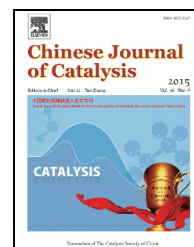


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Review (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

# Advances in visible light-mediated oxidative coupling reactions

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## ABSTRACT

A variety of visible light-mediated oxidative cross-coupling reactions featuring good atom/step economy and overall sustainability have emerged as efficient new methods for the construction of C–C bonds under mild conditions. Furthermore, a wide range of different oxidative cross-coupling reactions have been developed during the last 5 years using photoredox catalysis. This review provides a summary of recent advances in the field of photoredox-catalyzed oxidative cross-coupling reactions, and could be used as a reference guide or a platform to inspire the development of new photoredox-catalyzed oxidative cross-coupling reactions with improved efficiency and selectivity.

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## 1. Introduction

The development of efficient methods for the formation of new chemical bonds under mild and green conditions is one of the fundamental challenges of synthetic chemistry. Transition-metal catalyzed cross-coupling reactions have been proven to be powerful tools for the formation of C–C, C–N, C–O and C–S bonds, and reactions of this type have been widely applied in both academia and industry [1–6]. However, classic cross-coupling reactions between electrophiles and nucleophiles generally require separate pre-functionalization and de-functionalization steps, which can reduce the overall efficiency of the transformation. A new strategy has recently been developed to overcome this difficulty involving the oxidative coupling of two nucleophiles [7], where the use of hydrocarbons as nucleophiles is considered by many to be an ideal ap-

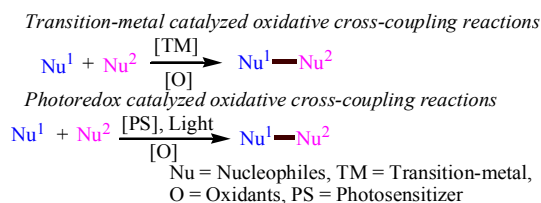
proach. There has been a recent increase in number of oxidative cross-coupling reactions being reported recently involving single electron transfer processes with first-row transition metal catalysts (i.e., Cu and Fe), and radical oxidative coupling reactions of this type represent a promising development in green chemistry [8].

With respect to the development of new sustainable and green synthetic methods, the application of visible light as a renewable source of energy has attracted significant interest from organic chemist working in a variety of different fields [9–12]. Based on photo-induced single electron transfer processes, visible light photocatalysis provides a new strategy for the oxidation of C–H bonds, and therefore represents an environmentally friendly approach to the construction of valuable chemicals under mild conditions. Although many organic molecules do not possess the structural features required to absorb

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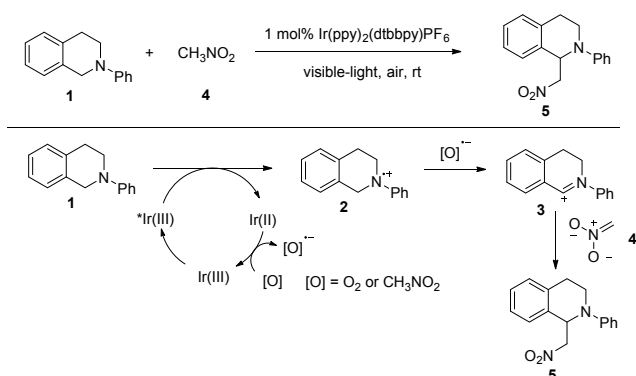
**Scheme 1.** Visible light-photocatalyzed oxidative cross-coupling reactions.

visible light, the use of visible light photocatalysts (photosensitizers) in conjunction with electron/energy transfer processes could allow for a wide variety of efficient photochemical reactions to be conducted under visible light irradiation conditions.

Although significant developments have been achieved in transition-metal catalyzed oxidative cross-coupling reactions, synthetic strategies based on visible light photoredox reactions have emerged as efficient pathways for the formation of new chemical bonds between two nucleophiles during the last few years. Based on the mild and environmentally benign features of photoredox catalysis and the synthetic step economy of oxidative coupling reactions, the utilization of visible light photo-induced single electron transfer processes in oxidative cross-coupling reactions continues to attract increasing levels of attention (Scheme 1). Furthermore, the increased interest in this area has led to the development of many different types of photocatalyzed oxidative coupling reactions during the last 5 years, including the visible light-photocatalyzed oxidation/coupling reaction of amines, photo-induced oxidative decarboxylative coupling reactions and cross-coupling hydrogen evolution (CCHE) reactions. To date, several important reviews have been published providing a summary of fundamental organic transformations [13–19]. The aim of this review, however, is to highlight the recent development of visible light-photocatalyzed oxidative coupling reactions.

## 2. Visible light-photocatalyzed oxidation of amines

### 2.1. Visible light-photocatalyzed oxidative cross-coupling reactions with iminium ions as intermediate



**Scheme 2.** Photoredox-catalyzed oxidative aza-Henry reaction.

The visible light-photocatalyzed oxidation of an  $sp^3$  C–H bond adjacent to the N atom of a tertiary amine would provide access to an activated iminium ion, which could be trapped with a wide range of different nucleophiles to yield the direct coupling products. Photocatalyzed oxidative cross-coupling pathways of this type have been shown to be powerful protocols for the functionalization of amines. For example, Stephenson et al. [20] reported an oxidative aza-Henry reaction under photoredox conditions in 2010, which proceeded via the formation of an iminium ion intermediate (Scheme 2). Notably, this work provided the first example of the visible light mediated functionalization of an  $sp^3$  C–H bond adjacent to a nitrogen atom. The results of this study also revealed that visible light and the catalyst were both required for a successful conversion, and that the absence of oxygen resulted in much lower yields of the product. Furthermore, it was revealed that oxygen and  $\text{CH}_3\text{NO}_2$  could both act as oxidants in this transformation. Based on a series of Stern-Volmer studies, the authors went on to propose a mechanism for this transformation. Briefly, visible light excitation of the  $\text{Ir}^{3+}$  catalyst followed by reductive quenching would lead to the formation of a radical cation of tetrahydroisoquinoline **2**. The authors proposed that oxygen could play a critical role in the reaction. The corresponding superoxide radical anion could abstract a H atom from the trialkylammonium radical cation to give the iminium ion. Nucle-



**Aiwèn Lei** received his PhD degree (2000) (with Prof. Xiyan Lu) at Shanghai Institute of Organic Chemistry, Chinese Academy of Science (CAS). He then moved to Pennsylvania State University, U.S.A., and worked with Prof. Xumu Zhang as a postdoctoral fellow. In 2003, he joined Stanford University, working with Prof. James P. Collman as a research associate. He became a full professor at College of Chemistry and Molecular Sciences, Wuhan University, China in 2005. His research focuses on: (1) oxidative-coupling, a novel approaches and understanding toward bond formations and (2) physical organic chemistry in modern coupling reactions. He has published more than 170 papers in international journals with a total SCI citation of > 4000, and the total impact factor over 1100. In 2007, he was hired as Luojia Distinguished Professor. In 2010, he won the National Science Fund for Distinguished Young Scholar. In 2012, he won the First Class Prize of Hubei Province Natural Science Award. In 2013, Prof. Lei attended the 15th Asian Chemical Congress and won the Asian Rising Star Award. **Then in 2014, he won the 4th Chinese Chemical Society–Royal Society of Chemistry Young Chemist Award.** In the same year, he has been selected as a Changjiang Scholar Chair Professor by the Chinese Ministry of Education.

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