論文 / 著書情報
Article / Book Information

題目(和文)	様々なカップリング反応を用いた新規光機能性多核錯体合成手法の開発
Title(English)	Development of synthetic methods for novel photofunctional multinuclear complexes using various C-C coupling reactions
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	化学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士　（　理学　） Doctor of
学生氏名： Student's Name	山﨑　康臣	指導教員（主）： Academic Advisor(main)	石谷　治　教授
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, some useful synthetic methods for various multifarious multinuclear complexes were reported. In particular, the new synthetic methods, so-called "*building block approach*", which utilize various C-C coupling reactions between metal complexes with functional groups as active moieties. The results are summarized as follows:

Chapter 1. The author overviewed reported synthetic methods for constructing multinuclear complexes, and pointed out synthetic problems derived from the ordinary synthetic methods using stepwise coordination of precursor metal complexes to the multidentate bridging ligands. The new synthetic methods using coupling reactions were proposed to enlarge variety of multinuclear complexes in this chapter.

Chapter 2. The Mizoroki-Heck reaction was firstly applied to coupling of different kinds of emissive metal complexes. By using two types of metal complexes as starting materials, i.e., metal complexes with vinyl groups and those with bromo groups, various hetero-trinuclear complexes were successfully synthesized. The reactions selectively proceeded with heating an MeCN solution containing the metal complexes, $Pd(OAc)_2$, PPh_3, and AcONa. During the reaction, injection of a small amount of O_2 (air) was required to promote the reaction. This method could be successfully applied to synthesis of various trinuclear complexes with strong absorption in a wide range of visible light and long emission lifetimes. The photocatalyst having one Re(I) catalyst unit and two photosensitizer units was one of the example, which showed photocatalytic ability for CO_2 reduction though the selectivity of CO_2 reduction and durability of the complex were not so high.

Chapter 3. Reaction conditions for the Mizoroki-Heck reactions with high selectivity and homo-coupling reactions were discussed. The homo-coupling reactions proceeded selectively in an MeCN solution containing complexes with bromo groups, $Pd(OAc)_2$, and AcONa by heating for several days. Under the same reaction condition, the Mizoroki-Heck reaction could be conducted with high selectivity in the presence of both a metal complex with bromo groups and an excess amount of metal complexes with vinyl groups. As described in the chapter 2, usage of the phosphine ligand as a reagent, the Mizoroki-Heck reaction proceeded selectively after injection of a small amount of air during heating the reaction solution. By utilizing combination of these three selective coupling reaction conditions, various novel multinuclear complexes, which could not be selectively obtained by using the ordinary synthetic methods, were successfully obtained in reasonable yields.

Chapter 4. The vinylene or ethynylene linkers in the bridging ligands of the multinuclear complexes synthesized by using various coupling reactions, e.g., the Mizoroki-Heck reaction, the olefin metathesis, and the Sonogashira coupling reaction, could be successfully converted to the corresponding saturated carbon chains by using photochemical hydrogenation reactions. This hydrogenation improved the photocatalytic abilities of the multinuclear metal complexes for CO_2 reduction. The reduction proceeded in an MeCN-pyridine-CF_3COOH (v/v/v = 3:1:0.1) mixed solution containing starting metal complexes and a sacrificial electron donor under visible light irradiation with high selectivity. The new hetero-trinuclear complex **Os-Re-Ru** was successfully synthesized by using stepwise Mizoroki-Heck reaction and the hydrogenation reaction. This complex showed strong absorption in a wide range of visible region because of the three different units. The photocatalytic ability was higher than **Os-Re** but slightly lower than **Ru-Re** probably because of deactivation processes derived from intramolecular energy or electron transfer. The reaction could be also achieved electrochemically. Bulk electrolysis was successfully applied in the presence of proton sources. These hydrogenation reactions should be applied for the various multinuclear complexes with a multiple bond or bonds in the bridging ligands.

Chapter 5. Ring-shaped multinuclear Re(I) complexes with a bromo group were synthesized by using thermal CO-ligand substitution reaction with Me_3NO. The Re(I) ring was successfully connected with a Ru(II) tris-diimine complex or another Re(I) ring by using the Mizoroki-Heck reaction or the homo-coupling. These results clearly indicate that multinuclear complexes can be also used as building blocks for synthesis of higher-order multinuclear complexes. Both synthesized multinuclear complexes with the Re(I) ring unit or units showed light-harvesting properties.

From the results described in this thesis, various metal complexes, i.e., not only mononuclear complexes but also multinuclear complexes, will be able to be selectivity connected with other metal complexes for constructing various multinuclear complexes. By combing these coupling methods with the hydrogenation reactions, the binding mode of the linkers in multinuclear complexes can be modified for tuning the photophysical properties and photocatalytic ability. Therefore, the synthesized multinuclear complexes will be able to be used for various purposes, such as photocatalysts, photosensitizers, light-absorbers, and light-harvesting systems. The synthetic methods and strategies developed in this thesis should enlarge variety of multinuclear complexes in terms of not only structures but also their functions.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).