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著者(和文)	納戸直木
Author(English)	Naoki Noto
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Type(English)	Outline

Study on Design of Strongly Reducing Organic Photoredox Catalytic Systems

(高還元力を示す有機フォトレドックス触媒系の設計に関する研究)

17D20517 Naoki Noto

School of Materials and Chemical Technology

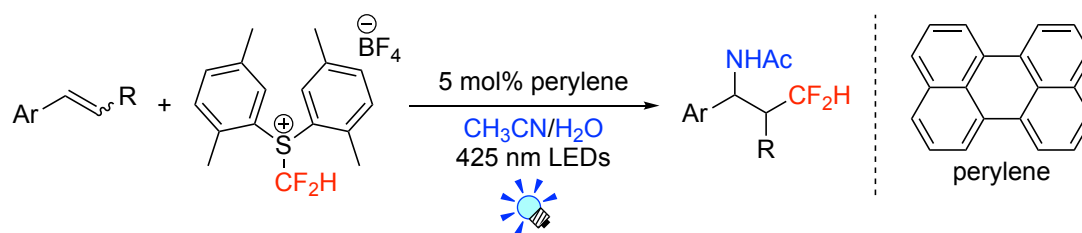
Department of Chemical Science and Engineering

Tokyo Institute of Technology

A controlled radical reaction has been regarded as a powerful tool in organic synthesis. Especially, photoredox catalysis is one of the most remarkable progresses in modern organic synthesis. For the past decade, the efficient single electron transfer processes brought about by photoredox catalysts have enabled various novel organic transformations under mild reaction conditions. However, in contrast to the great progress of photoredox “reactions”, precious metal complexes, which are generally expensive and harmful to human bodies, environment and properties of functionalized materials, are still used as photoredox “catalysts”. In addition, insufficient catalytic abilities of these precious metal-based photoredox catalysts seem to become a barrier to develop more widespread interesting photoredox reactions. Therefore, the Author started research for transition metal-free photoredox catalytic systems to solve the above-mentioned problems. The present thesis consists of two main topics. One is pursuit of highly reactive, strongly reducing organic photoredox catalysts (Chapters 2–4). Simple organic compounds are found to be effective promoters of radical fluoroalkylation reactions. Especially, 1,4-bis(diarylamino)naphthalene catalysts are promising ones which are readily accessible, and show much higher reducing power than the metal photoredox catalysts. The other is supramolecular photoredox catalyst in water (Chapter 5). A supramolecular photoredox catalyst composed of V-shaped aromatic amphiphiles and an organic photoredox catalyst works under very environmentally benign conditions. In addition to its good handling and reactivity, the designed supramolecular system can be applied to unique usages.

1. Metal-Free Di- and Tri-Fluoromethylation of Alkenes Realized by Visible-Light-Induced Perylene Photoredox Catalysis (Chapter 2)

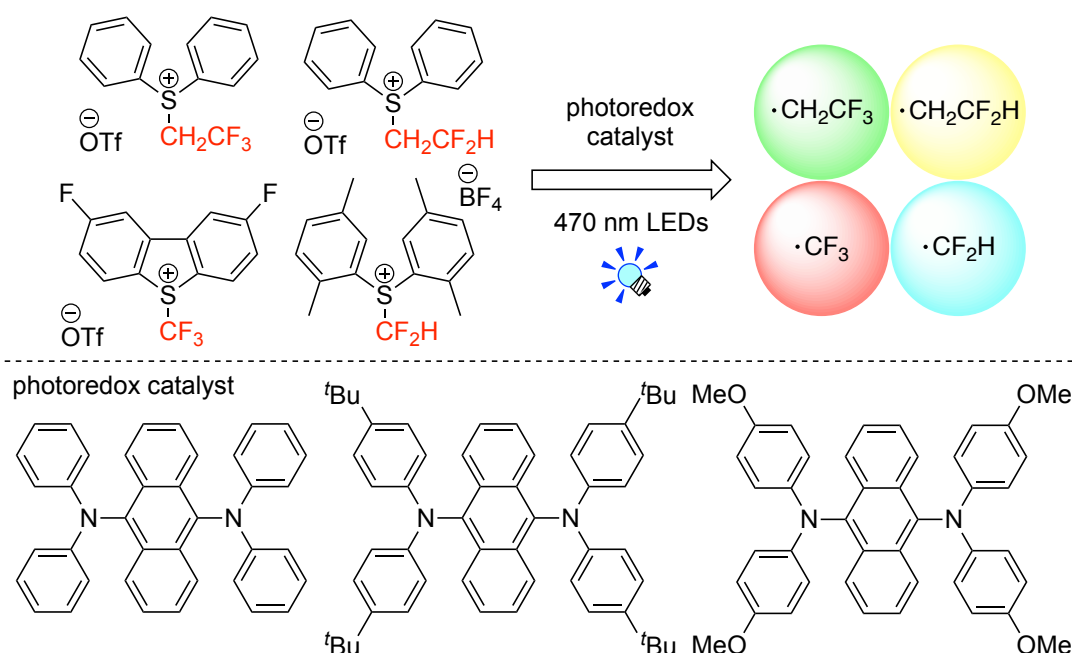
In Chapter 2, the Author describes *perylene catalyzed amino-difluoromethylation of alkenes* (Scheme 1). Perylene, a simple polycyclic aromatic hydrocarbon, turned out to be an excellent photoredox catalyst for radical difluoromethylation with a novel sulfonium-based difluoromethylating reagent. Furthermore, the strong reducing power of perylene was revealed by photo- and electro-chemical measurements. In addition to the titled amino-difluoromethylation reaction, application of perylene catalysis to other reactions was also discussed in this chapter.



Scheme 1. Perylene-catalyzed amino-difluoromethylation of alkenes.

2. Strongly Reducing (Diarylamino)anthracene Photoredox Catalyst for Metal-Free Visible-Light Photocatalytic Fluoroalkylation (Chapter 3)

In Chapter 3, *metal-free, reducing photoredox catalysis using 9,10-bis(diarylamino)anthracene derivatives* is described (Scheme 2). The problem of the sparingly soluble perylene in organic solvents, which hindered improvement of the catalytic activity by functionalization, was solved by the use of soluble and easily functionalizable anthracene, which allowed design of better organic photoredox catalysts as well. Next, the scope of the present photoredox catalysis was studied, and it turned out to be effective for various radical fluoroalkylation reactions.

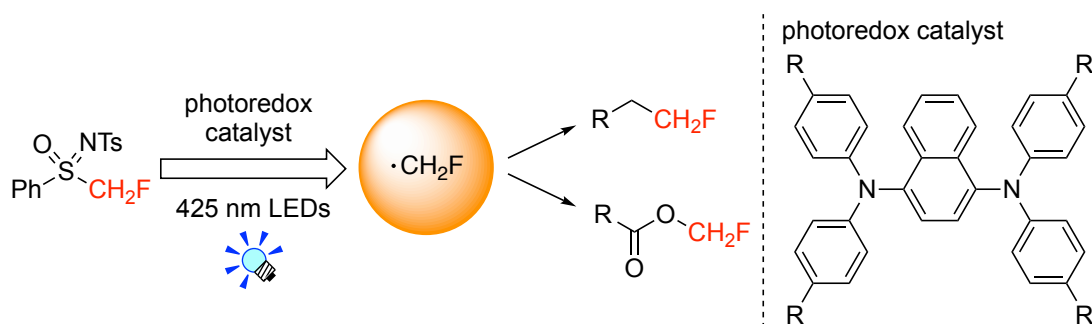


Scheme 2. Various fluoroalkylation with bis(diarylamino)anthracene derivatives.

3. Strongly Reducing (Diarylamino)naphthalene Photoredox Catalyst for Metal-Free Monofluoromethylation (Chapter 4)

In Chapter 4, the Author describes *new organic photoredox catalysts, where the anthracene*

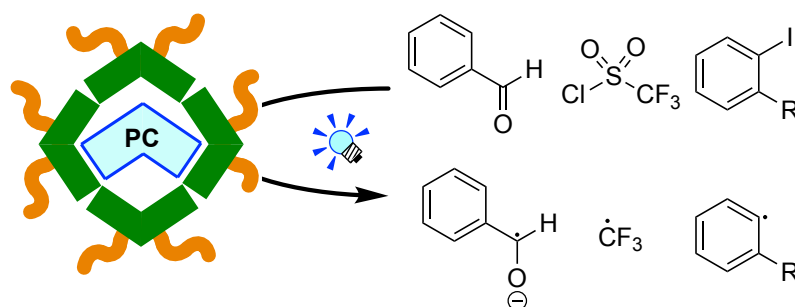
core of the catalysts discussed in the previous chapter is replaced by the naphthalene core (Scheme 3). Notably, these organic compounds turned out to be superior to the commonly used metal-based photoredox catalysts in terms of reducing power and the catalytic performance. The present organic photoredox catalysis enabled generation of the monofluoromethyl radical at room temperature, which was hard to achieve by conventional metal- and organic-photoredox catalysts. In addition to ordinary reactions for styrene derivatives, monofluoromethylation of the oxygen atom of a carboxylic acid was also achieved by combining copper catalysis.



Scheme 3. Radical monofluoromethylation with bis(diarylamino)naphthalene derivatives.

4. Transition metal-free supramolecular photoredox catalysis in water (Chapter 5)

In Chapter 5, the Author describes *transition metal-free supramolecular photoredox catalysis in water* (Scheme 4). Reactions in water with only visible light as the energy source in a manner similar to biosynthesis would be one of the goals for ideal organic transformation. The water-soluble and highly reactive photoredox catalyst was designed by supramolecular strategy with the V-shaped aromatic amphiphiles and a phenoxazine-based reducing organic photoredox catalyst, in contrast to the conventional functionalization strategy. In addition to its better reactivity toward photocatalytic pinacol coupling reactions than ordinary homogeneous reaction systems, unique utility of the present supramolecular photoredox catalysis such as recycling of the catalyst and substrate-selective reactions were notable.



Scheme 4. Supramolecular photoredox catalysis in water.