

Fluorinated analogs of polyhedral hydrocarbons, polyhedral fluorocarbons, have been predicted to localize an electron within their cages upon reduction. This property arises from a stabilized vacant orbital within the cage derived from multiple  $\sigma^*$  orbitals of C–F bond. This internal localization of electrons stands in stark contrast to common  $\pi$ -conjugated electron acceptors, however, polyhedral fluorocarbons have never been isolated because of the difficulties in introduction of multiple fluorine atoms.

The authors achieved the synthesis and characterization of perfluorocubane, as the first example of isolation of polyhedral fluorocarbon. The key to the successful synthesis was the efficient introduction of multiple fluorine atoms to cubane by liquid-phase reaction with fluorine gas. In addition to perfluorocubane, heptafluorocubane and hexafluorocubane were synthesized by this reaction.

The solid-state structure of each fluorinated cubanes was confirmed using x-ray crystallography, and a characteristic intermolecular interaction of fluorinated cubanes was disclosed. Their electron-accepting characters were corroborated electrochemically and spectroscopically, which demonstrated that the energy level of the lowest unoccupied molecular orbital (LUMO) decreases when the number of fluorine atoms increases. This result strongly supports the hypothesis that multiple  $\sigma^*$  orbitals of C-F bond make a low-lying LUMO to accept an electron.

Finally, the radical anion of perfluorocubane was examined by matrix-isolation electron spin resonance spectroscopy, which revealed that the unpaired electron accepted by perfluorocubane is located predominantly inside the cage.

Electron accepting molecules play essential roles in optical and electronic materials. Thus, the present study, which demonstrates that perfluorinated cage compounds act as novel electron acceptors, can be expected to pave the way for the molecular design of distinctive functional organic materials.