

Electron in a Cube: Synthesis and Characterization of Perfluorocubane as an Electron Acceptor

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The beautiful, highly symmetric structures of polyhedral molecules have long fascinated scientists. In a study recently published in *Science*, the group of Professor Midori Akiyama from The University of Tokyo (Japan) have succeeded for the first time in synthesizing a polyhedral molecule with all carbons fluorinated. Professor Akiyama explained: “Introduction of fluorine – one of the most peculiar and distinctive elements – into a molecule dramatically changes the properties of the compound itself. On the other hand, perfluorinated polyhedral molecules had been expected to capture an electron inside,¹ which was proven in this study by exploiting some of the unique features of fluorine atoms.”

Professor Akiyama acknowledged that her laboratory was founded at The University of Tokyo in 2017 with funding from AGC Inc., one of the world leading fluorine chemical companies. “What is quite special about our lab are the available facilities and techniques for the safe handling of elemental fluorine, a hazardous gas,” said Professor Akiyama. She continued: “Our mission has been the creation of novel and valuable fluorine chemistry via collaboration between the available and special combination of industrial and academic knowledge. During the survey of interesting structures

to be fluorinated, we found an extremely intriguing theoretical prediction about perfluorocubane as an electron acceptor by Dr. Irikura.¹ Then, we started to make it in the real world (Figure 1).”

Surprisingly, the group found that ‘radical’ fluorination of highly strained cubane derivatives could be achieved via the ‘PERFECT’ fluorination method,² and six or seven fluorine atoms could be introduced. The remaining one or two fluorine atom(s) were introduced using an electrophilic fluorinating reagent. “In the beginning, perfluorocubane was synthesized from hexafluorocubane, which can be obtained in higher yield and shorter steps,” explained Professor Akiyama. She continued: “Although perfluorocubane could be isolated via this route, the yield was actually rather miserable due to its high volatility. Then we changed the synthetic scheme to one starting from heptafluorocubane (Figure 2), which requires more preparative steps than hexafluorocubane to reach the target. This decision produced good fruit and the isolated yield of perfluorocubane increased nearly 20 times. We learned that ‘Haste makes waste’ from this experience.”

Theoretically, the radical anion of perfluorocubane had been expected to be stable as an isolated molecule in vacu-

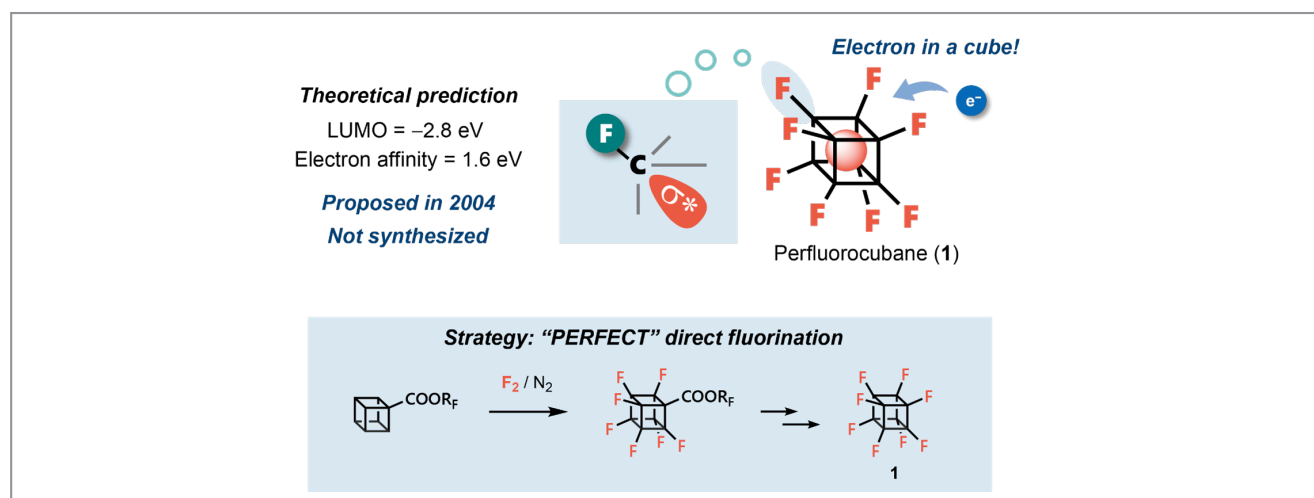


Figure 1 Structure of perfluorocubane (**1**) and its predicted properties, and synthetic strategy of **1** for this study. The energy level of **1** was calculated at the B3LYP/6-311++G(d,p) level of theory, and the predicted electron affinity has been reported previously.¹ From *Science* **2022**, *377*, 756–759. Reprinted with permission from AAAS.

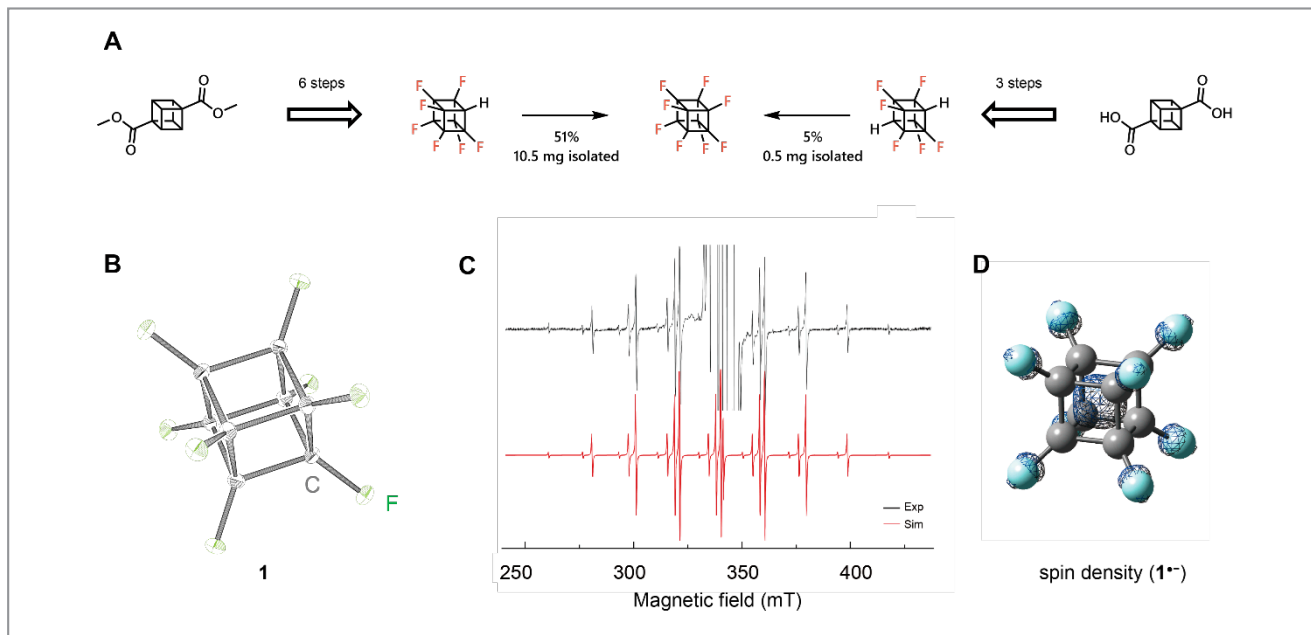


Figure 2 (A) Synthesis of perfluorocubane (**1**) from hepta/hexafluorocubane. (B) Crystal structure of **1** (ellipsoid probability, 50%). (C) ESR spectrum of **1** in a hexamethylethane matrix after γ -ray irradiation at 77 K (black) and simulated ESR spectrum (red) using $g = 1.9985$ and $a(^{19}\text{F}) = 19.62$ mT (8F). (D) Spin density (contour = 0.005) in the radical anion of **1**. From *Science* **2022**, *377*, 756–759. Reprinted with permission from AAAS.

um. However, the group's experiments revealed that a cyclic voltammogram in solution showed an irreversible reduction wave, which indicates the unstable nature of the radical anion when it interacts with ambient molecules.

"In the beginning, we were disappointed with this result; however, we could not give up trying to observe the radical anion," said Professor Akiyama. Then the group started collaborative research with Prof. Komaguchi at Hiroshima University (Japan) to carry out low-temperature matrix isolation ESR measurements. "One and a half years passed after the isolation of perfluorocubane; however, the ESR signal indicating generation of the radical anion was finally observed in December 2021!" revealed Professor Akiyama, continuing: "It must have been a Christmas present for us. Although we anticipated that highly symmetrical perfluorocubane would potentially show an isotropic spectrum even in the solid state, it was still fortunate that perfluorocubane actually rotates in the glass matrix and shows clear splitting of the signal (Figure 2)."

Professor Akiyama concluded: "In the future, it may be possible to apply perfluorocubane to electronics and spintronics materials, but for now our interest remains more scientific and fundamental, with questions such as: How does the electron trapped in a perfluorocubane behave? Can electrons be moved in and out? How does perfluorocubane inter-

act with other molecules? And so on. We believe this paper is the first step in opening up a whole new scientific area."

Mattias Farnok

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About the authors



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Kenji Komaguchi is an associate professor at Hiroshima University (Japan). He received his Dr. Eng. degree from Hiroshima University under the supervision of Prof. Masaru Shiotani (1994). After being a research fellow at the former Japan Atomic Energy Research Institute (Japan, 1995), he joined Hiroshima University (Japan) in 1996. He was a visiting researcher at Linköping University (Sweden) with Prof. Anders Lund in 2001. His research interests include structures, dynamics, and reactions of paramagnetic species, and their practical applications in photocatalysts, catalysts, solar cells, and deterioration of organic polymers.



Prof. M. Higashi

Masahiro Higashi received his Ph.D. from Kyoto University (Japan) in 2007 under the supervision of Prof. Shigeki Kato. Subsequently, he worked as a postdoctoral researcher in Prof. Donald G. Truhlar's group at the University of Minnesota (USA). In 2009, he joined Prof. Shinji Saito's group as a postdoctoral fellow at the Institute of Molecular Science (Japan). He then became an assistant professor at the University of the Ryukyus (Japan) as in 2013. In 2019, he joined Prof. Hirofumi Sato's group as an associate professor at Kyoto University (Japan). He is interested in the theoretical analysis of molecular mechanisms of chemical reactions and physical properties in condensed phases.



Prof. K. Nozaki

Kyoko Nozaki is a professor at The University of Tokyo (Japan). She graduated from Kyoto University (Japan) in 1986 and received her Ph.D. in 1991 from the same university. Since 1991, she was a faculty member at Kyoto University, moved to The University of Tokyo in 2002, and has been in her current position since 2003. Her research interest is focused on the development of homogeneous and heterogeneous catalysts for polymer synthesis and organic synthesis.

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Her achievements have been recognized with The Award of the Society of Polymer Science, Japan (2013), Chemical Society of Japan Award (2020), Distinguished Women in Chemistry or Chemical Engineering (2021), L'Oréal-UNESCO For Women in Science International Awards (2021), and Medal with Purple Ribbon (2022). She has been an International Honorary member of the American Academy of Arts & Sciences since 2021.



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Takashi Okazoe is a senior fellow researcher of Materials Integration Laboratories, AGC Inc. (Japan), as well as a part-time lecturer in Department of Chemistry & Biotechnology, School of Engineering, The University of Tokyo (Japan), where he leads collaborative research between AGC Inc. and The University of Tokyo. He graduated from Kyoto University (Japan) with a Master's degree in industrial chemistry in 1987. He joined Asahi Glass

Co., Ltd. (now AGC Inc.) and engaged in the development of fluorinated pharmaceuticals and the creation and development of a new perfluorination method 'PERFECT', and technology planning of AGC Chemicals. During that time, he obtained his Ph.D. from Kyoto University in 2009. As part of his technology planning of the academia–industry collaboration, he launched a social cooperation program 'Laboratory for Material and Life Sciences for Fusion of Fluorine and Organic Chemistry' at The University of Tokyo in 2017. Since then, he has stationed himself there to carry out joint research.