

RESEARCH

ORGANIC CHEMISTRY

Electron in a cube: Synthesis and characterization of perfluorocubane as an electron acceptor

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Fluorinated analogs of polyhedral hydrocarbons have been predicted to localize an electron within their cages upon reduction. Here, we report the synthesis and characterization of perfluorocubane, a stable 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. The solid-state structure of perfluorocubane was confirmed using x-ray crystallography, and its electron-accepting character was corroborated electrochemically and spectroscopically. 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.

For organic chemists, polyhedral molecules such as cubane (1), dodecahedrane (2), and buckminsterfullerene (3) represent attractive synthetic targets beyond their arguably subjective elegance. After the syntheses and structural characterizations of these polyhedral cages were achieved, interest quickly shifted to the possibility of encapsulating guests within their internal cavities. Early examples included the encapsulation of a variety of atoms in fullerene (4) and dodecahedrane (5) as well as the encapsulation of a molecule in fullerene (6, 7). Meanwhile, polyhedral fluorocarbons (CF)_n—i.e., the perfluorinated analogs of polyhedranes—have

become a focal point of attention and the subject of numerous theoretical studies (Fig. 1A). One of their most interesting features is their electron-accepting character inside their cage, which arises from a stabilized vacant orbital within the cage derived from multiple σ* orbitals of C–F bonds (8–10). This internal localization of electrons stands in stark contrast to common π-conjugated electron acceptors, which usually host electrons on their molecular surfaces. Although some experimental evidence that supports the formation of (CF)_n (where *n* = 20 or 60) has been reported (11, 12), isolation as a single isomer has not yet been achieved because of the difficulties associated

with the exhaustive fluorination of all cage vertices and the latent instability of (CF)_n on account of the overcrowded fluorine atoms (13–15). By contrast, perfluorocubane [(CF)₈, **1**], whose structure was proposed in 2004 (16), should be sufficiently stable for isolation given that the vicinal fluorine atoms are sterically less hindered than those in larger polyhedranes. Moreover, a theoretical study by Irikura (8) and our own density functional theory (DFT) calculations have suggested that **1** can be expected to exhibit pronounced electron-accepting character [electron affinity = 1.6 eV (8); energy of the lowest unoccupied molecular orbital (*E*_{LUMO}) = –2.8 eV; Fig. 1B]. Here, we report the synthesis, isolation, and characterization of **1** as a polyhedral fluorocarbon that can accept and store an electron within its internal cubic cavity (i.e., electron in a cube).

As a synthetic route to **1**, the stepwise introduction of eight F atoms onto cubane is impractical; in fact, only two F atoms have been successfully introduced into a cubane scaffold

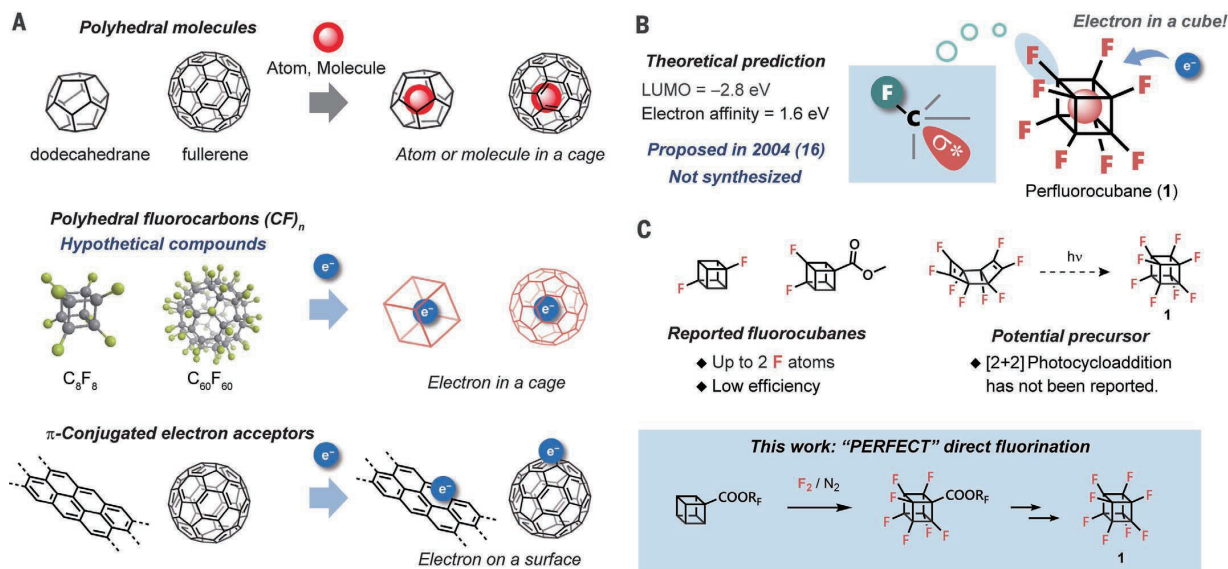


Fig. 1. A perfluorinated cube-shaped molecule accepts an electron inside its cage. (A) Schematic representation of the encapsulation of electrons, atoms, or molecules inside cage-shaped molecules. Polyhedral fluorocarbons can accept an electron inside their cage, whereas common π-conjugated electron acceptors usually store electrons on their surface. (B) Structure of perfluorocubane (**1**) and its predicted properties. 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 (8). (C) Previously reported related molecules and synthetic strategy for this study.