develop useful supramolecular structures, then exciting opportunities to engineer novel supramolecular assemblies for new applications are wide open.

Conflict of Interest: The authors declare no competing financial interest.

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