Confinement of an Electron in a Cuboid Molecule

—Success in Synthesis of Unprecedented Fluorine-Containing Molecules through Industry-Academia Collaboration—

1. Key points of the announcement

- The research group has succeeded in synthesizing "perfluorocubane," a cuboid molecule with fluorine atoms bonded at all vertices.
- The confinement of an electron in the inner space of a polyhedral molecule was observed for the first time.
- This achievement overturns the conventional wisdom of designing molecules to accept electrons and is expected to contribute to the development of materials science in the future.

2. Summary of the announcement

A research group led by Masafumi Sugiyama, a graduate student at the Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo; Project Assistant Professor Midori Akiyama (at the time of the research); Professor Kyoko Nozaki, Takashi Okazoe, a senior research fellow at AGC Inc. in joint research with Kenji Komaguchi, Associate Professor, Applied Chemistry Program, Graduate School of Advanced Science and Engineering, Hiroshima University; and Masahiro Higashi, Associate Professor, Molecular Engineering, Graduate School of Engineering, Kyoto University, has for the first time succeeded in synthesizing perfluorocubane, which has fluorine atoms bonded to all vertices and observing an electron confined inside it.

Polyhedral molecules with fluorine atoms bonded to all vertices were theoretically predicted to accept an electron in their interiors, but synthesis had not been achieved. The research group has succeeded in synthesizing the world's first perfluorocubane using the PERFECT method (Note 1) developed by AGC Inc. It also succeeded in observing the confinement of an electron inside this molecule. These results provide new possibilities for design guidelines for functional molecules that accept electrons.

The results of this research were published online in the journal *Science* on August 11, 2022 (EDT).

3. Details of the announcement

Polyhedral molecules such as cuboidal cubane, dodecahedral dodecahedron, and soccer ball-shaped fullerene have fascinated scientists around the world with their beautiful structures. Once advances in synthetic organic chemistry achieved the synthesis of polyhedral molecules, scientists' next interest turned to confining single particles in the inner space of polyhedral structures. Examples of confinement of metal atoms, noble gas atoms, hydrogen molecules, and water molecules into polyhedral molecules have been reported. On the other hand, quantum chemical calculations (Note 2) predicted that "when fluorine atoms are bonded to all the carbons at the vertices of a polyhedral molecule, an electron is confined to its inner space." This is because unoccupied molecular orbitals (Note 3), which contain no electrons, assemble inside the polyhedron to form a LUMO (Note 4), which can easily accept an electron (Figure 1). Although this phenomenon is very interesting, it has been difficult to synthesize polyhedral molecules with fluorine atoms bonded to all carbons, and been limited to the realm of theoretical prediction.

Against this background, the research group has synthesized perfluorocubane, in which fluorine atoms are bonded to all eight carbons of the cubane molecule. In previous studies, only a maximum of two of cubane's eight carbons have been introduced with fluorine atoms. Fluorine atoms are introduced one by one through multiple chemical reactions in the conventional method. As numerous steps are required to introduce eight fluorine atoms the synthesis of perfluorocubane had been thought to be an unrealistic endeavor. To overcome this, the group investigated a method to combine multiple fluorine atoms at once by using fluorine gas. In the field of synthetic organic chemistry, fluorine gas has rarely been used because it reacts explosively with organic compounds and is considered difficult to control. In response, AGC Inc. has developed the "PERFECT method," a technology for introducing fluorine atoms into organic compounds while controlling the reactivity of fluorine gas. In this study, this research group succeeded in simultaneously bonding seven fluorine atoms to cubane by using the PERFECT method (Figure 2). Further chemical reactions introduced the remaining one fluorine atom, achieving the synthesis of perfluorocubane. Single crystal X-ray structure analysis (Note 5) shows that fluorine is introduced at all vertices of cubane (Figure 2, right).

Electrochemical (Note 6) and spectrophotometric (Note 7) measurements demonstrated that, as expected, perfluorocubane has a molecular orbital that can easily accept an electron. The group also irradiated gamma-rays to give an electron to perfluorocubane and observed what chemical species are formed by low-temperature solid-phase matrix isolation ESR method (Note 8). The results show that the electron given to perfluorocubane is distributed mainly in the inner space of the cuboid (Figure 3).

Until now, the design guideline for molecules that accept electrons has always been to create a molecular orbital that can easily accept electrons by connecting multiple double bonds, as found in a benzene ring. In contrast, this research is significant in that it overturns the conventional wisdom in that it has developed a molecule that accepts an electron without using a double bond. In the future, the group will further investigate the behavior and reactivity of the electron confined in perfluorocubane to establish new scientific theories. Because molecules that accept electrons have applications in organic electronic materials, this study is expected to contribute to the development of materials science in the future.

This research was conducted in the "Laboratory for Material and Life Sciences for Fusion of Fluorine and Organic Chemistry," a Social Cooperation Program of the Department of Chemistry & Biotechnology, School of Engineering at the University of Tokyo funded by AGC Inc. The results of this research are the fusion of cutting-edge scientific knowledge from universities and specialized technology from companies. This research was also supported by Grants-in-Aid for Scientific Research for Early-Career Scientists (project numbers: JP19K15532 and JP21K14608), Dynamic Exciton: Emerging Science and Innovation (project numbers: JP20H05839 and JP21H05385), Grants-in-Aid for Research Fellowships for Young Scientists (project number: JP21J21713), Toyota Physical and Chemical Research Institute, The Hattori Hokokai Foundation, Iketani Science and Technology Foundation, and Koyanagi Foundation.

4. Announcement publication

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7. Glossary

(Note 1) The PERFECT (Perfluorination of an Esterified Compound then Thermolysis) method:
A method developed to convert all carbon-hydrogen bonds in an organic molecule to carbon-fluorine bonds.

(Note 2) Quantum chemical calculation: A method of analyzing the structure and properties of molecules by determining their electronic states through computer simulations.

(Note 3) Molecular orbital: The spatial distribution of electrons in motion within a molecule. Some molecular orbitals are actually occupied by electrons, while others are unoccupied.

(Note 4) LUMO: Lowest Unoccupied Molecular Orbital. The unoccupied molecular orbital that is not occupied by an electron and is the most receptive to electrons.

(Note 5) Single crystal X-ray structure analysis: A method to determine the structure and arrangement of molecules in a crystal by irradiating single crystals (crystals in which molecules are regularly arranged) with X-rays and measuring their diffraction.

(Note 6) Electrochemical measurement: A method of applying voltage to molecules in solution and measuring the current flowing through them. The ease of accepting electrons can be evaluated with this method.

(Note 7) Spectrophotometric measurement: A method of shining light on molecules in solution to determine the wavelength of light absorbed by the molecules. Molecules that are more receptive to electrons absorb light of longer wavelengths.

(Note 8) Low-temperature solid-phase matrix isolation ESR method: A method to observe unstable chemical species by generating the chemical species of interest at low temperatures in a reaction-inert solid medium, thereby suppressing their degradation. (ESR: Electron Spin Resonance)

8. Attachments

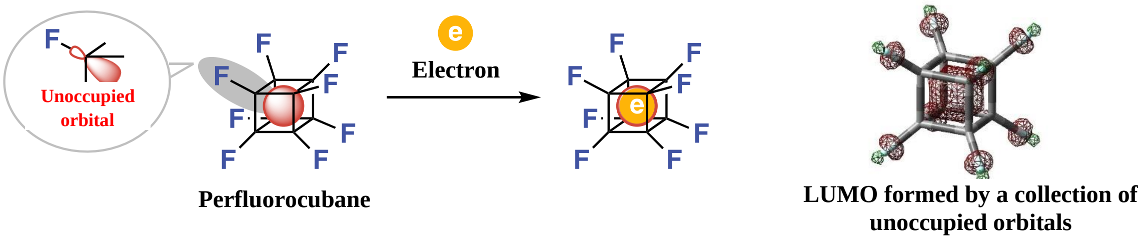

Figure 1: Mechanism of perfluorocubane accepting an electron and its LUMO distribution

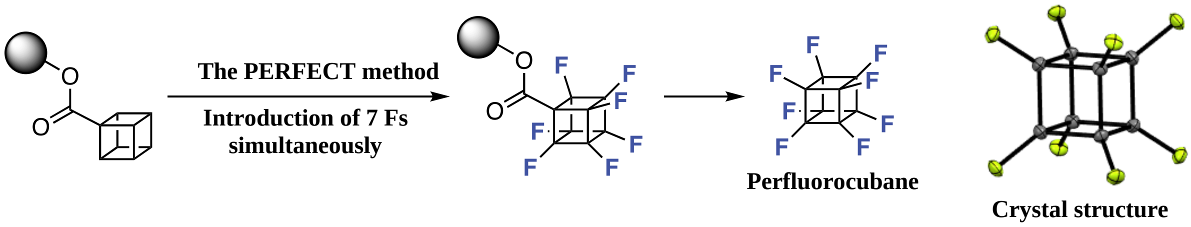

Figure 2: Synthesis and crystal structure of perfluorocubane

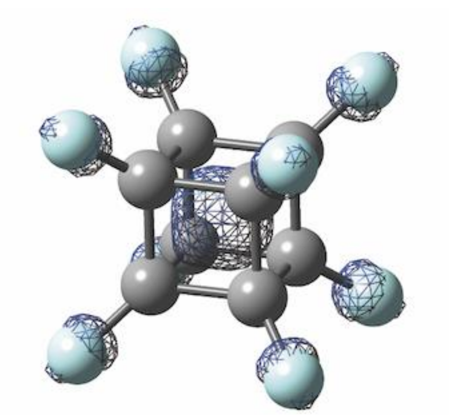

Figure 3: Distribution of an electron imparted to perfluorocubane