論文 / 著書情報
Article / Book Information

題目(和文)	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
Title(English)	Study on design of Strongly Reducing Organic Photoredox Catalytic Systems
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In recent years, photoredox catalysis is widely remarked as a powerful tool in organic synthesis. Photoredox catalysis can generate highly reactive but well-controlled radical species under mild conditions, and therefore a variety of photoredox reactions have been developed by numerous organic chemists. 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 the research of metal-free and powerful photoredox catalytic systems to solve the above-mentioned problems of photoredox catalysis. The present thesis consists of two main topics, i.e. pursuit of highly reactive, strongly reducing organic photoredox catalysts and supramolecular photoredox catalyst in water. Simple organic compounds such as perylene and bis(diarylamino)arene derivatives are found as 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 powers than the metal photoredox catalysts. 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.

Chapter 1 describes introduction including the above-mentioned aspects. The explanation in the first section includes the generally accepted mechanism and previous examples for the use of photoredox catalysis. Especially, photoredox reactions via the oxidative quenching cycle are mainly discussed. Second, the author explains organic photosensitizers reported previously. After general information about how to use organic photoredox catalysts, examples of strongly reducing organic photoredox catalysts are described to deepen understanding of the author's purpose in this thesis. Finally, the author shows organic reactions in water with the supramolecular strategy. Utilization of transition metal catalysts encapsulated in molecular hosts are mainly explained in this section.

In Chapter 2, the author describes perylene catalyzed amino-difluoromethylation of alkenes. 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. Although perylene's catalytic performance was limited, the study in this chapter was regarded as the start of the subsequent development for more reactive organic catalysts and transition metal-free supramolecular catalysts.

In Chapter 3, metal-free, reducing photoredox catalysis using 9,10-bis(diarylamino)anthracene derivatives is described. 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 such as tri- and di-fluoroethylation and tri- and di-fluoromethylation. Although the reducing power of the present catalyst was not superior to the conventional iridium catalyst, hints for the design of highly reactive organic photoredox catalysts were obtained through studies on the catalyst design and mechanism.

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. This change dramatically improved performance of the catalysts, and notably, they turned out to be superior to the commonly used metal-based photoredox catalysts in terms of reducing power and the catalytic performance. The present

strongly reducing 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 ordinarily reactions for styrene derivatives, monofluoromethylation of the oxygen atom of a carboxylic acid was also achieved by combining copper catalysis.

In Chapter 5, the author describes transition metal-free supramolecular photoredox catalysis in water. 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. Notably, this catalyst showed better reactivity toward photocatalytic pinacol coupling reactions than the homogeneous reaction systems in ordinary organic solvents. Additionally, unique utility of the present supramolecular photoredox catalysis such as recycling of the catalyst and substrate-selective reactions were notable.

The summary and outlook of the study are described in Chapter 6. The author has developed strongly reducing organic photoredox catalytic systems through the present study, indicating that (i) organic compounds can be more powerful than precious metal complexes as reducing photoredox catalysts, and (ii) the supramolecular strategy is very effective in catalyst design.