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Visible light induced 3d transition metal-catalysis: A focus on C-H bond functionalization.

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Abstract: *Transition metal catalysis under visible light irradiation has attracted considerable interest in the recent years. With the objective of breaking free from the use of noble metals, and as an alternative to traditional photoredox and dual catalysis, the implementation of this strategy with 3d transition metal complexes capable of both absorbing visible light and enabling catalysis has very recently led to the development of efficient photocatalytic systems for challenging organic synthesis, including C-H bond functionalization reactions.*

Introduction: Transition-metal photocatalysis has experienced tremendous developments in the last decades [1]. The most popular families of photocatalysts are Ru(II) polypyridyl and cyclometallated Ir(III) complexes owing to their strong absorbance in the visible light region where most organic molecules are transparent, and their sufficiently long-lived excited states to engage in outer-sphere electron or energy transfer to promote low energy reaction pathways [2,3]. Moreover, by merging photoredox catalysis and traditional transition metal-catalysis, the dual strategy has overcome intrinsic limitations of each approaches allowing for efficient and highly selective transformations that would be unfeasible under non-irradiative conditions [4,5]. Nevertheless, and despite remarkable achievement notably in combination with nickel catalysis [6,7], photoredox catalysis typically employs expensive organometallic complexes based on noble metals that are of economic and environmental concerns. Despite challenges associated with typically fast excited state deactivation and low photostability of 3d transition metal complexes [8], the long-standing interest in replacing noble metal in luminophores has led to recent discoveries of new photoactive complexes based on copper [9], nickel [10], cobalt [11], iron [12, 13], chromium [14, 15], and vanadium [16] exhibiting impressive photophysical properties whose applications as photoredox catalysts remain today relatively limited. On the other hand, a particular attention has been very recently given to visible light induced transition-metal catalysis, where the transition metal complex is capable of both absorbing visible light and enabling catalysis in the absence of an exogenous photosensitizer [17,18,19]. With the same objective of breaking free from the use of noble metals, the development of new photocatalytic systems solely based on abundant first-row transition metals has met with a number of resounding successes in very recent years [20]. The aim of this review is to highlight very recent advances in this emerging field of 3d transition metal catalyzed organic transformations under visible light with a special focus on C-H bond functionalization reactions.

Visible light induced copper catalysis: Among first-row transition metal, copper is by far the most studied alternative with already a variety of well-defined complexes capable of performing efficient transformation under visible light irradiation [21,22]. In a continuing effort to demonstrate the potential of copper-phenanthrolines complexes for visible light-mediated transformations, Reiser and co-workers recently reported on the use of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (dmp = 2,9-dimethyl-1,10-phenanthroline) as a low-priced and efficient photoredox catalyst for various atom transfer radical additions (Figure 1a) [23]. In this

concern, and inspired by the seminal work of Kochi [24], Wan and co-workers have recently developed the blue light-induced vicinal dichlorination of alkenes by chlorine atom radicals generated through ligand-to-metal charge transfer excitation of CuCl_2 (Figure 1b) [25]. More recently, Rovis and co-workers reported the photoinduced copper-catalyzed functionalization of unactivated $\text{C}(\text{sp}^3)\text{-H}$ bonds via the coupling of alkanes with electron deficient olefins (Figure 1c) [26]. The photoactive cuprate catalyst formed *in situ* from $\text{CuCl}_2/\text{LiCl}$ in acetonitrile undergoes ligand-to-metal charge transfer to generate chlorine radical capable of abstracting strong electron rich $\text{C}(\text{sp}^3)\text{-H}$ bonds. While blue light irradiation (440 nm) can promote the desired transformation, improved catalytic activities were obtained using near ultraviolet light (390 nm) at 60 °C. Closely related to this work, Hong and co-workers very recently demonstrated that the photoexcitation of the bench stable $\text{bpyCu}(\text{CF}_3)_3$ under blue light irradiation promotes trifluoromethylation of unactivated alkanes *via* the generation of trifluoromethyl radical as hydrogen atom transfer reagent (Figure 1d) [27].

Pioneered by the work of Fu and co-workers on photoinduced copper-catalyzed enantioselective cross-coupling reactions [28], the groups of Gong [29,30], Zhang [31] and Liu [32] recently contributed to the emergence of this research field by describing enantioselective alkylation of imine, dual carbofunctionalization of alkenes and decarboxylative alkynylation with terminal alkynes, respectively. The most recent example was reported in 2021 by Zhang and coworkers, who developed an asymmetric alkylation of azoles catalyzed by a copper(I)/carbazole-based oxazoline ligand system under visible light irradiation (Figure 1d) [33]. A large variety of azoles and secondary 1-arylalkyl bromide substrates were efficiently engaged in this asymmetric photocatalytic C-H functionalization process to afford the desired chiral alkylated azole products in good yields and up to excellent enantioselectivity. Preliminary mechanistic studies evidenced that both the *in situ*-formed $[\text{LCu}^{\text{I}}]$ and $[\text{LCu}^{\text{I}}\text{-azole}]\text{Li}$ complexes absorb visible light in the range of 400-500 nm and that the latter is likely the photoactive species due to a larger Stern-Volmer constant measured using 1-bromoethyl benzene as quencher.

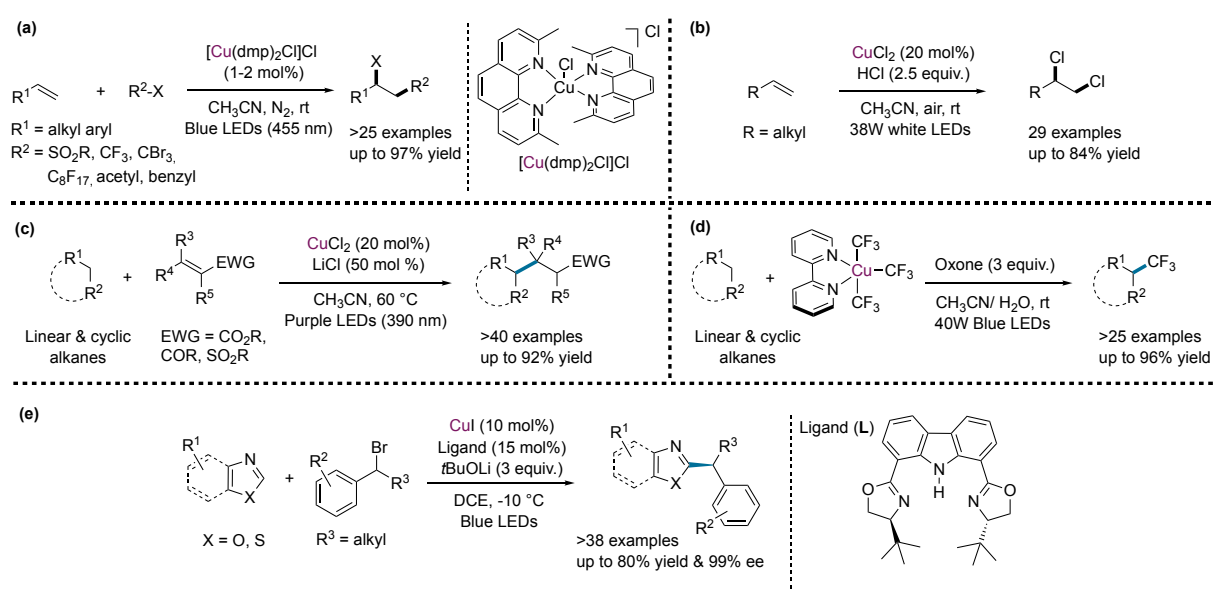


Figure 1. Visible light induced copper-catalysis

Visible light induced manganese catalysis: The use of manganese complexes in transition metal catalysis under visible light has recently emerged [34]. A relevant example was reported by Ackermann and co-workers who developed a visible light induced manganese-catalyzed C-H arylation in continuous flow (Figure 2a) [35]. Under blue light irradiation, $\text{CpMn}(\text{CO})_3$ as catalyst allowed for the efficient arylation at room temperature of arenes and heteroarenes using aryl diazonium salts. Interestingly, based on mechanistic studies, the authors proposed that both substrates coordinate the manganese metal center to form a photochemically competent complex able to undergo single electron transfer from its excited state to reduce the aryl diazonium salt and generate the corresponding aryl radical. In 2020, Qu, Li, Zhang and coworkers reported the selective chlorination of unactivated $\text{C}(\text{sp}^3)\text{-H}$ bonds of aliphatic amines catalyzed by $\text{Mn}_2(\text{CO})_{10}$ under blue light irradiation (Figure 2b) [36]. Visible light induced Mn-Mn bond homolysis affords $\text{Mn}(\text{CO})_5$ radical that abstracts the Cl atom of N-chlorosulfonamide to *in situ* generate amidyl radical undergoing 1,5-intramolecular hydrogen transfer followed by Cl atom transfer to produce the desired chlorinated product. The reaction performed under mild reaction conditions could notably provide efficient access to a large variety of alkyl chlorides in good yields. Very recently, Thomas and co-workers described a visible light induced manganese-catalyzed C-H borylation of furan and thiophene derivatives (Figure 2c). The photoactive Mn(I) hydride species, $\text{dmpe}_2\text{MnH}_3$, generated *in situ* from the dibromide precursor, $\text{dmpe}_2\text{MnBr}_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), in the presence of pinacolborane (HBPin) and sodium tert-butoxyde (NaOtBu), is prone to hydrogen loss that enables the catalytic C-H borylation process under visible light irradiation [37].

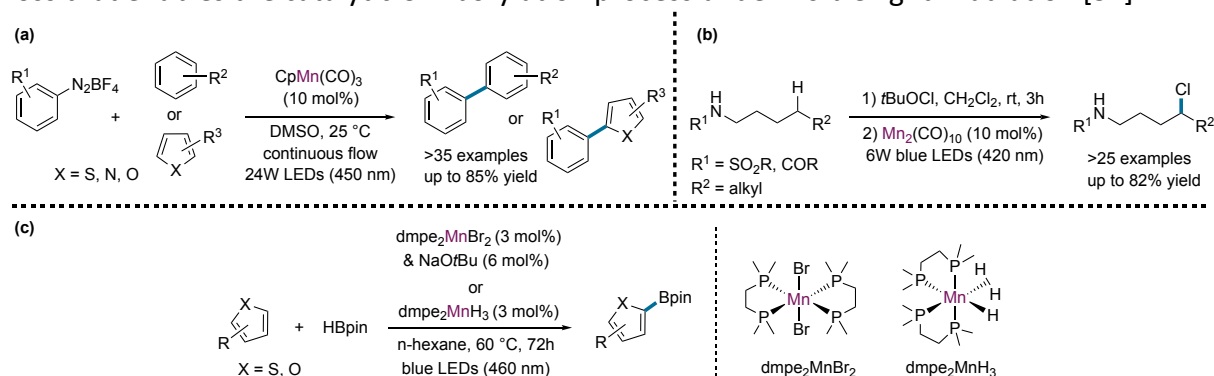


Figure 2. Visible light induced manganese-catalysis

Visible light induced iron catalysis: As an alternative to the challenging development of efficient Iron-based photosensitizers [12,13], new photocatalytic processes have been envisaged with the *in situ* formation of iron-substrate complexes that can generate radical species under visible light irradiation [38]. Inspired by the preliminary work of Sugimori [39], Jin and co-workers described in 2019 an efficient visible light-induced iron(II)-catalyzed decarboxylative alkylation of heteroarenes (Figure 3a) [40]. Also based on ligand-to-metal charge transfer of iron-carboxylates intermediates, Lei, Jin and coworkers have more recently developed an intramolecular aromatic C-H oxygenation of 2-biphenylcarboxylic acids catalyzed by $\text{Fe}(\text{NO}_3)_3$ / 2,2'-bipyridine-6,6'-dicarboxylic acid and sodium bromate as terminal oxidant that exhibits a broad functionality tolerance (Figure 3b) [41].

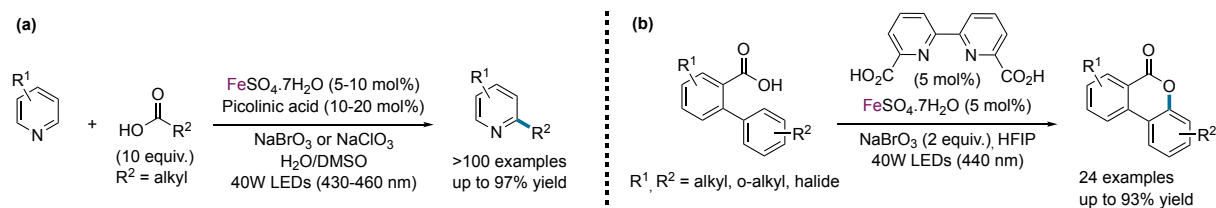


Figure 3. Visible light induced iron-catalysis

Visible light induced nickel catalysis: In comparison to the broad application of nickel complexes as cocatalysts in dual photoredox catalysis [6,7], only very limited examples refer to the solely used of nickel photoredox catalysts in organic transformations [42, 43]. Nevertheless, recent studies by Doyle [44] Scholes [45], and Xue [46,47] have notably opened new perspectives in cross-coupling reactions thanks to the employment of Ni^{II} -aryl halide complexes as pre-catalysts (Figure 4a). In 2020, Guo, Radius and Marder described a selective visible light-induced Ni-catalyzed borylation of chloroarenes [48]. Mechanistic investigations demonstrated that $\text{Ni}^{\text{I}}(\text{IMes})_2\text{Cl}$ generated *in situ* from $\text{Ni}(\text{IMes})_2$ (IMes = 1,3-dimesitylimidazoline-2-ylidene) is the catalytic active species that undergoes under visible light irradiation chlorine abstraction from aryl chlorides to produce $\text{Ni}^{\text{II}}(\text{IMes})_2\text{Cl}_2$ and aryl radical. The latter reacts with the anionic diborane $\text{B}_2\text{pin}_2(\text{OMe})^-$ formed from B_2pin_2 and KOMe (potassium methoxide) to afford the desired borylated product. Of particular interest, the authors also observed C-H bond borylation of chloroarenes to yield diborylated arenes as minor products (Figure 4b).

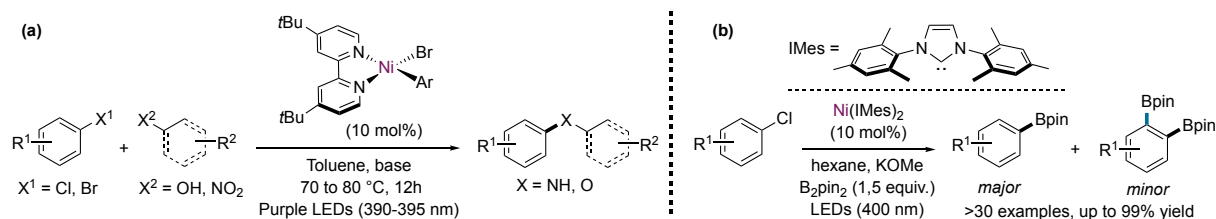


Figure 4. Visible light induced nickel-catalysis

Conclusion: First-row transition metal catalyzed organic transformations under visible light has recently emerged as a valuable alternative to traditional photoredox and dual catalysis that typically employ expensive organometallic complexes based on noble metals. Moreover, compare to ground stated transition metal catalysis, photoinduced 3d transition metal catalysis constitutes a greener approach allowing for milder reaction conditions, improved reactivity and selectivity, while enabling new challenging chemical transformations. Nevertheless, examples of photocatalytic processes solely based on 3d transition metal catalysts remains today relatively scarce and one might easily assume that it is only the beginning of the story.

Declaration of competing interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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