

Enlightening the Unconventional Photocatalytic Space in Organic Transformation

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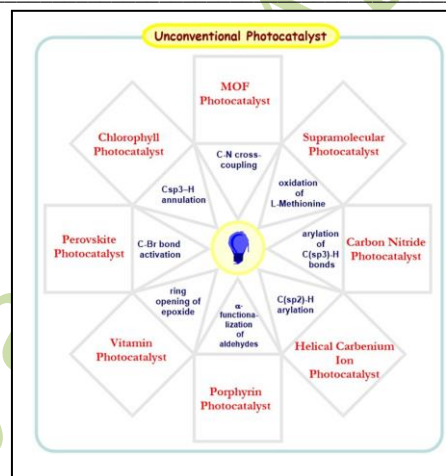
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Abstract

In recent years, organic photo-redox catalysts such as Ru or Ir-metal complexes and organic dyes have expanded the traditional catalytic toolbox due to their sustainability and environment friendliness. The central focus of this review is to explore unconventional photo-catalysts and their catalytic activity in organic transformations. However, an overview of such unorthodox photo-catalysts has been demonstrated herein to illuminate the photocatalytic space in organic synthesis.

Keywords: Photo-catalyst, Helical carbenium ion, Chlorophyll, Metal-Organic Framework, [2]Catenane, Porphyrin, Borane, Perovskite.



1. Introduction

Last few decades, visible-light-induced photo-redox catalysis has appeared at the forefront of modern organic synthesis due to high sustainability, diverse reactivity, and broad substrate tolerance^{1, 2}. The visible light-driven reaction strategy has become an excellent alternative to thermally driven traditional synthetic methodology because photon energy is converted to chemical energy. In principle, photo-catalysts absorb light having a particular wavelength and are excited from their ground state. After being excited, it can follow either an energy transfer (EnT) process or a single electron transfer (SET) process with the reactive substrate to drive a broad range of elegant transformations³⁻⁶. The photoactive molecules involving the energy transfer (EnT) process are titled as a photosensitizer, and the molecules involving a single electron transfer (SET) process are known as photo-redox catalyst⁷.

However, the ideal photo-catalysts are those which have a) strong absorption in visible light (above 400 nm), b) a stable, prolonged excited state lifetime (above one nanosecond), c) reliable oxidation and reduction potential, and d) stability under photocatalytic conditions (Figure 1)⁸. As shown in Figure 1, excited state PC^* directly transfers energy to organic substrates, which further takes part in the chemical reaction and excited state PC^* comes back to its ground state. Alternatively, it may follow oxidative and reductive quenching via SET process. Indeed, excited state PC^* is

either oxidized by the acceptor or reduced by the donor via SET process to generate oxidized PC^+ or reduced PC^- . Finally, PC was regenerated by a SET process with substrate and oxidized PC^+ /reduced PC^- . Subsequently, the resulting substrate (radical species) initiates a chemical reaction through a radical pathway. The most commonly used

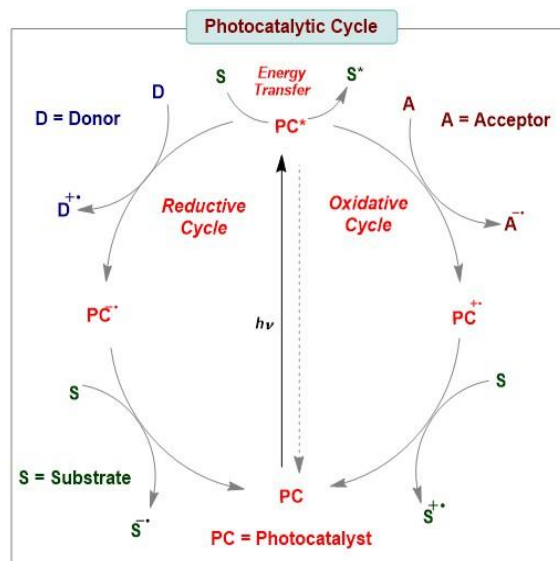


Figure 1. Photocatalytic cycles involving single electron transfer and energy transfer process.

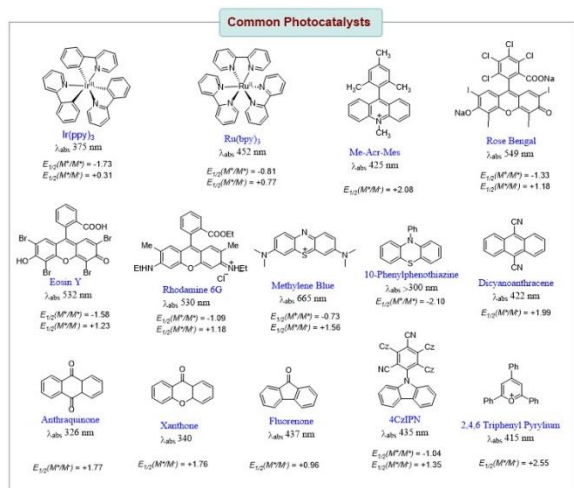


Figure 2. Commonly used organic photo-redox catalysts and their properties.

examples of photo-catalysts are iridium and ruthenium metal complexes, organic dyes like rose bengal, eosin Y, rhodamine, acridinium, pyrylium salts and cyano arenes etc., which has extensively been explored in photo catalysis (Figure 2)⁹. Pleasingly, MacMillan, König, Nicewicz, Fukuzumi, and many other renowned researchers across the globe have remarkably hit the area of photocatalytic research to unlock many challenges in designing complex molecular architectures^{1, 10-12}. Many reviews are also documented in literature which covers the basic concept of photo-catalysts and the utility of traditional photo-catalysts in organic synthesis^{1-4, 8-17}. Despite the substantial evolution in the last few decades in the field of organic photo-redox catalysis, there is still a lack of chemical space to assist the development of new photo-catalysts. To our best knowledge, there is no such review published in the literature that surveys the development of novel photo-catalysts in organic synthesis. This review aims to highlight a collection of such literatures on unusual or novel photo-catalysts used in organic transformation.

2. Unconventional photo-catalysis

The photocatalytic activity of different semiconductors, including carbon nitrides and perovskites, metal-organic frameworks, vitamin B₂ and supramolecular photo-catalysts, naturally occurring pigments like chlorophyll and metalloporphyrins, etc., in organic transformation, is covered in this section.

2.1 Porphyrin photo-catalyst in α -functionalization of aldehydes

Metalloporphyrins are a valuable scaffold used in controlling the biological system. But its catalytic space is not well recognized in organic synthesis. Gryko and co-workers

introduced tetraphenylporphyrin (H₂TPP) as an efficient photo-catalyst for the α -functionalization of aldehydes **1** with a diazo compound **2** which led to α -alkylated derivatives **3** in good yields (Figure 3)¹⁸. It was realized that porphyrin worked as a photosensitizer and a photo-redox catalyst. As porphyrins act as triplet photosensitizers, H₂TPP, after being in the excited

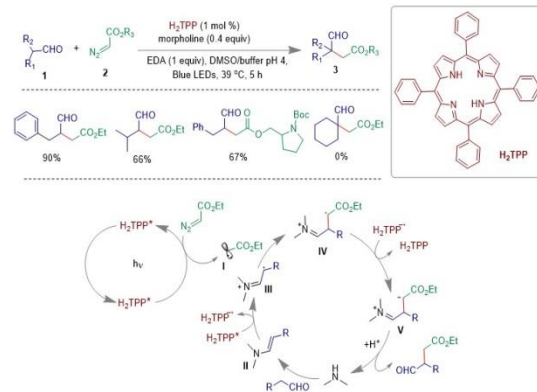


Figure 3. Gryko's work is based on a porphyrin photo-catalyzed α -functionalization of aldehydes¹⁸.

state, transferred its energy to EDA and generated triplet carbene **I**. On the other hand, enamine **II** was oxidized by the excited state H₂TPP to generate a radical cation **III** and a reduced form of porphyrin radical anion. Following, cation radical **III** reacted with triplet carbene **I** to produce **IV**. The final α -alkylated product was achieved by a SET process with porphyrin radical anion and protonation of intermediate **V**. However, porphyrin analogs are synthesized easily, and their electrochemical properties are modified by substituting the suitable group in the periphery, thus expected to be a new addition in photo-redox catalysis.

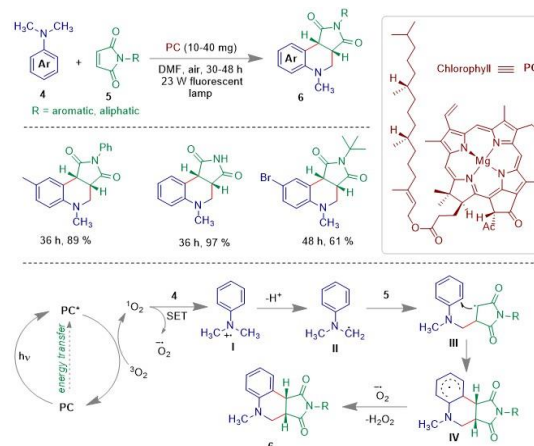


Figure 4. He and Guan's report on chlorophyll as photo-catalyst in the synthesis of tetrahydroquinolines¹⁹.

2.2 Chlorophyll photo-catalyst in the synthesis of tetrahydroquinolines

He and Guan experienced that chlorophyll, a natural pigment, can also be utilized as a photosensitizer for synthesizing tetrahydroquinolines **6** from maleimides **5** and *N,N*-dimethylanilines **4** (Figure 4)¹⁹. Chlorophyll followed the energy transfer mechanism after being excited by visible light. During the energy transfer pathway, excited state chlorophyll converted triplet oxygen to singlet oxygen by transferring energy. Following, singlet oxygen underwent SET process with the amine to generate amine cation radicals **I** and superoxide radical anion. The superoxide radical anion helped the proton transfer from amine **I** with the formation of α -aminoalkyl radical **II**. In the next step, the α -aminoalkyl radical attack **II** to maleimides **5** followed by intramolecular cyclization offered the intermediate **III**, which was instantly converted to the final tetrahydroquinoline product **6** by protonation of superoxide radical anion from **IV**. Thus it is anticipated that the utilization of natural pigment as a photo-catalyst will enlarge the library of photo-catalyst in organic synthesis.

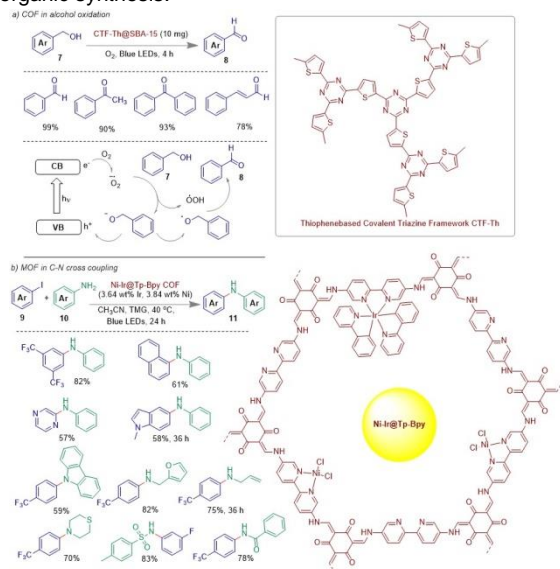


Figure 5. Zhang and Maji's individual report for selective oxidation of alcohol²² and C-N cross coupling²³.

2.3 Covalent organic framework (COF) photo-catalyst in alcohol oxidation and C–N cross-coupling reaction

Covalent organic framework are being also considered as visible light induced photo-catalyst due to the low band gap^{20, 21}. And photocatalytic efficiency could be tuned by modifying the donor acceptor backbone on the frame. Recently, Zhang group studied that covalent triazine-based frameworks could serve as photo-catalyst for the selective oxidation of alcohol **7** to aldehyde **8** and ketone (Figure 5a)²². As depicted from the mechanism, superoxide radical anion was generated by the visible light irradiation of photo-catalyst. Then, superoxide radical anion reacted with alcohol to produce alkoxide ion which was further oxidized by valance bond hole to generate benzyloxy radical. Finally aldehyde or ketone was produced from the reaction of $\cdot\text{OOH}$ and benzyloxy radical. Again, Maji and Banerjee group also envisioned that dual metallated organic framework (Ni-Ir@Tp-Bpy, where Tp=1,3,5-triformyl phloroglucinol and

Bpy=5,5'-diamino-2,2'-bipyridine) contributed as visible light photo-catalyst for the C–N cross-coupling of aryl iodide **9** and aryl amine **10** (Figure 5b)²³. Photoluminescence study showed that Ni-Ir@Tp-Bpy excited at 415 nm and emitted at 580 nm. Again, band gap was found to be 1.88 eV in the Ni-Ir@TpBpy COF. Thus it is expected that the utilization of metal or metal free covalent framework will boost the opportunity of environmentally benign photo-catalysts in organic synthesis.

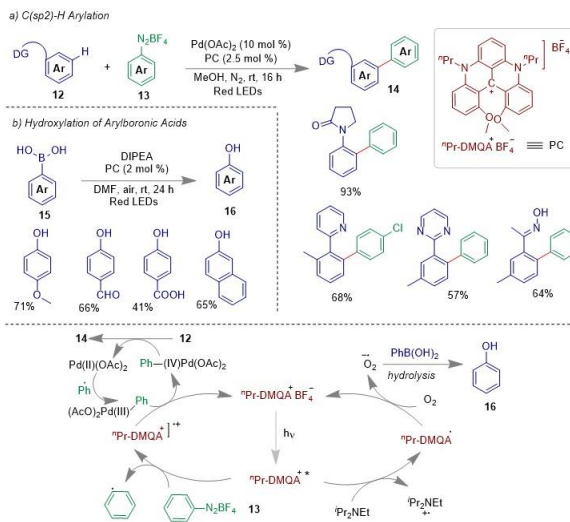


Figure 6. Gianetti's work based on helical carbenium ion photo-catalysis in C(sp²)-H arylation and hydroxylation of arylboronic acids²⁴.

2.4 Helical Carbenium Ion photo-catalyst in C(sp²)-H arylation and hydroxylation of arylboronic acids

Gianetti and co-worker have explored low energy red light induced helical carbenium ion catalyzed C–H arylation and hydroxylation reaction (Figure 6)²⁴. They have revealed that *N,N*-di-*n*-propyl-1,13-dimethoxyquinacridinium tetra fluoroborate (ⁿPr-DMQA⁺ BF₄[−]) was used for photo-oxidation and photo-reduction in hydroxylation of arylboronic acid and benzylic C(sp³)-H oxygenation. Again, oxidative C–H arylation with diazonium salt was also introduced by merging palladium metal-catalyst with carbenium ion. Mechanistically it has been proposed that carbenium ion photo-catalysts ⁿPr-DMQA⁺ was excited to its ⁿPr-DMQA⁺⁺ by red light at $\lambda_{\text{max}} = 640 \text{ nm}$. Next, excited ⁿPr-DMQA⁺⁺ took part in oxidative quenching with aryl diazonium tetra fluoroborate **13** to generate aryl radical. Then, the aryl radical was added to the Pd(II) to produce Pd(III) species which helped in regeneration of catalyst and formed a Pd(IV) intermediate. Finally, Pd(IV) intermediate produced C–H arylated product **14** by reductive elimination. On the other hand, ⁿPr₂NEt and O₂ acted as sacrificial reductant and oxidant for hydrolysis of boronic acid **15** to alcohol **16**, as depicted in Figure 6.

2.5 Supramolecular photo-catalyst in aerobic oxidation of L-Methionine

By leveraging the charge transfer interaction between the donor and acceptor, Stoddart and co-worker discovered that [2]catenane might be useful as a photo-catalysts for aerobic oxidation of organic sulfides (Figure 7)²⁵. The mechanical bonding interaction between two 4,4'-bipyridinium and two 1,5-dioxynaphthalene units led to [2]catenane which

helped to increase the absorption of visible light at low concentrations. However, the photo-induced electron-transfer (PET) process due to the narrowing of HOMO-LUMO and the formation of donor-acceptor charge transfer complexation in between cyclobis(paraquat-*p*-phenylene) and 1,5-dinaphtho[38]crown-10 afforded aerobic oxidation of L-methionine **17** to corresponding sulfoxide **18**. This photo-induced mechanical bonding interaction will pave new chances for stimulating the area of photo catalysis without using any external photosensitizer.

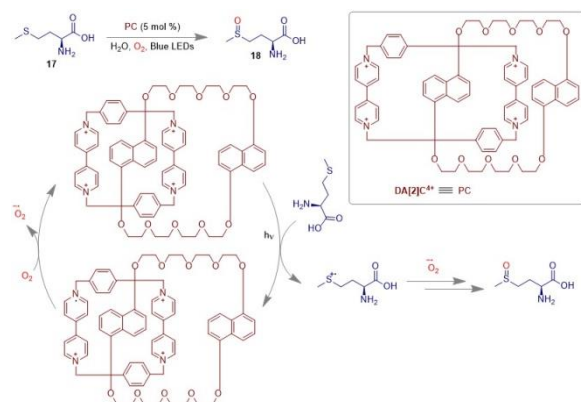


Figure 7. Stoddart's report on supramolecular photo-catalyst in aerobic oxidation of L-Methionine²⁵.

2.6 Borane photo-catalyst in aerobic sulfenylation of Indoles

Mostly Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ acts a Lewis acid and recently it is used as a frustrated Lewis pair²⁶. Generally borane compounds are stable under inert atmosphere²⁷. Tang and co-worker investigated that borane can also form an electron donor-acceptor (EDA) complex with N center of indole under oxygen and in the presence of visible light and facilitated the thioetherification reaction with thiophenol (Figure 8)²⁸. Mechanistically it has been shown that $B(C_6F_5)_3$ formed a charge transfer EDA complex **I** with indole upon irradiation of light. Consequently, a SET and back electron transfer (BET) process are feasible between EDA complex **I** and **II** of indole **19**. On the other hand, thiyl radical was generated from the reaction of thiophenol **20** and oxygen via intermediate **III**. Again regeneration of $B(C_6F_5)_3$ occurred through elimination of H_2O_2 from intermediate **IV**. Intermediate **V** which was generated from **II** reacted with thiyl radical to produce final product **21** via intermediate **VI**. However, this work unlocked the scope of borane catalyst under open atmosphere.

Figure 8. Tang's report on borane photo-catalyst in aerobic sulfenylation of indoles²⁸.

2.7 Carbon nitride photo-catalyst in arylation of $C(sp^3)-H$ bonds

Graphitic carbon nitride material grabbed enormous attention in the chemical community because of its mild reactivity and diverse application in catalytic transformation. König and co-workers have examined the mpg-CN photocatalytic arylation of aryl halide **9** in merging with nickel catalysis (Figure 9a)²⁹. It was mechanistically proposed that the aryl halide **9** first oxidatively added to the Ni(0) complex **I**, producing the Ni(II) complex **II**. As shown in Figure, complex

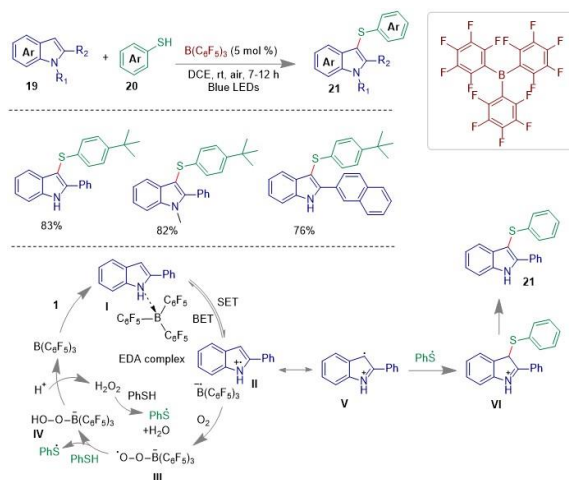


Figure 8. Tang's report on borane photo-catalyst in aerobic sulfenylation of indoles²⁸.

III was obtained by Ni(II) complex **II** via SET process with mpg-CN. Again, Ni(III) complex **III** experienced homolytic cleavage of Ni(III)-X, generating a halogen radical and DMA coordinated Ni(II) complex **IV**. Subsequently, hydrogen abstraction from DMA by halogen radical led to an α -carbon-centered radical with Ni(II) complex **V**, which again recombined to give the Ni(III) complex **VI**. Ni(III) complex **VI** reductively converted to Ni(I) complex **VII** with the desired product **23**. However, Ni(0) complex **I** was achieved by SET with conductance band electron on mpg-CN. It may also follow an energy transfer mechanism, as shown in another cycle. Interestingly, mpg-CN having a band gap of 0.39 eV, is involved in an energy transfer process to afford excited Ni(II) species **VIII**. Once again, homolytic cleavage of Ni(III)-X, hydrogen abstraction from DMA by halogen radical followed by recombination led to Ni(II) species **XI** via **IX** and **X** intermediates. Reductive elimination occurred from the electronically excited species **XII** by energy transfer (EnT), with mpg-CN providing the final product. Thus, it is assumed that this finding of organic semiconductors as photocatalyst will heal the photocatalytic application.

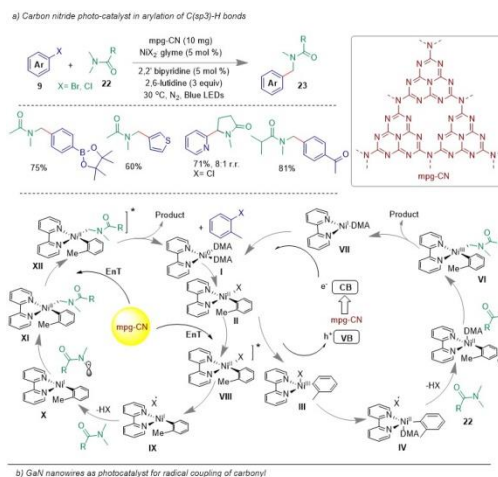


Figure 9. a) König and b) Li's individual reports on the use of carbon nitride²⁹ and GaN³⁰ as photocatalyst for the arylation of $C(sp^3)-H$ bonds and carbonyl couplings.

Again, Mi and Li also introduced GaN nanowires as a reusable photocatalyst for the synthesis of diol **24** from carbonyl compounds **8** (Figure 9b)³⁰.

2.8 Vitamin photo-catalyst in α -C-H functionalization of sulfides and ring opening of epoxide with an aryl halide

Procter and co-worker recently developed riboflavin (vitamin B₂) catalyzed α -C-H functionalization of Methionine analogues with inactivated alkenes (Figure 10a)³¹. Mechanistic study showed that photo irradiation of vitamin B₂ under blue LEDs led to excited PC^* which oxidized to sulfide **25** by furnishing a singlet state radical ion pair S_1 . Then intersystem crossing (ISC) promoted it to T_1 state which subsequently underwent proton transfer with PC^- to generate a reactive α -radical intermediate. Following highly α -radical intermediate attacked to alkene **26** resulting a radical intermediate. Finally, the parent product **27** was obtained from intermediate **I** with proton transfer and electron transfer by protonated PC^- . Thus photocatalytic activity of commercially available inexpensive riboflavin was introduced nicely. Again, Gryko group also disclosed vitamin B₁₂-Ni photo-redox catalyzed regio-selective ring-opening of epoxide of **28** by aryl halide **9** under the irradiation of blue LEDs (Figure 10b)³². However, Co complex of vitamin B₁₂ and NiCl₂·DME were used as dual catalyst in the presence of NMP solvent in water with Zn/NH₄Cl additive for the selective linear hydroxylated C-C coupled product **29**.

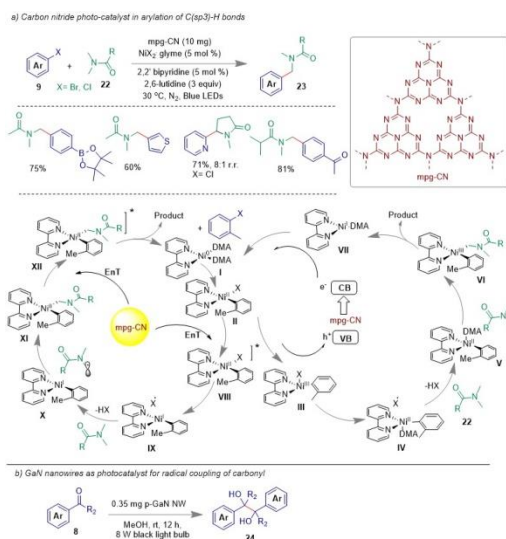


Figure 10. Procter's³¹ and Gryko's³² individual report for vitamin photo-catalyzed in α -C-H functionalization of sulfides and ring opening of epoxide with aryl halide.

2.9 Carbazole-cored organo photo-catalyst in reductive pinacol/imino-pinacol coupling

A newly designed benzoperylenecarbazole (BPC) organophotocatalyst by Maji group facilitated the reductive coupling of carbonyls **8** and imines towards the formation of pinacol **24** or imino-pinacol as the targeted product with reasonable yields (Figure 11)³³. The excited BPC reduced the carbonyl group to ketyl radical species. The BPC was regenerated by SET with DIPEA, and subsequently, DIPEA

was oxidized to radical-cation species. It is stated that noncovalent interactions between the methyl group of cationic radical of DIPEA **I** and aryl group of aldehyde accelerated the ketyl radical formation, which coupled homolytically to produce the final pinacol product **24** after protonation. This (BPC) organophotocatalyst was found to be a lower excited state oxidation potential (-2.0 V vs SCE) with a stable excited state lifetime (4.61 ns). Thus it is anticipated this newly developed organophotocatalyst will expand radical-based organic synthesis.

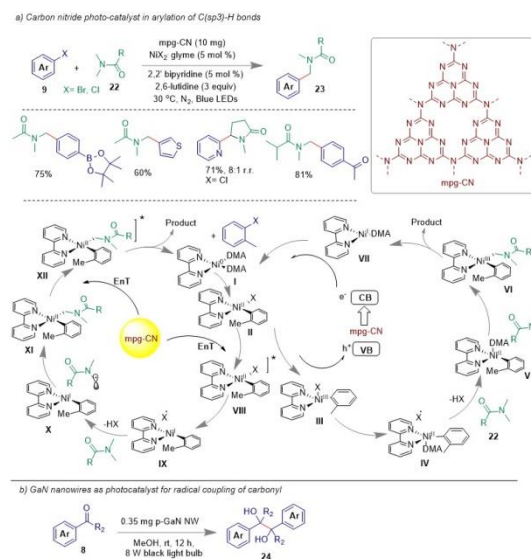


Figure 11. Maji's work based on organophotocatalyzed reductive pinacol/imino-pinacol coupling.³³

2.10 Perovskite photo-catalyst in C-Br bond activation

Perovskite having both effective charge separation and electron-hole diffusion, recently, they have been employed as photocatalyst for organic synthesis (Figure 12)³⁴. The photophysical properties of these perovskites materials i.e. the creation of electron/holes by absorption of photons in photovoltaics facilitate to produce reducing/oxidizing charges which is a desired phenomenon in photocatalytic organic synthesis. Mal and co-workers have developed CsPbBr₃ perovskite as an efficient and cost-effective visible light photo-catalyst for the synthesis of gem-dihaloenone **31** via C-Br activation of CBrX₃ (X = Br, Cl). Interestingly, the newly synthesized CsPbBr₃ responded in blue LEDs and sunlight, offering a variety of gem-dibromoenone and gem-dichloroenone with excellent yields. It was proposed that CX₃ radical, which was generated via the SET process with the conduction band of CsPbBr₃ reacted with terminal alkyne **30** to generate vinyl radical intermediate **II**. Following, radical intermediate **II** was further oxidized to vinyl radical intermediate **II** via SET with a valence bond in CsPbBr₃. Finally, gem-dihaloenone was found from the addition of H₂O and elimination of HX via intermediate **III**. The K₂CO₃ was used for the elimination of HX in the final step. The CsPbBr₃ perovskite photocatalyst has a photoluminescence lifetime is 12.5 ns with E_{ox} = +1.6 V. Therefore, it is believed that the development of CsPbBr₃ as photo-catalyst will advance the application of material chemistry for designing the new photo-catalyst in organic methodology.

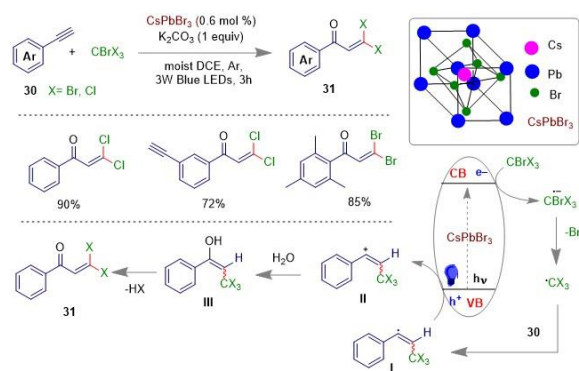


Figure 12. Mal's work based on CsPbBr₃ perovskite photocatalyzed synthesis of gem-dihaloenone.³⁵

3. Conclusions

In this review, we have emphasized uncommon photocatalysts and their application in organic synthesis. Various newly developed photo-catalysts like helical carbenium ion, semiconductors (carbon nitrides, perovskites), metal-organic frameworks, vitamins B₂ and supramolecular photo-catalysts, and naturally occurring pigments like chlorophyll and metalloporphyrins, etc. were utilized to accomplish many robust synthetic transformations such as C-H functionalization, C-X (X = C, N, S, Cl) cross-coupling, oxidation, reduction reactions. Thus we envisage that these unexplored photo-catalysts will spark the photocatalytic space by unlocking the streamlined bond routes in organic synthesis endeavors. It is also anticipated that this survey would benefit material chemists, inorganic chemists³⁶, and biologists in discovering novel photoactive molecules which will have potential applications as photo-catalysis.

4. Acknowledgement

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5. Conflicts of interest

There are no conflicts to declare.

6. Notes and References

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