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Chiba University

World's Smallest Molecular Machine: Reversible Sliding Motion in Ammonium-Linked Ferrocene

Researchers stabilized ferrocene molecules on a flat substrate for the first time, creating an electronically controllable sliding molecular machine

Ferrocene is a key molecule for developing molecular machines. However, it readily decomposes on the surface of flat noble metal substrates, marking a significant challenge. Now, for the first time, researchers stabilized ferrocene by linking it with ammonium salts and trapping them in a molecular film made up of cyclic crown ether molecules. The ammonium-linked molecule performs reversible lateral sliding motion upon the application of electrical voltage, representing the world's smallest molecular machine.

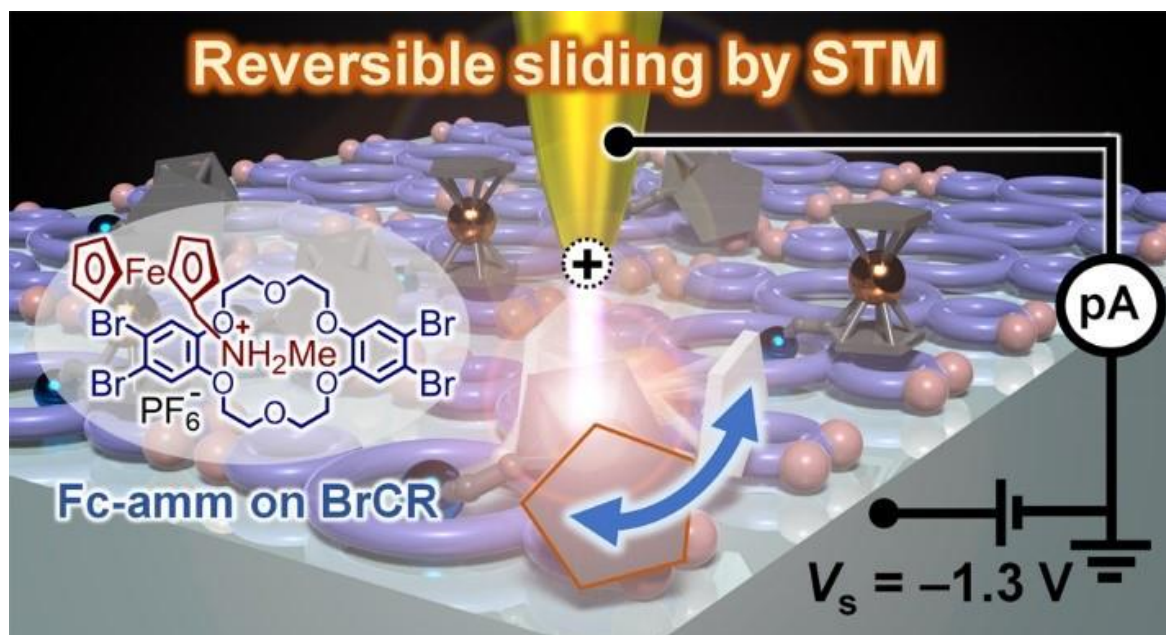


Image title: Lateral sliding of the ferrocene-based molecular machine

Image caption: The complex of ammonium-linked ferrocene (Fc-amm) and crown ether is assembled on a Cu(111) surface, and its sliding motion is activated by hole injection into the ferrocene group using scanning tunneling microscopy (STM).

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Artificial molecular machines, nanoscale machines consisting of a few molecules, offer the potential to transform fields involving catalysts, molecular electronics, medicines, and quantum materials. These machines operate by converting external stimuli, like electrical signals, into mechanical motion at the molecular level. Ferrocene, a special drum-shaped molecule composed of an iron (Fe) atom sandwiched between two five-membered carbon rings, is a promising foundational molecule for molecular machinery. Its discovery earned the Nobel Prize in Chemistry in 1973, and it has since become a cornerstone in the study of molecular machines.

What makes ferrocene so appealing is its unique property: A change in the electronic state of the Fe ion, from Fe^{2+} to Fe^{3+} , causes its two carbon rings to rotate by about 36° around the central molecular axis. Controlling this electronic state by an external electrical signal could enable precisely controlled molecular rotation. However, a major hurdle in its practical application is that it readily decomposes when adsorbed onto the surface of substrates, especially flat noble metal substrates, near room temperature, even under ultra-high vacuum conditions. A definitive method for anchoring isolated ferrocene molecules on a surface without decomposition has not been found, until now.

In a groundbreaking study, a research team led by Associate Professor Toyo Kazu Yamada from the Graduate School of Engineering at Chiba University, Japan, including Professor Peter Krüger from the Faculty of Engineering at Chiba University, Professor Satoshi Kera of the Institute for Molecular Science, Japan, and Professor Masaki Horie of National Tsing Hua University, Taiwan, has finally overcome this challenge. They have successfully created the world's smallest electrically controlled molecular machine. *"In this study, we successfully stabilized and adsorbed ferrocene molecules onto a noble metal surface by pre-coating it with a two-dimensional crown ether molecular film. This is the first direct experimental evidence of ferrocene-based molecular motion at the atomic scale,"* remarks Prof. Yamada. Their findings were published in the journal [Small on November 30, 2024.](#)

To stabilize the ferrocene molecules, the team first modified them by adding ammonium salts, forming ferrocene ammonium salts (Fc-amm). This improved durability and ensured that the molecules could be securely fixed to the surface of the substrate. These new molecules were then anchored onto a monolayer film made up of crown ether cyclic molecules, which were placed on a flat copper substrate. Crown ether cyclic molecules have a unique structure with a central ring that can hold a variety of atoms, molecules, and ions. Prof. Yamada explains, *"Previously, we found that crown ether cyclic molecules can form a monolayer film on flat metal substrates. This monolayer trap the ammonium ions of Fc-amm molecules in the central ring of crown ether molecules, preventing the decomposition of ferrocene by acting as a shield against the metal substrate."*

Next, the team placed a scanning tunneling microscopy (STM) probe on top of the Fc-amm molecule and applied an electrical voltage, which caused a lateral sliding motion of the molecules. Specifically, on applying a voltage of -1.3 volts, a hole (vacant space left by an electron) enters the electronic structure of the Fe ion, switching it from Fe^{2+} to Fe^{3+} state. This triggered the rotation of the carbon rings accompanied by a lateral sliding motion of the molecule. Density functional theory calculations showed that this lateral sliding motion occurs due to the Coulomb repulsion between the positively charged Fc-amm ions. Importantly, on

removing the voltage, the molecule returns to its original position, demonstrating that the motion is reversible and can be precisely controlled using electrical signals.

“This study opens exciting possibilities for ferrocene-based molecular machinery. Their ability to perform specialized tasks at the molecular level can lead to revolutionary innovations across many scientific and industrial fields, including precision medicine, smart materials, and advanced manufacturing,” says Prof. Yamada, highlighting the potential applications of their technology.

In summary, this study presents a crucial breakthrough in the design and control of molecular machines that can lead to significant advancements in numerous fields.

About Associate Professor Toyo Kazu Yamada

Dr. Toyo Kazu Yamada is currently an Associate Professor at the Graduate School of Engineering at Chiba University, Japan. He earned his Ph.D. (double degree) in 2004 from Radboud University Nijmegen, The Netherlands, and Gakushuin University, Japan. Additionally, he served as a Humboldt research fellow at the Karlsruhe Institute of Technology (KIT), Germany, from 2008 to 2010. His research primarily focuses on various aspects of materials science, encompassing single magnetic atoms and films, organic molecules, graphene nanoribbons, Fe/MgO interfaces, nanomagnets on an s-wave superconductor, and life molecules. His current research focuses on the functionality of a single magnetic atom or molecule on the surface of solid materials, such as magnetic substances and superconductors, as a quantum bit or quantum sensor for next-generation quantum computers.

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