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REVIEW ARTICLE

Advances in Green and Sustainable Photo Redox Catalysis for Organic Transformation

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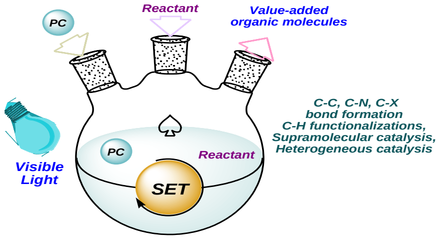
Abstract: Advances in visible-light-mediated photo redox catalysis have created anexceptional approach for small-molecule activation and new chemical bond formation in organic synthesis. This is analternative technique to generate new reactive intermediates and enable distinct synthetic strategies that were previously unthinkable. Of the many trademarks, photochemistry is often classified as “green” technology, promoting organic reactions under mild conditions without the necessity for potent and wasteful solvents, oxidants and reductants. This mini review coversthe overview of the primary principles of photoredox catalysis, discussing various metal-based and organophotocatalysts. It further surveys a variety of reactions, including trifluoromethylation, cyanation, C-H functionalizations, supramolecular catalysis, and heterogeneous catalysis in both aqueous and alcoholic mediums.



Keywords: *Photoredox catalysis, sustainable approach, single electron transfer.*

Contents

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1. Introduction

Photodynamic therapy (PDT) is a light-promoted approach that in the realm of synthetic chemistry, chemist typically utilizes pre-generated high-energy species, heat activation, or catalytic activation to facilitate the functionalization of molecules in organic synthesis when navigating reaction coordinates. However, there has been a recent upsurge in interest in unconventional chemical activation techniques, such as photochemical and electrochemical methods, aimed at providing novel pathways for retrosynthetic assessment. These emerging approaches have brought about significant changes in contemporary synthetic strategies. Notably, advancements in photochemical techniques have led to improved accessibility to highly reactive intermediates such as radical ions, radicals, and charge transfer complexes. Consequently, the photoredox process has opened new avenues for discovering reactions and developing bond disconnection tactics that were previously challenging or unattainable with traditional methods.[1]

In the last decade, synthetic photochemistry has experienced a revival, particularly focusing on establishing sustainable methods. Light-absorbing chromophores are commonly employed to facilitate a variety of organic transformations of small molecules that traditionally don’t react to light. In this process, called photocatalysis, chromophores typically facilitate either electron transfer (ET) or energy transfer (EnT) process. ET, also known as photoredox catalysis, operates by

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transferring single electrons based on the redox properties of both the excited photocatalyst (PC) and the reacting substrate. Photoredox reactions often require additional electron donors or acceptors to complete the catalytic cycle. Moreover, ensuring that the redox potentials of both the PC and the organic substrate are appropriately controlled, is crucial for successful photoredox catalysis (**Figure 1**).[2]

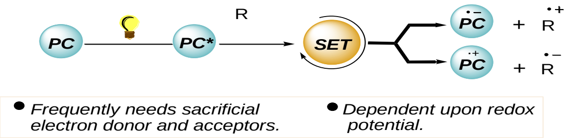


Figure 1.*Photo-redox process*

Photoredox-initiated reactions generally proceeded *via* utilization of two type of photocatalysts: transition metal-based inorganic photoredox complexes and organic dyes, also known as organic photoredox catalysts (**Figure 2**). Transition metal-based photoredox reactions typically utilize metal polypyridyl complexes, like Ru(II) polypyridine complexes or cyclometalatedIr(III) complexes. On the other hand, metal-free conditions make use of organic dyes such as eosin, rhodamine, 9-fluorenone, xanthone, methylene blue, rose Bengal, acridiniums, etc., which are proficient of absorbing visible light or near-visible light.[3]

Photoredox catalysts (PC) can harness visible light, which is a cost-effective, eco-friendly, and readily available source of sustainable energy. When exposed to visible light, PC generates long-lasting photoexcited states (PC*), which readily participate inbimolecular electron-transfer reactions, either releasing orcapturing electrons from molecules. In reductive quenchingcycles, PC* accepts an electron from a substrate (Sub) or a reductant (Red), forming the radical anion $[PC]^{\bullet-}$, followed by its oxidation. Alternatively, in oxidative quenching reactions, PC* transfers an electron to either a substrate (Sub) or an oxidant (Ox) in the reaction mixture, resulting in the formation of the radical cation $[PC]^{\bullet+}$, which is subsequently reduced. These single electron transfer (SET) events facilitate radical generation and provide new pathways for radical conversion in organic synthesis (**Figure 3**).[3,4]

In 1912, Giacomo Ciamician, a prominent figure in organic photochemistry, delivered an inspiring speech at the 8th International Congress of Applied Chemistry. Titled “The Future of Photochemistry,” Ciamician envisioned a future where clean and economical photochemical processes would replace high-energy synthetic methods in a new, environmentally conscious chemical industry.[5]This sustainable approach adheres to a set of guidelines aimed at reducing or eliminating the use of harmful toxic compounds throughout the chemical production process.

The pinnacle of sustainable chemical reactivity and the objective of green chemistry reflects photosynthesis. Recent progress in photochemical techniques, especially photoredox catalysis, appears to have advanced us toward this aim. Similar to how leaves intake air, these methods generate reactive radicals using coloured catalysts (like organic dyes or transition metal complexes) to absorb light and activate stable organic molecules through single-electron processes (oxidation or reduction).

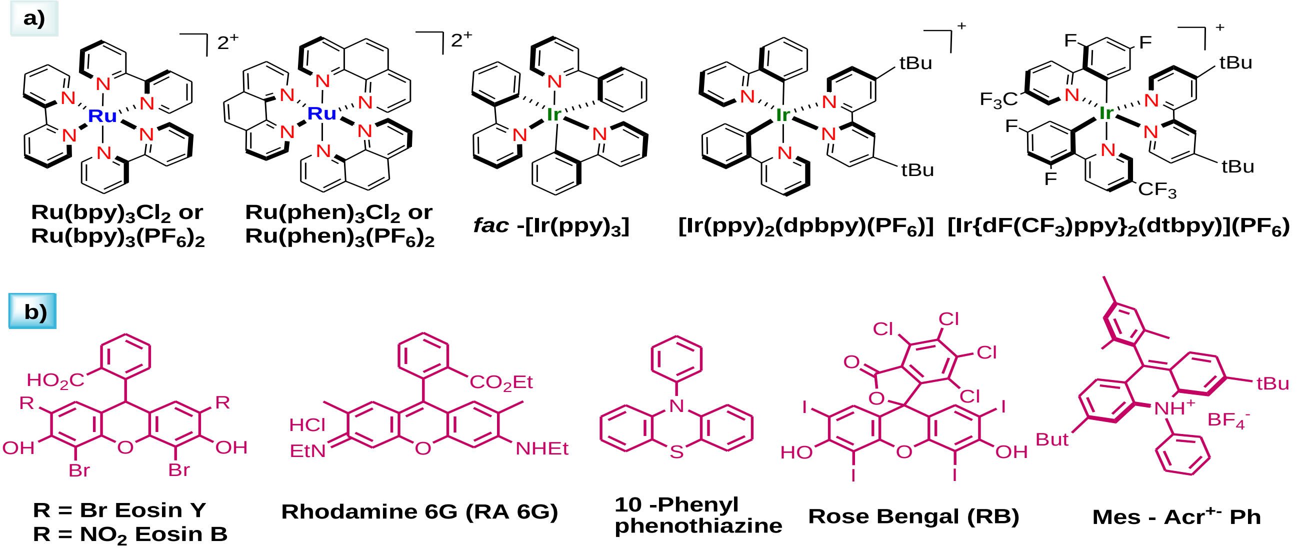


Figure 2. *Representative examples of photocatalyst*.

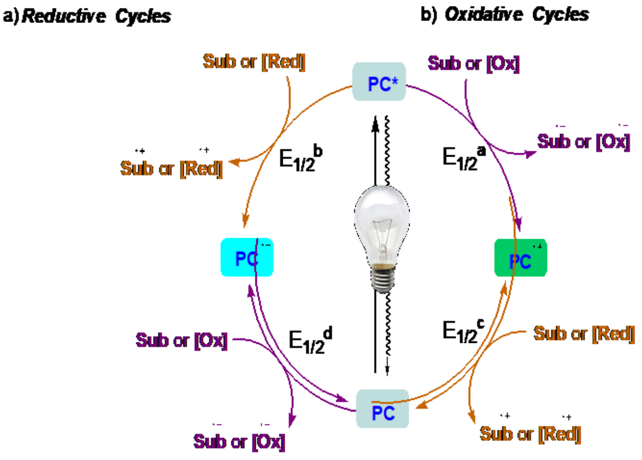
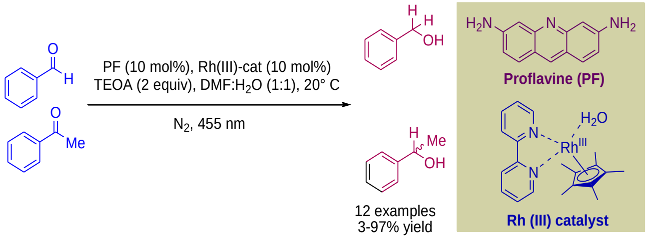


Figure 3. *The photoredox quenching cycles.*

The aim is to utilize water or alcohol as the reaction medium and harness visible light as the primary energy source, paving the way for innovative sustainable chemistry. This section delves into the latest developments in sustainable organic transformation through photoredox catalysis, outlining both the benefits and constraints associated with these catalysts.

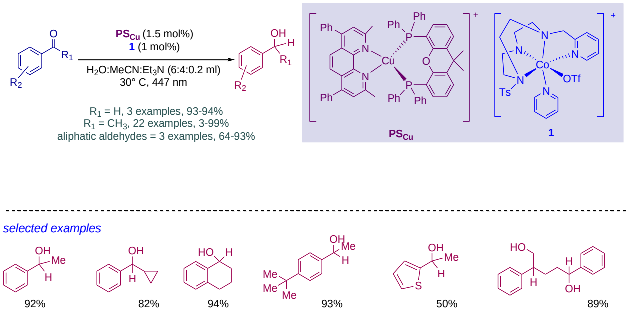
1.1 Water as a Hydride Source

Using proflavine (PF) as a photocatalyst, [Cp*Rh(III)(bpy)H]Cl as a mediator, and triethanolamine (TEOA) as a sacrificial electron donor leads to the selective reduction of aldehydes over ketones (**Scheme 1**).[6]In-depth mechanistic studies indicate that the primary reaction pathway entails the photochemical reduction of proflavine triplets, followed by the reduction of the Rh catalyst to produce reactive Rh(III)–H intermediate *in situ*. Water is essential in this process, providing the protons needed to form Rh(III)–H.



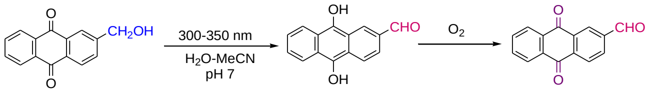
Scheme 1. *Photocatalytic generation of alcohols using Rh(III)–H species.*

Fillol's group reported a dual cobalt-copper photoredox catalyst that effectively reduces aldehydes and aromatic ketones to corresponding 1º and 2º alcohol in the presence of water as a hydride source and sacrificial electron donor (iPr_2EtN/Et_3N) when exposed to 447 nm light (**Scheme 2**).[7]Mechanistic investigations demonstrated that the reduction of the organic substrates is facilitated by the formation of a [Co–H] intermediate.



Scheme 2. *Dual catalysis for the photoreduction of aldehydes and aromatic ketones.*

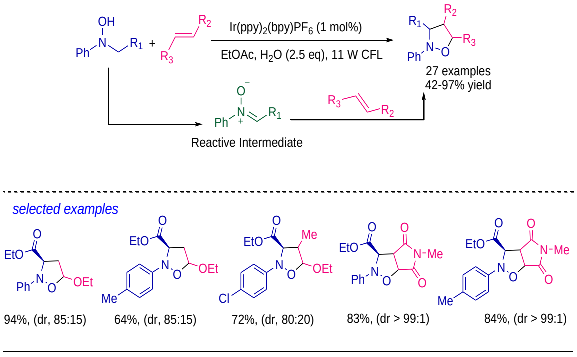
Wan and his team discovered that water is essential for an intramolecular reaction of 2-(hydroxymethyl)anthraquinone under UV light (300 – 350 nm) (**Scheme 3**).[8,9] This reaction results in an intramolecular redox product, which quickly oxidizes the anthraquinone derivative when it comes into contact with air or oxygen.



Scheme 3. *Intramolecular photoredox reaction in aqueous solution.*

1.2 Water Mediated Rate Acceleration in the Photocatalytic Synthesis of Isoxazolidines

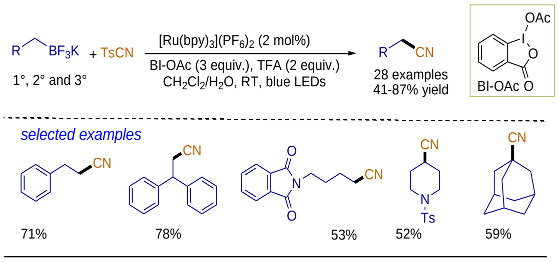
The study described an oxidative [3+2] cycloaddition reaction between *N*-alkyl-substituted hydroxylamines and alkenes. They used a 1 mol% $[Ir(ppy)_2(bpy)]PF_6$photoredox catalyst under an 11 W CFL light source in ethyl acetate solvent (**Scheme 4**).[10] Interestingly, they noticed that adding 2.5 equivalents of water to the reaction mixture sped up the reaction rate, giving the desired isoxazolidine products in good amounts. This finding suggests that water is essential to the reaction. To explain why water enhances the reaction rate, the authors proposed that the photoredoxcatalyst might split water, forming active species like $HO^•$, $HO^−$, and H_2O_2, which could participate in the reaction.[11,12]However, they dismissed the idea that substances like H_3O^+ and H_2O in the reaction mixture might catalyze the cycloaddition process.[13]



Scheme 4. [3 + 2] *cycloaddition reaction.*

1.3 Deboronative Cyanation

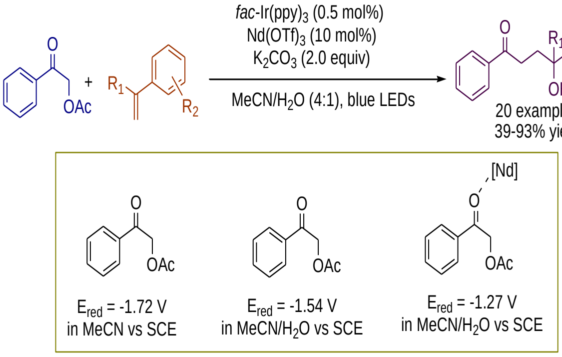
The mechanistic impact of the reaction has been overlooked in many photocatalytic methods that utilize water, either as a co-solvent or additive. It should be noted that radical precursors such as trifluoroborate salts, diazonium salts, and alkyl & aryl bromides are stable under aqueous conditions.[14] Alkyl nitrile was successfully generated through the direct photocatalytic cyanation reaction of alkyltrifluoroborates, utilizing $[Ru(bpy)_3](PF_6)_2$ as a photocatalyst, hypervalent iodine as an oxidant, and TFA as an additive (**Scheme 5**).[15] The reaction demonstrated tolerance towards various functionalities with a broad substrate scope. The involvement of an alkyl radical intermediate in the reaction was confirmed by trapping the free radical using a radical scavenger, TEMPO.



Scheme 5. *Deboronative cyanation reaction of alkyltrifluoroborates.*

1.4 LUMO Lowering Effect by Water

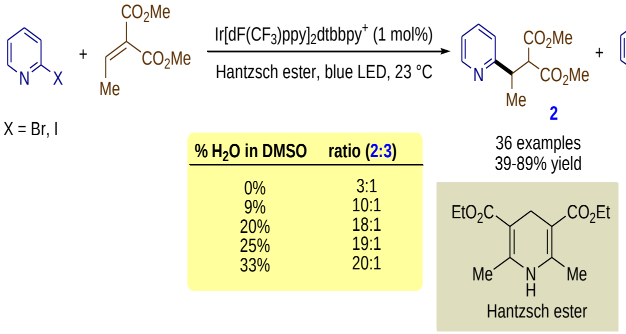
In the photocatalytic cross-coupling reaction between α-acetoxy acetophenones and styrene derivatives, a reduction in the lowest unoccupied molecular orbital (LUMO) energy level of the carbonyl was observed, resulting in the formation of 1,4-substituted products *via* Markovnikov functionalization (**Scheme 6**).[16] This coupling mechanism was achieved by deactivating the photocatalyst *fac*-$Ir(ppy)_3$ through oxidation, in combination with activating the carbonyl group in the presence of water and $Nd(OTf)_3$ serving as a Lewis acid catalyst. The inclusion of an aqueous medium, along with the water-compatible Lewis acid, amplified the reduction in LUMO energy levels of carbonyls, shifting the E_{red} of α-acetoxy acetophenones from -1.72 V to -1.27 V vs SCE. This enhancement facilitated a more energetically favourable electron transfer process, as evidenced by cyclic voltammetry and Stern–Volmer experiments. Significantly, the lack of the Lewis acid catalyst led to the inability to generate the 1,4-difunctionalized product.



Scheme 6. C–C *cross-coupling reaction.*

1.5 Water Influences Chemo selectivity

Water can serve not only as a solubilizer for polar substrates but also for its ability to act as a nonsolvent for lipophilic hydrophobic additives. Jui et al. showcased an impressive demonstration of these properties through the radical method for heteroaryl radical conjugate addition. A photocatalyst consisting of 1 mol% (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 was utilized, which is proficient in generating reductive 2-pyridyl radicals under blue LED irradiation. In their study, Hantzsch ester was employed to maintain redox neutrality by donating both an H-atom and an electron. The authors illustrated the solubility of the reactants by introducing water as a cosolvent, where the presence of Hantzsch ester enhanced the selectivity for the formation of the radical conjugate addition product over the reduction of nitrogen heterocycles (**Scheme 7**).[17]



% H_2O in DMSO	ratio (2:3)
0%	3:1
9%	10:1
20%	18:1
25%	19:1
33%	20:1

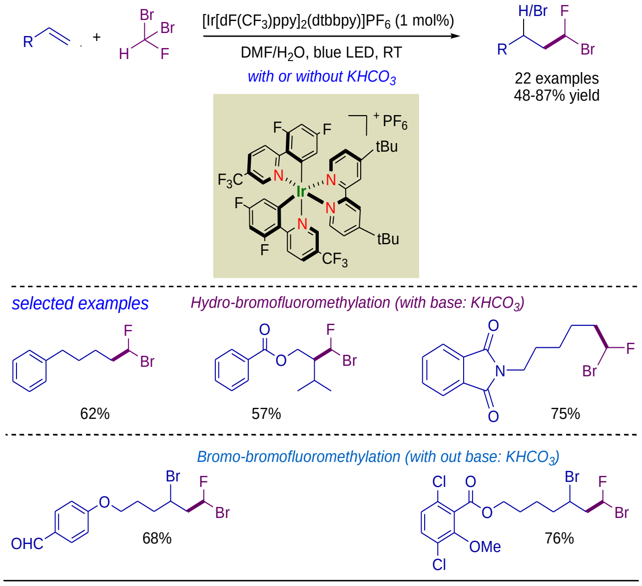
Scheme 7. *Heteroaryl radical conjugate addition.*

Qing recently unveiled an intriguing solvent effect in the chemoselective addition to alkenes. This involved a shifting from THF to a combination of DMF and water as the reaction solvent, facilitating the selective synthesis of dibromofluoromethylated products through radical addition of $CHBr_2F$ to alkenes under photoredox catalysis. Notably, the use of a 1:4 ratios of DMF to water yielded superior results for the desired product compared to alternative solvents (**Scheme 8**).[18]

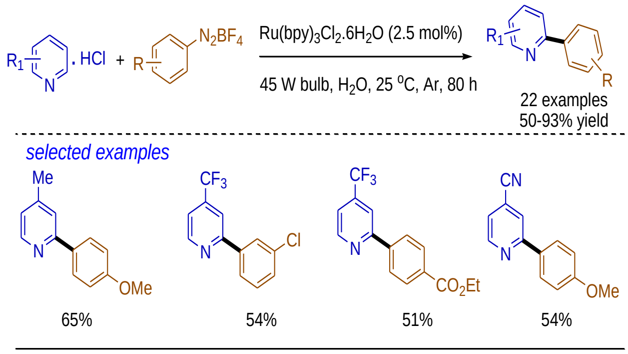
1.6 C-H Functionalisation of Heteroarenes in Water by Photoredox Catalyst

A new technique has been created for directly arylating C–H bonds in electron-deficient *N*-heteroarenes. This method uses aryldiazonium salts as coupling agents within a photocatalytic system. The photocatalyst, $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$, was activated using a 45 W LED bulb that emits visible light. This process successfully produced various aryl-heteroaryl structures (**Scheme 9**). Water was chosen as the solvent for its eco-friendly properties and its capacity to effectively dissolve and stabilize both the substrates and the catalyst.[19]

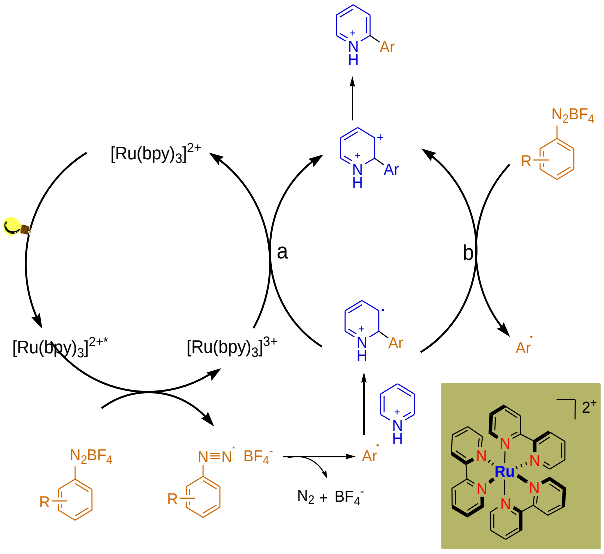
The mechanism was explored by introducing the radical quencher TEMPO into the optimized reaction conditions. The TEMPO experiments did not yield the desired product and confirm the presence of radical species in the reaction medium. In light of these findings, a mechanism was suggested with three pivotal steps: (1) the generation of the excited $[Ru(bpy)_3]^{II*}$ species by light irradiation of the $[Ru(bpy)_3]^{II}$ catalyst, (2) the formation of a phenyl radical through single electron transfer (SET) from $[Ru(bpy)_3]^{II*}$ to the aryldiazonium salt, leading to the oxidation of the catalyst to $[Ru(bpy)_3]^{III}$, and (3) the combination of the phenyl radical with pyridine hydrochloride resulting in another radical intermediate, which transforms into a carbocation *via* two possible pathways. Deprotonation of the intermediate yielded the coupling product (**Scheme 10**).[19]



Scheme 8. *Chemo selective addition of dibromofluoromethane to alkenes.*

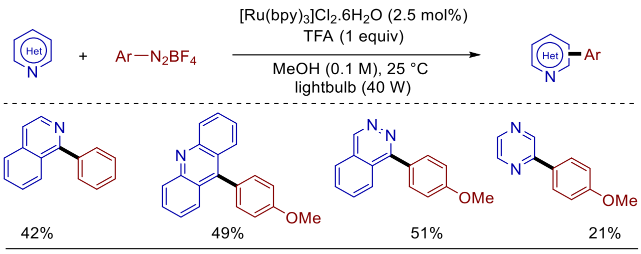


Scheme 9. *Synthesis of aryl-heteroaryl motifs.*



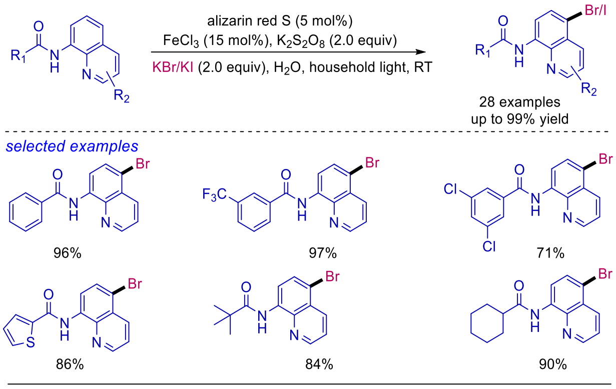
Scheme 10. *Plausible mechanistic pathway for arylation of heteroarenes.*

Lei *et al*. established a similar method to arylate isoquinolines using [Ru(bpy)$_3$]Cl$_2$·6H$_2$O as a photosensitizer (**Scheme 11**). Unlike the previous study, which employed pyridinium salts as the initial substrates, Lei group employed TFA for *in situ* protonation of the *N*-heterocycles in the reaction medium.[20]



Scheme 11. *Arylation of isoquinolines.*

1.7 Remote C-H Bromination

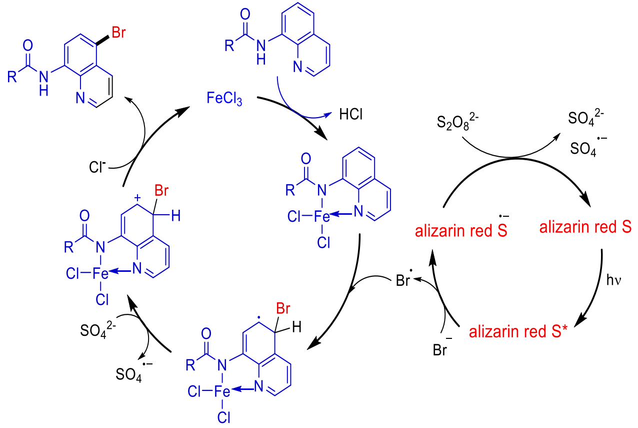


Scheme 12. *Synthesis of halogenated 8-aminoquinoline amides.*

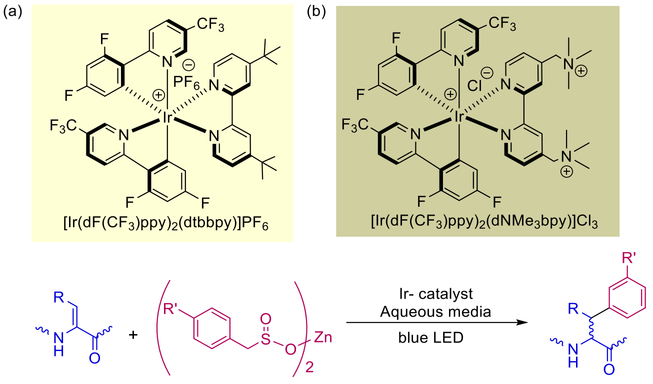
Research into visible-light photocatalysis that works well in water is a fascinating field. Pursuing these goals, scientists have created various photocatalysts that function in aqueous environments. One such catalytic system combines FeCl$_3$ with Alizarin Red S, a water-soluble organic photocatalyst, to carry out the C5–H halogenation of 8-aminoquinoline. This reaction achieved highly selective C5 halogenation of 8-aminoquinoline amides at room temperature, using K$_2$S$_2$O$_8$ as an oxidant and KBr as an additive, under the irradiation of standard household light in the presence of air (**Scheme 12**).[21]

The potential reaction pathway suggested by Wu and his team is illustrated in **Scheme 13**. In this pathway, the excited state of Alizarin Red S* generates a bromine radical (Br•) and an Alizarin Red S radical anion by reducing the bromide ion. With K$_2$S$_2$O$_8$ present, the Alizarin Red S radical anion undergoes oxidation, which completes the photocatalytic cycle and regenerates the ground state Alizarin Red S.

Most Ir- and Ru-polypyridyl complexes used as photoredox catalysts have limited solubility in water, ranging from less than 1 ppm to 1000 ppm, depending on their substituents and counterions. As a result, organic solvents are typically needed to dissolve both the catalyst and the substrates.[22]Despite this, using these complexes as catalysts has become appealing because they do not require an excess of oxidants. Roelfes and colleagues tackled the solubility issue by designing and synthesizing a water-soluble photocatalyst, [Ir(dF(CF$_3$)ppy)$_2$(dNMe$_3$bpy)]Cl$_3$, through ligand modification.[23] They replaced the *tert*-butyl groups on the ligand with quaternary ammonium groups to enhance water solubility. This newly developed catalyst has shown promise for modifying dehydroalanine (Dha) containing natural products in aqueous environments under physiological conditions and across a wide pH range (**Scheme 14**).

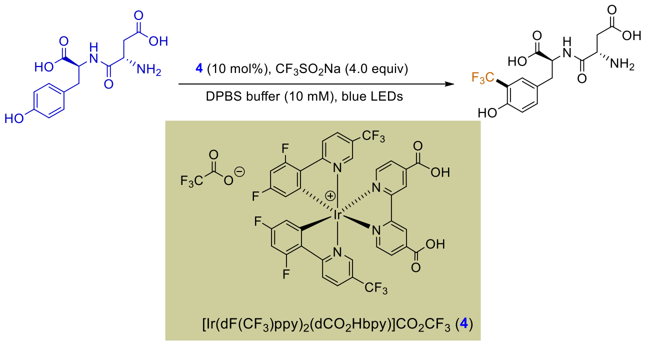


Scheme 13. *Probable reaction mechanism.*



Scheme 14. *Ir-catalysed modification of the Amino acid, (a) commercially available photoredox catalyst and (b) charged Ir(III)-based photoredox catalyst.*

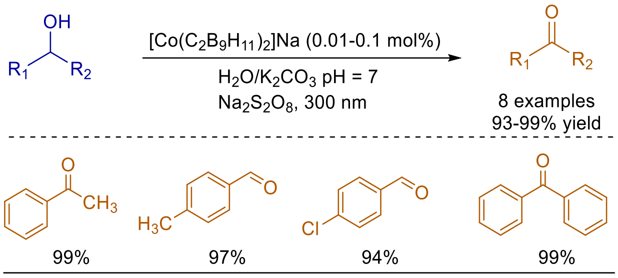
Conrad *et al.* Further advanced this field by designing similar heterolepticIr-complexes, incorporating carboxylate groups onto the bipyridyl ligands. This modification led to the creation of a new catalyst, [Ir(dF-(CF$_3$)ppy)$_2$(dCO$_2$Hbpy)]CO$_2$CF$_3$ (4), with enhanced water solubility. The performance of this photocatalyst was evaluated in the trifluoromethylation of polar molecules and peptides, using phosphate-buffered saline as the solvent. The Langlois reagent (CF$_3$SO$_2$Na) served as the CF$_3^•$ radical precursor, and a light source was used for photoexcitation (**Scheme 15**).[24]



Scheme 15. *Trifluoromethylation of biomolecule substrates.*

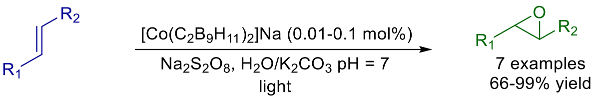
1.8 Metallacarboranes as Photoredox Catalyst in Water

A cobalt metallacarborane, [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]Na, which exhibits an unusual structure compared to established photoredox catalysts, facilitates hydrogen and dihydrogen bonding. This unique bonding contributes to its self-assembly properties,[25] water solubility,[26] and micelle formation.[27] The use of cobaltabisdicarbollide, [3,3'-Co(1,2-$C_2B_9H_{11})_2]^-$, along with its chloro derivatives, as photoredox catalysts in the oxidation of alcohols in water *via* single-electron transfer (SET) processes has been investigated by Teixidor and colleagues (**Scheme 16**).[28]



Scheme 16. *Metallacarborane catalysed oxidation reaction of alcohols.*

Researchers also examined the effectiveness of the same photocatalyst in generating epoxides from aromatic and aliphatic alkenes in water.[29] They noticed a significant increase in epoxide production with a short reaction time and minimal catalyst usage. The proposed mechanism suggests that when exposed to water and $S_2O_8^{2-}$ ions under light, the photoredox $[Co^{III}(C_2B_9H_{11})_2]^-$ catalyst oxidizes to form $[Co^{IV}(C_2B_9H_{11})_2]$, along with OH$^\bullet$ radicals, H+ ions, and SO_4^{2-} ions. Subsequently, the alkene undergoes oxidation by $[Co^{IV}(C_2B_9H_{11})_2]$, resulting in the creation of the corresponding epoxide through interaction with the hydroxyl radical (OH$^\bullet$) (**Scheme 17**).



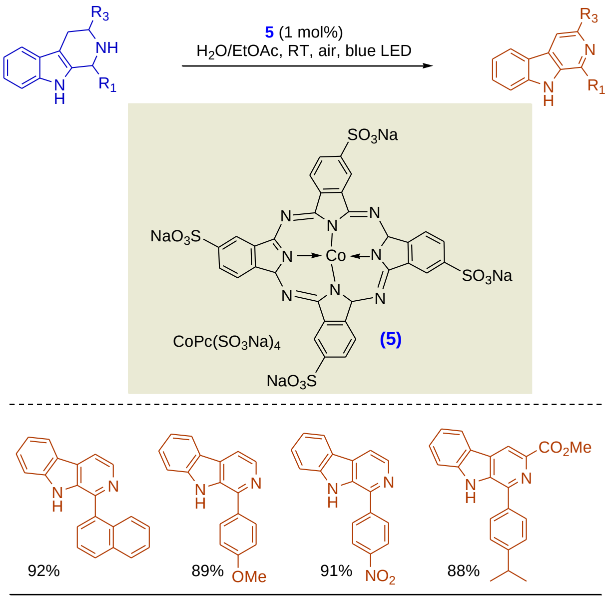
Scheme 17. *Alkene epoxidation.*

This metallacarborane was attached to silica-coated magnetic nanoparticles, resulting in a catalyst that can be easily separated using an external magnet.[30] A collaborative photoredox catalytic system was constructed using ruthenium-cobaltabis(dicarbollide), $[Ru^{II}(tryp)(bpy)(H_2O)][3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$, with the metallacarborane acting as the photoredox catalyst and Ru(II) serving as the oxidation catalyst, coupled by noncovalent contacts. This technique was utilised for the photooxidation of alcohols using ultraviolet light.[31] A water-soluble cobalt-based phthalocyanine photoredox catalyst (**5**) enabled the oxidative dehydrogenation of tetrahydro-(iso) quinoline, tetrahydro-β-carboline, and indoline derivatives in a biphasic media (**Scheme 18**).[32] This setup enabled easy product separation and permitted the catalyst to be reused up to five times while maintaining similar levels of reactivity.

1.9 Photoredox-Micellar Catalysis

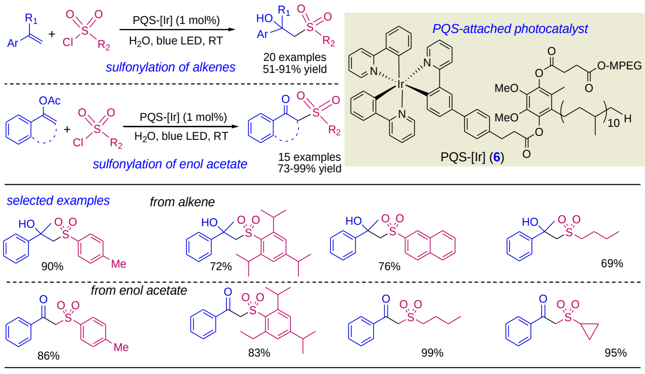
The field of synthetic organic chemistry has recently shown a growing interest in the development of water-soluble photocatalysts. Many substances commonly used in drug manufacturing, as well as certain photocatalysts, are not soluble in water, which hampers efforts to adhere to green chemistry principles. Integrating photoredox catalysis with micellar catalysis may provide a viable solution to this issue. Micelles, formed by adding surfactants to water, create an environment conducive to organic transformations in water. In 2018, Lipshutz and colleagues introduced a PQS–[Ir] photocatalyst.[33]

This catalyst is formed through the covalent binding of PQS (polyethyleneglycolubiquinol succinate, the reduced form of the dietary supplement CoQ_{10}) with the photocatalystIr$(ppy)_3$.



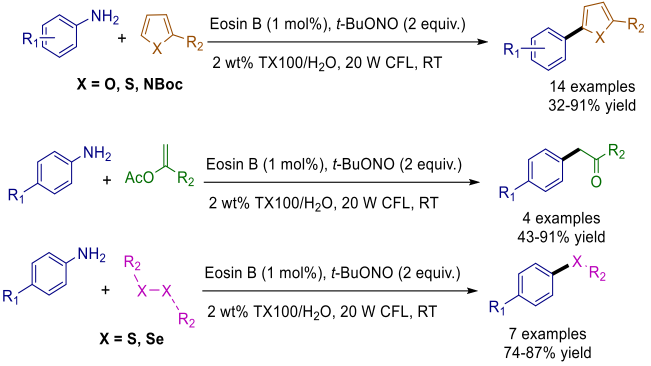
Scheme 18. *A photoredox catalyzed oxidative dehydrogenation N-heterocycles.*

This process leads to self-aggregation in an aqueous medium, producing nanomicelles. The amphiphilic PQS species includes a hydrophilic group (MPEG), a lipophilic side chain with 50 carbon atoms, and an –OH group located within the hydrophobic inner core where catalysis occurs. The efficiency of the newly developed PQS–[Ir] photocatalyst was investigated in the sulfonylation of alkenes and enol acetates, yielding the desired product with good efficiency (**Scheme 19**). Notably, this catalyst can be reused multiple times without compromising the product yield.



Scheme 19. *Sulfonylation of alkenes and enol acetates catalyzed by the PQS-[Ir].*

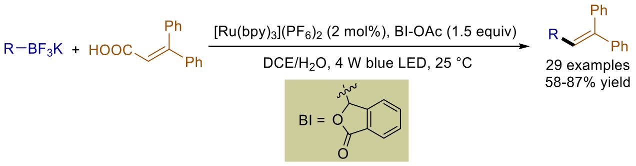
Organic dyes are frequently employed as photoredox catalysts due to their cost-effectiveness compared to precious metal-polypyridyl complexes.[34-37]Cai and Jiang's research team devised a micellar photocatalytic setup, utilizing an organic photoredox catalyst to arylate*in situ*-nitrosated aniline.[38] They employed commercially available Triton X-100 and Eosin B as the surfactant and photocatalyst, respectively, in the reaction conducted under the control of a 20 W CFL. Remarkably, the reaction proceeded smoothly at room temperature without the need for any organic cosolvent. Additionally, the authors investigated the synthesis of unsymmetrical sulfides and selenides from substituted disulfides/diselenides and anilines, as well as the [4+2] benzannulation of 2-aminobiphenyl with alkynes under their developed photocatalytic conditions (**Scheme 20**).



Scheme 20. *Arylation in photocatalytic conditions.*

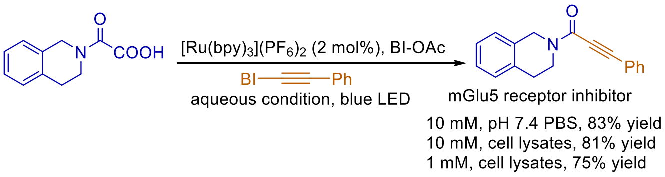
1.10 Dual Hypervalent Iodine Reagent and Photocatalyst Enabled Decarboxylation

Organic carboxylates, readily available and removable, serve as latent activating groups for constructing diverse organic motifs.[39] Typically, transition metal catalysts activate these carboxylates through coordination, necessitating strong oxidants or high temperatures to facilitate CO_2 extrusion.[40,41] Hypervalent iodine reagents (HIR) have garnered significant interest due to their similar activation properties to transition metals, enabling radical addition followed by subsequent decarboxylation under mild conditions. Building on this concept, researchers developed a photoredox system utilizing HIR with dual catalytic properties to promote decarboxylative radical alkenylation and ynonylation reactions.[42,43]Chen's group demonstrated alkyl-alkene synthesis *via* coupling alkyl trifluoroborate with aryl- or acyl-substituted vinyl carboxylic acids using a hypervalent iodine photocatalyst.[42] Optimal yields were achieved using blue LED irradiation with BI-OAc as the iodinating reagent in a DCE Medium at 25 ℃ (Scheme 21).



Scheme 21. Decaboxylative radical alkenylation reaction.

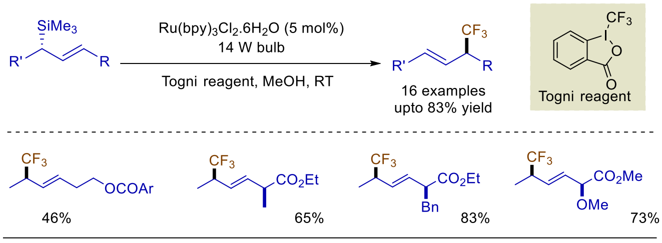
Furthermore, they have demonstrated the biological applications of the hypervalent iodine photoredox system in synthesizing biomolecules, such as the mGlu5 receptor inhibitor, under neutral aqueous conditions (**Scheme 22**).[44]



Scheme 22. *Synthesis of bioactive molecules in neutral aqueous medium.*

1.11 Photoredox Catalyst Mediated Trifluoromethylation in Alcoholic Medium

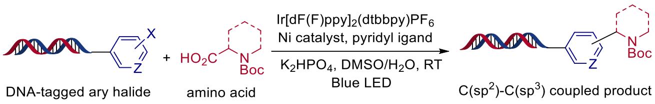
Gouverneur group introduced a trifluoromethylation approach for allylsilanes through photoredox catalysis, resulting in enantioenriched branched allylic-CF_3 products. The Togni reagent served as the $CF_3^{\bullet}$ radical source for the trifluoromethylation reaction in the presence of the photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$. This process was conducted in a methanolic or ethanolic medium and exposed to a household 14 W light bulb, as illustrated in **Scheme 23**.[45]



Scheme 23. *Trifluoromethylation of allylsilanes.*

1.12 Merging Nickel with Photoredox Catalysis in Water

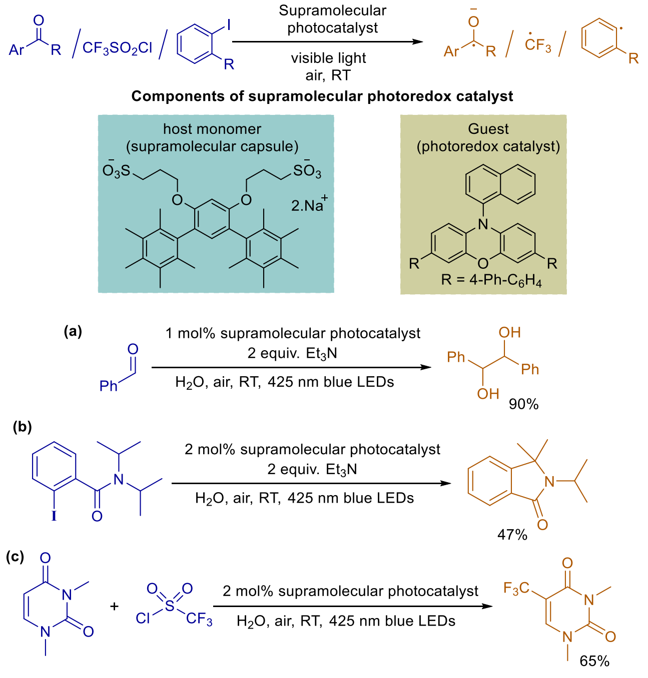
The fusion of transition metals with photoredox catalysts, known as metallaphotoredox catalysis, has surfaced as an intriguing method for the straightforward creation of complex structures pertinent to drug discovery. This approach holds promise as a valuable addition to DNA-encoded chemistry techniques. Recently, a breakthrough was achieved where amino acids underwent successful decarboxylation in aqueous conditions using an iridium-based photocatalyst. This process yielded the necessary C-centered radicals, which were subsequently integrated into various DNA-tagged radical acceptors.[46] Additionally, the same research group combined photoredox catalysts with nickel in water, facilitating DNA-compatible decarboxylative arylation reactions. Utilizing a novel nickel precatalyst featuring a pyridyl carboxamidine ligand in conjunction with an iridium-based photocatalyst, they achieved the synthesis of structurally diverse DNA-encoded libraries from readily available amino acids and a range of DNA-tagged aryl halides (Scheme 24).[46]



Scheme 24. *Decarboxylative arylation in aqueous medium.*

1.13 Supramolecular Photoredox Catalysis in Water

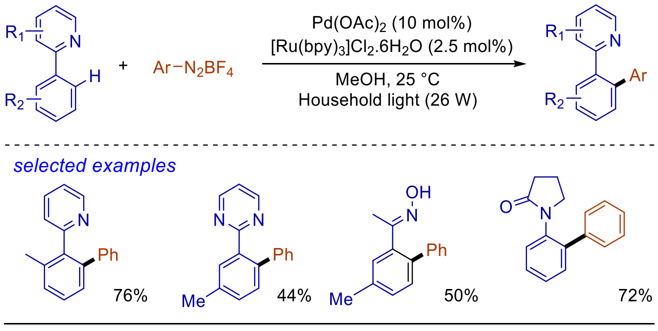
Supramolecular photoredox catalysis offers a metal-free approach in water for various photoredox reactions. Utilizing a nanosized supramolecular capsule containing V-shaped aromatic amphiphiles with pentamethylphenyl groups, it efficiently absorbs an organic photoredox catalyst in aqueous conditions, with the flexibility to modify the host-guest combination. Under visible light exposure, this catalyst effectively reduces organic compounds, generating a range of carbon-centered radicals like aryl, ketyl, and trifluoromethyl radicals in water (Scheme 25).[47] The ketyl radicals were applied to synthesize a series of pinacol derivatives (Scheme 25a), while the in situ generated aryl radical facilitated intramolecular cyclization through a 1,5-hydrogen atom transfer reaction (Scheme 25b). Additionally, the $CF_3^{\bullet}$ radical was utilized in trifluoromethylation of 1,3-dimethyluracil (Scheme 25c).



Scheme 25. *Supramolecular photoredox catalyst generates carbon-centered radicals in water*

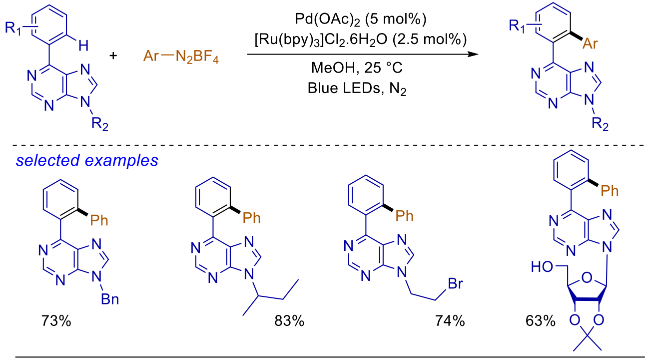
1.14. Dual catalysis for C−H bond activation

Diazonium salts could be utilized as one of the coupling partners for C-H activation reaction. In recent years, under photoredox conditions, it has acquired significant importance, particularly for the C–H bond activation. Sanford group described a visible light supported photoredox catalysis of $[Ru(bpy)_3]_2.6H_2O$, in combination with $Pd(OAc)_2$ as transition metal catalyst, which catalyzed the C–H arylation of the phenylpyridine derivatives at 25 ℃.[48] A variety of phenylpyridine derivatives with various functionalities and substituted aryl diazonium salts were successfully employed forthis method produced the desired product with yields ranging from moderate to good.(**Scheme 26**).



Scheme 26. *Arylation of phenylpyridines*

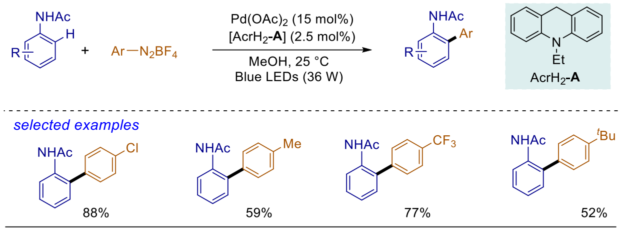
Succeeding this methodology, another work has been reported for *ortho* C−H Arylation of 6-arylpurine nucleosides attached arene system, using $[Ru(bpy)_3]_2.6H_2O$ as photoredox catalyst and $Pd(OAc)_2$ as metal catalyst. Diazonium salts were used as aryl source under irradiation of visible light (**Scheme 27**).[49]This arylation approach recommended a wide scope of substrates including functionalized purines which may be very important in medicinal chemistry.



Scheme 27. C−H *arylation of purine nucleosides.*

Recently, a dual catalytic system was developed that combines $Pd(OAc)_2$ as a metal catalyst with 9,10-dihydro-10-ethylacridine ($AcrH_2$-A) serving as an organic photoredox catalyst. This system facilitates the *ortho*-directed arylation of acetanilides and benzamides under mild reaction conditions. (**Scheme 28**).[50]

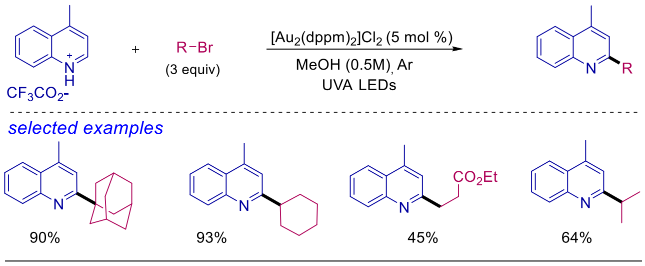
The arylation of *N*-heteroarenes can be accomplished using $[Ru(bpy)_3]_2.6H_2O$ as photosensitizer and aryldiazonium salts as the arylating coupling agent in the presence of household light bulb under inert atmosphere.[51]



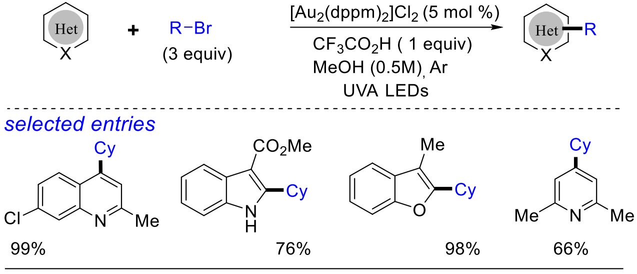
Scheme 28. C-H *Arylation of acetanilides.*

1.15 Au Catalysis

An unactivatedbromoalkanes effectively generates the alkyl radicals under light source and argon environment in the presence of a dimeric gold(I) photoredox catalyst, $[Au_2(dppm)_2]Cl_2$ in MeOH solvent. The generated alkyl radical species subsequently leads to direct C–H alkylation of various heteroarenes. This method is efficient for alkylation of heteroarenes in the absence of directing groups. [52] They first reported the 2-alkylation of lepidine-TFA salt with several bromoalkanes in the presence of MeOH as a green solvent with 5 mol% of $[Au_2(dppm)_2]Cl_2$ catalyst under UVA LEDs (365 nm) (Scheme 29). The applicability of this method was expanded for various heterocyclic coupling partners, such as benzofuran, indole or pyridine for the alkylation with bromoalkanes (**Scheme 30**).[52]

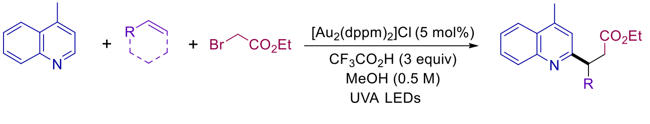


Scheme 29. *2-Alkylation of lepidine-TFA salt*



Scheme 30. *Alkylation of heterocycles*

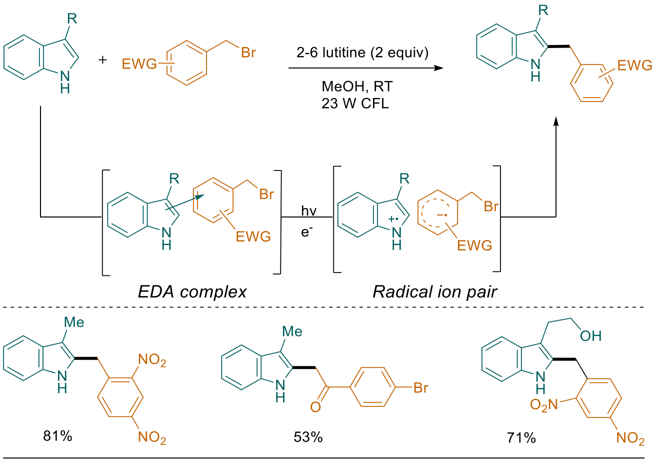
Furthermore, the same greener conditions can be utilized for alkylation of lepidine under multicomponent manner with an alkene and α-bromoester. The alkene is merged with the radical generated by the α-bromoester, ensuing in an alkylation at the C-2 position of heteroarenes unless this position is substituted (**Scheme 31**).[52]



Scheme 31. *Multicomponent reaction of lepidine*

1.16 Cross-coupling with EDA complex

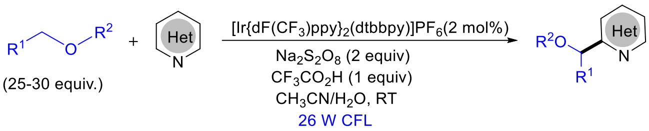
Melchiorre group developed the metal-free unique photoredox technique, engaging an electron donor-acceptor complex (EDA) formed between substituted indoles and electron-accepting benzyl or phenacyl bromides to accelerate the direct alkylation of indoles.[53] They isolated and characterized the reactive EDA complex that is generated by the interaction of 3-methylindole and 2, 4-dinitrobenzyl bromide by X-ray single-crystallographic technique.When exposed to visible light, this EDA complex produced a radical ion pair, enabling the formation of a benzyl radical anion. This radical then reacted with the indole, yielding benzylated indole in good yields, all without the need for an additional photosensitizer. The substrate scope depended on the substitution pattern of indole motif. C-2 substituted indole provided the C-3 alkylated indole and C-3 afforded C-2 selective product (**Scheme 32**).



Scheme 32. *2-Benzylation of indoles*

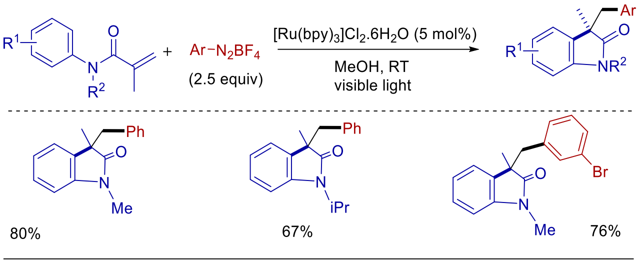
1.17 Double C-H Functionalization

The modification of two distinct carbon-hydrogen bonds could generate a new carbon-carbon bond. In 2015, MacMillan group revealed the formation of α-oxyalkyl radicals from several frequently used ethers through hydrogen atom transfer (HAT). Consequently, these radicals were combined with various heteroarenes engaging *via*Minisci-type approach. The process of HAT on dialkyl ethers, employing [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ as a photoredox catalyst, (NH$_4$)$_2$S$_2$O$_8$ as the oxidizing agent, and TFA in CH$_3$CN/H$_2$O under a 26 W CFL irradiation, facilitates the formation of α-oxyalkyl radicals, thereby enabling α-heteroarylation of ethers (**Scheme 33**).[54]



Scheme 33. *2-Alkylation of heteroarenes*

Fu and colleagues outlined a durable, environmentally friendly cascade process for the difunctionalization of *N*-arylacrylamides using aryldiazonium salts (**Scheme 34**). [Ru(bpy)$_3$]Cl$_2$ serves as a photoredox catalyst in methanol under visible light exposure, enabling the synthesis of 3,3-disubstituted oxindoles featuring a broad array of functionalities (e.g., F, Br, Cl, OMe, CN, CF$_3$, and pyridine). Importantly, no supplementary substances such as bases or reductants were necessary for the reaction to proceed.[55]



Scheme 34. *Difunctionalization of N-arylacrylamides*

2. Conclusion & Outlook

In recent times, photoredox catalysis has emerged as a potent tool in organic synthesis, driving rapid advancements in the field over the past few decades. Overall, it enables the execution of numerous coupling reactions under considerably milder conditions, often at room temperature, while accommodating a wide range of functional groups. This mini-review provides an overview of the fundamental principles of photoredox chemistry, discussing various metal-based and organophotocatalysts. It further explores a variety of reactions, including trifluoromethylation, cyanation, C-H functionalizations, supramolecular catalysis, and heterogeneous catalysis in both aqueous and alcoholic mediums.

Looking ahead, the focus will be on designing and developing new photoredox-mediated sustainable approaches for cascades and multicomponent reactions, particularly aiming at generating multiple C-C and C-heteroatom bonds. This area of research holds significant promise for laying the groundwork for constructing complex organic molecular architectures in a more environmentally friendly manner.

Author Contribution Declaration

Yafia and Partha designed the article, conceived the review plan and write-up strategy with the help of lead author Dr. Bera. The manuscript is finalized by Dr. Bera after discussing with all the authors.

Data Availability Declaration

Write here the data availability declaration. There are no new data were created hence data sharing is not applicable here.

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