

Study on Photocatalytic Reactions by Vitamin B12 Model Complex for Green Organic Synthesis

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論 文 名 : Study on Photocatalytic Reactions by Vitamin B₁₂ Model Complex for Green Organic Synthesis

ビタミン B₁₂ モデル錯体を触媒とした光増感型グリーン物質変換反応に関する研究
区 分 : 甲

論 文 内 容 の 要 旨

Vitamin B₁₂ is a term found in the nature as a cofactor of enzyme that plays a key role in the normal functioning of human body such as functionalizing the brain and nervous system. The natural vitamin B₁₂ derivatives catalyze various reactions, including 1,2-migration of the functional group, methyl-transfer reaction and dechlorination reaction, etc. These reactions are very interesting from the viewpoint of organic synthesis. The vitamin B₁₂ derivatives consist a cobalt ion bound to the tetrapyrrole ring (corrin ring) and a 5,6-dimethylbenzimidazole derivative. For the B₁₂ mimetic reactions, vitamin B₁₂ derivatives are usually reduced to a supernucleophilic Co(I) species and alkylated complexes with the Co-C bond are obtained from reacting with the corresponding substrate. Photochemical reduction method which is environment and economy friendly was investigated to generate the Co(I) species for the initiation of the catalytic reaction in this work other than chemical reduction or electrochemical reduction method, and catalytic reactions were developed. This work can be divided into three parts according to the photosensitizer and reaction type. The detail of this work is described as below.

Chapter 1 General introduction: research background and purpose were introduced.

Chapter 2 B₁₂(cobalamin)-TiO₂ hybrid catalyst, in which TiO₂ works as photosensitizer under UV light irradiation, has been reported to mediate various molecular transformations with the B₁₂ function. Most reactions are mediated by the cobalt-alkylated complex, which generally forms via the reaction of the Co(I) state of B₁₂ with substrate. Recently, B₁₂ inspired reaction for alkene reduction was reported. For the reaction, cobalt-hydride complex (Co-H complex), which forms by photochemically produced Co(I) state of B₁₂, is considered to mediate catalytic reactions. As has been widely known, C-F bond is the strongest bond in organic chemistry and elimination of fluorine under basic condition is often problematic in synthesis. Noteworthy, in this study, reduction of α -trifluoromethyl styrenes with C-F bond cleavage that produced *gem*-difluoroolefins was observed, which is a new type of B₁₂-TiO₂ catalyzed styrene reductive reaction. Furthermore, this study provides a mild and green way to synthesize *gem*-difluoroolefins, which is a useful intermediate in the synthesis of fluorinated compounds.

Chapter 3 Since UV-light accounts for only 5% of the solar light, the exploration of visible light which takes around 45% of the solar light has been a hot topic. Cyclometalated iridium(III) complexes have been rapidly developing due to their superior photophysical and photochemical properties. Consequently, they have been widely utilized as photoredox catalysts in the organic synthesis as well as serving as photosensitizers. It has been recognized that [Ir(C[^]N)₂(N[^]N)]⁺ chromophores (C[^]N=cyclometallating ligand and N[^]N=bidendate N₂ ligand) displayed considerably higher efficiencies with remarkably higher turnovers in homogeneous H₂-evolving photocatalytic systems working as photosensitizer than that obtained from the

typical metal bipyridyl complexes such as the $\text{Ru}(\text{bpy})_3^{2+}$ complex etc. In this part, a three-component catalytic system involving the B_{12} complex as a catalyst, cyclometalated iridium(III) complexes as a photosensitizer, and TEOA as a sacrificial reductant is reported. This catalytic system was applied to the visible light-driven dehalogenation of DDT, which is one of the most problematic POPs (persistent organic pollutants). A high catalytic efficiency with significantly enhanced turnovers, 10880, which ranks on the top of the reported ones was obtained. The 1,2-migration of the phenyl group of 2-bromomethyl-2-phenylmalonate was also conducted as a model reaction of the B_{12} -dependent enzyme

Chapter 4 Generally, catalytic systems involving natural B_{12} and its derivatives have been well investigated under anaerobic condition to avoid auto-oxidation of the supernucleophilic $\text{Co}(\text{I})$ species which plays a crucial role for the initiation of catalytic reactions. In 2015, our group found esters or amides formation by B_{12} - TiO_2 hybrid catalyst under aerobic condition with UV light ($\sim 5\%$ of the solar light) irradiation. Since then, to utilize the sunlight efficiently, we have been working on tuning the light region to visible light ($\sim 45\%$ of the solar light). In this part, the first visible light irradiated oxygen-controlled amides formation from trichlorinated organic compounds catalyzed by a B_{12} - $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ complex reaction system under aerobic condition is reported.

Chapter 5 Conclusion

In summary, UV light and visible light induced B_{12} -dependent catalytic reaction systems were constructed in this work. These reaction systems showed excellent performance during catalytic reactions, which happened easily under green and mild conditions such as room temperature, normal pressure and so on. Herein, this work might open the door for new synthetic methodologies in organic synthesis and degradation of permanent halogen contaminants. However, only UV light and visible light, which take around 50 percent of the sunlight, have been successfully developed as the energy source. To fully utilize the sunlight, we are dedicating to the development of near infrared and infrared light responsive photosensitizer.

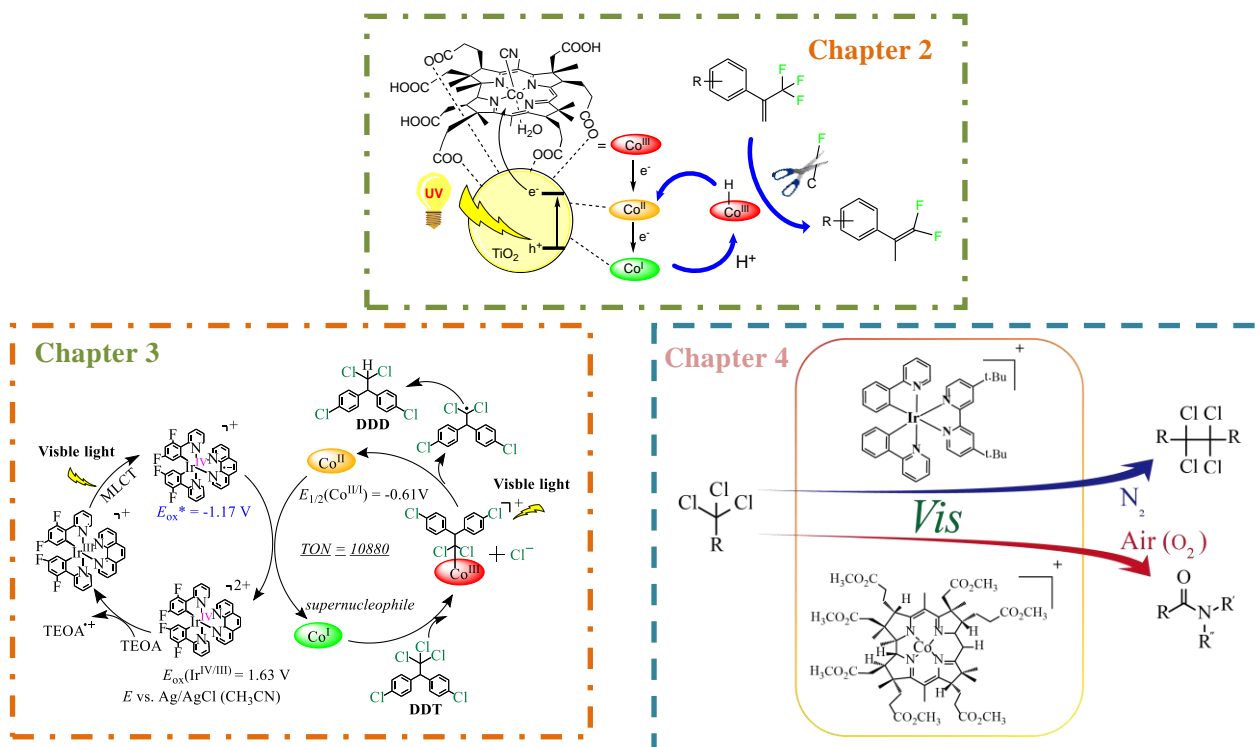


Figure 1 Reaction scheme of Chapter 2, 3 and 4.