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学位論文題目 The development of photo-induced perfluoroalkylation of anthracenes and structural investigation of perfluoroalkylated anthracenes

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1. Introduction

Organofluorine compounds have attracted considerable interest in the field of medicines and functional materials due to the atom's high electronegativity and small size. Therefore, the exploration of efficient methods for their synthesis has received much attention. Meanwhile, polycyclic aromatic hydrocarbons are an important class of compounds that have been widely used as organic semiconductors, organic electroluminescence materials, and fluorogenic dyes. Additionally, polycyclic aromatics having perfluoroalkyl groups (R_f) have been a focus of attention as organic semiconductor materials in recent years.

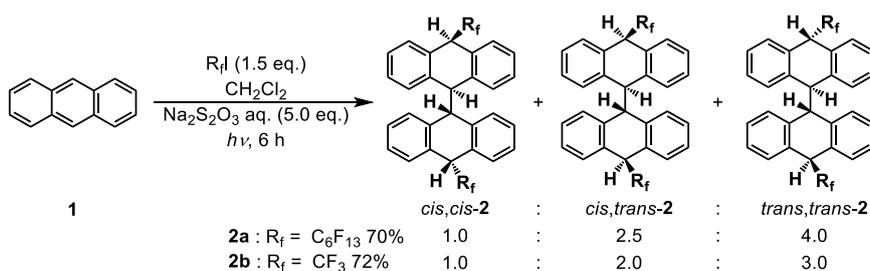
In this context, I have been attracted to the notion that the strongly electron-deficient R_f radicals would readily react with the electron-rich polycyclic aromatics. There have been only a limited number of reports on the perfluoroalkylation of polycyclic aromatics. Furthermore, these reactions proceed in low chemical yields and lack of regioselectivity. We have previously reported that perfluoroalkyl radicals generated by UV irradiation efficiently added to olefins in the presence of $Na_2S_2O_3$. Then, I investigated the perfluoroalkylation to anthracenes, which are stable and useful polycyclic aromatics under our photochemical conditions. I also tried to reveal the crystal structure of perfluoroalkylated anthracene synthesized by the reaction, because it is expected that fluorophilic effect could control molecular alignment.

2. Results and Discussion

In chapter 2, the perfluoroalkylation reaction to anthracene was described. The reaction of anthracene with a perfluoroalkyl iodide under our photochemical conditions resulted in the formation of the perfluoroalkylation–dimerization product 9,9',10,10'-tetrahydro-10,10'-bis(perfluoroalkyl)-9,9'-bianthracene (**2**) (Scheme 1). The reaction using various perfluorohexyl iodides as radical precursors smoothly furnished 9,9',10,10'-tetrahydro-10,10'-diperfluoroalkyl-9,9'-bianthracenes in high yields as a three diastereomer mixture (*cis,cis*, *cis,trans*, and *trans,trans* forms) due to the linkage of the two central cyclohexadiene rings. Furthermore, I

successfully obtained the details of crystal structures of all of these stereoisomers by X-ray analysis. Especially interesting were that 1) the two dihydroanthracene ring systems of the *trans,trans* diastereomers **2** are twisted by 74°

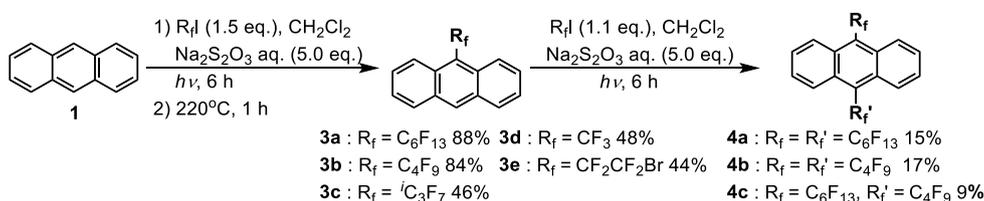
Scheme 1. Photoperfluoroalkylation of anthracene.



around the C-9–C-9' bond and 2) the racemic crystals of *trans,trans-2a* were obtained as a mixture of new types of atropisomers. In addition, NMR analysis as well as quantum chemical calculations led to the unequivocal expectation that *trans,trans-2a* underwent ring inversion of the cyclohexadiene ring and free rotation around the C-9–C-9' bond in solution was found to stop at temperatures as low as 233 K.

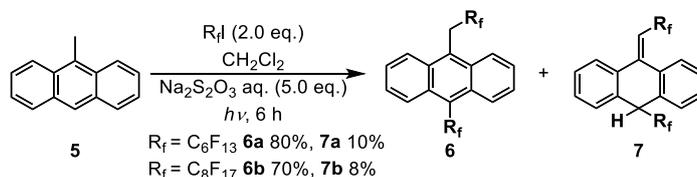
According to DSC analysis of **2**, I found that *trans,trans-2* and *cis,trans-2* were converted to *cis,cis-2*. Moreover, *cis,cis-2a* is converted to 9-perfluorohexyl anthracene (**3a**) at 260°C. The state of *trans,trans-2* changing into *cis,cis-2* was visibly observable as crystal growth by microscopy equipped with heating stage. Based on the result, one-pot process for the synthesis of 9-(perfluoroalkyl)anthracenes was achieved (Scheme 2). Finally 9,10-bis(perfluoroalkyl)anthracenes (**4**) was produced by continuous photoperfluoroalkylation of 9-(perfluoroalkyl)anthracene (**3**) (Scheme 2).

Scheme 2. Synthesis of 9,10-bis(perfluoroalkyl)anthracene.



In chapter 3, I described the results of photoradical perfluoroalkylation of 9-substituted anthracenes. The reaction of 9-methylanthracene with various perfluoroalkyl iodides smoothly furnished bis-perfluoroalkylated anthracene derivative **6** in high yields along with methylenedihydroacene type compound **7**.

Scheme 3. Photoperfluoroalkylation of 9-methylanthracene.



A further important point to note is that we successfully obtained the details of crystal structures of **4a** and **6a** by X-ray analysis. The F...F distances of both **4a** and **6a** are shorter than the sum of their van der Waals radii. The results suggested the fluororous interaction and the interaction affected the arrangement of molecular. In particular, comparing the UV/Vis spectrum of **4a** with anthracene, the 0-0 bands are red-shifted by 33 cm⁻¹. Besides, photoperfluoroalkylation of 9-substituted anthracenes which have hexyl, methoxy, acetoxy, chloro, bromo or iodo group also proceeded and new type perfluoroalkylated compounds were obtained.

In chapter 4, the results of the photoinduced reaction of heteroaromatics with perfluorohexyl were discussed. In particular, the reactions of naphtho[2,1-*b*:6,5-*b'*] dithiophene with perfluorohexyl iodide proceeded smoothly to give mono- and bis-perfluoroalkylated products. I then performed the X-ray single crystal structure analysis of products to discuss the influence of perfluoroalkyl chains on the product.

In conclusion, I provided a method of synthesizing perfluoroalkylated anthracenes and suggested a possibility of control molecular alignment by fluorophilic effect. These findings, lead to future development of material chemistry.