CHAPTER-6

Summary, Future Scope and Perspective

6.1. Conclusions

In this thesis, we have demonstrated the application of metal halide perovskite-based photocatalysts for the efficient synthesis of functionalized amines, amides, and dihydroisoquinolines either through C−N cross-coupling or by semidehydrogenation reactions. The C−N bond-formation reactions play a pivotal role in the synthesis of pharmaceuticals and fine chemicals. Conventionally, such transformations have relied on noble metal catalysts, which, despite their efficiency, are often cost-prohibitive and less sustainable for large-scale applications. Our findings underscore the potential of perovskite-based, earth-abundant semiconductor photocatalysts as a viable alternative for scalable, cost-effective, and environmentally friendly C−N bond formation. The target compounds, substituted amines, amides, quinolines, and DHIQ, are of significant importance in pharmaceutical development, peptide synthesis, agrochemicals, and various therapeutic agents, including antibacterial, anticancer, and antimicrobial drugs.

Although the optoelectronic properties of halide perovskite are suitable for the visible-light photoredox reactions, the major limitation originates from their inherent instability in the presence of moisture and protic solvents. Hence, the reaction protocol was designed such a way that it avoids the use of protic solvents or water. However, the conditions become more critical when H_2O is produced during the reaction as a part of O_2 activation process. This drawback severely restricts the wide applications of halide perovskite in organic transformations. To alleviate this issue, previously, the reactions were carried out in an inert atmosphere. This approach reduces the efficiency of the photocatalyst compared to the molecular O_2 activation mechanism. In this thesis, we have designed an alternative protocol of molecular O_2 activation to produce H_2O_2, avoiding the formation of H_2O in the reaction. This strategy helps to retain the structural integrity of the halide perovskites throughout the catalytic process. As a result, the catalysts showed improved stability and they were recycled for at least five times with a minimum loss in the photoactivity. Even the structural characterization of the used catalyst (after recycling) revealed its structural integrity.

Further, to enhance the photocatalytic performance, we have developed efficient photocatalyst systems employing strategies like (i) integration of metal complex as cocatalyst, (ii) heterojunction formation, and (iii) electronic band structure modulation. These modifications significantly improved charge carrier separation and hence photocatalytic activity. Interestingly, the metal complex also has a significant impact on the product selectivity through the HAT process.

Comprehensive photoelectrochemical and spectroscopic characterizations, including EIS, photocurrent measurements, and PL spectroscopy, confirmed enhanced charge separation and suppressed charge recombination. Additionally, femtosecond transient absorption spectroscopy revealed accelerated exciton relaxation dynamics, further validating the improved charge carrier kinetics in the optimized photocatalysts.

In **Chapter 2**, $CsPbBr_3$ QDs coupled with $Ni(dmgH)_2$ as a cocatalyst enabled efficient photoredox C–N coupling, delivering high amide yields (7% $[Ni]$-$CsPbBr_3$) due to optimal band alignment, rapid charge transfer, and suppressed trap-state recombination. To maintain perovskite stability, we implemented a robust strategy using non-polar solvents, controlled atmospheres, and avoiding water formation by employing molecular oxygen as an oxidant. The reaction proceeds via superoxide radical formation, yielding H_2O_2 instead of H_2O. The process proceeds under additive-free and mild conditions, with the catalyst demonstrating excellent recyclability, retaining its activity over five consecutive cycles without any loss of performance.

Similarly, in **chapter 3**, we have utilised $CsPbBr_3$ QDs catalyzed visible-light N-alkylation of amines with alcohols via a borrowing hydrogen mechanism. Here, the cobalt complex avoids the production of water in the reaction mixture, instead producing H_2 gas through the hydrogen borrowing process, and maintains $CsPbBr_3$ stability during the photoredox reaction. Cobaloxime cocatalysts enhanced charge separation and aldehyde formation, with [Co-4] achieving 97% selectivity due to favorable LUMO, tuned by the ligand backbone.

In **chapter 4**, we developed a heterojunction photocatalyst for selective DHIQ synthesis via semidehydrogenation of THIQs under visible light. The $CsPbBr_3$ activates $^3O_2$, while BiOBr tunes the valence band to facilitate the oxidation of THIQ to generate the radical cation and also facilitate the $^1O_2$ generation through the electron transfer process at the VB of BiOBr. The high electrophilic character of singlet oxygen enables selective THIQ dehydrogenation to DHIQ under mild conditions, minimizing over-oxidation and avoiding harsh reagents. To maintain perovskite stability, water formation was avoided by redirecting the reaction pathway toward H_2O_2 production via $^\bullet OOH$ radical intermediates.

Finally, in **chapter 5**, we successfully implemented lead-free perovskites (Cs_2CuBr_4), underscoring their potential as environmentally benign alternatives. Overall, this work paves the way for the development of stable, efficient, and sustainable perovskite-based photocatalysts for the photocatalytic amidation of alcohols through the activation of molecular O_2. In this chapter, we have explored how the electronic structures and particle size of the perovskite are tuned to the photoredox activity, with a more negative conduction band minimum and more positive valence band maximum, enabling efficient O_2 reduction to superoxide radicals, thereby enhancing C–N coupling activity.

6.2. Future scope and perspective

In this work, we have demonstrated the application of $CsPbBr_3$ as a photocatalyst, in conjunction with Ni and Co metal complexes (dmgH = dimethyl glyoximato), for the synthesis of functionalized amines and amides via C−N cross-coupling reactions. Additionally, we developed a Z-scheme heterojunction photocatalyst by combining $CsPbBr_3$ with BiOBr to enable the semidehydrogenation of THIQ to DHIQ. Moreover, we explored the use of a lead-free metal halide perovskite, Cs_2CuBr_4, for oxidative amidation of alcohols through C−N coupling. This thesis lays the foundation for future research, which could be extended to address the following directions:

(i) This work provides a foundation for future advancements in photocatalytic research. One promising direction involves the electronic modulation of $CsPbBr_3$ QDs through the incorporation of various transition metals and lanthanide ions (e.g., Mn^{2+}, Ni^{2+}, Zn^{2+}, Ce^{3+}) into the perovskite lattice. Such dopant engineering allows for precise tuning of the band structure and photoluminescence behaviour, which are critical parameters for enhancing charge separation dynamics, suppressing charge recombination, and improving electron mobility. These enhancements are pivotal for boosting photocatalytic performance in organic transformations and solar-to-chemical energy conversion applications.

(ii) Further research is necessary to explore Cs_2CuBr_4 and other transition metal-based lead-free halide perovskites as photocatalysts, with a focus on understanding their photoredox potentials and photophysical properties. A comprehensive investigation of these materials will facilitate their application in diverse areas such as solar energy conversion, photocatalytic organic transformations, water purification, and environmental remediation, including plastic degradation.

(iii) In addition, the Cu(I) center in Cs_2CuBr_4 exhibits a higher ability to activate molecular oxygen compared to the Pb(II) site in traditional lead-based perovskites. This inherent redox activity of Cu(I) offers a promising opportunity to exploit Cs_2CuBr_4 as a lead-free photocatalyst for the efficient generation of H_2O_2 under visible-light irradiation. Given the environmental and safety advantages of H_2O_2 as a green oxidant, future research can focus on optimizing the photocatalytic performance of Cs_2CuBr_4 for scalable H_2O_2 production.

(iv) Furthermore, the construction of heterojunction systems based on Cs_2CuBr_4 with suitable semiconductors presents a promising strategy to enhance photocatalytic efficiency by improving charge separation and suppressing recombination. By carefully selecting semiconductors with complementary band structures, type-II or Z-scheme heterojunctions can be engineered to facilitate directional charge transfer, thereby boosting redox potentials and overall activity. Future studies should focus on exploring the photophysical behavior, interfacial charge carrier dynamics, and lifetime of photoexcited species within these heterostructures. Such insights will be crucial for designing efficient photocatalytic systems tailored for selective organic transformations, under visible-light-driven C–N coupling, oxidative functionalization, and environmentally benign synthesis pathways.

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Professor Devender Singh
Dean (Academic Affairs)

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Ref. No. IIT(BHU)/TEC/Ph.D.Evl./CY/1495/1134

Dated: 10.10.2025

Dr. Arindam Indra
(Supervisor of Mr. Vishesh Kumar)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)

Subject : Oral Board of Mr. Vishesh Kumar – reg.

Dear Sir,

Consequent upon approval of constitution of following Oral Board, I am to send herewith the reports with encls. (IN ORIGINAL) of the Ph.D. Examiners of Mr. Vishesh Kumar to enable you to convene Oral Board at the earliest.

1. Dr. Arindam Indra, Department of Chemistry, IIT(BHU)
   (Supervisor) … Chairperson
2. Prof. Debabrata Maiti, IIT Bombay.
   (External Examiner from outside the Institute but within the country) … Member
3. Dr. Saravanakumar Elangovan, Department of Chemistry, IIT(BHU)
   (Internal Examiner from Deptt./School) … Member
4. Prof. Pralay Maiti, SMST, IIT(BHU)
   (External Examiner from within the Institute but outside the Deptt./School) … Member
5. Dr. Shreyans Kumar Jain, Deptt. of Pharmaceutical Engg. & Tech., IIT(BHU)
   (External Examiner from outside the Deptt./School or Internal Examiner from Deptt./School, IIT(BHU) … Member

You are requested to send the Report of Oral Examination to the undersigned on the prescribed format (**Ph.D. Form-7**) ***along with one hard bound copies of the approved thesis, a soft copy of the revised/amended thesis in Chapter wise and the original Thesis Evaluation Reports of External Examiners, in the enclosed envelop soon after Oral Board Examination for doing the needful at this end.***

A copy of provisions of Clause 11.5.3 of the Ordinance governing Post Graduate Programme is also appended herewith

Yours faithfully,

Dean (Academic Affairs)

Encls.: 1. Format of Oral Board Exam. Report
2. Examiners' Reports
3. One copy of Thesis for candidate.

Copy forwarded for favours of information and necessary action to : ***CONFIDENTIAL***

1. Dr. Saravanakumar Elangovan, Department of Chemistry., IIT(BHU) along with a copy of Ph.D thesis.
2. Prof. Pralay Maiti, SMST, IIT(BHU) along with a copy of Ph.D thesis.
3. Dr. Shreyans Kumar Jain, Deptt. of Pharmaceutical Engg. & Tech., IIT(BHU) along with a copy of Ph.D thesis.
4. The Head, Department of Chemistry, IIT(BHU)

Dean (Academic Affairs)

INDIAN INSTITUTE OF TECHNOLOGY
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Ph.D. EXAMINATION

Recommendation on Ph.D. Thesis

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Ref. No.: IIT(BHU)/TEC/Ph.D.Evl./CY/1495

1. Name of Candidate : Mr. Vishesh Kumar
2. Registered for Ph.D. Degree in : Chemistry
3. Department/School : Chemistry
4. Title of Thesis : Tuning Charge Transfer Dynamics in Halide Perovskites for Improved Photoredox Organic Reactions
5. Details of Examiner : Prof. Debabrata Maiti

Please give your **specific recommendation** by ticking ( ) any one of the following, with signature underneath and enclose your **detailed report** on separate sheet(s) with your signature, name and address.

Please specify the Category under which the Thesis should be placed.

EXAMINER'S REPORT

Chapter 1 deals with the study of the optical properties of metal halide perovskites, along with their various applications in energy conversion processes such as solar cells, photocatalytic CO2 reduction, and photoredox organic transformation reactions.

Chapter 2 deals with some Ni(II) complexes-$CsPbBr_3$ quantum dots (QDs) used for visible-light- driven photoredox C–N coupling. The cocatalyst $Ni(dmgH)_2$ (dmgH = dimethylglyoximato) significantly enhances the photocatalytic performance of QDs, enabling the synthesis of a wide range of amides. Additionally, $Ni(dmgH)_2$ facilitates the activation of molecular O_2 to generate superoxide radicals, which initiate the radical-mediated C–N coupling pathway. The catalyst was found to be recyclable five times with a minimum loss of its initial activity.

Chapter 3 is a study of the importance of Co(II) complexes that tunes the product selectivity in the N-alkylation of amines via photoredox catalysis using lead halide perovskites. $CsPbBr_3$ QDs were employed for the selective N-alkylation of amines with alcohols by modulating the LUMO energy of cobaloxime cocatalysts. This was achieved by altering the electronic environment around the Co center, thereby tuning the LUMO energy barrier. Moreover, product selectivity can be easily controlled by adjusting the electronic environment of the Co catalyst.

Chapter 4 deals with the importance of singlet oxygen generation for the selective semidehydrogenation of tetrahydroisoquinoline using a Z-scheme CsPbBr3/BiOBr heterojunction photocatalyst. This system combines BiOBr nanosheets with CsPbBr3 QDs, enabling efficient conversion of THIQ to 3,4-dihydroisoquinoline (DHIQ). The internal electric field at the interface drives electron transfer from the conduction band of BiOBr to the valence band of CsPbBr3, promoting effective charge separation.

Chapter 5 shows the studies on the introduction of a lead-free metal halide perovskite (Cs2CuBr4) as a visible light-driven photocatalyst for oxidative amidation of alcohols *via* molecular oxygen activation. The author also modulated the band structure of Cs2CuBr4 by altering synthesis methods. Enhanced charge separation and reduced recombination in Cs2CuBr4-1 further improved its photocatalytic performance under visible light.

Chapter 6 of this thesis establishes halide perovskites as efficient, sustainable photocatalysts for visible-light-driven C–N bond formation. A stabilization strategy using non-polar solvents and controlled atmospheres overcomes moisture sensitivity. Cocatalyst integration, heterojunctions, and band engineering enhance light absorption and charge dynamics, confirmed by spectroscopic analyses. Lead-free perovskites further demonstrate eco-friendly potential, advancing perovskite photocatalysis for pharmaceutical and fine chemical synthesis.

A nice, uniform presentation with elegant figures and tables make this thesis easy to read and attractive.

There are only few minor issues, as mentioned bellow, that need to be addressed before this thesis can be accepted in its final form.

1. In chapter 2 optimization table (page 43), the author should check the yields of the products by some other techniques (e.g, NMR, GC, HPLC etc.).
2. In chapter 2 table 2.4 (page 52), the first chemical structure is not visible, kindly change it.
3. In chapter 3 table 3.4 (page 77), the author should mention the C-F coupling in the 13C data of compound 3g.
4. In chapter 5 table 5.5 (page 123), the author should mention the C-F coupling in the 13C data of compound 3h and 3i.
5. The colour combination of schemes needs to be improved.
6. The first introduction chapter and last conclusion chapter needs to be shortened.
7. Kindly provide a better zoomed version and higher resolution of all spectroscopic data.

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Place : -Mumbai- -

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(Signature of Examiner)

Name & Address of the Examiner

Prof. Debabrata Maiti

Professor, Department of Chemistry

IIT Bombay

Encl. : (a) Detailed Report on separate sheet(s)

(b) List of points for clarification

(c) Suggestions for modification etc.

Recommendation on Ph.D. Thesis

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1. Name of Candidate : Mr. Vishesh Kumar
2. Registered for Ph.D. Degree in : Chemistry
3. Department/School : Chemistry
4. Title of Thesis : Tuning Charge Transfer Dynamics in Halide Perovskites for Improved Photoredox Organic Reactions
5. Details of Examiner : Prof. Davide Ravelli

Please give your **specific recommendation** by ticking ( ) any one of the following, with signature underneath and enclose your **detailed report** on separate sheet(s) with your signature, name and address.

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EXAMINER'S REPORT

The thesis submitted by Mr. Vinesh Kumar deals with the development of synthetic methodologies based on heterogeneous photocatalytic manifolds mediated by perovskite materials. After an in-depth introduction, the thesis is articulated in four different chapters, that tackle different transformations with different strategic approaches. Thus, chapter 2 deals with amidation reaction via perovskite-Ni dual catalysis, while chapter 3 studies amines alkylation with alcohols via a hydrogen borrowing strategy triggered by a dual perovskite-Co system. Chapter 4 then studies the semi dehydrogenation of tetrahydroisoquinoline by a composite perovskite/BiOBr material forming a Z-scheme heterojunction. Finally, chapter 5 described a different amidation protocol taking place thanks to a lead-free, Cu-based perovskite. Insightful conclusions and perspectives close the manuscript.

Overall, I read the thesis with much interest, and I found it robust, very well-articulated and organized, and exhaustive. In addition to the preparative part, the different projects present a thorough characterization of the material and are typically supplemented by dedicated mechanistic and control experiments, also demonstrating the recyclability of the material.

Overall, I find that the thesis can be processed further, only requiring minor revisions, which have been indicated in the attached version of the thesis. Most of the points raised are intended to improve readability and require specifying additional aspects/details. A few minor issues have been found in the description of the reaction mechanisms, for which the candidate is invited to double check the precise redox balance of the different steps encountered along the synthetic transformation.

Contd....2

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Ph.D. EXAMINATION

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Place : PAVIA, ITALY

Date : 22ND AUGUST 2025

Name & Address of the Examiner

Prof. Davide RAVELLI
Department of Chemistry, University of Pavia
Viale Taramelli 12, 27100 Pavia - Italy

Encl. : Annotated copy of the THESIS

EXTRACTS FROM
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1. The Ph.D. oral examination will be an open examination. The supervisor/ programme coordinator will be the Chairman of the oral board and will fix the date of the oral examination and intimate the date to the Academic Section.
2. If a member of the oral board, communicates in advance, his/her inability to be present or fails to be present on the specified date and time, the Chairman, Senate may appoint another member in his/her place, in consultation with the thesis supervisor(s)/programme coordinator, Head of the Department/Coordinator of the School and Dean of Academic Affairs.
3. Each member of the oral board will be given a copy of the thesis along with the entire set of thesis examiner's reports and modifications thereto, if any, at least one week before the date of the oral examination.
4. The oral board shall
    - i) examine the thesis reports,
    - ii) examine if necessary modifications suggested by the thesis examiners have been incorporated,
    - iii) elicit the candidate's replies to the questions raised by the thesis examiners,
    - iv) authenticate the work as the student's own,
    - v) judge if the presentation of the work by the student and the answers to the questions asked have been satisfactory, and
    - vi) give a report of the examination, which will be communicated by the supervisor(s)/ programme coordinator to the Dean of Academic Affairs through the Convener, DPGC through the Chairman, SPGC.
5. If all, except at most one member, declare the student as passed, the student shall be deemed to have passed.
6. If a candidate has not passed, the oral board will specify whether
    - i) the candidate may be given another chance to appear in the oral examination and will specify the approximate date for re-examination. The original oral board will conduct the re-examination unless a different oral board is approved by the Chairman, Senate. In the re-examination, the board will declare whether the student has passed or failed as per the criteria laid down above but will not recommend holding a third oral examination.
    - ii) the candidate is declared to have failed.
7. On receipt of the report that the student has passed the oral examination, Dean of Academic Affairs will recommend to the Senate for the award of Ph.D. degree.
8. If the candidate has failed, the matter will be brought to the attention of the Senate for further action.
9. The Chairman, Senate may order a special procedure for the evaluation of a Ph.D. thesis to protect the work of classified nature involving national security and sovereignty and/or to protect the intellectual property rights of the candidate, the supervisor and the Institute.

* * *