Synthesis and Properties of Perfluorocubane

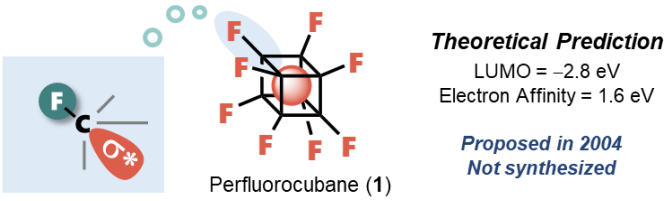
([1]*Graduate School of Engineering, The University of Tokyo*, [2]*AGC Inc.*) ○Masafumi Sugiyama,[1] Midori Akiyama,[1] Yuki Yonezawa,[1] Kyoko Nozaki,[1] Takashi Okazoe[1,2]

Keywords: *Cubane; Fluorine; Electron acceptor; Single crystal x-ray diffraction analysis*

The electronic and optical properties of organic molecules are dominated by their frontier orbitals and the orbitals which possess close energy levels to frontier orbitals. For π-conjugated molecules, the energy levels of the orbitals can be modulated by extension of π-conjugation and/or introduction of heteroatoms. Therefore, most of functional organic molecules have consisted of π-conjugated scaffolds, namely, they mostly possess carbon–carbon or carbon–hetero atom multiple bonds. Contrary to this trend, there is a possibility to utilize σ* orbitals to form a stabilized vacant orbital and modulate properties of molecules. Fluorine makes the antibonding σ* orbitals of C–F single bonds polarizing to the carbon, because fluorine is the most electron negative atom.[1] Thus, appropriate molecular designs to gather multiple σ* orbitals of C–F bonds inside a cyclic or cage-shaped molecule would give a novel type of stabilized vacant orbital, which will accept an electron. One of the most ideal molecules to prove this hypothesis is perfluorocubane (**1**), predicted to possess high electron affinity of 1.6 eV and an unprecedentedly lower lying vacant orbital (E_{LUMO} = −2.8 eV).[2] Accordingly, **1** will possibly work as a novel class of electron acceptor without any π-conjugation. Consequently, synthesis of **1** would disclose the novel science field utilizing σ orbitals.

We achieved the first synthesis and structure determination of perfluorocubane (**1**), which has not been synthesized even after 17 years from the first proposal of its structure.[3] The key step was liquid-phase direct fluorination of cubane derivatives with fluorine gas, which allowed efficient introduction of multiple fluorine atoms. Its structure was determined by the single crystal X-ray diffraction analysis, NMR spectroscopy and Raman spectroscopy. Physical properties of neutral perfluorocubane were investigated by photochemical and electrochemical measurements.

Furthermore, the radical anion of **1** was observed using a matrix-isolation ESR technique, which suggested that an electron was accepted inside the cage of **1**.



(1) O'hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308–319. (2) Irikura, K. K. *J. Phys. Chem. A* **2008**, *112*, 983–988. (3) Kato, T.; Yamabe, T. *J. Chem. Phys.* **2004**, *120*, 1006–1016.

Acknoledgement

We thank Prof. Dr. Komaguchi (Hiroshima University) for matrix-isolation ESR measurement.