

論文内容の要旨

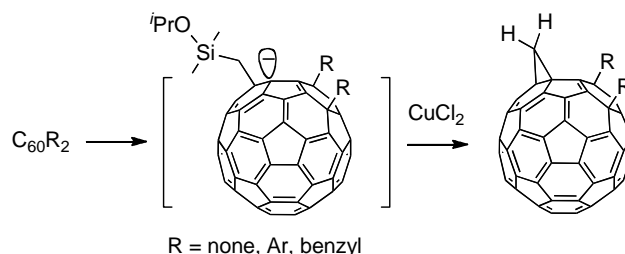
論文題目 Regioselective Functionalization of Fullerenes through Cationic Species
(カチオン性中間体を経る位置選択的なフラーレンの官能基化に関する研究)

氏名 張 瑛

In this thesis, I demonstrated a concise and efficient way to generate fullerene cationic species which are generally considered to be difficult due to the electronegative nature of the fullerene moiety, through the oxidation of fullerene anion and fullerene dimer with Cu(II) salts. This new method for generation of fullerene cationic species shows a widespread application in functionalization of fullerene to afford a range of new fullerene derivatives which may serve as promising electron-acceptor materials in organic photovoltaic (OPV) devices.

In Chapter 2, I described a regioselective new method for synthesis of novel methanofullerenes through the addition of a silylmethylmagnesium chloride to fullerene followed by oxidation of the anionic intermediate with CuCl_2 . The present method is efficient and scalable and does not give any regioisomer or multiadduct. Interestingly, the reaction with 1,4-diorgano[60]fullerene also proceeded smoothly to give a diastereomerically pure 56π -electron methanofullerene derivatives, $\text{C}_{60}\text{R}_2(\text{CH}_2)$. The introduction of the methylene group raises the LUMO level and the J_{sc} and V_{oc} values, thereby increasing the power conversion efficiency of organic photovoltaic devices that utilize these new fullerene derivatives.

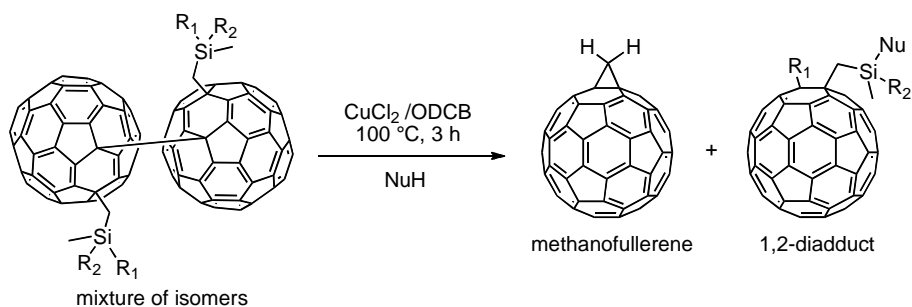
Scheme 1.



In Chapter 3, I described a new Cu(II)-assisted aryl, and allyl-migration from silicon to carbon on fullerene core that occurs on both silylmethylfullerene dimers and mono silylmethylfullerenes. The reaction provides a concise, regioselective and efficient

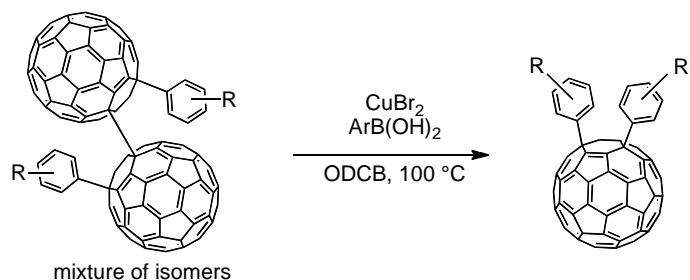
way to synthesize non-cyclic 1,2-diadducts that are otherwise difficult to access.

Scheme 2.



In Chapter 4, a new concise and efficient way to synthesize symmetric and non-symmetric 1,4-diaryl[60]fullerene derivatives through the reaction of fullerene dimers and aryl boronic acids in presence of copper(II) salts was described. These new 1,4-diaryl[60]fullerene derivatives also have a 58π -electron system and show LUMO levels comparable to that of phenyl C61-butyric acid methyl ester (PCBM), which makes them to be attractive candidates as n-type semiconductors in organic solar cell research.

Scheme 3.



In Chapter 5, I described a regioselective and efficient synthetic way for 5 and 7-membered-ring 1,2-diorgano[60]fullerene derivatives through a fullerene cation intermediate generated by oxidation of fullerene radical with $Cu(II)$ salt and I_2 .

Scheme 4.

