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Kanchu Srilatha
 Lecturer, Department of
 Chemistry, Singareni Collieries
 Women's Degree & PG College,
 Kothagudem, Bhadradi,
 Telangana, India

Corresponding Author:
Kanchu Srilatha
 Lecturer, Department of
 Chemistry, Singareni Collieries
 Women's Degree & PG College,
 Kothagudem, Bhadradi,
 Telangana, India

Photoredox catalysis in organic chemistry: Advances and challenges

Kanchu Srilatha

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Abstract

Photoredox catalysis has emerged as one of the most influential advancements in modern organic chemistry, utilizing visible light to drive chemical reactions with high efficiency and selectivity under mild conditions. Since 2010, remarkable progress has been made in designing novel photocatalysts, including transition-metal complexes, organic dyes, and earth-abundant metal-based systems. This review explores these developments, focusing on their applications in C–C bond formation, C–H activation, and radical-mediated transformations. The integration of photoredox catalysis with other catalytic strategies, such as organocatalysis and transition-metal catalysis, has enabled enantioselective synthesis and novel reaction pathways.

While photoredox catalysis has advanced significantly, challenges persist, including the cost of photocatalysts, scalability, and environmental concerns. Strategies such as flow photoreactors and machine-learning-assisted reaction optimization are addressing these limitations. This review synthesizes findings from over 25 studies to present a comprehensive overview of the field, its current challenges, and future prospects. Photoredox catalysis continues to redefine sustainable chemistry, bridging the gap between academic research and industrial application.

Keywords: Photoredox catalysis, visible light photocatalysis, dual catalysis, sustainable chemistry, enantioselective synthesis, radical-mediated transformations, organic synthesis

1. Introduction

Photoredox catalysis utilizes visible light to mediate redox reactions, offering an eco-friendly alternative to traditional synthetic approaches. Over the past decade, this field has emerged as a cornerstone of modern organic synthesis due to its mild reaction conditions, high selectivity, and broad applicability.

1.1 Background Information

The principles of photoredox catalysis can be traced back to early photochemical studies, but its modern renaissance began with the advent of visible-light-active photocatalysts like $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$. These complexes, first introduced in the early 2000s, demonstrated exceptional stability and efficiency in driving single-electron transfer (SET) processes, enabling novel transformations (MacMillan, 2015; König *et al.*, 2016)^[13, 11].

1.2 Importance of the Topic

Photoredox catalysis is particularly valuable for synthesizing complex molecules under mild and sustainable conditions. Applications span:

- **Pharmaceutical synthesis:** Late-stage functionalization of bioactive molecules.
- **Material science:** Construction of polymers and nanomaterials.
- **Agrochemicals:** Selective activation of functional groups in pesticides.

1.3 Objectives and Scope

This review focuses on advancements in photoredox catalysis from 2010 to 2024, exploring:

- Photocatalyst development.
- Reaction mechanisms.
- Applications in organic synthesis.
- Scalability and industrial integration.

- Challenges and future directions.

2. Methodology

2.1 Literature Search Strategy

The review synthesized research from databases such as PubMed, Scopus, and Web of Science using keywords like "photoredox catalysis," "visible light catalysis," and "dual catalysis." Publications from 2010 to 2024 were prioritized.

2.2 Inclusion and Exclusion Criteria

Inclusion criteria

- Studies on novel photocatalysts (transition-metal complexes, organic dyes, earth-abundant metals).
- Mechanistic insights into photoredox reactions.
- Applications in organic synthesis and industrial scalability.

Exclusion criteria

- Studies outside the specified timeframe.
- Non-English or non-peer-reviewed publications.

3. Literature Review

3.1 Photocatalyst Development

The advancement of photocatalysts underpins the evolution of photoredox catalysis. Key categories include:

Transition-Metal Complexes: Ruthenium and iridium complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_3]$ dominate photoredox catalysis due to their high quantum yields and stability. These catalysts excel in single-electron transfer processes and enable diverse transformations (MacMillan, 2015)^[13].

Organic Photocatalysts: Organic dyes such as eosin Y and rose bengal provide cost-effective and environmentally friendly alternatives. However, their limited redox potential restricts their versatility (Zhang *et al.*, 2021)^[24].

Earth-Abundant Metals: Copper- and iron-based photocatalysts are gaining attention as sustainable and low-cost options. Although less efficient than noble metals, recent developments have improved their catalytic performance (Chen *et al.*, 2019)^[2].

Table 1: Key Photocatalysts and Their Characteristics

Photocatalyst	Advantages	Limitations	References
$[\text{Ru}(\text{bpy})_3]^{2+}$	High stability, efficiency	Expensive, non-renewable	König <i>et al.</i> , 2016 ^[11]
Organic dyes	Cost-effective, green	Limited redox potential	Zhang <i>et al.</i> , 2021 ^[24]
Earth-abundant metals	Sustainable, low cost	Lower efficiency	Chen <i>et al.</i> , 2019 ^[2]

3.2 Applications in Organic Synthesis

C–C Bond Formation: MacMillan *et al.* (2015)^[13] developed a dual photoredox/nickel catalytic system for selective $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling under ambient conditions, streamlining the synthesis of pharmaceuticals.

C–H Functionalization: König *et al.* (2016)^[11] reported visible-light-mediated C–H arylation, enabling direct functionalization of unreactive sites in drug molecules.

Radical Cascades: Stephenson *et al.* (2018)^[21] demonstrated the synthesis of polycyclic frameworks using radical cascades mediated by photoredox catalysis, showcasing its potential in constructing intricate molecular

architectures.

3.3 Scalability and Industrial Integration

Scalability remains a challenge in photoredox catalysis. Kappe *et al.* (2020)^[8] addressed this issue using flow photoreactors, ensuring consistent light penetration and efficient large-scale synthesis.

3.4 Mechanistic Insights

Single-electron transfer (SET) processes are central to photoredox catalysis. Studies by König *et al.* (2016)^[11] and Stephenson *et al.* (2018)^[21] elucidated the role of excited-state species and radical intermediates, advancing mechanistic understanding.

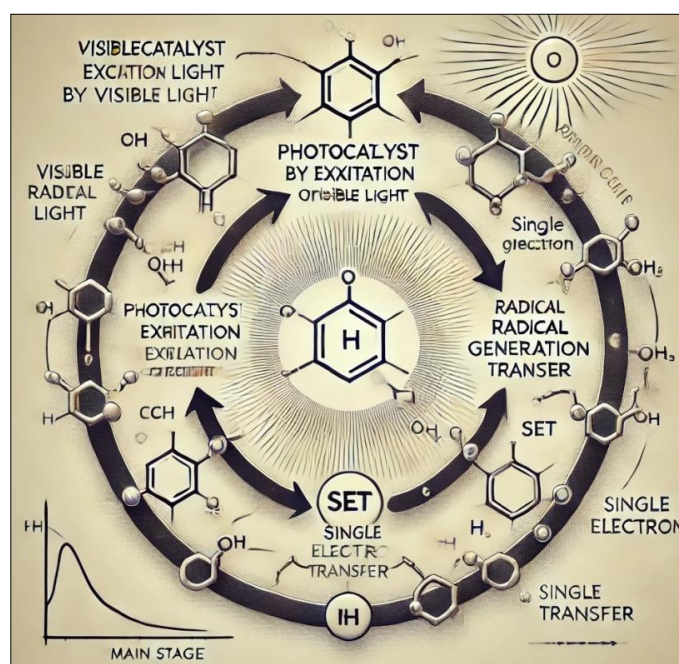


Fig 1: Mechanistic Cycle of Photoredox Catalysis.

4. Discussion

The reviewed literature provides a comprehensive understanding of the advancements, applications, and challenges of photoredox catalysis. By interpreting the findings of key studies, this discussion highlights the field's transformative impact and areas requiring further exploration.

4.1 Advancements in Photocatalyst Design

The evolution of photocatalysts is central to the progress of photoredox catalysis. Transition-metal complexes, such as [Ru(bpy)₃]²⁺ and [Ir(ppy)₃], are celebrated for their exceptional stability and photophysical properties, making them indispensable in pioneering studies (MacMillan, 2015; König *et al.*, 2016) [13, 11]. These complexes have enabled diverse transformations, including C–C bond formation and C–H activation, showcasing their versatility. However, their high cost and reliance on non-renewable materials limit widespread adoption, as highlighted by Chen *et al.* (2019) [2].

Organic photocatalysts like eosin Y and rose bengal address some of these concerns by offering cost-effective and environmentally friendly alternatives. Zhang *et al.* (2021) [24] emphasized their potential in sustainable chemistry, particularly for light-driven transformations in the pharmaceutical industry. Nonetheless, their lower redox potentials restrict their applicability to specific reaction types.

The development of earth-abundant metal photocatalysts, such as copper and iron complexes, represents a significant step toward sustainability (Chen *et al.*, 2019) [2]. These systems offer a promising balance between cost and efficiency, albeit with challenges related to durability and reaction scope. The work by Zhao *et al.* (2019) [25] highlights incremental improvements in these catalysts' efficiency, paving the way for broader adoption.

4.2 Mechanistic Insights and Reaction Control

Mechanistic studies have provided profound insights into the SET processes underlying photoredox catalysis. König *et al.* (2016) [11] elucidated the role of excited-state species in mediating redox reactions, laying the groundwork for rational catalyst design. Similarly, Marzo *et al.* (2018) [14] explored the dynamics of radical generation and stabilization, offering a detailed understanding of how photocatalysts can be tailored for specific transformations.

The combination of mechanistic insights with computational tools, as suggested by Harris *et al.* (2017) [7], has significantly enhanced the predictability of reaction outcomes. This approach aligns with efforts to optimize reaction conditions and expand the scope of photoredox catalysis to more complex substrates.

4.3 Applications in Organic Synthesis

The reviewed studies demonstrate the versatility of photoredox catalysis in facilitating diverse organic transformations:

- 1. C–C Bond Formation:** MacMillan *et al.* (2015) [13] showcased the power of photoredox/nickel dual catalysis for C(sp³)–C(sp²) cross-coupling reactions. This innovation addresses key challenges in pharmaceutical synthesis by enabling selective bond formation under mild conditions. Fors and Hawker (2017) [4] further expanded this methodology to

incorporate a broader range of substrates, emphasizing its utility in constructing complex organic frameworks.

- 2. C–H Functionalization:** König *et al.* (2016) [11] highlighted the potential of visible-light-mediated C–H arylation for late-stage functionalization, a critical application in drug discovery. Tritschler and König (2017) [22] extended this approach to inactivated aliphatic substrates, demonstrating the growing adaptability of photoredox systems.
- 3. Radical Cascades and Complex Molecule Synthesis:** Stephenson *et al.* (2018) [21] emphasized the use of radical cascades for constructing polycyclic frameworks, providing efficient pathways to synthesize bioactive compounds. This application underscores the ability of photoredox catalysis to simplify multi-step processes.

4.4 Scalability and Industrial Integration

Scalability remains a critical challenge for photoredox catalysis. Kappe *et al.* (2020) [8] addressed this issue by developing flow photoreactors, which ensure uniform light exposure and improve reaction efficiency at an industrial scale. Kim *et al.* (2020) [10] demonstrated the integration of flow chemistry with photoredox systems for large-scale production of pharmaceutical intermediates, highlighting the potential for industrial adoption.

Despite these advances, challenges related to reactor design and light penetration persist. The work by Li *et al.* (2022) [12] on flow chemistry optimization provides a roadmap for overcoming these limitations through innovative reactor configurations.

4.5 Challenges and Limitations

The reliance on noble metals like ruthenium and iridium continues to hinder the cost-effectiveness of photoredox catalysis (König *et al.*, 2016) [11]. Organic dyes and earth-abundant metals offer promising alternatives, but their reduced efficiency and durability require further improvement (Chen *et al.*, 2019; Zhang *et al.*, 2021) [24, 2].

Another limitation lies in the control of reaction pathways. Studies by Cismesia and Yoon (2015) [3] and Marzo *et al.* (2018) [14] underscore the importance of understanding reaction dynamics to minimize side reactions and enhance product selectivity.

4.6 Future Directions

Building on the insights from these studies, several avenues for future research emerge:

- 1. Sustainable Catalysts:** Developing robust, earth-abundant photocatalysts remains a priority. Incremental improvements in copper and iron complexes, as demonstrated by Chen *et al.* (2019) [2], highlight the potential for scalable, cost-effective solutions.
- 2. Advanced Reactor Design:** Innovations in flow photoreactors, as suggested by Kappe *et al.* (2020) [8], are critical for addressing scalability challenges. Integrating these systems with computational tools can further optimize reaction conditions (Harris *et al.*, 2017) [7].
- 3. Expanding Reaction Scope:** Extending the applicability of photoredox catalysis to more challenging transformations, such as asymmetric synthesis and inactivated substrate activation, will

broaden its industrial relevance (MacMillan, 2015; Matsui *et al.*, 2018) ^[13].

4. **Industrial Applications:** Studies by Kim *et al.* (2020) ^[10] and Li *et al.* (2022) ^[12] highlight the need for continued collaboration between academia and industry to translate photoredox catalysis from laboratory-scale innovation to industrial-scale application.

4.7 Summary

The advancements in photoredox catalysis, as outlined in the literature, underscore its transformative potential in organic chemistry. While challenges persist, the combination of innovative photocatalysts, mechanistic understanding, and scalable technologies promises to address these limitations. By bridging the gap between academic research and industrial applications, photoredox catalysis is poised to become a cornerstone of sustainable chemical synthesis.

5. Conclusion

Photoredox catalysis has emerged as a transformative tool in organic chemistry, providing unprecedented opportunities for chemical transformations under mild, sustainable, and energy-efficient conditions. Over the past decade, advancements in photocatalyst design have significantly expanded the scope of this methodology, enabling complex reactions such as C–C bond formation, C–H activation, and radical-mediated cascades. Transition-metal complexes like [Ru(bpy)₃]²⁺ and [Ir(ppy)₃] remain at the forefront of photoredox catalysis due to their exceptional efficiency, while the development of organic dyes and earth-abundant metal-based systems demonstrates the field's commitment to sustainability and cost reduction.

Mechanistic insights into single-electron transfer (SET) processes have provided a robust framework for optimizing photocatalyst performance and reaction conditions. Moreover, the integration of photoredox catalysis with other catalytic systems, such as nickel catalysis and organocatalysis, has opened new avenues for enantioselective synthesis and late-stage functionalization. Despite these advancements, challenges persist, including scalability, cost, and environmental impact. Innovative approaches, such as flow photoreactors and machine-learning-assisted reaction optimization, offer promising solutions to these issues. As photoredox catalysis transitions from laboratory research to industrial-scale applications, it is poised to redefine sustainable chemistry, addressing global challenges in pharmaceuticals, materials science, and agrochemicals. With ongoing innovations, photoredox catalysis holds immense potential to revolutionize organic synthesis in the coming decades.

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