

Development of Novel Advanced Functional Porous Materials for Heterogeneous Catalysis and Arsenic Remediation for Safe Drinking Water

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis submitted in partial fulfillment of the requirements of the degree of

Doctor of Philosophy

द्वारा / By

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शोध प्रबंध पर्यवेक्षक : प्रो. सुजीत के. घोष

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भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2024

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Indian Institute of Science Education and Research (IISER), Pune

Certificate

I certify that the thesis entitled “*Development of Novel Advanced Functional Porous Materials for Heterogeneous Catalysis and Arsenic Remediation for Safe Drinking Water*” submitted by *Mr. Gourab Kumar Dam* represents his original work which was carried out by him at IISER, Pune under my guidance and supervision.

The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institutions. I further certify that the above statements made by him/her in regard to his/her thesis are correct to the best of my knowledge

A handwritten signature in blue ink, appearing to be 'S. Ghosh', with a long horizontal line extending to the right.

Date: 08.10.2024

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I declare that this written submission represents my idea in my own words and where others' ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this thesis is the original work done by me under the guidance of Prof. Sujit K. Ghosh.

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Acknowledgement

I would like to seize this opportunity to convey my profound appreciation to my PhD supervisor, **Prof. Sujit K. Ghosh**, for his unwavering faith and consistently supportive throughout my PhD tenure. He has been a steadfast source of motivation and a diligent mentor who instilled the work ethic and freedom for work that is essential for the development of scientific demeanor and aptitude. His guidance has enabled me to develop into an independent researcher, challenging me to surpass my capabilities in order to achieve excellence in my field. I am grateful for your unwavering support, your confidence in me, and your ability to maintain a positive attitude in all circumstances, sir.

I deeply former director Prof. J. B. Udgaonkar and current director Prof. Sunil S. Bhagwat for providing a state-of-art institute maintaining a vibrant research environment. I am also extremely grateful to my research advisory committee (RAC) members, **Dr. Benudhar Punji (NCL, Pune)** and **Dr. Moumita Majumder (IISER, Pune)** for their insights and valuable suggestions during the annual RAC meetings and during informal discussions. I am thankful to the former chair chemistry Prof. H. N. Gopi and present chair chemistry Prof. Nirmalya Ballav and all other faculty members in the department of chemistry for fostering a vibrant scientific environment in the department and being reachable for any queries. I would like to convey my sincere gratitude to Ma'am (Dr. Sudarshana Mukherjee) and I wish both Suvan and Suyash all the best for their future.

The PhD experience has been enriched by each and every member (present and alumni) of the '**Microporous Materials Lab**' group or I say a family far from home. I would like to thank all of them, Dr. Aamod V. Desai, Dr. Partha Samanta, Dr. Samraj Mollick, Dr. Shivani Sharma, Dr. Tarak Nath Mandal, Dr. Arunabha Sen, Dr. Subhajit Dutta, Dr. Sumanta Let, Dr. Sahel Fajal, Dr. Writakshi Mandal, Dr. Debanjan, Dipanjan, Kishalay, Dibya, Anirban, Dipayan, Dr. Sagarmani Rasaily, Rafael, Vartika, Yashasvi, Sudip, Supriti, Shalu, Riddhi who have contributed significantly at different stages in varied capacities. Of them, I would like to sincerely thank and acknowledge Sumanta Da, Subhajit Da and Sahel Da for taking me under their wings during the salad days of my PhD journey and for numerous scientific discussions which fostered my understanding. In particular, I would like to convey my sincere gratitude for my super senior Aamod da for his continuous guidance, care and support throughout this long journey of doctoral research, **Subhajit Da**, for your guidance in the Doctoral journey with those long memorable walks through the nature. Specially, **Sumanta Da**, for being my mentor to

this new path of my life. I want to give you tons of thanks for giving me opportunities to work with you and let me be your companion towards a new field, which I believe will give a new direction in our lab. I missed those discussion about Bengali Natok, Sunday Suspense with chilled Beer which makes these journey memorable with you. It was really an amazing as well as a learning experience to work with all of you. Apart from their mentorship, I have been fortunate to have developed a strong personal equation with each of them. Apart from my seniors, I would like to mention my endless appreciation to all my current lab members and my juniors, because without them this journey would not have been as exciting and memorable as it has been. A very special thanks to **Kishalay** and **Anirban** for being part of my journey in IISER Pune and for giving me a sweet test of companions. Without them my journey will not be easy, thank you guys for being part of my life. I will miss the cooking nights, football nights and specially the nights with Beer, Rum and Music. I will miss these two beep-beep soul in my life. Also, I want to give a special thanks to excellent talented M.Sc student **Vartika**, who completed her M.Sc thesis and several projects with me, which helps me a lot in this journey.

For the smooth progress in a long course, the support of administrative and technical staff is paramount. I thank Anuradha ma'am and Dr. Umeshareddy Kacherki for library assistance. I would like to acknowledge Mr. Anil Prathashetti, Mr. Yathish T. S., Mr. Prashant Badgujar, Mr. Mahesh Jadhav, Sandeep Kanade, Mrs. Megha Paygude, Mr. Nilesh Dumbare, and Mr. Parveen Nasa, Mr. Ravinder Malothu, Mr. Nifin Dalvi, Mr. Sandeep Mishra for technical support. I would like to thank Mr. Mayuresh Kulkarni, Mr. Sanjay Meena, Mr. Ganesh Dimbar, Mr. Tushar Kurulkar, and Mrs. Sayalee Damle for their prompt administrative support at multiple occasions. I also express my gratitude to CSIR, India for research fellowship for the entire tenure at IISER. I thank American Chemical Society (ACS), John Wiley & Sons (Wiley-VCH), Royal Society of Chemistry (RSC) for publishing several research and review articles.

I am indebted to all my teachers who have directly or indirectly influenced my PhD journey, especially, Hamid Kaku, Badal Kaku, Rahul Da, Gopal Da, Rangalal da, and Nilasish Sir. A special note of thanks to **Sukumar Sir**, whose love and support in my down time has inspired me. **Dr. Akhilesh Kumar Singh**, my M.Sc projects supervisor, a special thanks to him for giving me opportunity in his research group. How I forgot **Muktar Da** and **Rabi Da**, two great seniors in my M.Sc Lab at IIT Bhubaneswar? You two introduce a positive attitude to life and research into me which helps me a lot in my research carrier.

In Bachelors time I am very fortunate to meet Subhasis, Pratibha, Desoshree, Arup, Ankita, Arnab as my companion over the journey. Specially **Subhasis**, being roommate, we share everything and with no time we became Best Friend. He supported in every situation and motivated me a lot. I spend best part of life in the Master's in IIT Bhubaneswar with some best souls of the universe. Agniva, Dheer, Dipanjali, Kaushiki, Sharmistha, Soumen, Jeetu, Rathore, Supriyo, Anup, all gives me a sweetest test of life. Special thanks to **Agniva** and **Dheer**, for keeps me motivating me, we spend very high nights with long walk and discussion. This part is incomplete without my childhood and school friends, Rana, Fatik, Rimo, Sahen, Rocky, Suman, Rajesh. Specially **Rana, Fatik** and **Rajesh**, these three is the backbone of my journey, I want them to thank for being supportive in every situation in my life. One of the best things happened in IISER Pune, meet **Charu Shakuntala**, a great friend and greatest human being I have ever met. I missed those late-night walks after beer, even after your leaving for Denmark, you keep motivating me. One day we will travel to Banaras, Lahore and to the Mountains.

I thank each and every member (past and present) of Prof. Pinaki Talukder, Prof. Nirmalya Ballav and Prof. Pramod Pillai group for their constant support and understanding in allowing us to access their instrumental facility freely. I was an integral part of Chemphilic Team-2022 which was indeed a momentous experience.

The special person of my life, I want to give a deepest gratitude to my partner, **Pratibha**, for my biggest supporter through all the ups and downs of my journey. From the long nights of work to the moments of doubt, you were always there to cheer me on and your belief in me, gave me the motivation to keep moving forward. Thank you for your love, patience, and constant encouragement, your companionship, and for being my rock throughout this challenging but rewarding journey.

Lastly, I am indebted to my family for being the invisible backroom support, without whom this could not have been completed. **Maa-Baba** gives me freedom in life to choose whatever I want; From my earliest days, you instilled in me the values of hard work, perseverance, and the importance of education. You have been my constant source of support throughout this journey, always believing in me even when I struggled to believe in myself. Your sacrifices and unwavering faith in my abilities have made this accomplishment possible. **Didi**, the journey from childhood to adulthood with her, makes me blessed every day. I owe everything I have achieved to your love and support. I believe I will make them a happy and proud family.

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6. Summary and Future Outlook

Synopsis

The foundational basis of the work presented in this thesis is the rational design, development, and synthesis of advanced functional porous materials (AFPMs), targeting applications in heterogeneous organo-catalysis, photocatalysis and water detoxification. While traditional porous materials are indispensable in everyday life, achieving precise, on-demand functionality with these materials remains a formidable challenge. Advanced Functional Porous Materials (AFPMs), which encompass a broad spectrum, are primarily categorized into metal-organic frameworks (MOFs) - inorganic-organic hybrid porous materials formed via coordination bonds between inorganic metal ions and organic ligands, metal-organic polyhedra (MOPs) – discrete molecular structure consists of metal node and organic linkers, and porous organic materials (POMs), constructed through robust covalent bonds between organic building blocks extending across the solid framework. Porous organic materials mainly categorized into two types of materials, covalent organic framework (COFs), mainly crystalline in nature and porous organic polymer (POPs), mainly amorphous in nature. These materials provide a platform for function-driven design, tunable synthesis, and flexible pore composition, alongside the modulation of physical and chemical properties, enabling detailed exploration of host - guest interactions based on structure - property relationships. Porous organic polymers (POPs), which offer precise molecular-scale control to create tailored "nanospace" with adjustable porosity and specific chemical functionalities, have demonstrated significant potential in applications such as gas storage and separation, catalysis, energy storage, photoluminescence, drug delivery, and the detection and removal of pollutants from water. However, despite these advances, the rational design of task-specific, advanced porous organic polymer composites for wastewater remediation and environmentally benign heterogeneous catalysis remains largely unexplored. The crux of this thesis work revolves around systematic approach toward developing strategically synthesized function-led AFPMs and their composite materials zeroing on heterogeneous catalysis and water contaminants sequestration. Thus, designed advanced functional porous solids were utilized to address two excellent applications. Attempts were made to develop series of potent porous organic polymers and composite catalyst for organic transformation and sustainable photosynthesis of H_2O_2 from air and sunlight. Furthermore, to combat arsenic water pollution, ionic metal organic framework and ionic porous organic polymers bearing specific functional group were introduced for selective detection and sequestration of organic arsenic pollutants from water.

Chapter-1: Introduction

The topic starts by providing a comprehensive treatment of porous materials, which include both naturally existing porous compounds and advanced porous materials (APMs), including inorganic-organic hybrids and porous organic materials (POMs). The present study provides a concise overview of the synthesis and

structural properties of inorganic-organic hybrid structures, namely metal-organic frameworks (MOFs) and metal-organic polyhedra (MOPs), as well as their prospective applications. Various types of porous organic materials (POMs), including covalent-organic frameworks (COFs), porous aromatic frameworks (PAFs), covalent triazine frameworks (CTFs), hydrogen-bonded organic frameworks (HOFs), porous organic polymers (POPs), and porous organic cages (POCs), are further discussed, emphasizing their wide range of applications. The primary emphasis is on improved metal organic framework and porous organic polymers and their suitability for specific applications, with a special attention on the role of MOFs and POPs as exceptional materials in heterogeneous catalysis and water purification. Furthermore, the thesis presents a summary of the advancements achieved in the development of purpose-oriented sophisticated porous organic polymers, specifically designed for certain purposes.

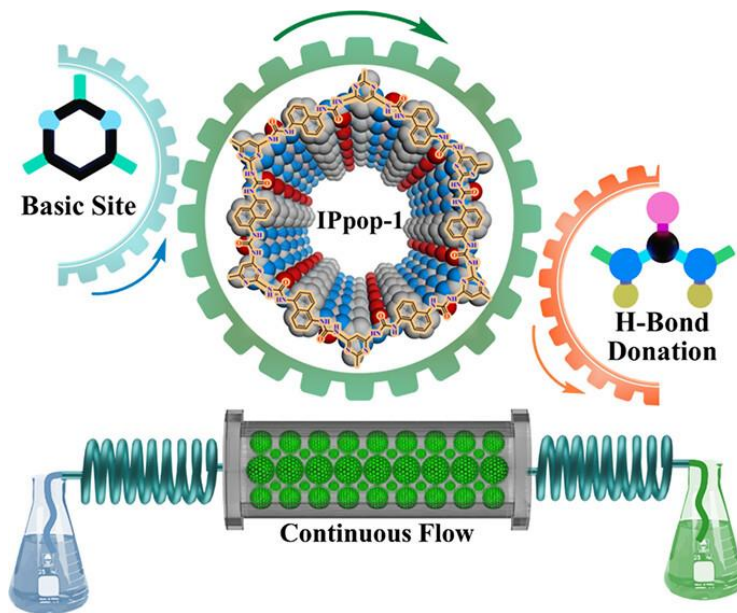
Part-I: Function-led Design and Syntheses of Porous Organic Polymers as Sustainable Heterogeneous Catalyst

The heterogenization of homogeneous molecular catalysts by immobilizing them onto a support matrix has emerged as a promising strategy to create chemically homogeneous yet structurally heterogeneous solid catalysts. Heterogeneous catalysts offer several advantages over their homogeneous counterparts, including facile separation after the catalytic reaction, reusability, and suitability for flow chemistry applications. However, challenges such as increased catalyst costs, reduced activity, and limited accessibility of active sites to substrate molecules present significant bottlenecks in heterogeneous catalysis. Therefore, careful consideration must be given when selecting a support matrix for the immobilization of homogeneous molecular catalysts. Porous organic polymers (POPs), with their intrinsic properties such as high surface area, synthetic tunability, and chemical stability, represent an ideal support matrix for immobilizing catalytic sites via straightforward methods. This section focuses on the development of efficient heterogeneous catalysts using POPs as the support matrix. This segment of the thesis is separated by two separate chapters, chapter-2 and chapter-3. Chapter-2, describe the successful design and synthesis of a porous organic polymer consists of urea functionalization and pyrimidine moiety, its composite preparation and utilization in H-bond donating Friedel-Craft alkylation and multi-component Michael-Knoevenagel condensation reaction under flow condition. In chapter-3, a series of imidazoline porous organic polymer via tuning halide ion was synthesized to carry out the photocatalytic production of H_2O_2 from Air, water and sunlight.

Chapter-2: Urea Tethered Porous Organic Polymer (POP) as Efficient Heterogeneous Catalyst for Hydrogen-Bond Donating Organocatalysis and Continuous Flow Reaction

Hydrogen bond donating (HBD) heterogeneous organocatalysis has come to light as a powerful surrogate to Lewis acid activation toward manufacturing biologically important C–C bonds. Notwithstanding the emergence of urea as a functionally diverse moiety to drive homogeneous HBD reactions, its catalytic competency is often muted by self-quenching behavior. Keeping this in perspective, spatial isolation of catalytically active urea functionality inside a porous framework can alleviate this pitfall, rendering a potential solution. The current work reports the fabrication of a porous urea network (IPpop-1) as a superior heterogeneous HBD catalyst toward Friedel–Crafts alkylation of β -nitrostyrene and indole (yield up to 99%) under mild conditions advocating green chemistry. Experimental evidence that supports the critical step of the catalytic reaction leading to a plausible mechanism was unveiled along with theoretical assistance. Additionally, the versatile bifunctional nature of the catalyst was established from its competence in catalyzing multicomponent Knoevenagel–Michael condensation as well as cyanosilylation reactions efficiently. One-pot cascade catalysis was also achieved under milder reaction conditions with excellent product yields exploiting the dual active sites of IPpop-1. Pertaining to practicality, spherical composite beads were fabricated to perform continuous flow multicomponent Knoevenagel–Michael condensation without compromising the catalytic activity of IPpop-1. Furthermore, regeneration of the spent catalyst (up to 10 cycles) and scalability combined with wide substrate tolerance manifested conceptual feasibility of the polymer catalyst.

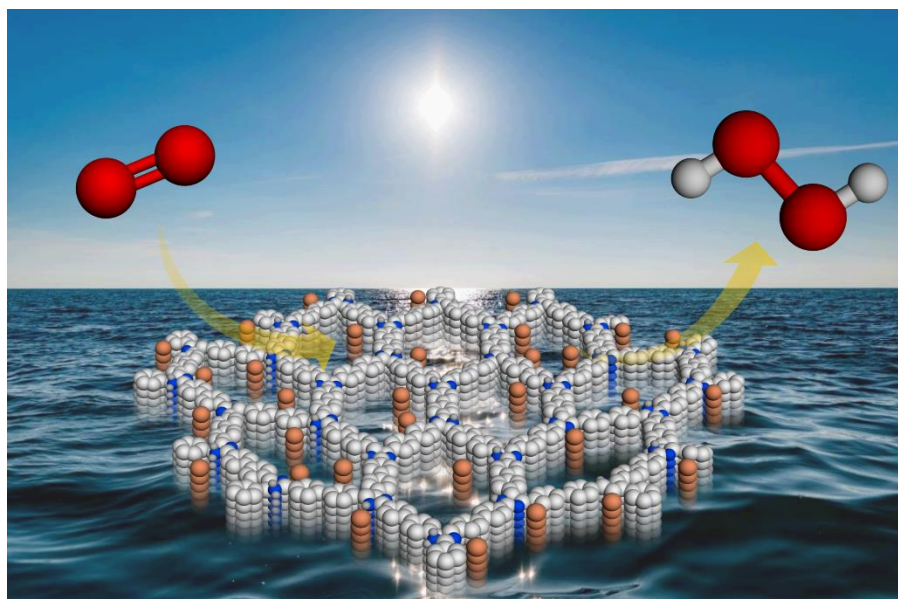
(*ACS Sustainable Chem. Eng.* 2024, 12, 8, 3000–3011)



Chapter-3: Halide Ion Tuning in a Imidazoline Porous Organic Polymer for Photosynthesis of H_2O_2 from Sunlight, Air and Seawater

Solar photocatalysis from air and seawater has gained attention as an environmentally sustainable method for hydrogen peroxide (H_2O_2) production. However, the complexity and high cost associated with the structural design of photocatalysts have hindered their widespread practical use. The photocatalytic reduction of oxygen to generate H_2O_2 presents a promising pathway for providing oxidants applicable across various industrial processes. Porous organic polymers (POPs) are suitable candidate for this photoproduction due to their structure-property correlation yet to explore. In this work we develop three imidazole porous organic polymers tuning the halide ion inside the cationic polymeric network. In seawater under sunlight irradiation and air the production rate reaches $58654 \mu\text{M h}^{-1} \text{g}^{-1}$ for IPM-402F, followed by 45573 and $55070 \mu\text{M h}^{-1} \text{g}^{-1}$ for IPM-402Cl and IPM-402Br, respectively. Although highest results were found in O_2 saturated H_2O -ethanol (9:10) mixture at 450 nm. IPM-402F can produce $535133 \mu\text{M h}^{-1} \text{g}^{-1}$ followed by 477759 and $529058 \mu\text{M h}^{-1} \text{g}^{-1}$ for IPM-402Cl and IPM-402Br, respectively. Highest %AQY and SCC was found 26.36 and 1.233 for IPM-402F. Different control experiments with electrochemical studied showed photocatalytic H_2O_2 production is direct ORR process by IPM-402Xs. DFT calculation was performed to evaluate the role of the solvent molecules in the mechanistic pathway.

(Manuscript Under Preparation)



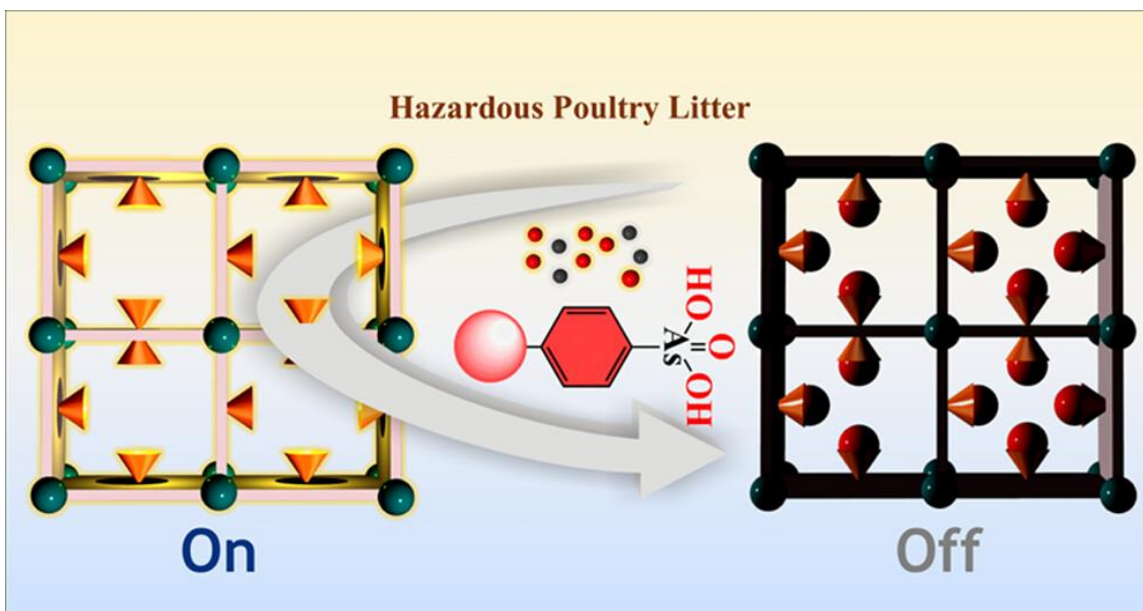
Part-II: Fabrication of Task Specific Porous Materials Towards Detection and Remediation of Toxic Organic Arsenic in Water for Safe Drinking Water

Water pollution has become one of the most critical challenges facing humanity in the 21st century. The removal of toxic contaminants from water to achieve purification has attracted significant global research attention. However, despite ongoing efforts, the fight against water pollution remains incomplete, as many key pollutants remain unaddressed, posing a continued threat to billions of people. In response to this urgent issue, the potential of ionic metal organic framework (iMOF) and ionic porous organic polymer (iPOP) is being investigated as a promising solution for the detection and sequestration of harmful water contaminants. This segment also contains two separate chapters. Chapter-4 summarizes the developments of aromatic sulfonic acid decorated highly luminescent ionic metal organic framework (iMOF-12C) for selective detection of organic arsenic from water. Chapter-5 contains the study of design and synthesis of an ionic adaptable urea functionalized porous organic polymer (IPiPOP-3U) towards organic and inorganic arsenic decontamination from water and mechanistic insight.

Chapter-4: Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water

Drugs containing organic arsenic moiety are extensively utilized as food additives in the poultry industry, and release of these organic arsenics through poultry litter to natural water bodies can prove fatal and noxious to the ecosystem. Pertaining to this, sensitive detection of organic arsenic drugs in a selective manner from livestock waste water remains pivotal but indeed very challenging. In this work, we explored a cationic MOF, viz., iMOF-12C, as a fluorescence sensor toward precise recognition of organic arsenic molecules such as roxarsone (ROX) and nitarsone (NIT). Here we explore the potential of ionic MOFs for the first time toward recognition of organic arsenic drugs. iMOF-12C displayed excellent potency as a suitable sensory material toward selective detection of both ROX and NIT in water medium. The quenching efficiency of iMOF-12C toward ROX and NIT recognition was found to be 78 and 82%, respectively. The limit of detection (LOD) of iMOF-12C for ROX and NIT was calculated as 3.95 and 1.35 ppb, respectively, well below WHO's safety limit. Further, for practical application, iMOF-12C-based mixed-matrix membranes (MMM) were casted, which showed excellent organic arsenic detection in water. The findings of this work highlight the potential of iMOF-12C toward real-time detection of organic arsenic molecules in water bodies.

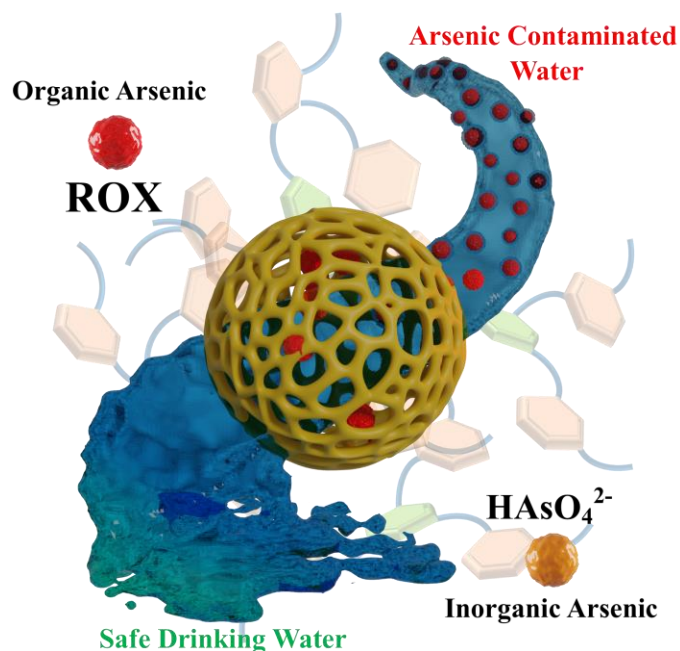
(*ACS Appl. Opt. Mater.* **2023**, 1, 7, 1217–1226)



Chapter-5: A Chemically Robust Urea Tethered Adaptable Ionic Porous "Nanotrap": Ultrafast Organic and Inorganic Arsenic Water Decontamination

Poultry industry widely make use of organoarsenic compounds as feed additives. Consequently, their release into wastewater can be the genesis of serious poisoning of the ecosystem. Roxarsone (ROX), a typical aromatic organoarsenicals, on account of being an emerging micropollutant, is imperative to remove from water as it can be degraded into extremely toxic inorganic arsenic compounds poisoning the ecosystem. Therefore, it is topical to design and develop potent materials with high affinity towards organic and inorganic arsenic species which still remains very challenging. Herein, we report amalgamation of ionicity and anchoring adaptable functionality tethered covalently to ensure structural robustness in a single material. IPiPOP-3U bearing urea functionality-based “nano-trap” displayed outstanding organoarsenic adsorption competence in terms of ultrafast uptake (up to 99% removal in 30 seconds) and excellent capacity (833 mg/g for ROX). The practical applicability of IPiPOP-3U was verified with trace concentration studies and flow-through experiments. It also displayed unaltered sorption efficiency in various real-world water samples, while the mechanistic aspects were disseminated with the aid of extended X-ray absorption fine structure (EXAFS) in combination with theoretical studies. The thermodynamic feasibility ROX capture by IPiPOP-3U was further probed by isothermal titration calorimetry (ITC). Additionally, IPiPOP-3U also showed remarkable performance towards the removal of inorganic arsenic, i.e., arsenate (HAsO_4^{2-}) with high uptake capacity (264 mg/g) with excellent cycling performance (up to 10 cycles).

(Manuscript Under Revision)



Chapter-6: Summary and Future Outlook

In this section, an effort to summarize the insights gained through the library of task-specific Advanced functional porous materials and their composites reported in chapters 2-5 have been made. The crucial role of some key design parameters as well as post-polymerization structure modulation have been discussed. Apart from highlighting the importance of function-led designing for crafting task-specific AFPMs, judicious structural modifications to achieve desired chemical as well as non-native functionality is briefly summarized. The experimental outcomes of the current thesis work on Advanced functional porous materials and their composites aimed at eco-friendly heterogeneous catalysis and water detoxification is documented in comparison to state-of-art materials. The rational design of task specific materials can come forth as a new paradigm as potent materials toward task-specific applications.

Abbreviations

g	Gram
mg	Milligram
mL	Milliliter
mM	Millimolar
cm	Centimeter
RT	Room Temperature
Anal.	Analysis
min	Minutes
h	Hour
$\mu\text{M h}^{-1} \text{g}^{-1}$	Micromolar / hour - gram
ppm	Parts per million
ppb	Parts per billion
ns	Nano seconds
MOF	Metal-Organic Framework
MOP	Metal-Organic Polyhedra
MOG	Metal-Organic Gel
COF	Covalent-Organic Framework
POP	Porous organic polymer
iPOP	Ionic porous organic polymer
PAF	Porous aromatic framework
COP	Covalent-Organic Polymer
CMP	Conjugated microporous polymer
AFPM	Advanced Functional Porous Material
UV-Vis	Ultraviolet–visible spectroscopy
SC-XRD	Single Crystal X-Ray Diffraction
PXRD	Powder X-Ray Diffraction
TGA	Thermo-gravimetric Analysis
FESEM	Field Emission Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance
CP-MAS	Cross Polarization Magic Angle Spin
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
XPS	X-ray photoelectron spectroscopy
TPD	Temperature programmed desorption
ITC	Isothermal Titration Calorimetry
DRS	Diffuse Reflectance Spectroscopy

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<https://pubs.acs.org/doi/10.1021/acssuschemeng.3c06108>

Chapter 4:

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<https://pubs.acs.org/doi/10.1021/acsaom.3c00115>

Research Publication

(† indicates equal contribution)

Included in Thesis:

1. Urea-Tethered Porous Organic Polymer (POP) as an Efficient Heterogeneous Catalyst for Hydrogen Bond Donating Organocatalysis and Continuous Flow Reaction.
Gourab K. Dam,[†] Sumanta Let,[†] Vartika Jaiswal, and Sujit K. Ghosh.
ACS Sustainable Chem. Eng., **2024**, 12, 8, 3000–3011.
2. Halide Ion Tuning in an Imidazoline Porous Organic Polymer for Photosynthesis of H₂O₂ from Sunlight, Air and Seawater
Gourab K. Dam, Sumanta Let, Saurav Parmer, Vartika Jaiswal, Kishalay Biswas, Sudip Maity, Vidhya Avasare and Sujit K. Ghosh.
(Manuscript Under Preparation)
3. A Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water.
Gourab K. Dam, Sahel Fajal, Subhajit Dutta, Sumanta Let, Aamod V. Desai and Sujit K. Ghosh.
ACS Appl. Opt. Mater., **2023**, 1, 7, 1217–1226.
4. A Chemically Robust Urea Tethered Adaptable Ionic Porous "Nanotrap": Ultrafast Organic and Inorganic Arsenic Water Decontamination.
Gourab K. Dam, Sumanta Let, Vidha Bhasin, Sahel Fajal, Kishalay Biswas, Mandar M. Shirolkar, Dibyendu Bhattacharyya, and Sujit K. Ghosh.
(Under Revision)

Not Included in Thesis:

5. Ultrafast Photocatalytic Decontamination of Mustard-Gas Simulant and Thermodynamic Insight by Metal-free Imidazoline Porous Organic Polymer.
Gourab K. Dam,[†] Vartika Jaiswal,[†] Sumanta Let, Anirban Roy and Sujit K. Ghosh.
(Under Revision)
6. New Approach to Photocatalytic Degradation of Nerve agent by Zr-MOF@Imidazoline POP, A MOF-Porous Organic Polymer Composite.
Gourab K. Dam,[†] Vartika Jaiswal,[†] and Sujit K. Ghosh.
(Manuscript Under Preparation)
7. Palladium anchored N-Heterocyclic Carbene in a Porous Organic Polymer (POP): A Heterogeneous Composite Catalyst for Eco-Friendly C-C Coupling.
Sumanta Let,[†] **Gourab K. Dam**,[†] Partha Samanta, Sahel Fajal, Subhajit Dutta and Sujit K. Ghosh.
J. Org. Chem., **2022**, 87, 24, 16655–16664.
8. Organic porous heterogeneous composite with antagonistic catalytic sites as a cascade catalyst for continuous flow reaction.
Sumanta Let, **Gourab K. Dam**, Sahel Fajal and Sujit K. Ghosh.

Chem. Sci., **2023**, *14*, 10591-10601.

9. Unraveling Mechanistic Insights in Covalent Organic Frameworks for Highly Efficient Sequestration of Organic Iodides from Simulated Nuclear Waste.
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10. Chemically Robust Functionalized Covalent Organic Framework for Highly Efficient and Selective Separation of Bromine.
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(Under Revision)
11. Functionalized Ionic Porous Organic Polymers Exhibiting High Iodine Uptake from Both the Vapor and Aqueous Medium.
Arunabha Sen, Shivani Sharma, Subhajit Dutta, Mandar M. Shirolkar, **Gourab K. Dam**, Sumanta Let, and Sujit K. Ghosh.
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12. Imidazolium Functionalized Chemically Robust Ionic Porous Organic Polymers (iPOPs) toward Toxic Oxo-pollutants Capture from Water.
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13. Efficient Capture of Trace Acetylene by an Ultramicroporous Metal–Organic Framework with Purine Binding Sites.
Shivani Sharma, Soumya Mukherjee, Aamod V. Desai, Matthias Vandichel, **Gourab K. Dam**, Ashwini Jadhav, Gabriele Kociok-Köhn, Michael J. Zaworotko and Sujit K. Ghosh. *Chem. Mater.*, **2021**, *33*, 14, 5800–5808.
14. Hemilabile Binding of Acetylene in an Amide-Rich Ultramicroporous MOF Enables Strong Acetylene Selectivity.
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15. A nano-molar level fluorogenic and oxidation state-selective chromogenic dual reversible chemosensor for multiple targets, $\text{Cu}^{2+}/\text{S}^{2-}$ and $\text{Fe}^{3+}/\text{F}^-$ ions.
Sayed Muktar Hossain, **Gourab K. Dam**, Sagarika Mishra, Akhilesh Kumar Singh.
New J. Chem., **2020**, *44*, 15186-15194.
16. Neutral nitrogen donor ligand-based MOFs for sensing applications. (Review)
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17. Ionic Metal-Organic Frameworks (iMOFs): Progress and Prospects as Ionic Functional Materials.
(Review)
Subhajit Dutta, Yogeshwar D. More, Sahel Fajal, Writakshi Mandal, **Gourab K. Dam** and Sujit K. Ghosh.
Chem. Commun., **2022**, 58, 13676-13698.

Instrumental Techniques

1. ^{13}C CP-MAS Nuclear Magnetic Resonance (NMR) Spectroscopy: Solid-state ^{13}C cross-polarization magic-angle-spinning (CP-MAS) spectra were acquired on a Bruker 500 MHz NMR spectrometer with a CP-MAS probe. Carbon chemical shifts are expressed in parts per million (δ scale). The ^{13}C chemical shifts were externally referenced to tetramethylsilane ($\delta = 0.0$ ppm).

2. Fourier Transform Infrared Spectroscopy (FT-IR): The IR Spectra were acquired by using Bruker Alpha-II ECO-ATR spectrophotometer using solid sample in $550\text{--}4000\text{ cm}^{-1}$ range.

3. X-ray photoelectron spectroscopy (XPS): As-obtained powder samples was stuck to conductive paste and then measured by X-ray photoelectron spectroscopy using K-Alpha+ model (Thermo Fischer Scientific, UK) with Al $K\alpha$ source.

4. Thermogravimetric analysis (TGA): Thermogravimetric analyses were performed using Perkin-Elmer STA 6000 TGA analyzer by heating the samples from 30 to $800\text{ }^{\circ}\text{C}$ under N_2 atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

5. Field emission scanning electron microscopy (FESEM): The morphology of the materials was investigated with a Zeiss Ultra Plus field-emission scanning electron microscope (FESEM) with an integral charge compensator and embedded EsB and AsB detectors (Oxford X-max instruments 80 mm^2 (Carl Zeiss NTS, GmbH). The elemental analysis was carried out using voltage of 15 KV equipped with an EDX detector. Data acquisition was performed with an accumulation time of $>600\text{ s}$.

6. Transmission electron microscopy (TEM): For high-resolution TEM analysis, all the samples were dispersed in isopropanol (0.5 mg/mL) and sonicated for 15 minutes. Then, the samples were left undisturbed for 2 minutes, and the upper part of the solution was taken for preparing TEM samples on a lacey carbon-coated copper grid (Electron Microscopy Science). TEM imaging was performed on the HRTEM (JEM-2200FS, JEOL) operating at acceleration voltage of 200 kV.

7. Powder X-ray diffraction (PXRD): Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advanced X-ray diffractometer at room temperature using Cu $K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) at a scan speed of $0.5\text{ }^{\circ}\text{ min}^{-1}$ and a step size of 0.01° in 2θ .

8. Low temperature adsorption-desorption isotherm measurements: N_2 and CO_2 gas adsorption-desorption measurements were performed at 77K and 195K respectively, using the BelSorp-Max instrument (Bel-Japan). Prior to adsorption measurements, the activated samples were heated at $120\text{ }^{\circ}\text{C}$ under vacuum for 12 hours using BelPrepvacII.

9. Temperature-programmed desorption (TPD) measurements: The temperature programmed desorption (TPD) study was done using CHEMBET™ TPR/TPD, QUANTACHROME.

10. Proton (¹H) nuclear magnetic resonance (NMR) spectroscopy: All ¹H spectra were recorded on Bruker 400 MHz spectrometer. The chemical shifts (δ) in ppm were referenced to the residual signal of deuterium solvents (¹H NMR in CDCl₃, ¹H NMR in CDCl₃ and DMSO-d₆ equivalent mixture). The multiplicities of the peaks are s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet).

11. Zeta potential: Zeta potential measurements were performed on Malvern Zetasizer Nanoseries ZS90. Solvent – water.

12. UV-visible absorption spectra: UV-vis absorption studies were performed on a Shimadzu UV1900 UV-Vis spectrophotometer in an optical quartz cuvette (10 mm path length) over the entire range of 200-800 nm.

13. Diffuse reflectance spectroscopy (DRS): DRS spectra and corresponding absorbance spectra was collected on a Shimadzu UV-3600i UV/Visible/NIR Spectrophotometer with solid sample.

14. Fluorescence: Fluorescence emission spectra and PLE was collected on a HORIBA Fluoromax+ solid sample and solvent dispersed samples.

15. Photoelectrochemical measurements: Photocurrent and EIS were measured in 0.5 M sodium sulfate solution (pH=6.8) through the traditional three-electrode system in the CHI 760E electrochemical workstation. The working electrode is FTO glass plate coated with catalyst slurry, the counter electrode is platinum foil, and saturated Ag/AgCl as reference electrode.

16. Electrochemical measurements: All the electrochemical measurements and RRDE experiment was performed in a CHI760E electrochemical workstation (Sinsil International) equipped with RRDE-3A (ALS Japan). RRDE electrode measurement: length: 25 mm, OD: 12 mm, ring OD: 7.0 mm, ring ID: 5.0 mm and disk diameter: 4.0 mm.

17. Inductively coupled plasma atomic absorption/emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS): ICP-AES analysis was performed on ARCOS, Simultaneous ICP Spectrometer. ICP-MS was performed on Quadrupole inductively coupled plasma mass spectrometry (Q-ICP MS; Thermo Scientific iCAP Q) instrument. Multielement standards were purchased from inorganic ventures.

18. Isothermal Titration Calorimetry (ITC): The ITC experiments were performed on a Malvern MicroCal PEAQ-ITC microcalorimeter having 20 (19+1) injection cycle method capacity, the sample

volume of 280 μL with a sample cell size of 200 μL and injection syringe volume of 40 μL for each set of experiments.

Chapter 1

Introduction

1.1. Porous Materials: A Brief Account

Porosity is an inherent characteristic found in all things. Traditionally, porous materials have to have persistent, linked potential voids that are open to gas molecules or liquids. Since ancient Egypt,¹ naturally occurring porosity has been used for cooling, filtration, and water purification. It is often found in biological tissue, rocks, charcoal, soils, and other materials. But it's important to understand that porous materials have been around for a lot longer than we may realize. Ancient Egyptian texts, like the ones found in the Ebers papyrus, which was written approximately 1500 BC, mention treatments for dyspepsia that include porous charcoal.² The use of charcoal for water purification is also referenced in ancient Hindu literature.³ In order to extend the shelf life of drinkable water, the British navy also burned the inside of their wooden barrels during early expedition.⁴ Together with a few pioneering studies on charcoal adsorption, zeolites—a Greek term meaning "zeo" (to boil) and "lithos" (stone)—were emerging as a distinct class of porous materials in the second half of the 20th century.⁵ Along the same line, past few decades have seen a remarkable upsurge in terms of evolution of porous materials. Rational construction of materials with porosity ranging from micro-, meso- to nano-scale have commanded tremendous research attention all over the world owing to their various intriguing applications.⁶ Chronologically diverse class of porous materials have been documented in scientific literature. Mesoporous clay, activated carbons (AC), zeolites, aluminophosphates (ALPOs) and porous silica stand amongst the early and well-known porous materials.⁷⁻⁹ The use of porous solids is not just restricted to sorption and catalysis in the modern world due to rising demand; they have also found extensive use in a number of other industries, such as renewable energy, environmental remediation, and healthcare.¹⁰ In general, based on the size of the pores or the separation between the pore's opposing surfaces, porous materials are classified as microporous for those having pores smaller than 2 nanometers (nm), those with pores ranging from 2 to 50 nm are referred to as mesoporous materials while macroporous materials contain pores larger than 50 nm. Porous solids have long been necessary for day-to-day living and have had a profound effect on our culture. However, because the structure-property link is still unclear, obtaining target-specific applications with such standard porous materials is almost difficult. Thus, the creation of novel porous materials that enable molecular-level fine-tuning of order and intended functionality becomes crucial. The ability to create customized materials for challenging and appealing applications that are challenging to accomplish with traditional porous solids is made possible by exquisite command of the porous materials framework. In the last twenty years or more, there has been a cautious reorientation toward the synthesis of innovative materials through the use of designed and functional building blocks. Advanced functional porous materials (AFPMS) are the broad name used to describe these materials.¹¹⁻¹³ These APMs have led to a rebirth in both chemistry and material engineering since their discovery. This is further underscored by the ever-growing global community of researchers working on

this emerging field, which offers scientists the opportunity to explore virtually every chemical or structural property in this class of materials. In contrast to traditional porous solids, an intriguing new class of porous materials that complement or even outperform them may be created thanks to the distinct chemistry of both organic and inorganic materials, or the combination of the two.¹⁴⁻¹⁶

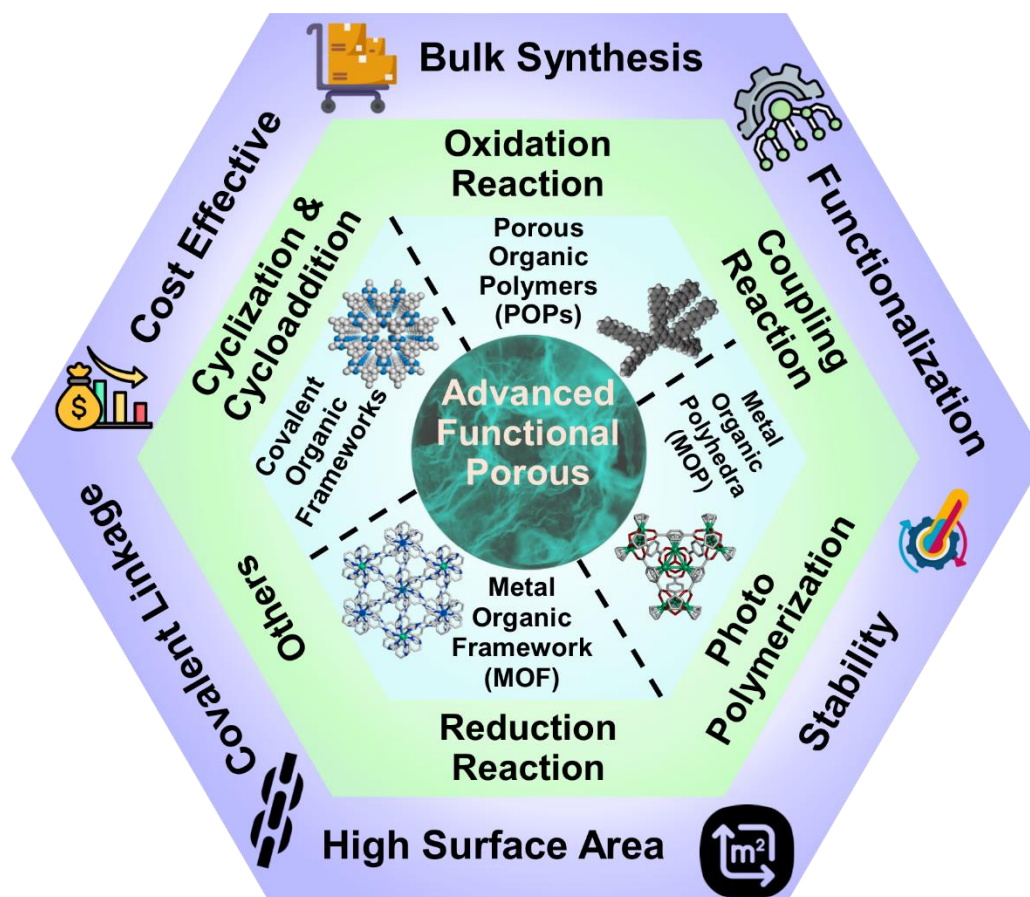


Figure 1.1. Details of Advanced Functional Porous Materials (AFPMs)

1.2. Advanced Functional Porous Materials (AFPMs)

Because of their unique properties and the benefits, they provide for accurate molecular-level control, advanced functional porous materials (AFPMs) (Figure-1.1) have attracted a great deal of attention in recent years from researchers worldwide. AFPMs may be carefully created and produced. They are distinguished by having a high specific surface area and custom pores. These materials can also be made into thin films, monolithic aerogels, or molecular beads to make them processable and useful in real-world applications. AFPMs are notable for their ability to respond to external stimuli by reversibly switching between their open and closed porous forms. The availability of a variety of simple synthetic pathways for generating

AFPMs is a trait that sets them apart from traditional porous solids and accounts for their advantage over them.¹⁷

Generally speaking, there are two ways to build AFPMs. Using inorganic metal nodes and functional organic synthons, one may create organic-inorganic hybrid porous structures. The second approach uses covalent bonds and noncovalent interactions to join only organic functionalized molecular blocks to form metal-free porous organic materials. These allow for a general classification of the advanced functional porous material (AFPM) (Figure-1.2) domain into two categories: pure organic porous materials and inorganic-organic hybrid porous materials. Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), metal-organic gels (MOGs), and metal-organic polyhedra (MOPs)¹⁸⁻²⁰ are a few examples of the wide range of

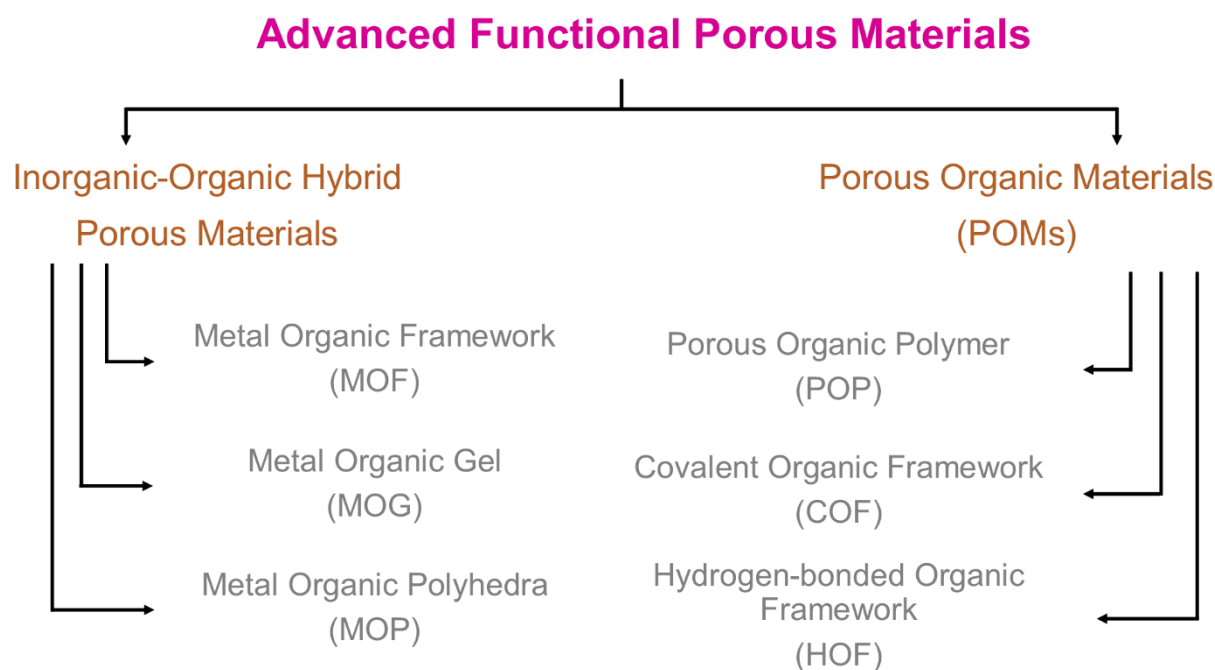


Figure 1.2. Classifications of Advanced Functional Porous Materials (AFPMs)

materials that make up the inorganic-organic hybrid porous materials. Conversely, pure organic porous materials include covalent organic frameworks (COFs), hydrogen-bonded organic frameworks (HOFs), supramolecular organic frameworks (SOFs), porous organic cages (POCs), and porous organic polymers (POPs) etc.²¹⁻²⁴

The key advantage of employing these strategies is the ability to carefully select functional moieties for synthesizing AFPMs, thereby imparting a task-specific nature to these materials. The building blocks are designed with application-specific functionality incorporated into the framework backbone, creating a

porous scaffold that is interactive and functional based on the specific application requirements. Porous materials are a diverse class of substances characterized by the presence of voids, pores, or cavities within their structure. These voids create an internal surface area, often significantly larger than the external surface area, and can be tailored for specific applications. Porous materials find extensive use in various fields, including chemistry, materials science, geology, environmental science, and engineering. Here's a more detailed exploration of porous materials.

1.2.1. Inorganic-Organic Hybrid Porous Materials

Inorganic-organic hybrid porous materials are a flexible class of advanced materials distinguished by the incorporation of both inorganic and organic ingredients into a single porous structure. These materials combine the complimentary qualities of inorganic components (metal ions, metal clusters, or oxides) with the flexibility, tunability, and functional variety of organic ligands. The exact assembly of these building blocks permits the creation of materials with adjustable porosity, large surface area, and variable chemical reactivity. As a result, inorganic-organic hybrid porous materials have enormous promise in a variety of applications, such as gas storage, catalysis, chemical sensing, and drug delivery.²⁵⁻²⁷ Their hybrid nature enables the fine-tuning of structural and functional features, providing a foundation for customized materials science solutions. Metal-organic frameworks (MOFs), metal-organic gels (MOGs), and metal-organic polyhedra (MOPs) are three major classes of these materials, each with its own set of structural characteristics and uses. This versatility makes them ideal for a wide range of technical and industrial applications.

1.2.1.1. Metal Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are a pioneering class of advanced porous materials that have sparked widespread interest due to their distinct structural and functional features. These crystalline materials, which are frequently classified as a subclass of coordination polymers, are made up of metal ions or metal-oxide clusters that have been coordinated with organic ligands to create highly organized, three-dimensional networks with intrinsic voids. The resultant frameworks have extraordinary porosity, as seen by finely constructed pore architectures and extraordinarily large surface areas, which frequently exceed those of typical porous materials. The flexibility of MOFs stems from their adjustable features, which enable exact control over pore size, chemical activity, and structural topology.

Metal-organic frameworks (MOFs) are categorized into three distinct generations based on their behavior following desolvation. First-generation MOFs lose structural integrity upon removal of guest molecules, resulting in framework collapse. Second-generation MOFs, however, maintain their structural integrity post-desolvation, preserving their porous architecture. In contrast, third-generation MOFs, often referred to

as "dynamic frameworks," exhibit structural flexibility. These frameworks undergo a reversible transformation to an alternate structure upon desolvation but can revert to their original configuration when exposed to appropriate conditions, such as re-solvation. This reversible dynamic behavior adds a level of adaptability that is particularly valuable for responsive and smart material applications. A crucial approach for enhancing MOF functionality is post-synthetic modification (PSM), which involves chemically modifying pre-synthesized MOFs to introduce new functional groups without altering their crystalline structure. PSM allows for the generation of structurally similar but functionally distinct MOFs, offering a route to materials that may be challenging to synthesize via conventional methods. This technique enables the precise incorporation of functionalities, making it a powerful tool for the rational design of MOFs with tailored properties.

MOFs can also be classified based on their charge characteristics into neutral and ionic MOFs (iMOFs). Neutral MOFs typically arise when organic linkers, often containing carboxylate ($-\text{COOH}$) groups, coordinate with metal nodes in a neutral electrostatic configuration. iMOFs, on the other hand, are divided into *cationic* and *anionic* frameworks, depending on the net charge of the structure.²⁸⁻²⁹ The charge of iMOFs plays a critical role in influencing their interactions with guest molecules, making them useful for applications such as ion exchange, separations, and catalysis. Due to their unique structural properties, including high surface areas, tunable pore sizes, and versatile functionalization, MOFs are applied across a wide range of fields. One of the most prominent applications is in gas storage and separation, where MOFs leverage their large surface areas and tunable porosity to selectively adsorb gases such as hydrogen, methane, and carbon dioxide, making them ideal for energy storage and carbon capture technologies. Luminescent MOFs (LMOFs), which emit light upon excitation, are employed in sensing applications for detecting various analytes. These materials have potential in fields such as

molecular recognition and host-guest chemistry, owing to their ability to interact with specific guest molecules. In catalysis, MOFs act as heterogeneous catalysts, with their metal nodes or clusters serving as active sites for various chemical reactions, including organic transformations, photocatalysis, and electrocatalysis. The porous nature of MOFs also makes them valuable for drug delivery systems, where they can encapsulate and release therapeutic agents in a controlled manner. Additionally, MOFs play a significant role in environmental applications, such as water purification, by selectively adsorbing and removing contaminants from aqueous systems. In the context of energy and environmental technologies, MOFs are explored for their potential in clean energy applications. They are used in the development of advanced conductors, electrochemical devices, supercapacitors, and composite materials incorporating nanoparticles. These properties position MOFs as critical materials in the advancement of technologies for energy storage, conversion, and environmental remediation. The classification of MOFs into different

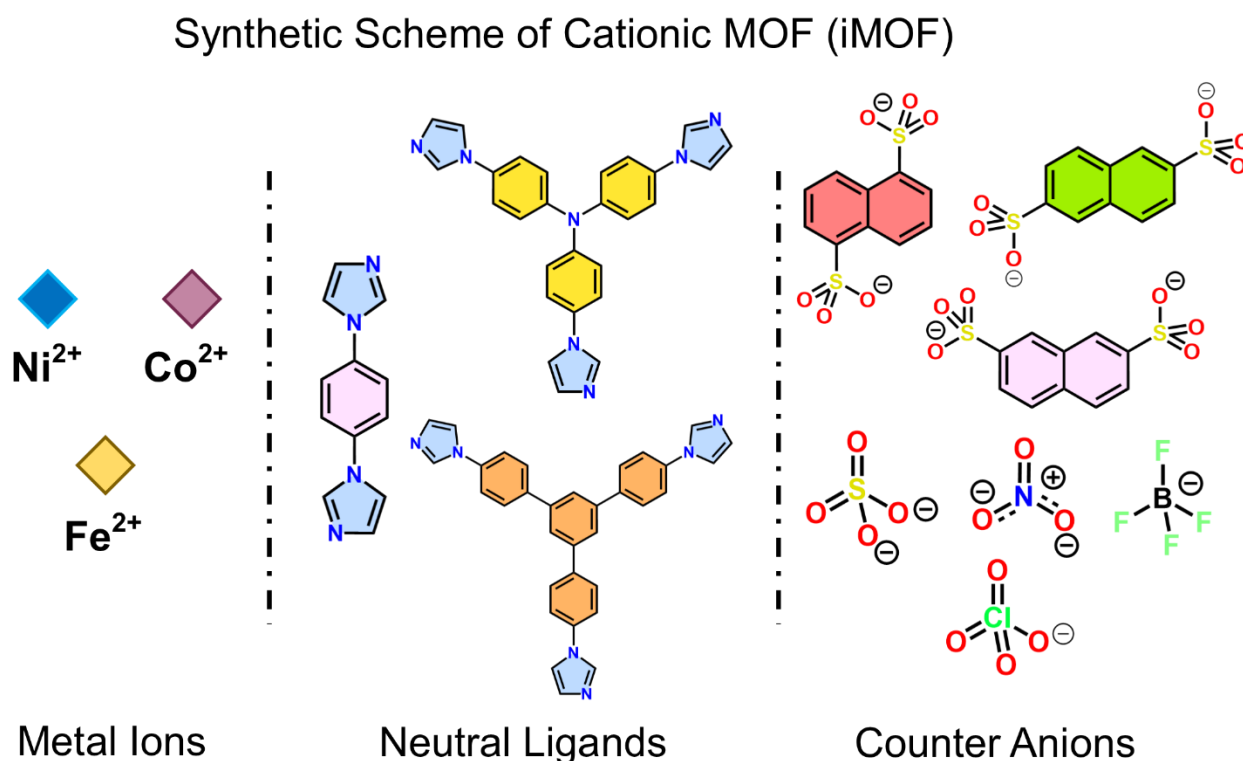


Figure 1.3. Synthetic Scheme of Cationic Metal Organic Framework

generations based on desolvation behavior, along with their functional versatility, underscores their adaptability for a broad range of scientific and technological applications.³⁰⁻³²

However, challenges such as stability and scalability continue to drive ongoing research in the field of MOFs. Efforts are directed towards enhancing their stability under various conditions and developing scalable synthesis methods to unlock their full potential for practical applications. As researchers delve deeper into the intricacies of MOFs, the possibilities for innovation and discovery in materials science seem boundless, positioning MOFs as a cornerstone in the quest for advanced materials with unprecedented properties and applications.

1.2.1.1.1. Cationic Metal Organic Frameworks (iMOFs)

Typically, ionic MOFs form due to presence of uncompensated framework charge and therefore necessitating extra framework ions either negative or positive to maintain the overall charge neutrality.³³⁻³⁵ On the basis of the residual charge of the framework backbone, ionic MOFs are classified into two, anionic and cationic MOFs. The framework backbone of cationic MOFs possesses a net positive charge which is counterbalanced by the uncoordinated anions present inside the pores. The counter anions typically remain free inside the porous channels of the framework or can coordinate to the metal center via weak

electrostatic interactions. In recent years, cationic MOFs have exhibited extraordinary potential toward applications like sensing, environmental pollutant capture, catalysis etc. Owing to its' several advantages such as pre-functionalized cationic framework backbone, uncoordinated polar functional anions inside the pores etc., cationic MOFs are regarded as the next generation anion exchange material for various environmental applications. Despite of such huge potential, exploration of cationic MOFs in the domain of industrial separation and aquatic remediation is at very nascent phase which is the one of the prime objects of this thesis work. Cationic MOFs can be synthesized either by pre-synthetic approach or by post-synthetic modifications of a secondary functionality in a neutral framework.³⁶⁻⁴³ The main design strategy of cationic MOFs is based on pre-synthetic ligand designing in which neutral N-heterocyclic donor moiety linked ligands are mainly utilized. Representative examples of such N-donor ligands are presented in Figure 1.3. In this regard, five-member terminal donating groups such as imidazole, triazole, pyrazole etc. are preferred owing to smaller size and stronger binding ability over the six membered heterocycles such as pyridine, pyrazine etc. The vicinity of the coordination sphere of the central metal will be strengthened by using such lesser bulky 5-membered N-heterocyclic moieties which can result into a higher density of the ligand moieties around the central metal centers, enabling hexa-coordination to the metal nodes and shielding from the influence of external species. Further, the coordination number of the particular metal ion gets satisfied by solely the functional ligands and the metal center gets covered by the high number of 5-membered rings, which acts as shield here from water molecules, imparting hydrolytic stability in the MOF. Another approach to synthesize cationic MOFs via pre-synthetic approach is to utilize cationic imidazolium moieties in the ligand backbone. Such ligands comprise of positively charged nitrogen atom which intrinsically impart cationic nature to the framework. Moreover, Carboxylic acid-based ligands are also employed to synthesize cationic MOF *via* pre-functionalization approach. In this method, the carboxylic acid ligands having nitrogen heteroatom (e.g. pyridine moiety) appended can be reacted with alkyl halide (R-X) moieties via nucleophilic substitution which yield in N-R⁺X⁻ moiety, having the halide (X⁻) anions uncoordinated inside the pores. On the other hand, post-synthetic modification (PSM) of neutral MOFs is another effective technique of synthesize cationic MOFs. For example, PSM-based approach can be employed for oxidation of metal centres such as Fe²⁺ to convert into oxidised metal centre Fe³⁺, which will result in a requirement of extra negative charge to balance the overall framework's charge. Oxidation of such MOFs can result in generation of cationic frameworks containing extra-framework anions to balance overall charge.

1.2.1.2. Metal Organic Gels (MOGs)

Metal-organic gels (MOGs) represent a cutting-edge class of materials that amalgamate the unique characteristics of metal-organic frameworks (MOFs) and soft materials like gels. These intriguing materials exhibit a gel-like consistency while incorporating the inherent porosity and structural features of MOFs.

MOGs are formed through the self-assembly of metal ions or clusters with organic ligands, resulting in a three-dimensional gel network.⁴⁴⁻⁴⁶ The gelation process involves the formation of a viscoelastic structure, typically induced by factors like temperature, solvent conditions, or pH. What distinguishes MOGs is their dual nature – the ability to retain the ordered porosity of MOFs while displaying the deformability and responsiveness typical of gels. This combination of attributes renders MOGs highly adaptable for various applications. The synthesis of MOGs involves carefully selecting metal ions and organic ligands to achieve the desired gelation behavior. The resulting gel-like structures can be tuned to have specific mechanical properties, making them suitable for applications ranging from drug delivery to sensing. The porous nature of MOGs opens up possibilities for controlled release of encapsulated substances, making them promising candidates for targeted drug delivery systems. Additionally, their responsiveness to external stimuli, such as changes in temperature or pH, can be harnessed for applications in sensors and actuators. MOGs also hold potential in environmental and catalytic applications, leveraging their porosity and gel-like nature for efficient adsorption and separation processes. The combination of structural versatility and soft, gel-like characteristics positions MOGs as multifunctional materials with broad implications across fields such as materials science, chemistry, and biotechnology.⁴⁴⁻⁴⁶ As research in this emerging field advances, the exploration of novel metal-organic gel systems and their innovative applications is expected to expand, unlocking new avenues for responsive and adaptable soft materials in diverse technological realms.

1.2.1.3. Metal Organic Polyhedra (MOPs)

The term metal-organic polyhedra (MOP) was first introduced in the early 21st century. Unlike, MOFs, metal-organic polyhedra (MOPs) stand out as a captivating and intricate class of coordination compounds that form three-dimensional structures resembling polyhedra through the coordination-assisted self-assembly of metal ions or clusters with organic ligands.³⁴⁻³⁷ These polyhedral assemblies exhibit a diverse range of architectures, from simple geometric shapes to more complex structures with multiple metal nodes and ligands. The synthesis of MOPs involves carefully orchestrated coordination interactions between metal centers and organic ligands, leading to the formation of well-defined polyhedral structures. The nature of the metal ions and ligands used in the synthesis imparts specific properties to the resulting MOP, including porosity, functionality, and reactivity. MOPs find applications in various fields, including gas storage, catalysis, and sensing, owing to their well-defined structures and tunable properties. Their geometric precision and potential for functionalization make them promising candidates for the design of advanced materials with tailored properties, contributing to the growing landscape of supramolecular chemistry and materials science.⁴⁷⁻⁵⁰ As researchers continue to explore the vast design

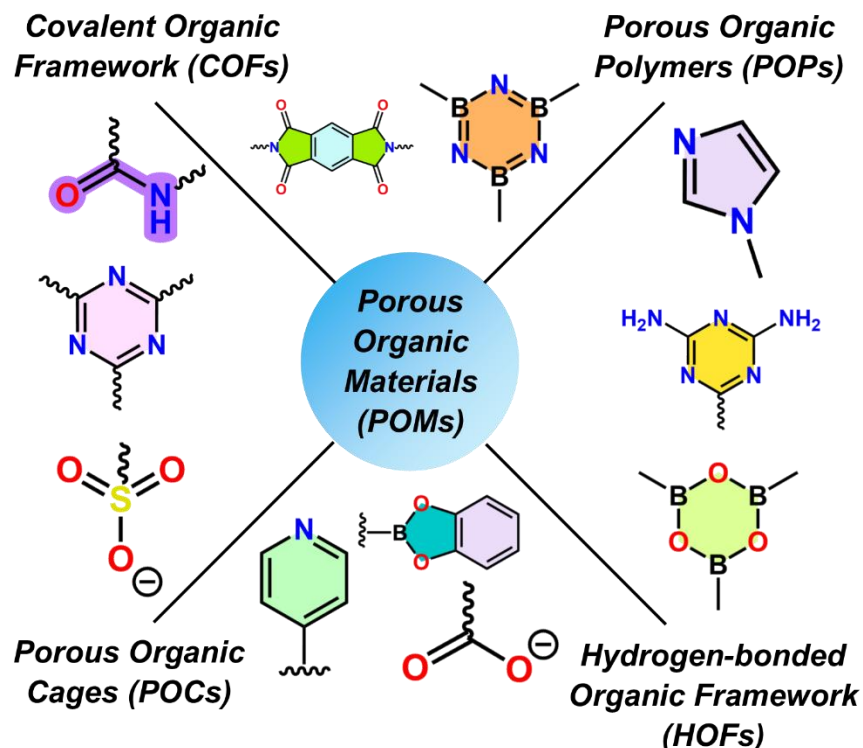


Figure 1.4. Classifications of Porous Organic Materials and Functionalization

space of MOPs and their applications, these structures hold promise for innovations in diverse technological and scientific domains.

1.2.2. Porous Organic Materials (POMs)

Porous organic materials (POMs) are distinct from other APMs (e.g., MOFs, MOP etc.) as they are crafted solely from purely organic constituents linked by strong covalent bonds. The metal free nature of these materials and abundance of lightweight carbon throughout the frameworks render them as low-density materials. There is a plethora of synthetic techniques available that can be used to create POMs which ultimately dictate the structural ordering of these framework materials. Consequently this leads to the development of crystalline POMs such as covalent-organic frameworks (COFs), porous organic cages (POCs) or hydrogen-bonded organic frameworks (HOFs) while amorphous POMs encompasses porous organic polymers (POPs), polymer of intrinsic microporosity (PIM) etc.⁵¹⁻⁵⁵ POMs are frequently cited as having a combination of both chemical and thermal stability, a vast array of organic functionalities, and extended pi-conjugated frameworks as their main advantages over other APMs materials (Figure 1.4).

1.2.2.1. Covalent Organic Framework (COFs)

Covalent Organic Frameworks (COFs) stand at the forefront of advanced porous materials, representing a unique class characterized by their crystalline structures and covalent bonds linking organic building blocks. COFs are meticulously designed and synthesized through the formation of robust, ordered networks, where the organic components are connected by strong covalent bonds, leading to a stable and porous framework. The modular nature of COFs allows for precise control over their pore size, shape, and functionality, offering unprecedented tunability.⁴⁵⁻⁴⁸ This characteristic tunability, coupled with their high surface area, positions COFs as versatile materials with applications across various domains. They find utility in gas storage, catalysis, sensing, and molecular separation due to their tailored porosity, allowing for selective adsorption and controlled release of molecules. COFs also exhibit promise in electronic and optoelectronic devices, as their crystalline structures facilitate charge transport. Additionally, the potential for functionalization and post-synthetic modifications enhances their adaptability for diverse applications, such as drug delivery systems and water purification.⁵⁶⁻⁵⁹ As research continues to unveil new synthetic strategies and further elucidate the structure-property relationships of COFs, these materials emerge as important contributors to the advancement of materials science, offering solutions to challenges in energy, environment, and technology.

1.2.2.2. Hydrogen-bonded Organic Framework (HOFs)

Another recently-emerging crystalline member of POMs is called HOFs. Hydrogen bonds and noncovalent interactions stabilize the organic building blocks that are primarily used to form HOFs.⁶⁰⁻⁶² HOFs are constructed from monomers containing an acceptor and donor moiety for hydrogen bonds.⁶³ HOFs are often constructed using functional groups including diaminotriazine (DAT), guanidinium-organo sulphonate moieties, carboxylic acid and amide-based moieties, and nitrogen heterocyclic moieties. The stability and management of hydrogen bonding during network propagation dictate the basic principle of HOF creation. Following the creation of HOFs with permanent porosity, the hydrogen bond assisted supramolecular architecture must continue to be stable in order to access the porous spaces formed following guest solvent removal. Together, these elements provide functional HOFs for applications including molecular identification and sustainable energy. Until now, gas molecule separation has made use of HOFs, particularly in the separation of hydrocarbons and carbon dioxide from nitrogen. Furthermore, HOFs have been employed for renewable energy applications like proton conduction and for the detection and encapsulation of different compounds like enzymes.

1.2.2.3. Porous Organic Polymer (POPs)

Porous organic polymers (POPs) are a broad family of amorphous APMs that are composed of polymeric structures to which functional organic moieties, including as heterocycles, macrocycles, and fused aromatic

systems, have been covalently attached. Among modern porous materials, POPs with benefits like huge surface area, on-demand tuneable pore surfaces, and ease of design and synthesis provide these covalently tethered porous materials a significant and practical advantage.⁶⁴⁻⁷⁰ Because of their structure with stronger covalent bonds, porous organic polymers show much better physiochemical stability than their congener MOFs. POPs include a broad range of materials, including conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), hyper crosslinked polymers (HCPs), and porous aromatic frameworks (PAFs). POPs are often seen to be primarily amorphous in form. Having said that, it should be noted that stability is a crucial need for their application in real time, and their strong nature and outstanding physiochemical stability make them perfect sorbent materials. "Performance property correlation" becomes more important than "structure-property correlation" in such applications, such as wastewater remediation.⁷¹⁻⁷² These organic porous compounds can be synthesized through a variety of organic reactions, both in solution and in the solid state, including Friedel Crafts reactions for HCPs, trimerization of nitrile functionalities for CTFs, and various kinds of organometallic cross-coupling reactions for PIMs, PAFs, and CMPs, such as Sonogashira-Hagihara coupling, Yamamoto coupling, and Suzuki coupling etc.⁷³⁻⁷⁵ The judicious choice of reactive functional synthons promotes the growth of infinite network structure. POPs can be two dimensional or three dimensional in nature depending on the composition of the

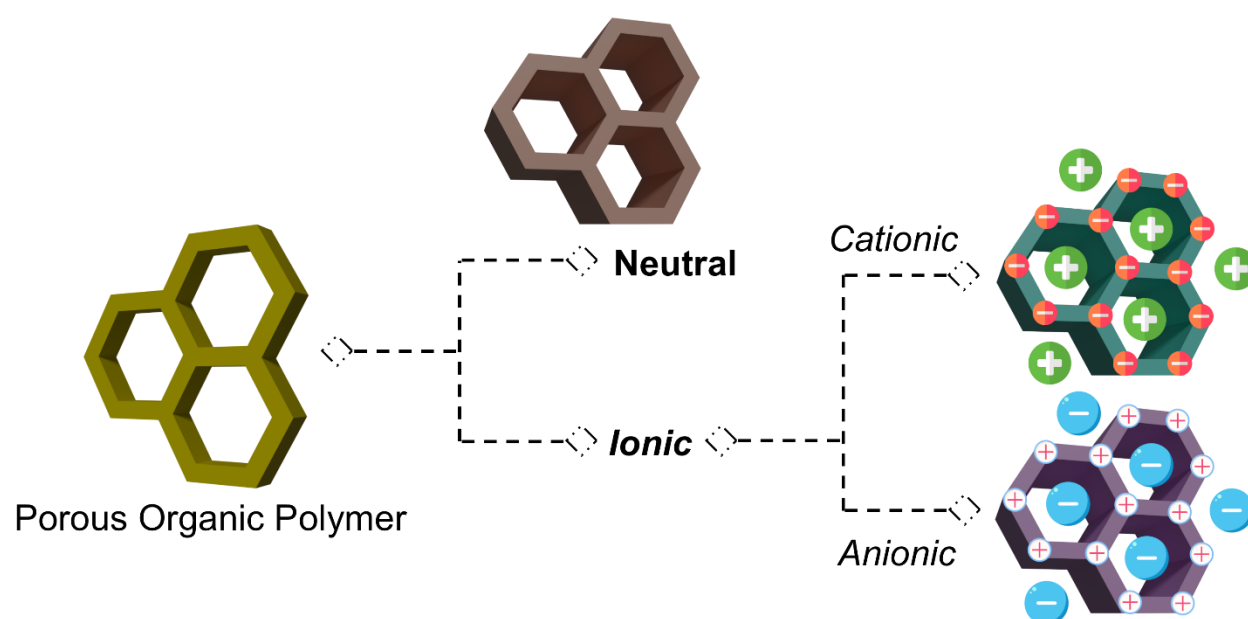


Figure 1.5. Classifications of Porous Organic Polymers

building blocks and the freedom of rotation of the hanging chemical bonds.⁷⁶ The main benefit of POPs is that they feature characteristics of both porous materials and organic polymers. While the polymeric backbones create rigid structural architectures, the presence of porous voids provides enough space for

host-guest interaction. This porosity of POPs can be tuned and optimized by varying the following aspects: the structure and shape of the monomers, the method of synthesis, and the reactivity of the constituents.⁷⁷⁻

⁷⁸ The concentration of the starting material, the volume of solvent and catalyst (if applicable), and the temperature can all have a little effect on the porosity of the POPs that are produced. POPs are known for their robust character, which relates to good durability in a range of hostile chemical conditions, and huge surface area, which accounts for outstanding porosity.

1.2.2.3.1. Ionic Porous Organic Polymer (iPOPs)

Alongside neutral POP networks, it is also possible to design and construct charged polymeric frameworks with free counter ions in these organic materials by meticulously selecting synthetic pathways and building blocks (Figure 1.5). Generally, there are two approaches to achieve the desired functionality and charge across the extensive networks of porous organic polymers: the pre-synthetic method and the post-synthetic modification (PSM) approach. The careful choice of molecular building blocks and synthetic pathways is essential in the pre-synthetic phase for introducing charged functionality within the porous network. Nonetheless, given that pre-synthetic functionalization of porous polymers can often be complex and not readily attainable, post-synthetic modification has emerged as a crucial strategy for developing task-specific porous organic polymers. It is crucial to note that post-synthesis structural engineering has emerged as a highly intriguing approach recently, allowing for the incorporation of desired functionality and electrostatic charge into the POPs for customized applications. However, ionic porous organic polymers (iPOPs), which constitute a subgroup of the extensive POP family, have been significantly less investigated and examined compared to their neutral counterparts.

1.3. Applications of Advanced Functional Porous Materials (AFPMs)

Advanced functional porous materials (AFPMs) have seen significant advancements over the past few decades, particularly in the refinement of synthetic strategies and precise control over morphology. Through the incorporation of tunable porous structures and specific functionalizations, these polymers can now be designed with high precision at the molecular level. Their preparation often involves copolymerization with multifunctional monomers, as well as post-synthetic modification to introduce desired properties. As a result, AFPMs are emerging as versatile materials with broad potential applications, including gas storage, catalysis, water purification, molecular separation, chemical sensing, and drug delivery (Figure-1.6). Due to their adaptable physical and chemical properties, Advanced functional porous materials, such as their efficacy in gas storage (e.g., hydrogen and methane) and selective separation of gases like carbon dioxide. Furthermore, the tunability of AFPM porosity allows for the maximization of accessible surface area, enhancing physisorption processes. To exploit stronger chemisorption interactions between guest

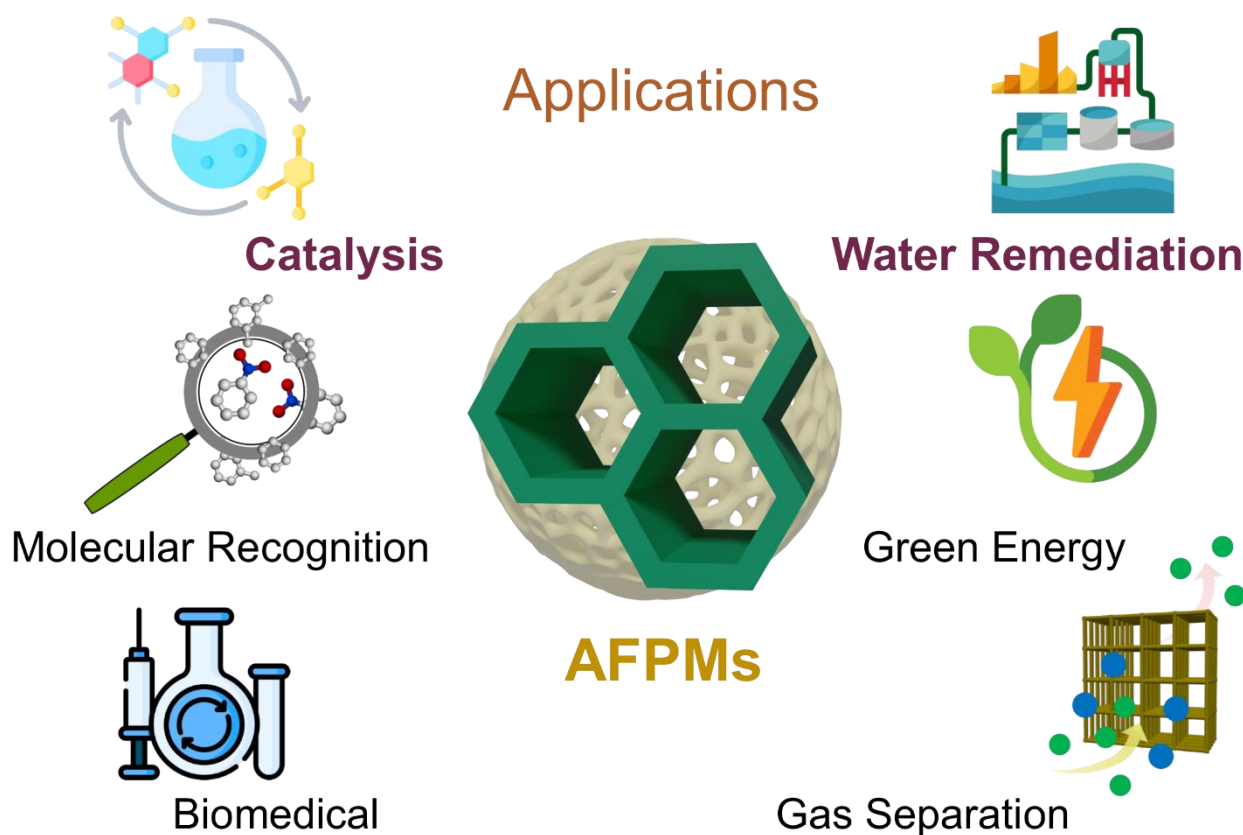


Figure 1.6. Applications of Advanced Functional Porous Materials (AFPMs)

molecules and the polymer matrix, the internal pore environment can be further tailored by functionalizing the pore walls, leading to improved gas adsorption capabilities. AFPMs also serve as robust support matrices for heterogeneous catalysis due to their structural stability, excellent reusability, and large pore sizes, which facilitate the incorporation of catalytically active molecules, making them highly suitable for catalytic applications. The uniform, spatially isolated distribution and high density of catalytically active sites within Advanced functional porous materials (AFPMs) make them highly promising candidates for heterogeneous catalysis. The incorporation of hydrophilic or hydrophobic functional groups within the porous structure facilitates the diffusion of a wide range of guest molecules, enhancing the polymers' efficiency in molecular recognition processes. This functionality enables AFPMs to be highly effective in applications such as molecular separation, toxic analyte sensing, and the selective capture of target molecules from both aqueous and organic media. Furthermore, the extended conjugation present within the rigid backbones enhances the photophysical properties of APMSs, making them suitable for light-harvesting and other photoactive applications. The deliberate introduction of specific functional groups further broadens the utility of these materials, particularly in various electrochemical processes, by enhancing their performance in energy-related and catalytic applications.

1.4. Heterogenous Catalysis by AFPMs

Catalysis is indispensable to modern life, serving as a foundational technology across various essential processes. Heterogeneous catalysis, in particular, is favored due to its ease of separation from reaction products, operational simplicity, reduced catalyst cost, and suitability for continuous flow systems. A current trend in catalysis involves the immobilization of homogeneous catalysts onto heterogeneous supports, aiming to combine the chemical specificity of homogeneous catalysts with the practical advantages of heterogeneous systems (Figure 1.7). However, this approach presents several challenges, including reduced catalytic efficiency, instability, and increased cost, which hinder the large-scale industrial use of immobilized molecular catalysts. The decline in catalytic efficiency can often be attributed to limited accessibility of the active sites and alterations in the chemical microenvironment upon immobilization. Moreover, this process frequently necessitates pre-functionalization of either the catalyst precursor or the support matrix, which typically involves labor-intensive, multi-step synthetic procedures. The complexity and expense of such catalysts further reduce the economic viability of heterogenized homogeneous systems in chemical synthesis.

Given these constraints, the strategy of catalyst immobilization must be approached with care. It is essential that the chosen method is not only synthetically accessible and cost-effective but also retains high catalytic activity and design flexibility. Additionally, the anchoring of active catalysts onto solid supports should maintain or even enhance the overall stability of the system, ensuring that catalytic efficiency remains uncompromised. Fortunately, advancements in materials chemistry continue to provide alternative approaches to address these issues, offering potential pathways to optimize catalyst design and performance.⁷⁹⁻⁸² In this context, Advanced functional porous materials (AFPMs) have attracted considerable interest owing to their appealing characteristics and straightforward synthesis process. The significant characteristics, including a large specific surface area, high physicochemical stability, adjustable pore size, and the ability for surface modification, along with scalable synthesis, have positioned AFPMs as a central topic of interest in heterogeneous catalysis. Nonetheless, a significant drawback of polymer-supported heterogeneous catalysts is their expense of monomers. The significant costs primarily stem from labor-intensive synthetic methods, especially in the post-immobilization phase, along with frequently inadequate catalyst loadings that lead to diminished catalytic efficiency. The bottom-up synthetic approach for AFPMs presents a more efficient and streamlined pathway for the development of heterogeneous catalysts.⁸³⁻⁸⁶ This approach enables the integration of substantial catalyst loadings, increased surface area, and superior catalytic efficiency. This enables the development of robust, task-oriented polymeric structures with a high concentration of catalytically active sites. Moreover, the reusability of AFPMs presents a compelling approach

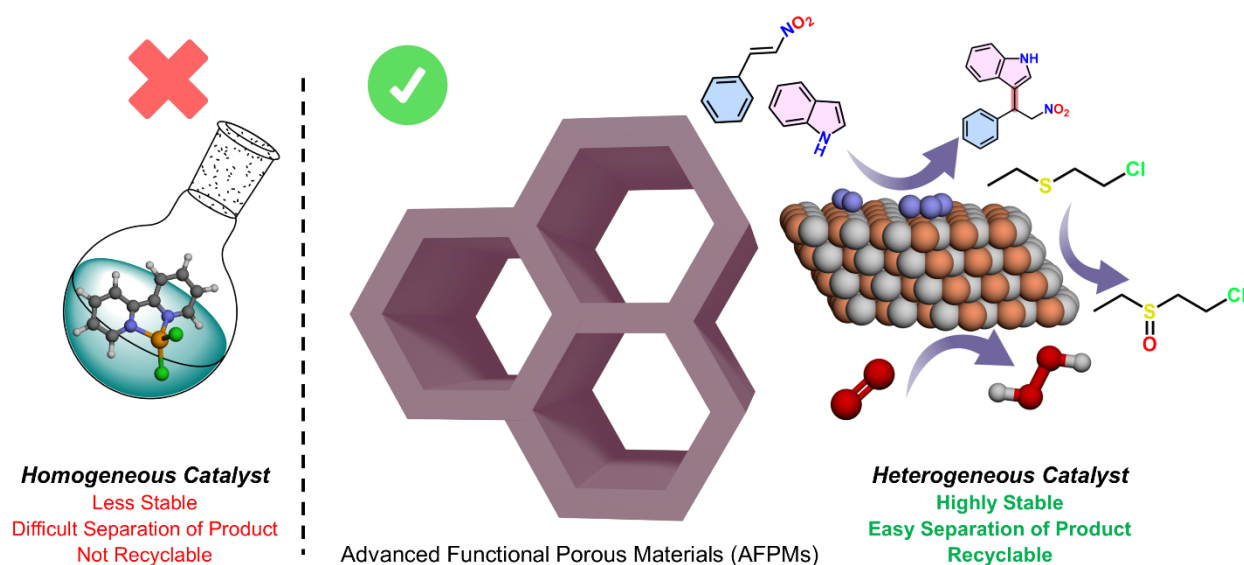


Figure 1.7. Catalytic Applications of Advanced Functional Porous Materials (AFPMs)

to addressing the enduring challenge of cost efficiency in solid catalysts. Bottom-up strategies offer the ability to customize the porous structures and surface chemistry of AFPMs to fulfill particular catalytic needs, facilitating the creation of function-oriented frameworks that exhibit a variety of functionalities for catalytic uses. The elevated specific surface area, precisely defined pore surfaces, and meticulously engineered frameworks of AFPMs render them exceptionally advantageous for heterogeneous catalysis. Nonetheless, even with advancements in the design and synthesis of AFPM-based solid reagent catalysts, numerous challenges persist, including intricate synthetic pathways, reliance on hazardous solvents, and the requirement for elevated operating temperatures, all of which hinder their alignment with environmentally friendly chemistry principles. Consequently, creating effective AFPM-based heterogeneous catalysts that can facilitate organic transformations under mild conditions while utilizing environmentally friendly solvents is of utmost significance. Tuning of different functional group into the framework, can bring photo and redox activity to AFPMs, which also helps to photo and electrocatalytic energy conversion under very mild and green condition.⁸⁷⁻⁸⁹ Furthermore, the synthetic methods for these catalysts should be simple and capable of being scaled up effectively. The design rationale in this thesis is built upon these considerations, emphasizing the creation of effective, eco-friendly AFPM catalysts aimed at achieving sustainable chemical transformations (Figure-1.8).

The use of AFPMs in organocatalysis exemplifies a flexible and eco-friendly method in catalysis, utilizing the unique structural characteristics of these materials. AFPMs demonstrate significant surface areas, adjustable pore dimensions, and customizable frameworks, allowing for the integration of various catalytic active sites. The characteristics enable improved reactivity, selectivity, and recyclability in heterogeneous

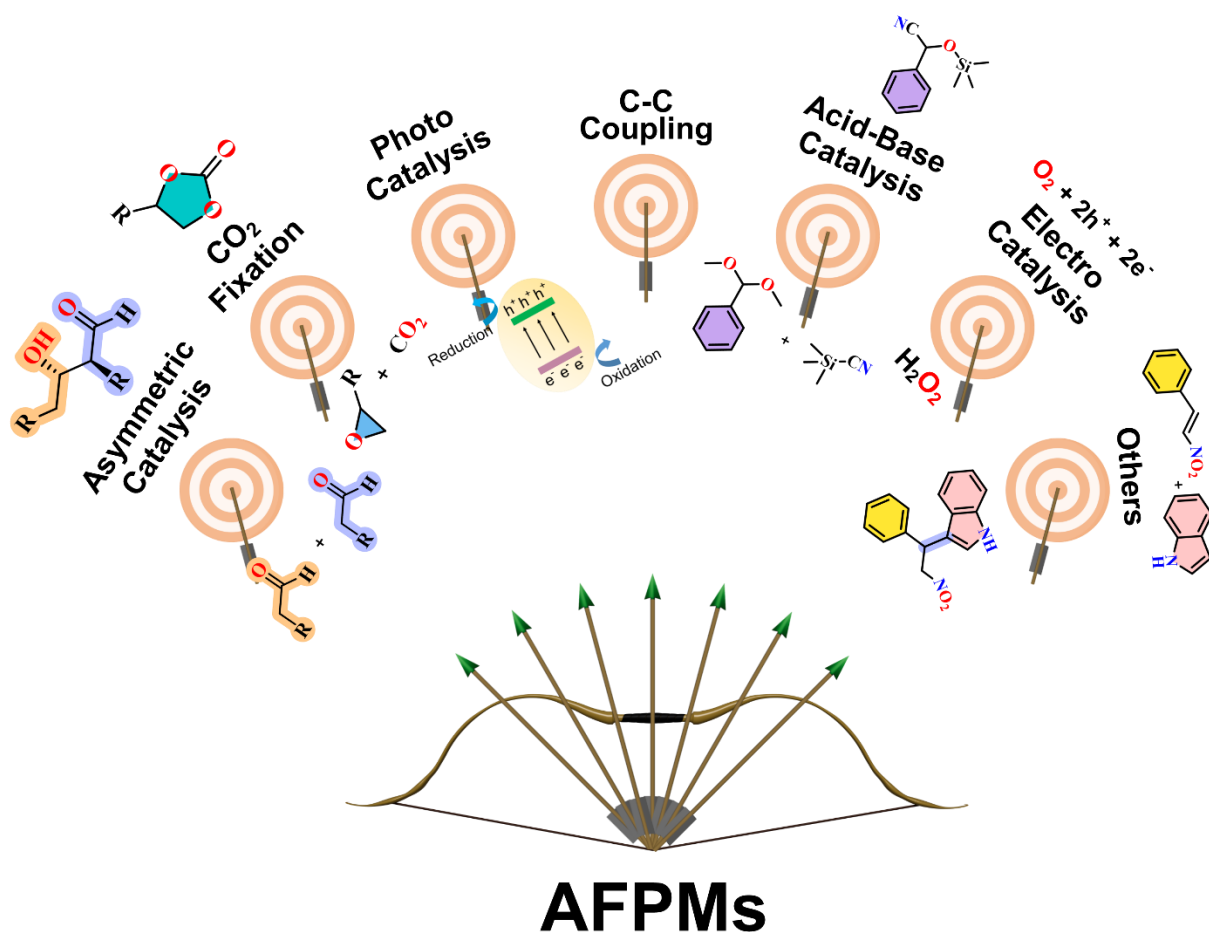


Figure 1.8. Different Types of Catalysis by AFPMs

catalysis. AFPMs have been utilized in numerous organocatalytic transformations, including carbon-carbon bond formation, asymmetric synthesis, oxidation and reduction reactions, as well as photocatalytic processes. The unique benefits of AFPMs, such as their stability, modularity, and ease of recovery, make them highly effective instruments for a variety of catalytic applications in both green and industrial chemistry.

Surface Area and Pore Volume:

High surface areas (often >1000 m²/g) and tunable pore volumes are critical for facilitating substrate accessibility to catalytic sites, thereby enhancing the overall reaction rate. In catalytic applications such as C–C coupling reactions,⁹⁰ Chiral reaction,^{91, 92, 93, 94, 95} and oxidative processes, larger surface areas enable higher turnover frequencies.

Pore Size Distribution:

Tunable mesoporous (2–50 nm) and microporous (<2 nm) structures within POPs can be optimized to accommodate a wide range of substrates. For example, larger pore sizes are beneficial in catalyzing reactions with bulky substrates, such as in the Diels–Alder reaction or asymmetric catalysis, while micropores are ideal for gas-phase reactions like CO₂ fixation^{96, 97, 98, 99} or hydrogenation.

Functional Group Density:

The loading and distribution of catalytically active sites, such as organocatalysts (e.g., amines, imidazoles, thioureas), metal-free catalytic centers, or redox-active sites, are vital for catalytic efficiency. High functional group density enhances reactivity, particularly in catalytic systems like Michael addition or aldol reactions, where strong nucleophilicity or electrophilicity is required.

Thermal and Chemical Stability:

POPs display excellent thermal and chemical stability under harsh reaction conditions, such as elevated temperatures and extreme pH. This stability makes them suitable for applications in oxidative catalysis (e.g., alcohol oxidations) and challenging environments (e.g., acid-catalyzed esterifications or hydrolysis).

Catalyst Recyclability and Longevity:

A major advantage of POP-based catalysts is their ability to be recycled and reused without significant loss of activity. This is particularly important in large-scale industrial applications, such as in Friedel–Crafts reactions or polymerization processes, where cost-effective catalyst recovery is essential. The stability of POPs ensures their catalytic performance is retained across multiple cycles.

Diffusion Kinetics:

The diffusion of reactants and products through the porous network can significantly affect the catalytic performance. Optimizing the polymer structure to minimize diffusion limitations is critical in reactions involving larger molecules, such as in enantioselective catalysis and tandem reactions, where multiple steps occur within the same catalytic site.

Photocatalytic Applications:

POPs, when functionalized with photosensitizers or light-absorbing moieties, can facilitate light-driven catalytic reactions. This includes the photocatalytic H₂O₂ production,^{100, 101, 102, 103, 104, 105} degradation of pollutants, CO₂ reduction, and water-splitting reactions. The porous architecture allows for efficient light penetration and maximizes interactions between the photosensitizer and the substrate.

Environmentally Benign Catalysis:

POP-based organocatalysts often enable reactions under mild conditions, reducing the need for hazardous solvents and reagents. For example, they have been employed in asymmetric organocatalysis for pharmaceutical synthesis, CO₂ capture and conversion into value-added products, and biocatalytic transformations in aqueous media, supporting green chemistry principles.

1.5. Water Pollutants Remediation by AFPMs

Water is an indispensable resource for all living organisms, and the United Nations (UN) projects that global water consumption will increase by 20-55% by 2050.¹⁰⁶ Concurrently, the rise in environmental pollution has emerged as a critical global issue, necessitating urgent attention toward pollutant remediation.¹⁰⁷⁻¹⁰⁸ The rapid growth in the world population, coupled with increased energy and resource consumption, poses a significant threat to the sustainability of life for future generations. Among various forms of environmental degradation, water pollution has become a primary concern. The increasing contamination of freshwater sources and the excessive use of water are exerting detrimental effects on Earth's aquatic ecosystems. Notably, wastewater effluents from diverse industries, along with radioactive waste from nuclear power plants,

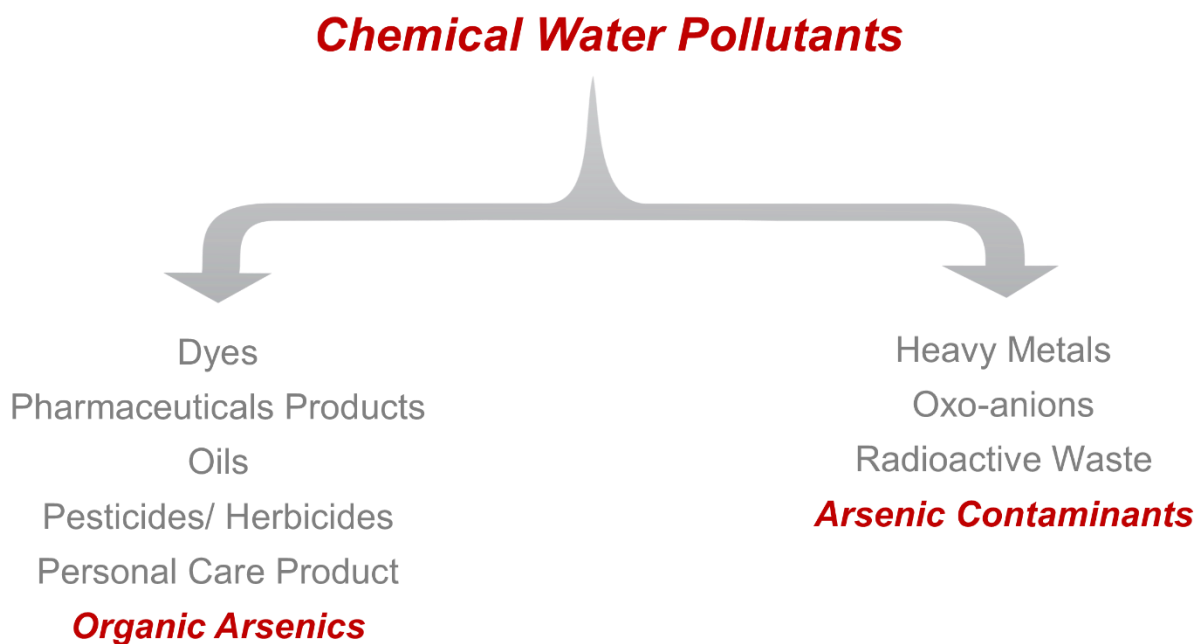


Figure 1.9. Different Types of Water Pollutants

represent major contributors to water pollution. Globally, nearly 2 million people die annually from waterborne diseases such as diarrhea and infections related to poor hygiene, primarily caused by widespread water contamination. According to the Safe Drinking Water Act (SDWA), water pollutants encompass a

wide range of chemical, physical, and biological substances that compromise water quality.¹⁰⁹ Water pollution is generally classified into several categories, including physical, chemical, and pathogen-related pollution, each having significant environmental and health impacts. Among these, chemical water pollution, caused by the release of toxic and hazardous chemical species, is one of the most severe and life-threatening threats to living organisms. Chemical pollutants in water are broadly categorized into organic and inorganic contaminants. Organic pollutants include a diverse range of compounds such as synthetic dyes, personal care products, polyaromatic hydrocarbons, herbicides, pesticides, oils, detergents, and pharmaceutical substances. These pollutants primarily originate from industrial processes, domestic activities, agriculture, and related sectors. Inorganic contaminants (Figure-1.9), on the other hand, encompass toxic metal cations such as mercury (Hg^{2+}), cadmium (Cd^{2+}), and lead (Pb^{2+}), as well as radionuclides like uranium (UO_2^{2+}), strontium (Sr^{2+}), and cesium (Cs^+). Additionally, heavy metal oxo-anions, such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), arsenate (AsO_4^{3-}), and various radioactive anions like pertechnetate ($^{99}\text{TcO}_4^-$),¹¹⁰⁻¹¹³ contribute significantly to water contamination. Many of these substances are listed as "priority pollutants" by the United States Environmental Protection Agency (US EPA). In comparison to organic pollutants, inorganic contaminants persist much longer in the environment, rendering them highly toxic and challenging to remediate. Their resistance to degradation and the difficulty of converting them into non-toxic species exacerbate the environmental risks they pose. Both organic and inorganic pollutants are often carcinogenic and pose severe ecological and public health hazards. Consequently, the safe disposal and management of these pollutants are of paramount scientific interest, as their persistent presence threatens ecological balance and the well-being of ecosystems.

1.5.1. Organic Arsenic as Water Pollutants

The ongoing increase in water pollution has emerged as a pressing threat to the global population and has spurred extensive research efforts worldwide. Arsenic (As), recognized as a "class A" carcinogen to all forms of life, presents a direct threat to the global environment in cases of contamination. Long-term exposure to arsenic can result in the development of arsenic poisoning, which may lead to neurological disorders, cancer, cardiovascular disease, skin lesions, and even death in infants. Three individuals have made significant contributions to the detection and removal of arsenic from the environment. Despite this, most of these studies have focused on inorganic arsenic, while its organic counterpart has received comparatively less attention. Four Organic arsenic acids (OAAs) have demonstrated significant utility in the poultry industry as effective feed additives for promoting weight gain, managing intestinal parasites, preventing dysentery, and serving as antibacterial agents over the years. The widespread application of these organoarsenics inevitably leads to associated damage to the ecological environment. Furthermore, the introduction of these water-soluble organic arsenic compounds into the surrounding environment can lead

to both abiotic and biotic processes that facilitate biogeochemical transformation. This results in the conversion into highly mobile and toxic inorganic arsenite (As [III]) and arsenate (As [V]), which increases the presence of inorganic arsenic compounds in the habitat, thereby contaminating soil and groundwater and posing a threat to human health. Roxarsone (4-Hydroxy-3-nitrophenyl arsonic acid, known as ROX) serves as a prominent example of aromatic organoarsenicals, which are produced in large quantities and widely used as additives in poultry feed. Seven Over the past years, there has been a notable rise in the amount of ROX utilized in feed additives. Nevertheless, the significant quantity of ingested ROX in animals is minimally absorbed in tissues and is excreted with manure, resulting in arsenic concentrations that can reach up to 1000 $\mu\text{g/kg}$, which greatly exceeds the 0.5 ppm safety limit established by the World Health Organization (WHO). Therefore, it is essential to isolate and separate soluble ROX prior to its transformation into more dangerous and highly toxic inorganic arsenic.¹¹⁴⁻¹²⁰

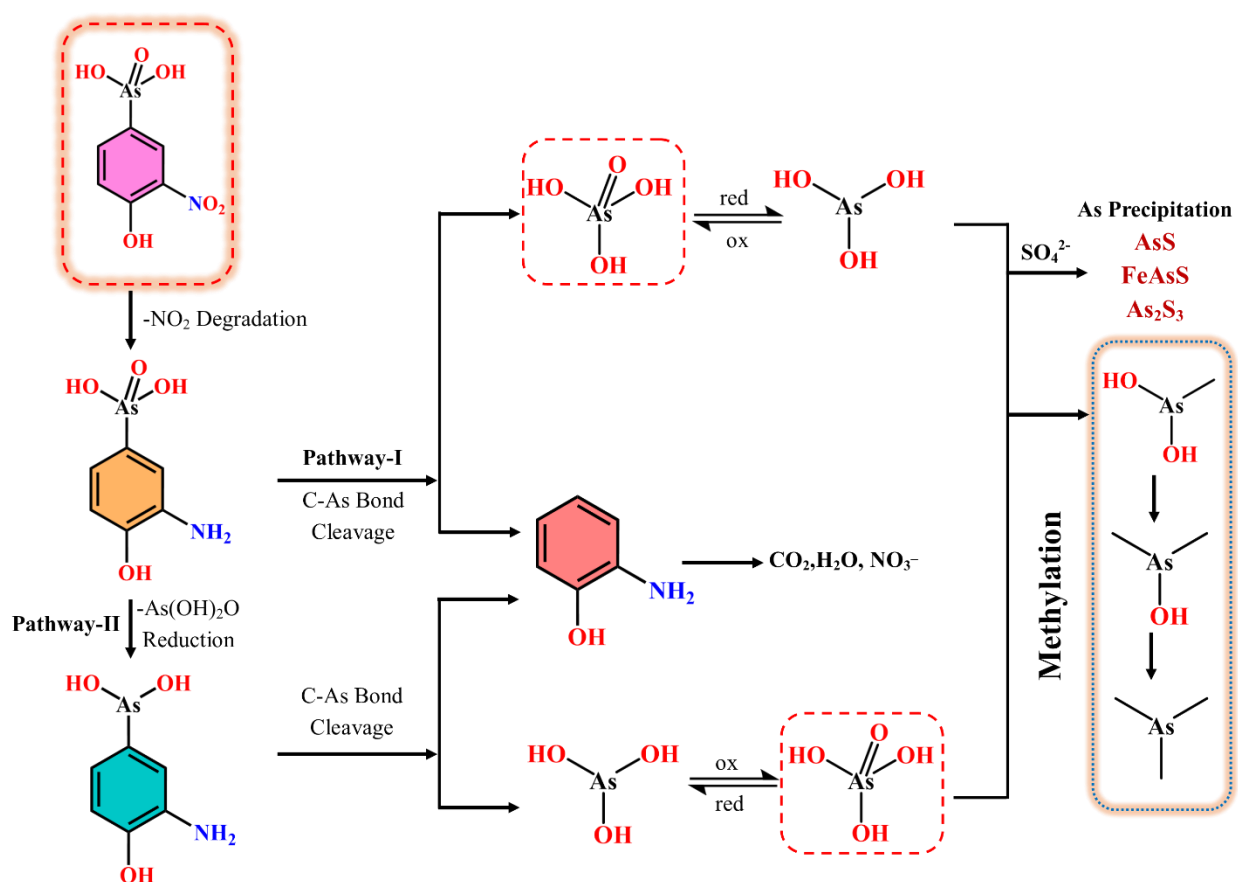


Figure 1.10. Microbial transformation pathway of ROX under anaerobic conditions. (Ref 121)

Access to clean, potable water is fundamental for survival, making the recycling and purification of water a crucial strategy for mitigating water pollution. In this regard, the efficient sequestration of toxic water contaminants stands as a top-tier scientific challenge requiring immediate attention. For the successful

removal of water pollutants, two key factors must be considered: first, the employed methods must be straightforward, highly potent, and capable of rapidly and efficiently targeting specific analytes. Second, the materials used must demonstrate long-term stability and durability in aqueous environments, while maintaining high selectivity for the targeted contaminants. Among various approaches, adsorption-based pollutant trapping presents a particularly effective and cost-efficient alternative to traditional methods such as membrane filtration, sedimentation, coagulation, and precipitation for the selective removal of toxic water pollutants.¹¹⁴⁻¹¹⁵ Consequently, the development of high-performance adsorbent materials has become a pressing research priority. Current materials used for adsorption, including zeolites, inorganic clays, activated carbons (AC), layered double hydroxides (LDHs), and resins, often fall short in terms of selectivity, capacity, and adsorption kinetics.¹¹⁶

In this context, advanced functional porous materials (AFPMs) have emerged as promising candidates for addressing water pollution. AFPMs combine the advantages of advanced porous materials like metal-organic frameworks (MOFs) with the benefits of traditional adsorbents. Being composed entirely of organic units linked through robust covalent bonds, AFPMs offer exceptional tunability and can be chemically functionalized to meet specific needs. Recently, ion-exchange-based sorbent materials, which operate through electrostatically driven adsorption mechanisms, have shown considerable promise in the detoxification of water by selectively adsorbing toxic pollutants. Despite these advancements, the development and large-scale application of such materials for wastewater remediation are still in the early stages. This thesis aims to build upon this opportunity by focusing on the rational design of task-specific ionic metal-organic framework (iMOFs) and ionic porous organic polymers (iPOPs), with the goal of accelerating their potential for highly selective and efficient sequestration of water contaminants. By leveraging the unique properties of iAFPMs, this work seeks to advance the field of water purification through innovative material design.

1.6. Thesis Overview

The main focus that comes under the purview of the present thesis work primarily revolves around the design and syntheses of task-specific advanced functional porous materials (AFPMs) including cationic metal-organic framework (iMOFs) and ionic porous organic polymers (iPOPs) as well their composites aimed at eco-friendly heterogeneous catalysis and potent water remediation applications. Function-led design of task-specific AFPMs was achieved by investigating some key design parameters such as judicious choice of suitable monomers, strategic post-polymerization structure modulation to impart desired charge & functionalities toward target-specific applications. Leveraging on the molecular level control that AFPMs can offer, tailor made “nanospace” both in terms of porosity, electrostatics and desired chemical functionalities was realized in all the scientific works presented in the current thesis. The overall thesis has

two sections each of which is further sub-divided into two chapters. The first part of the thesis work describes AFPMs being used strategically as the ideal support matrix to generate superior heterogeneous organocatalyst and photocatalyst. Following this, the second part focuses on development & investigation of AFPMs to combat water pollution, a pressing global problem that calls for immediate mitigation

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Part - I

Function-led Design and Syntheses of Porous Organic Polymers as Sustainable Heterogeneous Catalyst

Contemporary existence is inconceivable without catalysis and has become essential to our fundamental necessities for survival. The rapid expansion of the global economy and the continuously growing population necessitate the urgent establishment of a highly efficient and sustainable chemical industry using environmentally friendly methods of chemical and the sustainable energy conversion. One approach to meet this goal is to create innovative catalysts that demonstrate high efficiency in terms of product yield, selectivity and atom economy, therefore reducing the associated costs.¹ The underlying design principle for catalyst development is to create materials with uniformly exposed active sites to facilitate selective reactions and get the desired result. Unlike its homogeneous sibling, although having more active sites, historically, more trial-and-error experimentation has been required to develop different catalysts. Nevertheless, they frequently exhibit significant benefits compared to homogeneous catalysts, including ease of separation, recyclability, and sustainability.^{2,3} Towards this particular path, Advanced Functional Porous Materials (AFPMs) have been discovered to possess catalytic potential as optimal substrates for metal nanoparticles or complexes, as well as metal-free organocatalysts.^{4,5} Due to their intrinsic durability and exceptional porosity, AFPMs are highly appealing as heterogeneous catalysts. Furthermore, the simple ability to include ligands into the structures of AFPMs enables the practicality of developing catalysts with a single atom. AFPMs consisting of clearly defined isolated active catalytic centers serves as the connection between homogeneous and heterogeneous materials. The development of AFPMs-based heterogeneous catalysts to facilitate organic transformations and photocatalytic O_2 into H_2O_2 under moderate and environmentally acceptable conditions is of great significance from the standpoint of green chemistry and energy requirements.⁶ Nevertheless, the catalysts that have been created often need elevated reaction temperatures or the use of hazardous organic solvents. Through the careful selection of monomers and smart post-synthesis engineering, it is possible to produce highly effective heterogeneous catalysts for chemical transformations and energy conversion under environmentally benign reaction circumstances.

This section contains two chapters, i.e. chapter 2 and chapter 3. In chapter 2, a urea functionalized porous organic polymer was synthesized containing Urea moiety, act as a H-bond donating site with pyrimidine backbone, act as a basic site to drive Friedel-Craft alkylation and Michael-Knoevenagel condensation under flow condition. In chapter 3, halide ion tuning in an imidazoline porous organic polymer was synthesized towards photocatalytic H_2O_2 production under sunlight and air from sea water.

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Chapter 2

Urea Tethered Porous Organic Polymer (POP) as Efficient Heterogeneous Catalyst for Hydrogen-Bond Donating Organocatalysis and Continuous Flow Reaction

2.1. Introduction

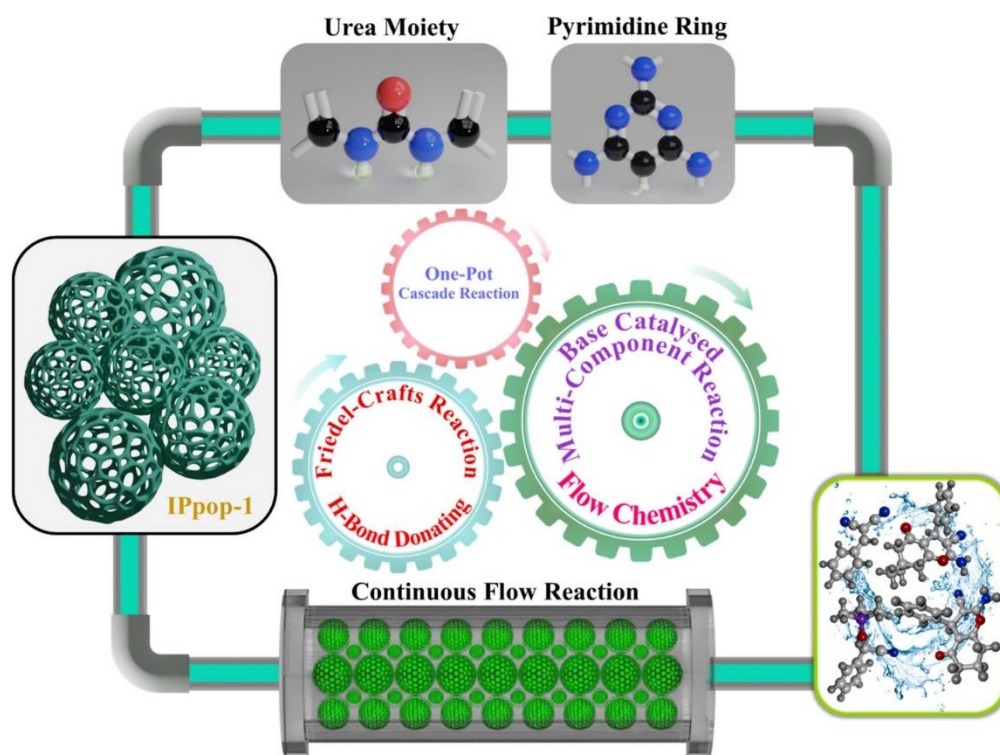
Chemical reactions often necessitate additional energy input to surmount the barriers to activation energy. Apropos of that, introduction of a suitable catalyst enables accelerated chemical conversion under milder conditions through bypassing these energy barriers. Modern human life has become unimaginable beyond catalysis, a technology central to our fundamental requirements of livelihood.¹ Over the years, homogeneous catalysts have emerged showcasing their excellent activity and selectivity in numerous chemical reactions. Having said that, obvious pitfalls such as complex recyclability issue, costly nature, as well as tedious purification and isolation of desired products (particularly in pharmaceutical synthesis) have largely thwarted their advancement both in chemical industry and academia.² To combat these impediments, efforts have been put forward worldwide toward developing efficient heterogeneous catalysts that offer facile recyclability along with designable and easily accessible active sites.³⁻⁷ Along this line, diverse porous architectures such as zeolites,^{8,9} mesoporous silica,¹⁰ metal-organic frameworks,¹¹ covalent organic frameworks^{12,13} as well as porous organic polymers (POPs)¹⁴⁻¹⁸ have surfaced as a competent solid support matrix in heterogeneous catalysis. Among them, POPs have shown tremendous potency in the field of heterogeneous catalysis providing leverage with their following unique features: (1) Akin to its homogeneous counterparts, POPs allow easy integration of diverse task-specific functional groups with their synthetic tunability.^{19,20} (2) Their insoluble and robust nature offer easy regeneration, while wettability of POPs can be engineered conveniently, enabling enhanced mass transfer to boost catalytic performance.²¹ (3) Harnessing confinement at the nanoscale with regard to space as well as electronic characteristics aid in yielding better activity in terms of yield and product selectivity.²² Additionally, framework stability, high permanent porosity, and function-led designability advocate POPs to be a fitting material as innovative heterogeneous catalysts.^{23,24}

Pertaining to the critical role of H-bonding in multifarious natural processes, hydrogen bond donating (HBD) organocatalysis has emerged as a potent biomimetic surrogate to enzyme catalysis in the past decade.²⁵⁻²⁷ Among various reported HBD catalysts that can mimic biological machinery, urea as well as thiourea groups as the key functional moiety have dominated this research area.²⁸⁻³¹ The rationale behind this can be correlated with their ability for two-point hydrogen bonding via acidic N-H bonds. Plentiful bond-forming reactions [e.g., Friedel-Crafts (FC) reactions,³² Diels-Alder reactions,³³ Mannich reactions,³⁴ Claisen rearrangements,³⁵⁻³⁷ Strecker reactions,³⁸ etc.] have been shown to be efficiently catalyzed by several homogeneous HBD catalysts.

Howbeit, the competency of urea-based homogeneous HBD catalysts in terms of H-bond donors is predominantly attenuated owing to their self-association through intermolecular H-bonding, resulting in declining substrate-catalyst recognition, leading to quenched catalytic activity.³⁹⁻⁴³ To this end, strategic

fabrication of materials that can bypass the bottleneck of this malign self-association that aids in substrate recognition toward “turned-on” catalytic efficiency is of utmost necessity.

Building on this perspective, we envisioned that anchoring HBD catalytic sites inside the nanospace of a porous polymer could emerge as a promising route for fabricating enzymeregiscent superior heterogeneous catalysts. Along this line, in the present work, we report the simple and easy fabrication of a porous urea network-based heterogeneous composite catalyst illustrating excellent catalytic potency toward the ecofriendly HBD FC reaction between indole and β -nitrostyrene. Additionally, owing to the presence of bifunctional catalytic sites, IPpop-1 displayed excellent performance toward basecatalyzed multicomponent reaction along with cyanosilylation (acid-catalyzed), as well as one-pot cascade catalysis advocating its versatile nature as a heterogeneous catalyst. The practical applicability and potency of the polymer catalyst were also established from its competence in continuous flow catalysis toward multicomponent Knoevenagel-Michael Condensation (Scheme 2.1). Furthermore, the catalytic competency of IPpop-1 featuring substrate scope, recyclability in combination with scalability, and practicality by virtue of constructing microstructure composite beads without compromised catalytic activity was also established.



Scheme 2.1: Schematic Illustration of Multifunction Catalytic Sites, Multifunctional Activity, and Multicomponent Flow Catalysis of by IPpop-1.

2.2. Experimental

2.2.1. Materials

Starting materials, 1, 5-diisocyanatonaphthalene and 2, 4, 6- triaminopyrimidine were purchased from Tokyo Chemical Industry (TCI India). DMF, THF, Methanol, Ethanol and remaining solvents were obtained locally. These chemicals were used without further purification.

2.2.2. Synthesis

2.2.2.1. Synthesis of IPpop-1: In a 100 mL two-neck round bottom flask, 2,4,6- triaminopyrimidine (2 mM, 500 mg) and 1,5-diisocyanatonaphthalene (6 mM, 1.26 g) was added under N₂ atmosphere. To it 30 mL anhydrous N, N-Dimethylformamide was added and stirred until all substrate were dissolved. Then the R.B. Flask containing reaction mixture was placed into oil bath of temperature of 120 °C for 48 hours. On completion of reaction, the precipitate was filtered and washed with DMSO, DMF, THF, 1,4-Dioxane, Chloroform and Methanol repeatedly. Thus, obtained solid material was subject to Soxhlet extraction in methanol for 24h to remove the high boiling solvent from the porous network of IPpop-1. This solvent exchanged phase was heated at 130 °C under vacuum overnight to obtain the guest free desolvated phase for further works.¹

2.2.2.2. Synthesis of Composite Bead: The IPpop-1 composite bead was prepared by reported protocol with slight modification. Generally, 50 mg of IPpop-1 was dispersed in 1 mL of 20 mg/mL sodium alginate aqueous solution under stirring. Meanwhile, the curing solution was prepared by dissolving 188 mg of anhydrous calcium chloride in 30 mL of polyacrylic acid aqueous solution (108 mg in 30 mL H₂O). Next, the alginate suspension was dropped by 1000 microlit pipette tip into the curing solution. After shaping, the beads were collected and washed with distilled water for several times. Followed by a freeze-drying step, the spherical IPpop-1 beads were obtained.

2.2.3. Methods

2.2.3.1. IPpop-1 Catalyzed Friedel-Craft Alkylation: To a 15 mL screw cap glass drum vial, β -nitrostyrene (0.1 mM, 1 equiv.) and Nheterocycles (0.15 mM, 1.5 equiv.) and 10 mg of IPpop-1 were added followed by 2 mL Ethanol. Then the capped reactor was placed into oil bath and then stirred at 50 °C for 12 hours. After completion of reaction, the reaction mixture extracted with CHCl₃ (3 $\times$ 5 mL), the organic layer was dried over Na₂SO₄. After evaporation of the solvent under vacuum, the crude product was analysed by ¹H NMR to determine the product yield.

2.2.3.2. IPpop-1 Catalyzed Cyanosilylation Reaction: The mixture of aromatic aldehyde (0.5 mM, 1 equiv.), Me₃SiCN (1 mM, 2 equiv.) and IPpop-1 (5 mg) was stirred in a glass vial without any solvent in

room temperature for 8 hours. After completion of reaction, the crude product extracted with CHCl_3 (3×5 mL), the organic layer was dried over Na_2SO_4 . After evaporation of the solvent under vacuum, the crude product was analysed by ^1H NMR to determine the product yield.

2.2.3.3. IPpop-1 Catalyzed Three Component Reaction: Aromatic aldehyde (0.3 mM, 1 equiv.), 1,3-Dicyclohexanedione / Dimedone (0.3 mM, 1 equiv.), malononitrile (0.3 mM, 1 equiv.), IPpop-1 (10 mg) and 2 mL ethanol was placed in a screw cap vial. Then the reaction mixture was stirred in room temperature for 2 hours. After completion of reaction, the mixture was filtered and washed with ethanol 2-3 times. Then evaporated the solvent under vacuum and the product was analysed by ^1H NMR.

2.2.3.4. Scaled Up Three Component Reaction: The scaled up three component Knoevenagel-Michael addition reaction was carried out by increasing the amount of substrate, catalyst and solvent by 20 times. In a typical reaction condition, 200 mg IPpop-1, 1.11 g 4-bromobenzaldehyde, 841 mg dimedone, 400 mg malononitrile and 40 mL ethanol was placed into a 100 mL round bottom flask and stirred in room temperature for 2 hours. Then the reaction mixture was filtered and washed with ethanol. The crude product was obtained by evaporation of solvent under vacuum and analysed by ^1H NMR.

2.2.3.5. Continuous Flow Three Component Reaction: For Flow Chemistry we used Ravel Peristaltic Pump (Model No: RH-P110L-50) for control the rate of reaction mixture flow. We used 300 mg of composite bead for the Flow reaction. The catalyst bed volume was 9.11 cm^3 . Mixture of 4-bromobenzaldehyde (1.35 g, 7.5 mM), Dimedone (1.05 g, 7.5 mM), malononitrile (500 mg, 7.5 mmol) in ethanol solution (125 mL) was pumped through the spiral transparent glass tube reactor which is evenly charged with a mixture of IPpop-1 beads at room temperature with a flow rate of 0.5 mL min^{-1} .

2.2.3.6. IPpop-1 Catalyzed One-Pot Cascade Catalysis Reaction: In a 10 mL glass vial with a magnetic stirrer coupled with temperature controller, the one-pot deacetalization-Knoevenagel condensation reaction was carried out. 4-bromobenzaldehyde dimethylacetal (0.5 mM), malononitrile (0.5 mM), 5 mg IPpop-1 and 2 mL H_2O were put into the reactor and stirred at 60°C for 16 hours. Then reaction mixture was filtered and extracted with CHCl_3 (3×5 mL), the organic layer was dried over Na_2SO_4 . Final Product was obtained by evaporation of solvent under vacuum. The starting substrate, intermediate product, and final product compositions were determined by ^1H NMR in CDCl_3 to test the conversion of the reaction. The conversions of the starting substrate dimethylacetal and the intermediate product aldehyde were calculated by ^1H NMR by comparing the integral of the phenylic proton from the final product benzylidene ethyl cyanoacetate (7.72 ppm) with the phenylic proton of the 4-bromobenzaldehyde dimethylacetal (5.35 ppm) and 4-bromobenzaldehyde (9.96 ppm).

2.2.3.7. Photoluminescence Experiment: 1.5 mg of IPpop-1 was dispersed in 2 mL ethanol and placed into the PL instrument under stirring condition. The data was collected by incremental addition of 1 mM solution of different analytes (β -nitrostyrene, indole, pyrrole) at excitation of 370 nm.

2.3. Results and Discussion

2.3.1. Synthesis and Structural Characterization of the Catalyst

Toward the construction of a multifunctional heterogeneous catalyst, our focus was introducing HBD sites and basicity in a singular material. Along this line, we chose 2,4,6-triaminopyrimidine as the basic site, and after the solvothermal reaction⁴⁴ (Figure 2.1a and Appendix Scheme 2.1) with 1,5-diisocyanatennaphthalene, we obtained the poly urea network bearing the urea moiety, resulting from the condensation reaction between amine and isocyanate, with the H-bond donor site as well as free pyrimidine nitrogens acting as the basic functionality. After its successful construction, the dual-catalytic sites of the heterogeneous catalyst IPpop-1 were extensively characterized to understand the structural details through various techniques, including solid-state ¹³Cp-MAS NMR, FTIR, TGA, FESEM, TEM, XPS, low temperature nitrogen (N₂) gas sorption measurements, CHN elemental analysis, temperature-programmed desorption (TPD), etc. ¹³C CP-MAS NMR spectroscopy presented evidence of successful condensation of the starting material and the formation of the poly urea network. The presence of seven main broad peaks in ¹³Cp-MAS was observed that authenticated the formation of the network. Peaks at ~69 ppm validates the free sp² carbon from the pyrimidine ring, while the peaks at ~183 and ~189 ppm confirmed the formation of urea functionality, coming from the -C=O of the urea moiety connected to the sp² carbon atom between two nitrogen atoms of the pyrimidine ring and the -C=O of another two urea moieties connected to other two sp² carbons of the pyrimidine moiety, respectively. Peaks at ~193 and ~197 ppm were attributed to the pyrimidine ring in the IPpop-1 framework due to sp² carbon atoms between two nitrogen atoms in the pyrimidine ring and the sp² carbon atom from the pyrimidine ring, respectively. Peaks at ~157 and ~164 ppm substantiated the two terminal sp² carbons of the naphthalene ring. Additionally, the broad peaks at ~119, ~125, ~130 ppm, and ~133 ppm were corroborated with the other aromatic sp² carbon from the naphthalene ring (Figure 2.1b).⁴⁴ FTIR spectra of IPpop-1 also validated the successful formation of the poly urea network by the condensation reaction between amine and isocyanate. The peaks at ~3313 to 3443 cm⁻¹, corresponding to the primary -NH₂ group from 2,4,6- triaminopyrimidine, and the peak at ~2250 cm⁻¹ for the -N=C=O group were found to diminish along with the formation of the peak at ~1635 cm⁻¹, assigned to the -C=O group of the urea moiety, while a peak at ~1224 cm⁻¹ can be attributed to the -C-N group of pyrimidine (Figure 2.1c), indicating the successful poly urea network fabrication. The robustness of IPpop-1 was evaluated from TGA. From the TGA profile, we observed an initial loss of ~20%

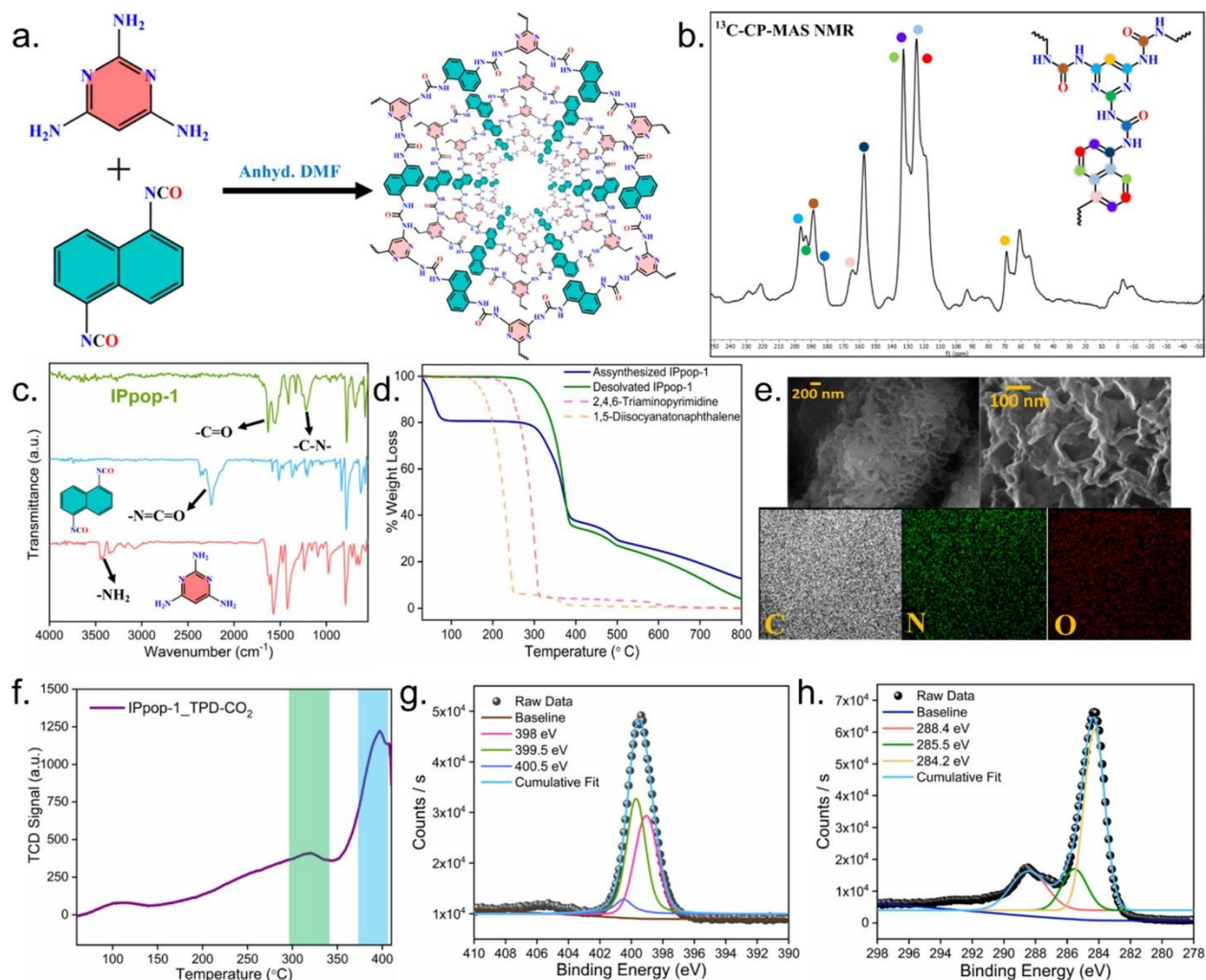


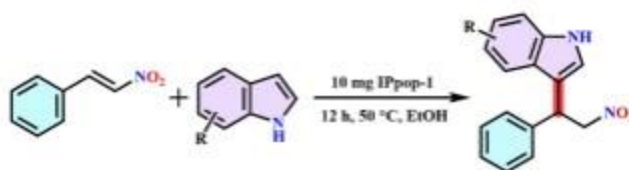
Figure 2.1. (a) Synthetic scheme for the synthesis of IPpop-1, (b) ^{13}C CP-MAS NMR of IPpop-1, (c) FT-IR spectra of 2, 4, 6-triaminopyrimidine (red), 1,5-diisocyanatennaphthalene (blue), and IPpop-1 (green), (d) TGA profile of 2, 4, 6-triaminopyrimidine (dotted pink), 1,5-diisocyanatennaphthalene (dotted orange), as-synthesized IPpop-1 (blue), and desolvated IPpop-1 (green), (e) FESEM images and elemental mapping of pristine IPpop-1, and (f) CO_2 -TPD profile of IPpop-1. Deconvoluted XPS spectra of IPpop-1: (g) nitrogen and (h) carbon.

under 80°C which is attributed to the loss of trapped solvents inside the framework. In the desolvated phase, we observed no gradual weight loss up to 300°C , suggesting robustness and thermal stability of the IPpop-1, while continuous loss beyond 300°C signified the decomposition of the organic framework (Figure 2.1d). The surface morphology and the presence of the compositional elements were evaluated by FESEM and TEM analyses. Flower petal-like morphology was revealed by the FESEM images of IPpop-1. A closer look reveals that the layers are stacked to each other (Figures 2.1e and Appendix Figure 2.8). With the aid of elemental analysis, energy-dispersive X-ray spectroscopy, and corresponding mapping, the

elemental composition of IPpop-1 was evaluated. IPpop-1 showed that C, N, and O were present and distributed uniformly across the polymer matrix (Figures 2.1e and Appendix Figure 2.9). The transmission TEM images confirmed the layer structure of the IPpop-1 network (Appendix Figure 2.10). The presence of bifunctional sites in the network was further evaluated by TPD. CO₂-TPD profile exhibited two peaks at 320 and 397 °C corresponding to strong Lewis basic sites coming from the pyrimidine nitrogens present in the IPpop-1 network, while the NH₃-TPD profile revealed three peaks at 109.7, 320, and 397.4 °C corresponding to acidic sites originating from the -NH group of the urea moiety (Figures 2.1f and Appendix Figure 2.11). Furthermore, XPS was employed to evaluate the surface composition and the chemical state of the elements in IPpop-1. The survey scan shows three peaks around ~399, ~284.8, and ~531 eV that are characteristic and correspond to nitrogen (N), carbon (C), and oxygen (O) respectively, present in the IPpop-1 network (Appendix Figure 2.12). The high-resolution peaks were further deconvoluted for a detailed analysis of the chemical state of the elements. The N 1s peak consisted of three peaks at 398, 399.5, and 400.5 eV assigned to the sp² aromatic -C=N, sp² aromatic -C-N from the pyrimidine ring, and -C-NH from the urea moiety, respectively (Figure 2.1g). C 1s peak was fitted into three different peaks at 284.28, 285.54, and 288.4 eV which correspond to sp² aromatic -C=C, sp² aromatic -C=N/-C-N of the pyrimidine ring, and -C=O of the urea moiety (Figure 2.1h). Additionally, O 1s peak was fitted at 531.27 eV which corroborated with the presence of only one type of oxygen in the network coming from -C=O of the urea moiety (Appendix Figure 2.13). Low-temperature N₂ adsorption profile of IPpop-1 showed type IV adsorption isotherm with H3-type hysteresis loop (Appendix Figure 2.14) suggesting the hierarchical pore distribution.⁴¹ The BET surface area of IPpop-1 was found to be 98 m²g⁻¹, while the average pore diameter of 4.5 nm and the total pore volume of 0.22 cm³ g⁻¹ were calculated. The NLDFT pore size distribution plot indicated the predominant abundance of mesopores in IPpop-1 (Appendix Figure 2.15). Also, the CHN elemental analysis illustrated the percentage of respective elements of %C 61.85, %N 21.81, and %H 4.62 to be present in IPpop-1. Additionally, solid-state UV-vis spectra showed that IPpop-1 has absorption maxima around ~350 nm (Appendix Figure 2.16), and the solid-state fluorescence spectra showed the emission maxima around ~445 nm (Appendix Figure 2.17). Overall, all these observations obtained from the structural analysis confirm the concurrent presence of both HBD acidic and base catalytic sites.

2.3.2. H-bond Donating FC Alkylation

HBD FC alkylation between aromatic compounds and electron-deficient alkenes is a critical C-C bond formation reaction that has been widely used in synthetic chemistry. Successful incorporation of urea moiety as an HBD catalytic site into a polymer backbone significantly increases the catalytic activity by avoiding the self-quenching of HBD moiety, a common phenomenon observed in the homogeneous catalyst. FC reaction between indole and β -nitrostyrene has gained considerable significance owing to its



Entry	R	Product	Yield (%)
1	-H		86.8
2	2-CH ₃		>99
3	1-CH ₃		97.5
4	2-Ph		>99
5	6-Cl		73.5
6	5-F		84
7	1H-Pyrrole		91.4
8	2,4-dimethyl-1H-pyrrole		>99

Table 2.1. Substrate Scope for IPpop-1-Catalyzed FC Alkylation Reaction; Condition: N-Heterocycles (0.15 mmol), β -Nitrostyrene (0.1 mmol), EtOH (2 mL), Temperature (50 °C), Catalyst Amount (10 mg); Yield Determined from ^1H NMR.

importance in the synthesis of indole-based alkaloids and tryptamine derivatives.¹ Due to the weaker nucleophilicity of indole, in general, the FC reaction between β -nitrostyrene and indole proceeds somewhat slowly. Crafting heterogeneous catalysts to activate electrophilic β -nitrostyrene toward the nucleophilic addition of indole via hydrogen bonding is one potential solution to overcome this issue. Motivated by this structural trait featuring spatially isolated urea functionality, we investigated the HBD catalytic activity of IPpop-1. Initially, a series of control experiments were performed to determine the optimal condition for

the reaction. As shown in Appendix Table 2.1, different solvent and reaction conditions were tested to arrive at the best conditions for the FC reaction with 10 mg of IPpop-1 catalyst, 0.225 mM (1.5 equiv) indole, and 0.15 mM (1 equiv) β -nitrostyrene. At room temperature, toluene and acetonitrile as the solvent produced no significant yield of the desired product (Appendix Table 2.1, entry 1, 2). However, at room temperature, when ethanol was used as solvent, the yield was found to be 21.3% (Appendix Table 2.1, entry 3). The FC reaction with toluene at 50 °C yielded 22.5% of the product (Appendix Table 2.1, entry 4), whereas in acetonitrile, no promising yield was observed (Appendix Table 2.1, entry 5). Finally, we observed the best activity of IPpop-1 with a product yield of 86.8% in ethanolic condition at 50 °C after 12 h of reaction (Appendix Table 2.1, entry 6), while without the catalyst, no product formation was observed (Appendix Table 2.1, entry 7) which also confirmed the catalytic activity of IPpop-1. After the optimal reaction conditions for the FC reaction were identified, the substrate scope for IPpop-1 with various indole derivatives and β -nitrostyrene was investigated to evaluate the versatility of IPpop-1. Table 1 shows the catalytic performance potency of IPpop-1 over a wide substrate range bearing diverse functionality when tested with different indole derivatives, and in every case, good-to-excellent yield was calculated by ^1H NMR. Only indole as substrate showed a pretty good yield of 86.8% (Table 2.1, entry 1). When the indole derivative had an electron-withdrawing group (-F, -Cl etc.), a slight decrease in the product yield was observed (Table 2.1, entries 5, 6). On the other hand, indole derivatives with an electron-donating group (-1 CH₃, -2 CH₃, -2 Ph etc.) show excellent performance with product yield >97% (Tables 1 and 2). We also performed the FC alkylation with pyrrole derivatives. Only 1H-pyrrole gives a yield of 91.4% (Table 2.1, entry 7), whereas 2, 4-dimethyl-1H-pyrrole gives a product yield of >99% (Table 2.1, entry 8). This advocates for the versatile nature of IPpop-1 as a heterogeneous catalyst and its profound usefulness in the synthesis of indole and pyrrole-based alkaloids with biological importance. From a sustainability point of view, the recyclability of the catalyst is not only crucial but also a necessity. IPpop-1 can be easily recovered after every cycle and can be reused just by washing with MeOH and drying at 75 °C under vacuum. IPpop-1 exhibit an excellent reusability even after 10 catalytic cycles with 76.4% yield of the final product after the 10th cycle (Appendix Figure 2.18, 2.19), which makes the IPpop-1 a robust and sustainable heterogeneous catalyst toward catalysis for FC alkylation reaction. Overall, the excellent catalytic competence of IPpop-1 featuring broad substrate scope and reusability makes it a potent HBD heterogeneous catalyst.

2.3.3. H-bond Donating Green Cyanosilylation

Cyanosilylation is the most typical process for the synthesis of cyanohydrins, one of the most useful synthons in organic synthesis and life science, and has recently gained interest in the industry on account of being the precursor of α -hydroxy acids, α -hydroxy aldehydes, β -amino alcohols, and other chemicals.

Trimethylsilyl cyanide is used as an eco-friendly alternative to harmful chemicals like HCN, NaCN, or KCN to craft C-C bonds in the nucleophilic addition process that produces cyanohydrins. Lewis acids, organic-inorganic salts, or nucleophilic catalysts have all been used as electrophilic catalysts to activate different carbonyls for cyanosilylation reactions effectively. The urea moiety also can serve as a catalytic site for promoting cyanosilylation reaction in the form of a HBD catalyst owing to its acidic -NH bond. HBD cyanosilylation reaction is in its nascent phase and therefore provides a scope for exploration improvement. Optimization of reaction condition was performed by taking 0.5 mM 4-bromobenzaldehyde (1 equiv), 1 mM Me₃SiCN (2 equiv), and 5 mg of IPpop-1 as a catalyst without any solvent system at room temperature. From the NMR titration studies, we observed the full conversion of the reactant aldehyde to the cyanohydrin trimethylsilyl ether product after 8 h (Appendix Figure 2.20). Additionally, from the time-dependent ¹H NMR study, we observed an exponential decay of the starting material (cyan traces), while a gradual increase in the concentration of the desired product (violet traces) confirmed successful conversion (Appendix Figure 2.21). This catalytic performance can be attributed to the outstanding ability of IPpop-1 to function as an HBD solid acid catalyst. This observation inspired us to broaden the scope of the substrate by performing cyanosilylation with other carbonyl compounds containing a variety of functional groups. It was seen that the carbonyl moiety containing electron-withdrawing groups such as -CN, -Br, -F, -Cl, and -NO₂ showed excellent yield irrespective of their position (-ortho, -meta, and -para) (Appendix Table 2.2, entries 3b, 3c, 3d, 3e, 3f, 3g, 3h, 3l, 3m, 3o, and 3p). Likewise, electron-donating group-substituted benzaldehyde displayed exception yields (Appendix Table 2.2, entries 3i, 3j, and 3k). Additionally, the bulky substrate bearing two benzene rings (biphenyl-4-carboxaldehyde and 1-naphthaldehyde) shows >99% of product yield, validating the potency of IPpop-1 as a HBD catalyst for the synthesis of cyanohydrins under green eco-friendly condition. The plausible reaction mechanism of IPpop-1-catalyzed cyanosilylation on the basis of H-bonding between the acidic -NH group of urea moiety and the oxygen of aromatic aldehyde, leading to the activation of the aldehyde oxygen that further reacts with Me₃SiCN to form cyanohydrins, is proposed from literature reports (Appendix Figure 2.22). Recyclability is another criterion to show the heterogeneity of the catalyst for real-world application. IPpop-1 shows an excellent recyclability toward cyanosilylation reaction even after five cycles with insignificant change in the yield of the product (Appendix Figure 2.23), making it a suitable heterogeneous catalyst.

2.3.4. Base-Catalyzed Multicomponent Knoevenagel-Michael Condensation

Numerous naturally occurring compounds contain 4H-pyran and its derivatives, which feature important biological properties and have found a wide range of usages in pharmaceuticals as antibacterial, anticancer, and antiallergic medicines. The most utilized method for the synthesis of 4H-pyran derivatives involves a Lewis base catalyzed three-component reaction involving cyclic 1,3-diketones, aryl aldehydes, and

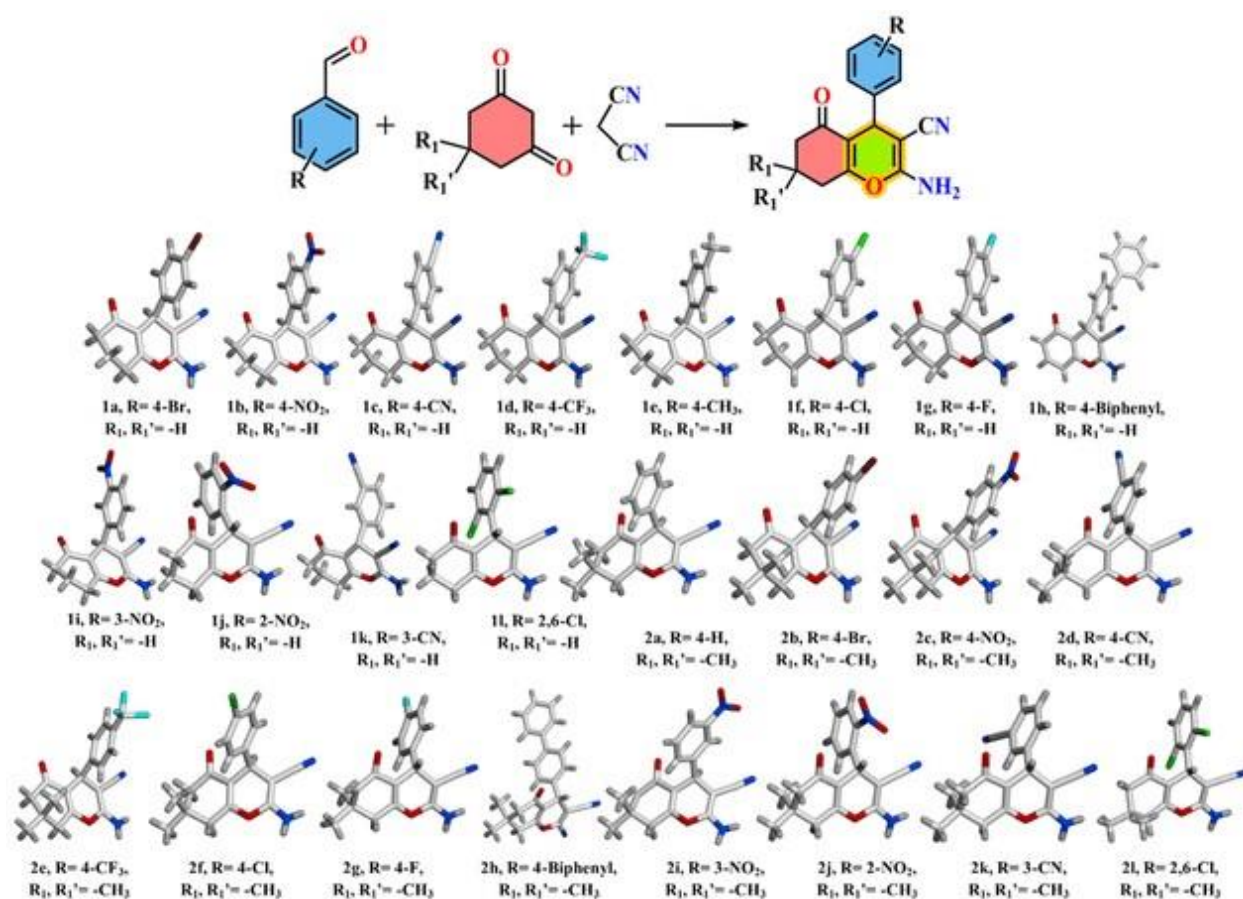


Table 2.2. Single-Crystal Structures of the Products for Multicomponent Knoevenagel-Michael Condensation.

malononitrile and is carried out under various reaction conditions.⁷¹ Most of these methods are nongreen and uses toxic piperidine and trimethylamine in a volatile organic solvent along with several other reagents like HMTAB, TEBA, Re(PFO)₃, NaBr, etc. As IPpop-1 has abundant two strong Lewis basic sites coming from the pyrimidine ring, we tried to investigate the greener approach toward the synthesis of 4H-pyran derivatives by optimization of the reaction condition. To attain the ideal reaction condition, a series of control experiments were carried out initially by taking 0.3 mM 4-bromobenzaldehyde (1 equiv), 0.3 mM dimedone (1 equiv), and 0.3 mM malononitrile (1 equiv) in ethanolic solution at room temperature. It was found that with increasing amount of the catalyst, the product yield was increased in a certain time (Appendix Table 2.3, entries 1-5). We observed the best activity in terms of product yield by using 10 mg of IPpop-1 catalyst in 8 h in ethanolic solution at room temperature (Appendix Table 2.3, entry 11). The ¹H NMR titration further shows the gradual product formation rate at different time intervals (Appendix Figure 2.24). Also, the multicomponent reaction was performed in various solvent mediums differing in polarity under the same reaction condition, and it was found that excellent yield >99% in the polar protic solvent

like methanol (Appendix Table 2.3, entry 12) and ethanol (Appendix Table 2.3, entry 11), while it gave average yield in a polar aprotic solvent. Suboptimal activity was observed, in acetonitrile, with a product yield of 46.5% (Appendix Table 2.3, entry 13), while in THF, the product yield was 50% (Appendix Table 2.3, entry 14). Interestingly, in a nonpolar solvent, i.e., toluene, there was no product formation (Appendix Table 2.3, entry 15). Next, with the best-optimized reaction condition that allows the usage of ethanol as a green solvent, we tested the substrate scope of IPpop-1 for this reaction. The substrate investigation is expanded by including a variety of aromatic aldehydes with electron-withdrawing and electron-donating substituents along with the combination of two 1,3-diketones (1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione) in order to explore the universality of the reaction (Table 2.2 and Appendix Table 2.4). Satisfyingly, in all cases, the product yield was excellent (>99%), as calculated from ^1H NMR. To our delight, we were also able to obtain single crystals of all multicomponent reaction products that enabled us to determine their structure unambiguously (Table 2) showcasing the proficiency of IPpop-1 as a solid catalyst for base-catalyzed multicomponent condensation to synthesize the 4H-pyran derivatives. Additionally, the heterogeneity of IPpop-1 was investigated by removing the polymer catalyst through filtration after 45 min. Afterward, the reaction was permitted to proceed with the liquid supernatant, but no increment in the product yield was seen, indicating that the reaction was occurring in a heterogeneous manner (Appendix Figure 2.25). Scalability is a further essential component of a superior catalyst and is a widely desired feature. In order to evaluate the effectiveness of our catalyst on a large scale (20 times higher scale), we isolated 2.24 g of the product after 8 h of the reaction with an excellent yield, highlighting its potential toward scaled-up reaction (Appendix Figure 2.26). Reusability of IPpop-1 toward multicomponent reaction was also evaluated. After each catalytic cycle, the catalyst was recovered by centrifugation and washed with acetone followed by drying at 80 °C for 5 h. IPpop-1 demonstrated excellent recyclability performance with >99% yield of the final product even after 10 cycles (Appendix Figure 2.27, 2.28). These findings unequivocally demonstrate the robustness, sustainability, and recyclability efficiency of IPpop-1 toward multicomponent Knoevenagel-Michael condensation reaction.

2.3.5. Continuous Flow Base-Catalyzed Multicomponent Knoevenagel-Michael Condensation

Motivated by its satisfying catalytic performance, we further evaluated the conceptual viability of IPpop-1 by carrying out the basecatalyzed multicomponent Knoevenagel-Michael condensation under continuous flow condition. In this context, a doublecross-linking strategy that involved poly acrylic acid (PAA), CaCl_2 as source of Ca^{2+} ions, and sodium alginate with H_2O as the solvent was used to convert IPpop-1 polymer powder into millimeter-sized processable composite beads (Figure 2.2a, 2.2c, 2.2d). After their successful synthesis, a custom-made spiral microglass reactor was filled with 275 mg of polymer beads for the continuous flow reaction. Typically, a continuous flow of ethanolic mixture solution of 4-

bromobenzaldehyde, dimedone, and malononitrile were injected into the microreactor, while the desired end product was collected at the reactor outlet. Under an optimized reaction condition, an ethanolic solution (120 mL) of 4-bromobenzaldehyde (1.35 g), dimedone (1.05 g), and malononitrile (0.5 g) were injected at a flow rate of 0.5 mL min⁻¹ at room temperature to achieve the continuous conversion into the final product. After every 25 mL of flow of the solution, ¹H NMR was recorded (Appendix Figure 2.30), while the cumulative product was collected all together. Interestingly, we collected the final product 2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4Hchromene-3-carbonitrile on a gram scale (2.67 g) with 95.6% yield. Also, we explored the influence of the flow rate on conversion by performing the reaction with a different flow rate of 1 mL/min. We found that by increasing the flow rate from 0.5 to 1 mL/min, there was almost no change in % yield of the desired product (Appendix Figure 2.29) which indicates the potency of IPpop-1 toward the catalytic three-component reaction under dynamic condition. These observations further punctuate the scope and competence of IPpop-1 continuous flow catalysis (Figure 2.2b), further illustrating its potency as a superior catalyst pertaining to industrial relevance as well as conceptual feasibility.

2.3.6. One-Pot Cascade Deacetalization-Knoevenagel Condensation

After successfully investigating the potency of IPpop-1 as a bifunctional H-bond donor as well as a base heterogeneous catalyst, we further carried out the one-pot cascade deacetalization-Knoevenagel condensation reaction to check the antagonistic catalytic property of IPpop-1. The first step, i.e., deacetalization to the aldehydes, is an acid-catalyzed reaction that can be performed by the -NH groups of the urea moiety due to its acidic nature, while the second step, Knoevenagel condensation, can be promoted by the pyrimidine moiety, which can act as a basic site. Malononitrile (0.5 mmol) and 4-bromobenzaldehyde dimethyl acetal (0.5 mmol) in 2 mL of water were chosen as the standard reaction conditions, with the catalyst concentration of IPpop-1 being 5 mg. The reaction was performed at 60 °C for 16 h and formation of the product was monitored through time dependent ¹H NMR by plotting the consumption of 4-bromobenzaldehyde dimethyl acetal into the intermediate 4-bromobenzaldehyde and finally to the desired 4-bromobenzylidenemalononitrile formation (Figure 2.3a). From the kinetics plot (Figure 2.3b), we observed an exponential decay of the starting material (blue traces) from its initial value. After 8 h, ~75% dimethyl acetal was consumed, while after 16 h, all of the starting material was consumed. Additionally, we observed an exponential increment in the product formation (orange traces) over the course of the time until it reaches saturation. In the context of the formation of the intermediate product, aldehyde, we conclude that the first step, the deacetalization reaction, is pretty sluggish compared to the second step, i.e., Knoevenagel condensation. From ¹H NMR, it is clear that the formation of the intermediate aldehyde is slow, and after its formation, the intermediate is readily converted to the final product which

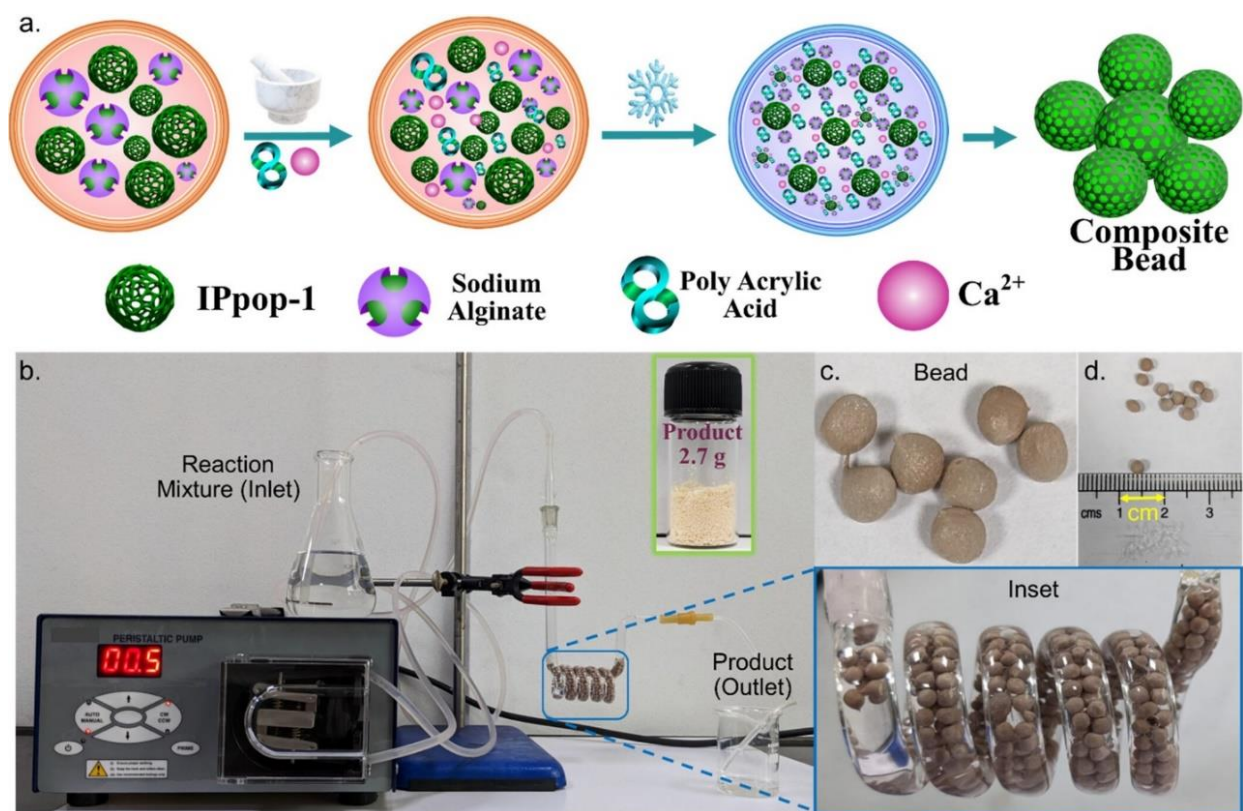


Figure 2.2. (a) Schematic illustration of PAA-alginate- Ca^{2+} bead formation synthesis from IPpop-1 powder. (b) Continuous flow reaction setup for the large-scale synthesis of multicomponent reaction (inset, product). (c, d) Optical photograph of composite beads.

also confirmed that the activity of urea moiety as the acid catalyst is slower in the first step compared to the base driven catalytic activity of pyrimidine in the second step (Appendix Figure 2.31). We performed two reactions with 4-bromobenzaldehyde dimethyl acetal and benzaldehyde dimethyl acetal, and in both cases, we found the extremely high yield of the product of >99%. To check the heterogeneity of the catalyst IPpop-1, we performed the hot-filtration test and removed the catalyst from the reaction mixture after 4 h via filtration and allowed the reaction to proceed without the catalyst, but no significant increase in the % yield of the product formation was observed (Appendix Figure 2.32). This indicates the heterogeneous nature of the catalyst. The reusability of IPpop-1 toward one-pot cascade reaction was also performed after collecting the catalyst via centrifugation, washing with methanol, and drying at 75 °C in a hot air oven. IPpop-1 shows an excellent catalytic activity toward cascade reaction even after five cycles with a yield of 98% (Figure 2.3c), confirming the sustainability of the polymer catalyst.

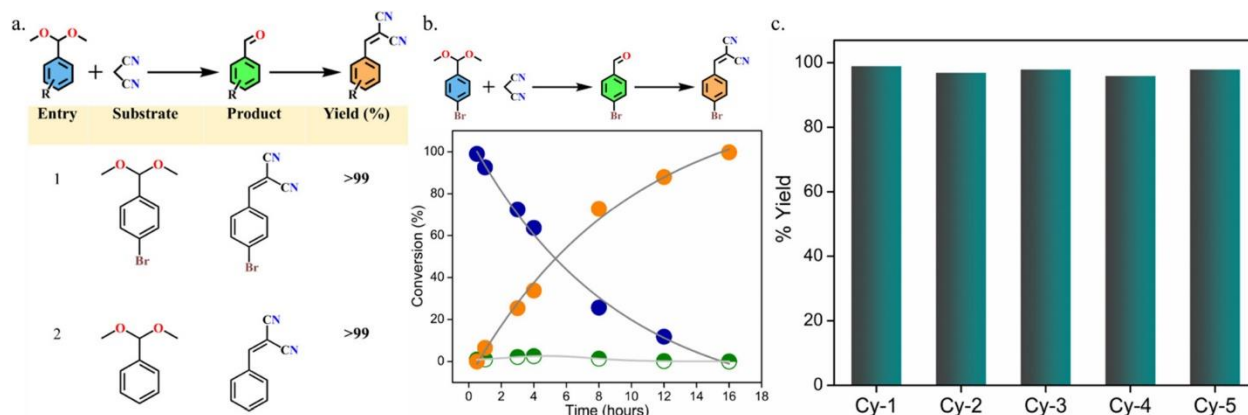


Figure 2.3. (a) Product list of substrate scope for the one-pot cascade reaction, (b) catalytic performance of IPpop-1 over time toward the one-pot cascade reaction monitored by ^1H NMR, and (c) recyclability of IPpop-1 for the one-pot cascade reaction.

2.3.7. Insight into Mechanistic Overview

Mechanism is an effective way to explain the formation of different products aided by different catalytic systems. The catalytic activity of IPpop-1 toward FC alkylation was investigated in detail to propose the plausible mechanistic cycle (Appendix Figure 2.33). We propose that the polymer containing a urea moiety forms a six membered (non-hydrogen bearing, considering -NH as a single atom) cyclic hydrogen-bonded complex with a nitro group of the substrate β -nitrostyrene. In the catalytic process, it is assumed that the -NH group coming from the urea functionality interacts with the nitro group of the β -nitrostyrene via hydrogen bonding, increasing the electrophilic nature of the -C=O group of the urea moiety. This increase in the electrophilic character of the -C=O group in turn favors the attack from indole to β -nitrostyrene. Considering the electronic nature of the catalyst and substrate, interaction of β -nitrostyrene (-NO₂ group) with the -NH group and indole (-NH group) with the -C=O group not only increases the nucleophilicity but also brings the substrate closer to each other which facilitates the formation of the product. Further, in order to confirm the mechanistic pathway, we further studied the interaction between β -nitrostyrene and the IPpop-1 via fluorescence spectroscopy. Briefly, 1.5 mg of finely ground IPpop-1 was taken in a cuvette with 2 mL of ethanol, and to this freshly prepared ethanolic solution, analytes (1 mM) were added under stirring condition. As shown in Figure 2.4a, IPpop-1 shows quenching in fluorescence intensity (430 nm) upon incremental addition of the ethanolic solution of β -nitrostyrene (25 μL each time), while there was no change in the fluorescence intensity upon addition of indole or pyrrole excitation experiment (PLE) to study the change in energy between pristine IPpop-1 and β -nitrostyrene treated IPpop-1 in ethanolic

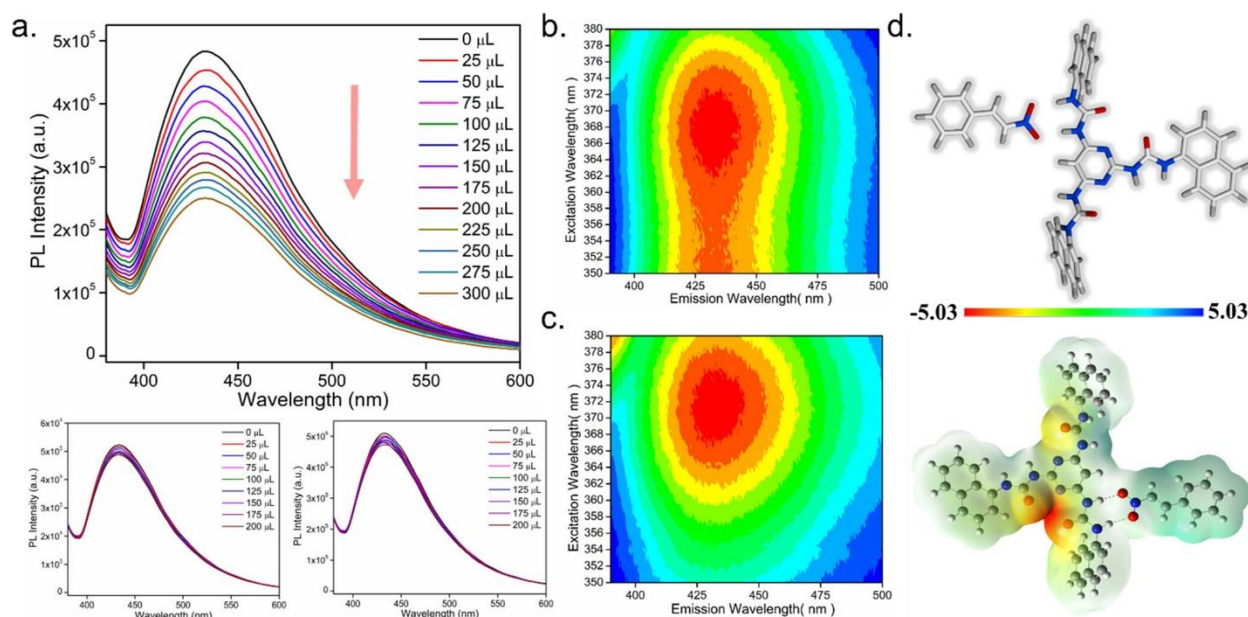


Figure 2.4. (a) Fluorescence titration of IPpop-1 with different analytes, (b, c) PLE spectrum of pristine IPpop-1 and after addition of β -nitrostyrene, and (d) optimized structure and ESP diagram of IPpop-1 with β -nitrostyrene.

medium. The emission spectra were recorded from 390 to 500 nm by exciting IPpop-1 in the range of 350–380 nm. We found that the pristine IPpop-1 has absorbance in the range from 350 to 365 nm, which changes significantly to 375 nm in β -nitrostyrene-treated IPpop-1, while the emission in both the cases remained constant at $\sim$ 435 nm. This bathochromic shift further confirmed the strong interaction between β -nitrostyrene and IPpop-1 leading to adduct formation. With this proposed mechanism, we also performed the theoretical calculation by employing density functional theory calculations using the B3LYP-31g* basis set with Gaussian 9 software package. The adduct complex between the urea moiety of IPpop-1 and the $-\text{NO}_2$ group of the β -nitrostyrene also supports and validates the plausible mechanism (Figure 2.4b–2.4d). These findings clearly indicate that IPpop-1 forms an adduct H-bonded complex with β -nitrostyrene and facilitates the FC reaction.

2.3.8. Post-catalytic Characterizaion

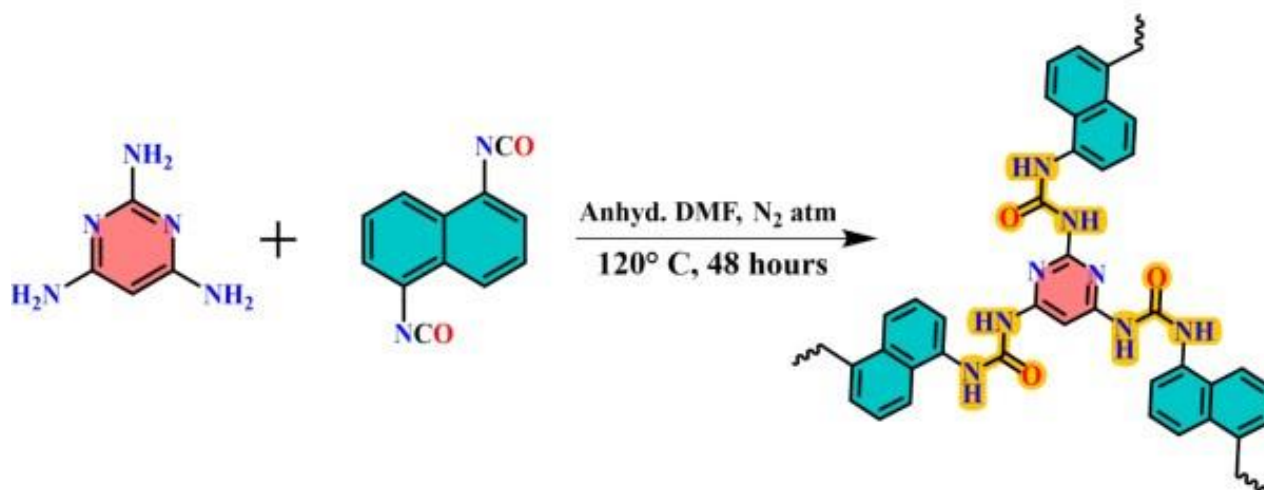
Pertaining to the stability of the polymer catalyst, the structural robustness of IPpop-1 was evaluated through several techniques. After performing the catalytic reactions IPpop-1 was subjected to ^{13}CP -MAS NMR, FTIR, FESEM, EDX analysis, etc. As shown in Appendix Figure 2.34, the SS- ^{13}CP -MAS NMR spectra of spent IPpop-1 match well with the pristine spectra displaying similar characteristic peaks that confirm the retention framework structure post catalytic cycles. A similar observation was found in the FTIR measurement where we acquired almost identical spectra as compared to the fresh catalyst bearing

all characteristic stretching vibrations (Appendix Figure 2.38). Additionally, no significant changes in the surface morphology was revealed from the FESEM images of the spent catalyst, advocating its robust nature (Appendix Figure 2.35, 2.36). The EDX spectra of reused IPpop-1 also presented an abundance of all compositional elements in the expected distribution (Appendix Figure 2.37). With this, we also take the optical picture of the composite bead used in the continuous flow reaction, and it was clear that after the reaction, the composite bead retained its shape and structural integrity (Appendix Figure 2.39). Overall, the postcatalysis stability of IPpop-1 was established from a combination of experiments which make it a potent and superior heterogeneous catalyst from the sustainability perspective (Appendix Table 2.5).

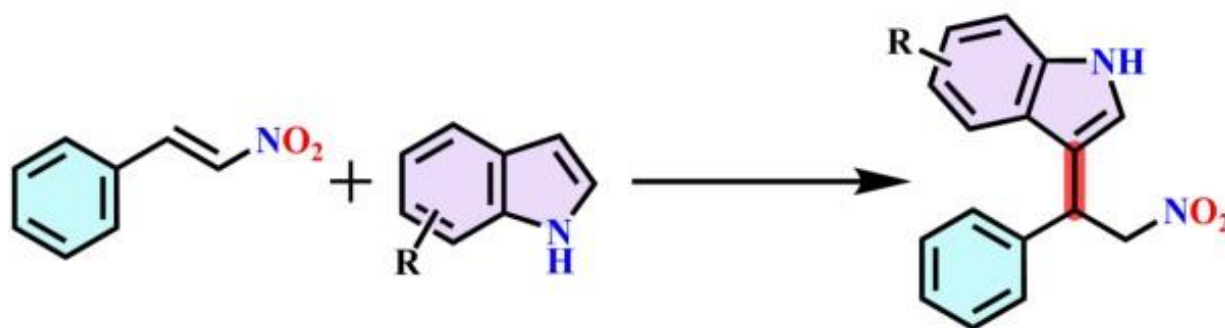
2.4. Conclusion

In a nutshell, we have reported an easily synthesized porous urea network (IPpop-1) that has been shown to be a highly potent heterogeneous HBD catalyst. The anchoring of active urea motifs in spatially isolated close proximity throughout the tailor-made nanospace of the porous polymer catalyst enables bypassing the catalyst deactivation prevailing in homogeneous HBD catalyst systems. IPpop-1 displayed excellent catalytic activity toward FC alkylation of β -nitrostyrene and indole, featuring broad substrate scope, recyclability, as well as scalability. The underlying mechanism at play was disseminated from direct experimental findings, which was further supported by theoretical insights. In addition, the presence of bifunctional sites in the polymer catalyst made it an ideal candidate to promote one-pot cascade catalysis along with Knoevenagel condensation and cyclosilylation reactions with excellent product yields. Base-catalyzed multicomponent Knoevenagel-Michael condensation could also be carried out with outstanding efficiency in IPpop-1 advocating its multifunctionality. Finally, the practical relevance pertaining to processability was also enforced by fabricating composite beads of the polymer to promote multicomponent Knoevenagel Michael condensation under flow catalysis without any trade off in its catalytic activity.

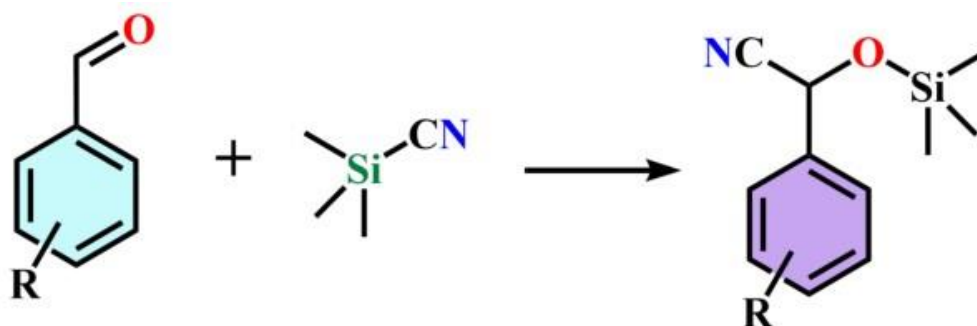
2.5. Appendix Section



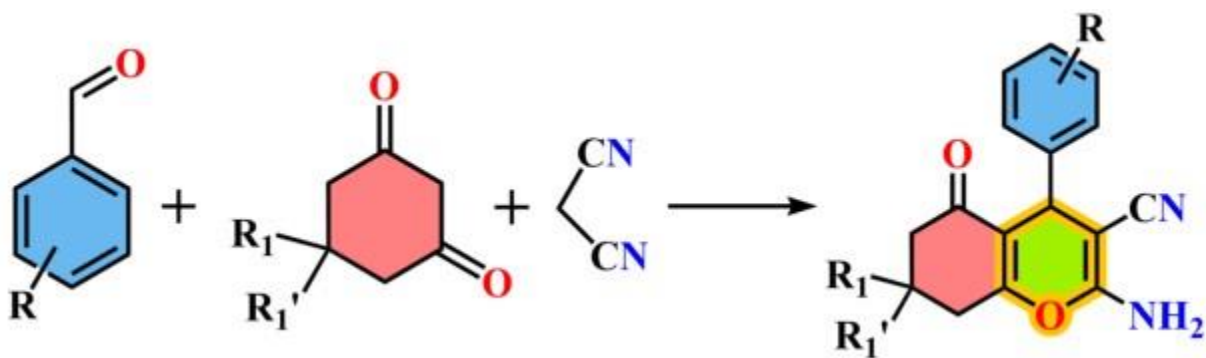
Appendix Scheme 2.1: Synthetic scheme of IPpop-1



Appendix Scheme 2.2: IPpop-1 catalyzed Friedel-Craft alkylation



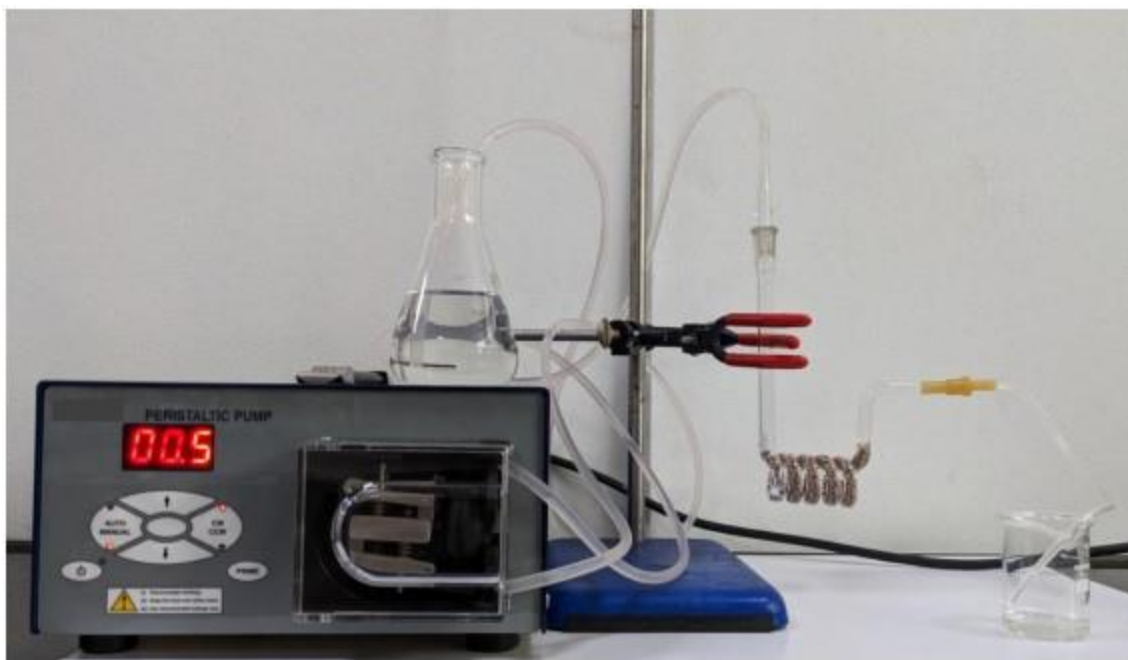
Appendix Scheme 2.3: IPpop-1 catalyzed cyanosilylation reaction



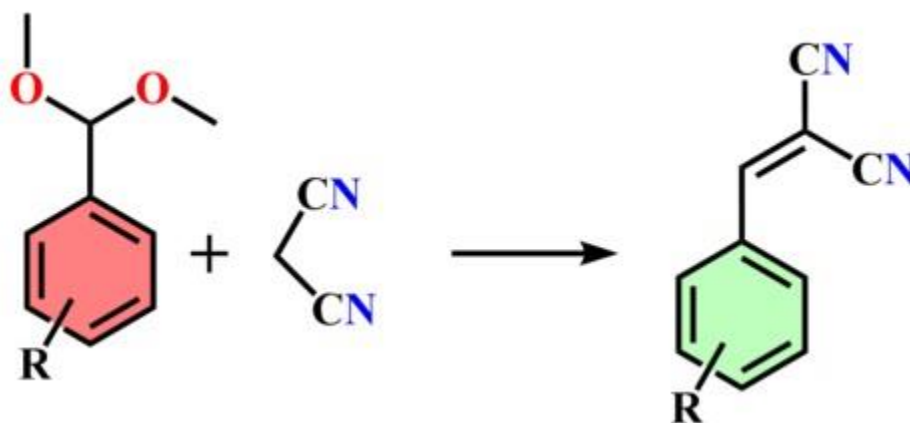
Appendix Scheme 2.4: IPpop-1 catalyzed three component reaction



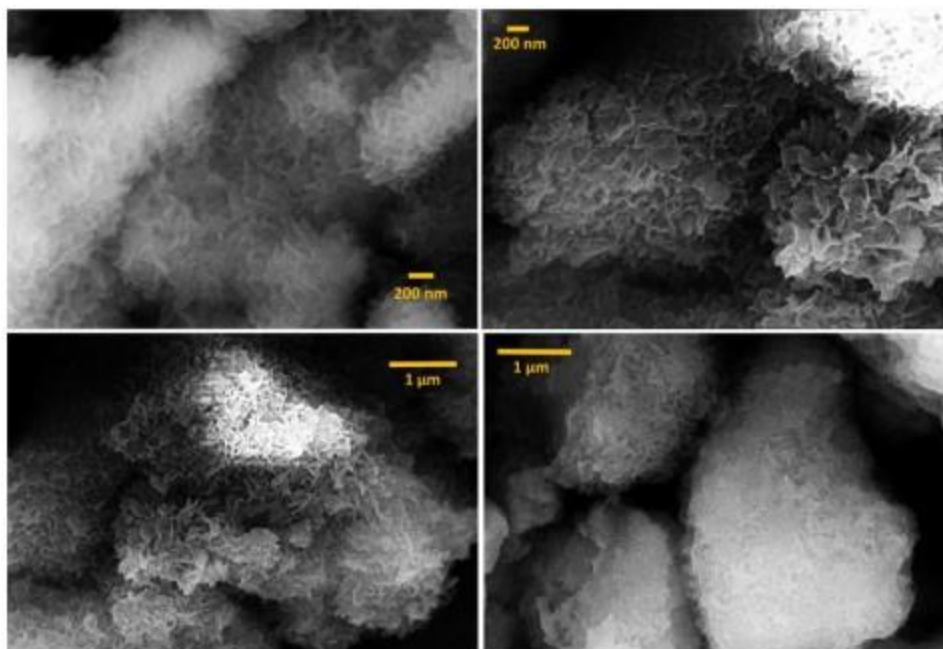
Appendix Scheme 2.5: Digital photograph of continuous flow reactor



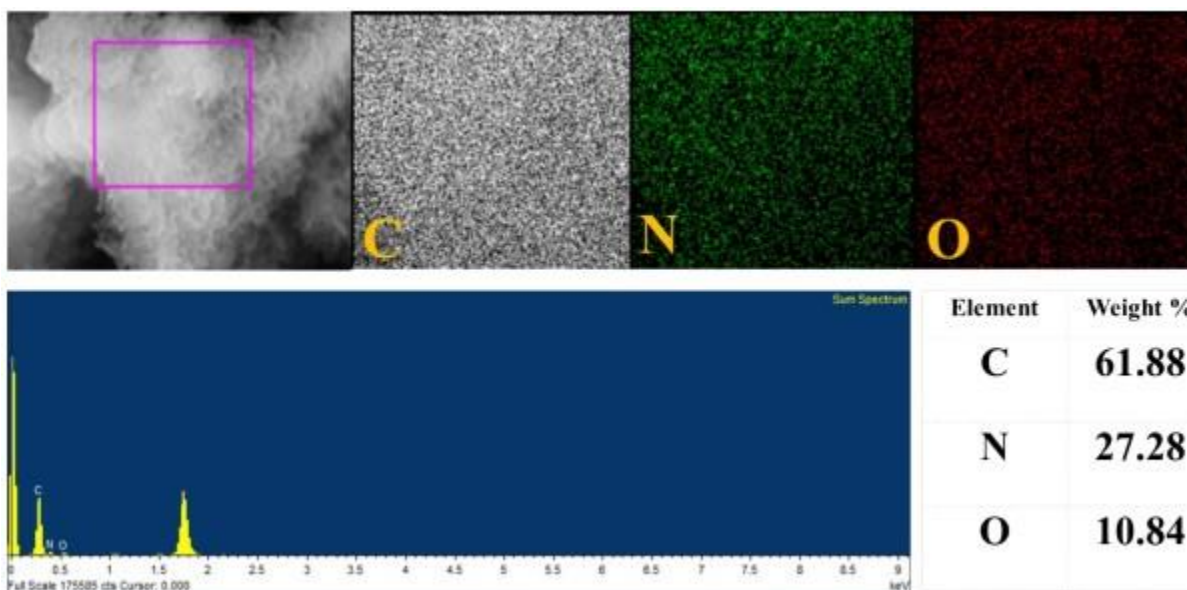
Appendix Scheme 2.6: Digital photograph of continuous flow set up



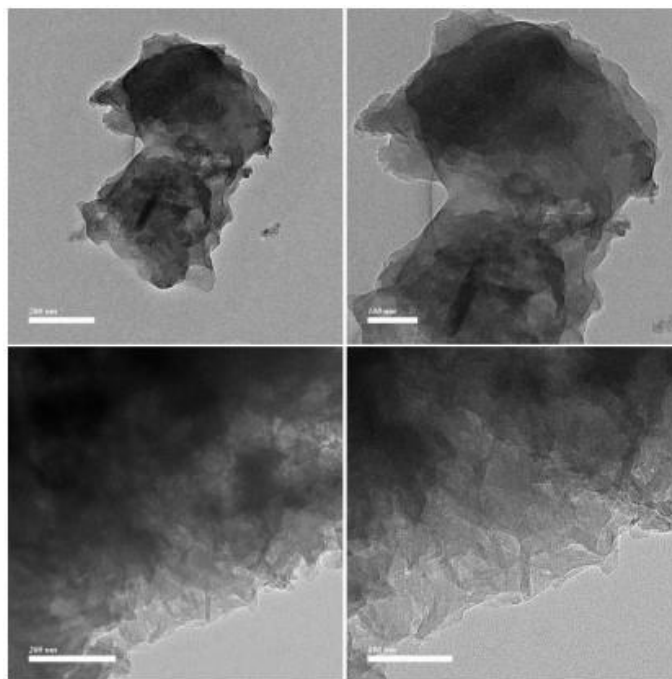
Appendix Scheme 2.7: IPpop-1 catalyzed one-pot cascade catalysis reaction



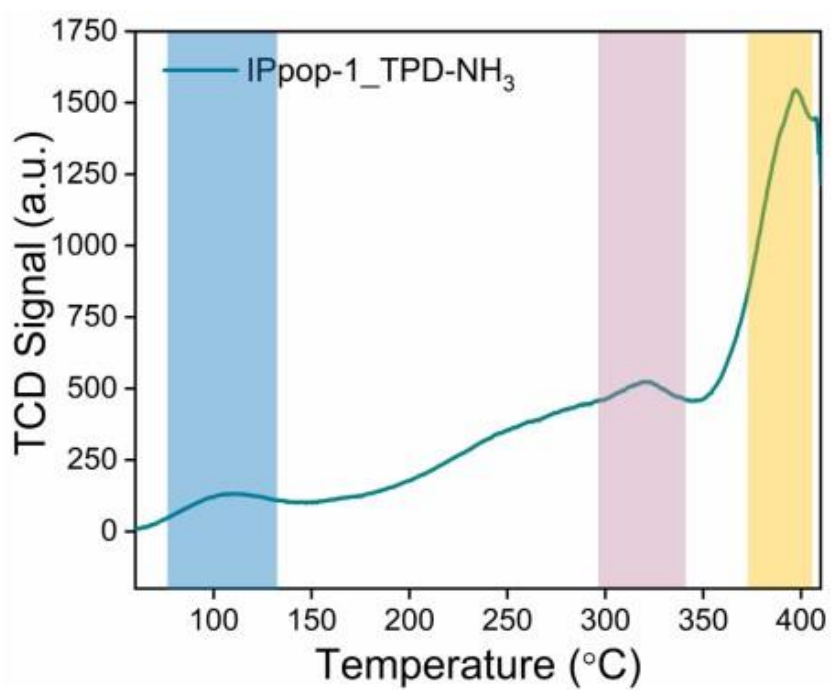
Appendix Figure 2.8: FESEM images of IPpop-1



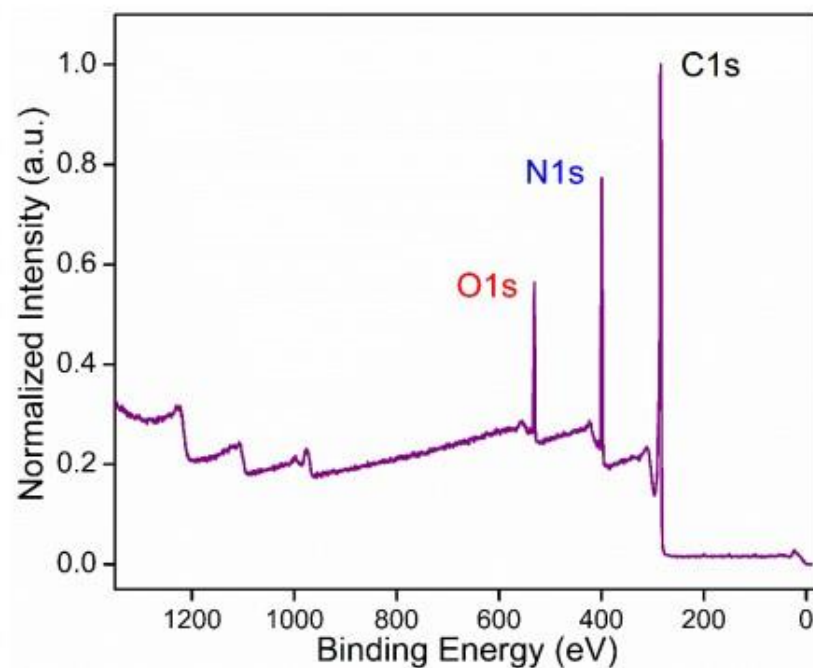
Appendix Figure 2.9: EDX analysis and elemental mapping of IPpop-1



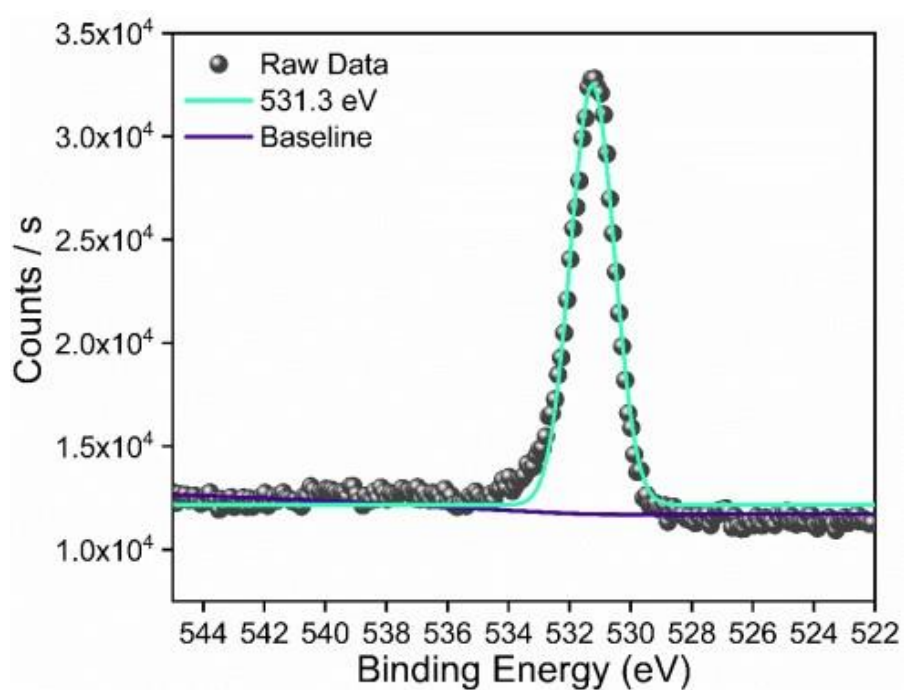
Appendix Figure 2.10: TEM images of IPpop-1



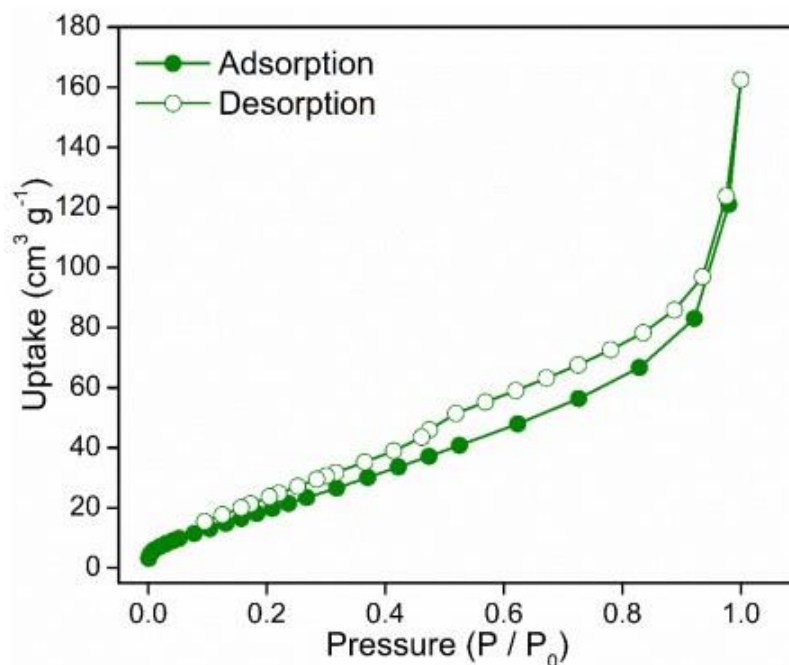
Appendix Figure 2.11: NH_3 TPD profile of IPpop-1



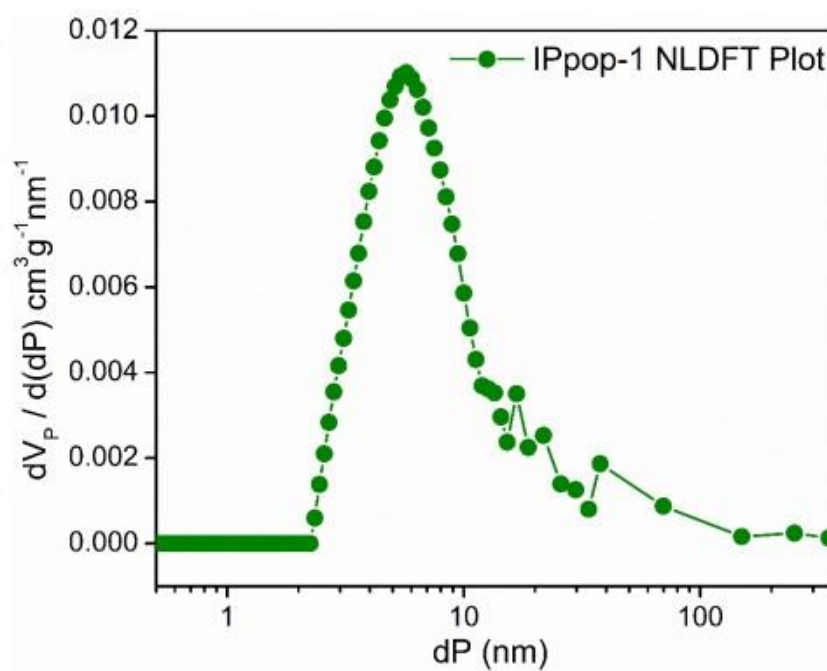
Appendix Figure 2.12: XPS survey spectra of IPpop-1



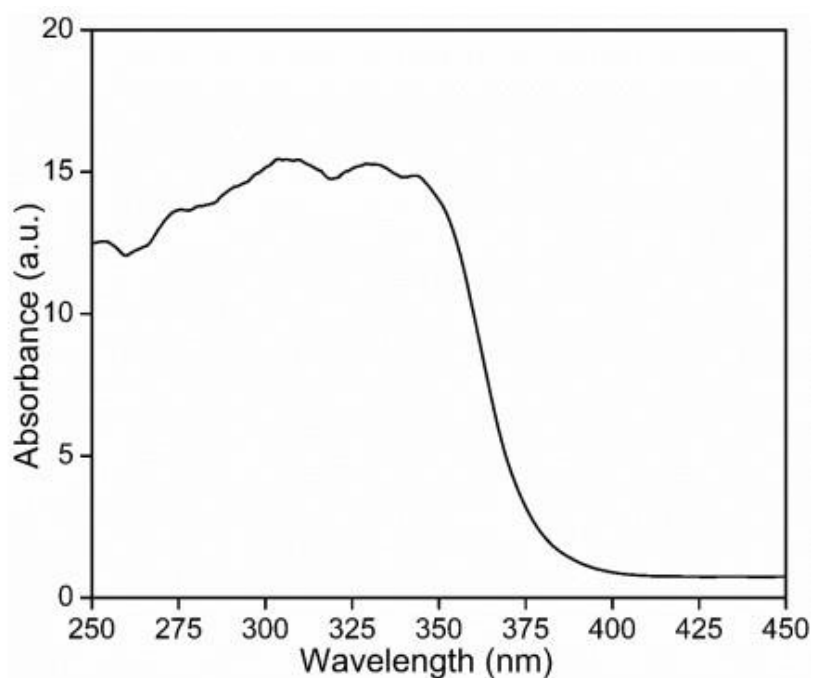
Appendix Figure 2.13: Deconvoluted O1s XPS spectra of IPpop-1



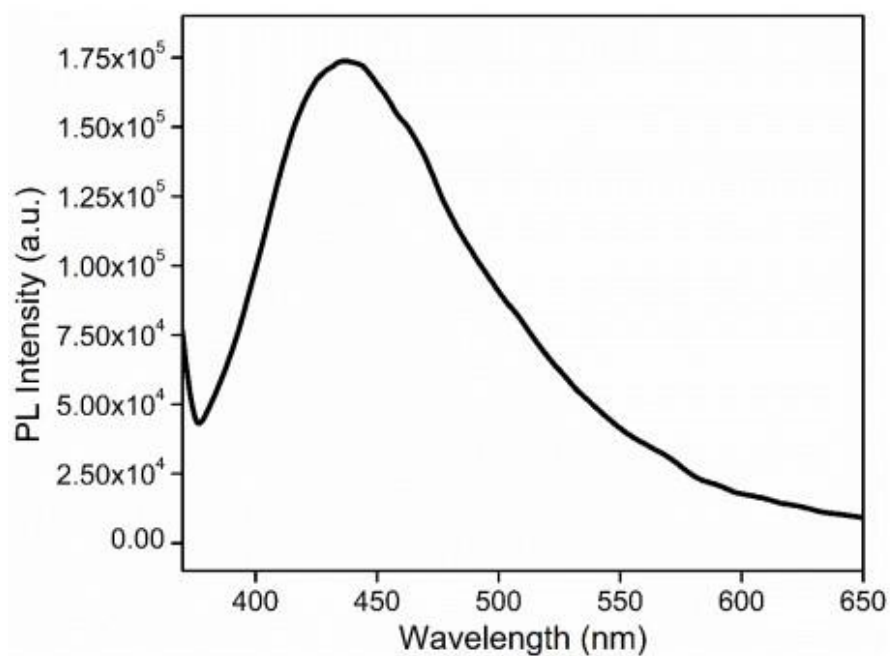
Appendix Figure 2.14: N_2 adsorption at 77K of IPpop-1



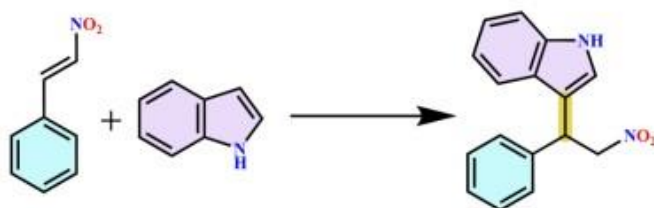
Appendix Figure 2.15: NLDFIT plot for pore size distribution of IPpop-1



Appendix Figure 2.16: Solid state UV-Vis spectra of IPpop-1

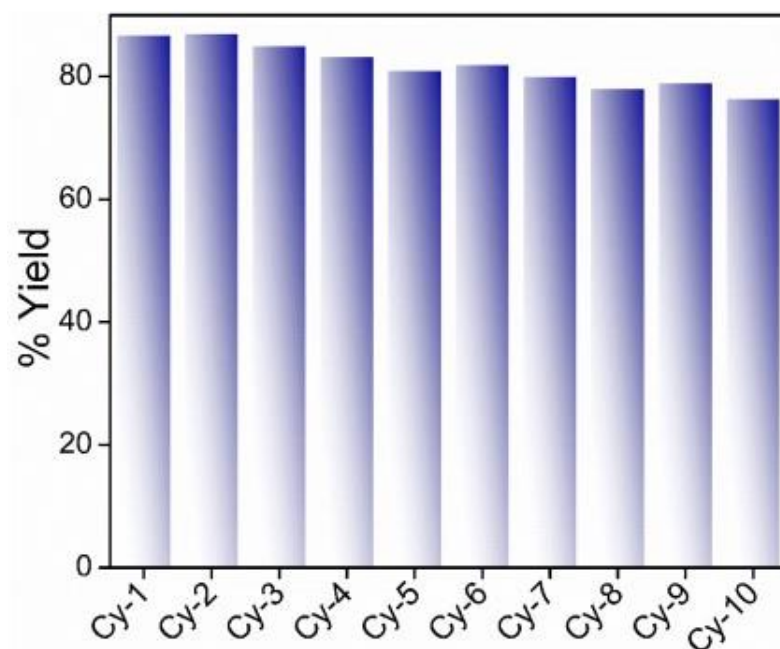


Appendix Figure 2.17: Solid state fluorescence spectra of IPpop-1

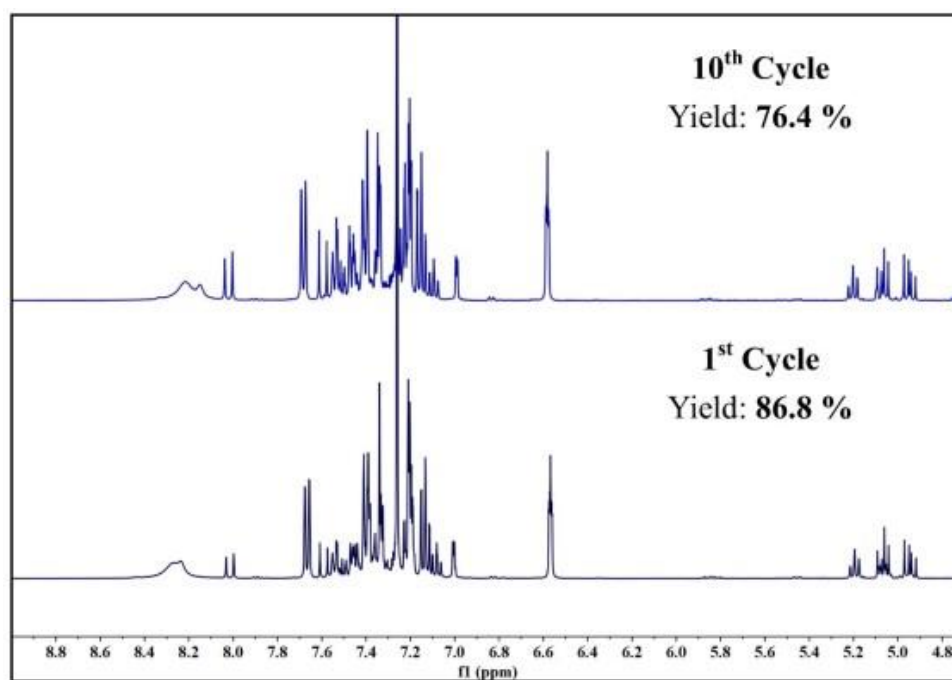


Entry	Solvent	Catalyst Amount (mg)	Time (hour)	Temp (°C)	Yield (%)
1	Toluene	10	12	R.T.	NA
2	Acetonitrile	10	12	R.T.	NA
3	Ethanol	10	12	R.T.	21.3
4	Toluene	10	12	50	22.5
5	Acetonitrile	10	12	50	NA
6	Ethanol	10	12	50	86.8
7	Ethanol	NA	12	50	NA

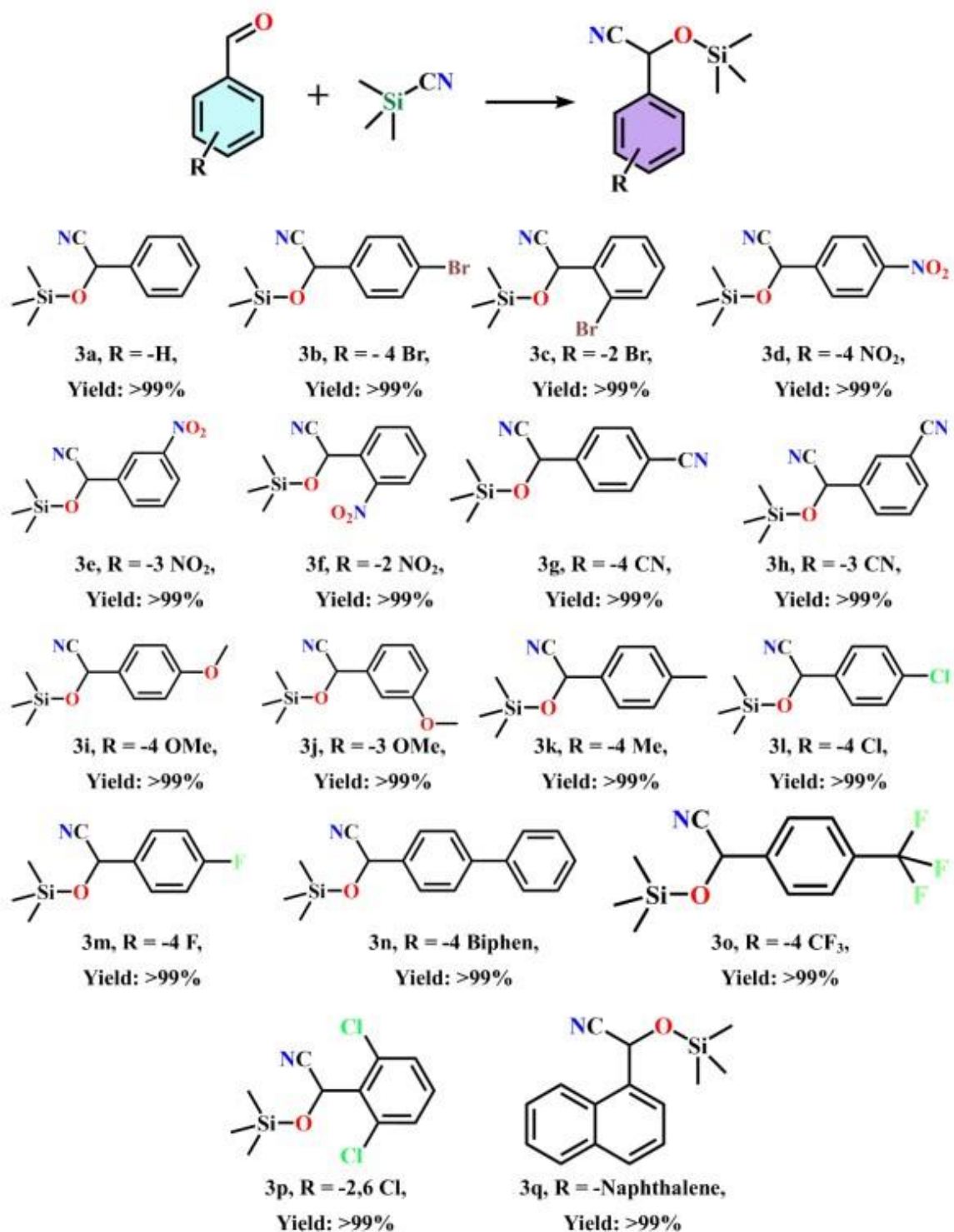
Appendix Table 2.1: Optimization table of IPpop-1 catalysed FC alkylation



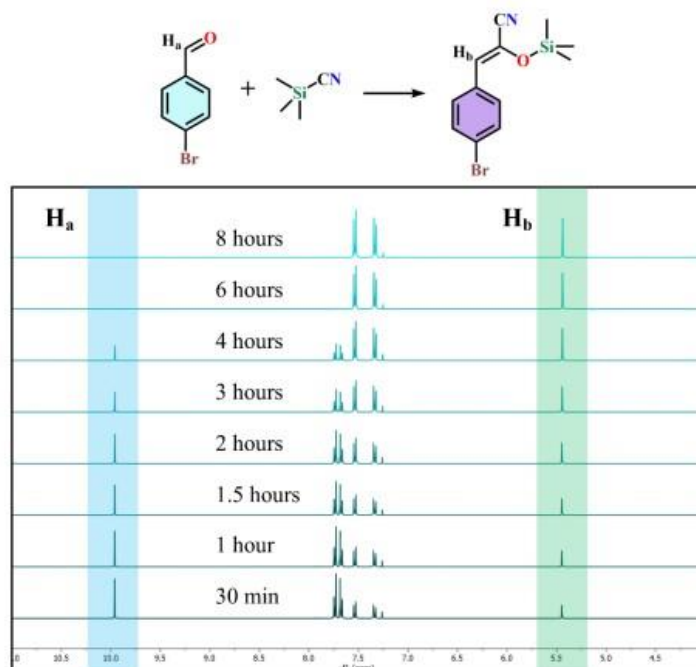
Appendix Figure 2.18: Recyclability of IPpop-1 catalysed Friedel-Crafts alkylation reaction



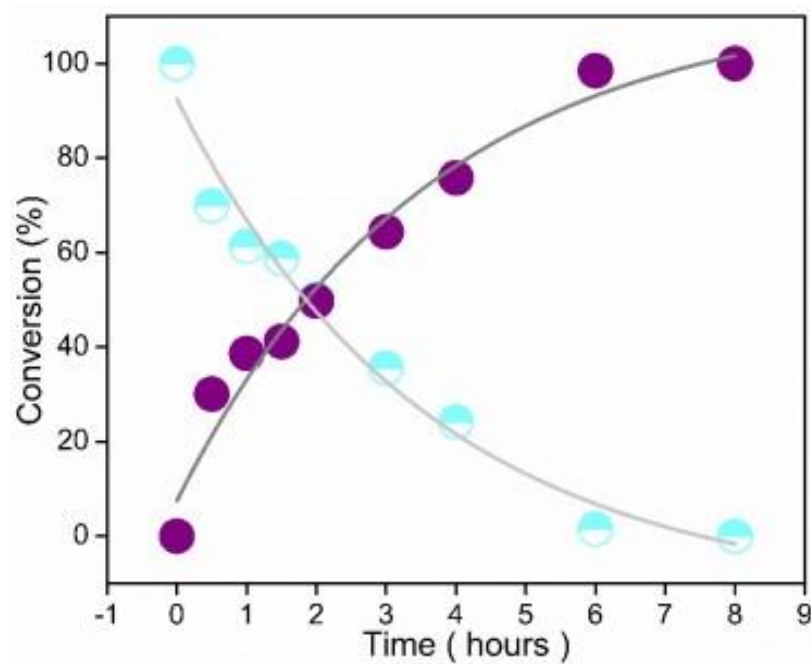
Appendix Figure 2.19: ^1H NMR spectra of recycled FC product catalysed by IPpop-1



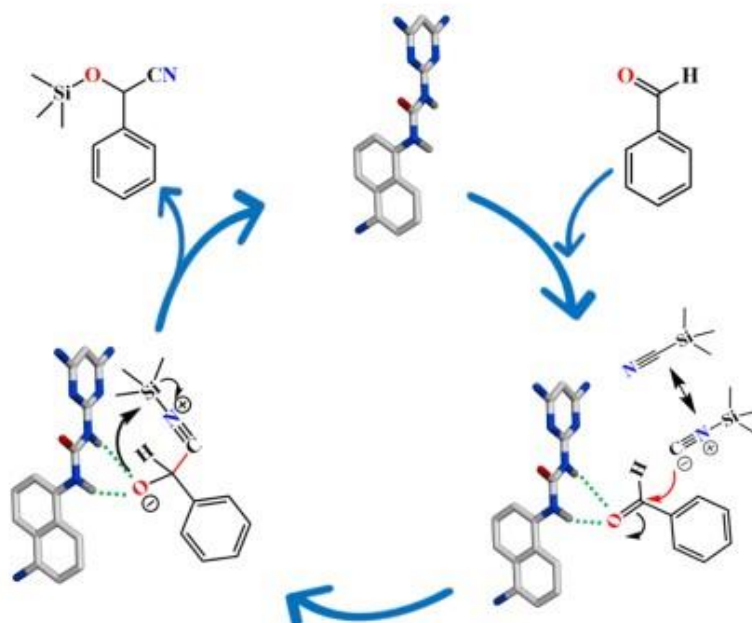
Appendix Table 2.2: Product list of IPpop-1 catalysed cyanosilylation reaction



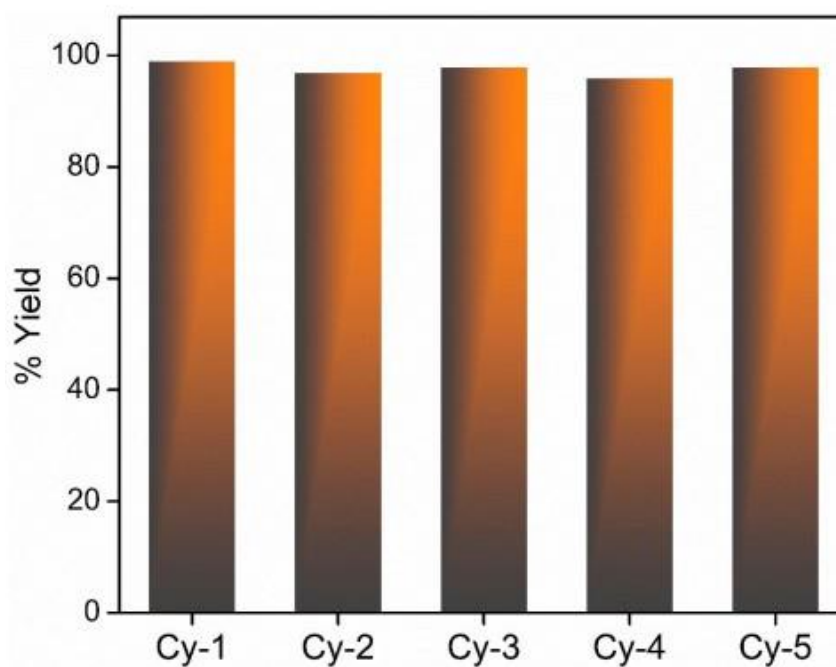
Appendix Figure 2.20: Time dependent ^1H NMR spectra of IPpop-1 catalysed cyanosilylation reaction



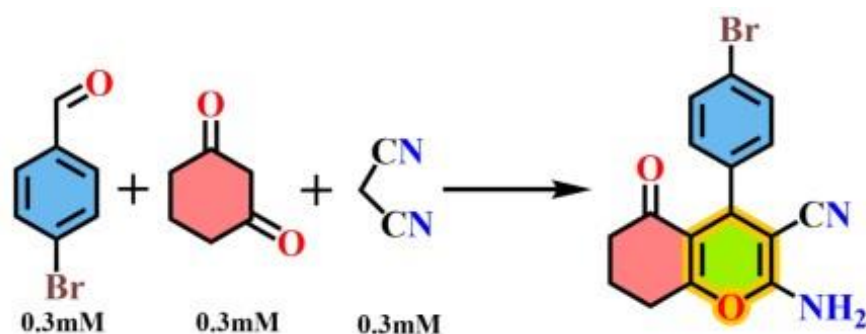
Appendix Figure 2.21: Time dependent catalytic performance of IPPOP-1 catalysed cyanosilylation reaction



Appendix Figure 2.22: Plausible mechanism of IPpop-1 catalysed cyanosilylation reaction

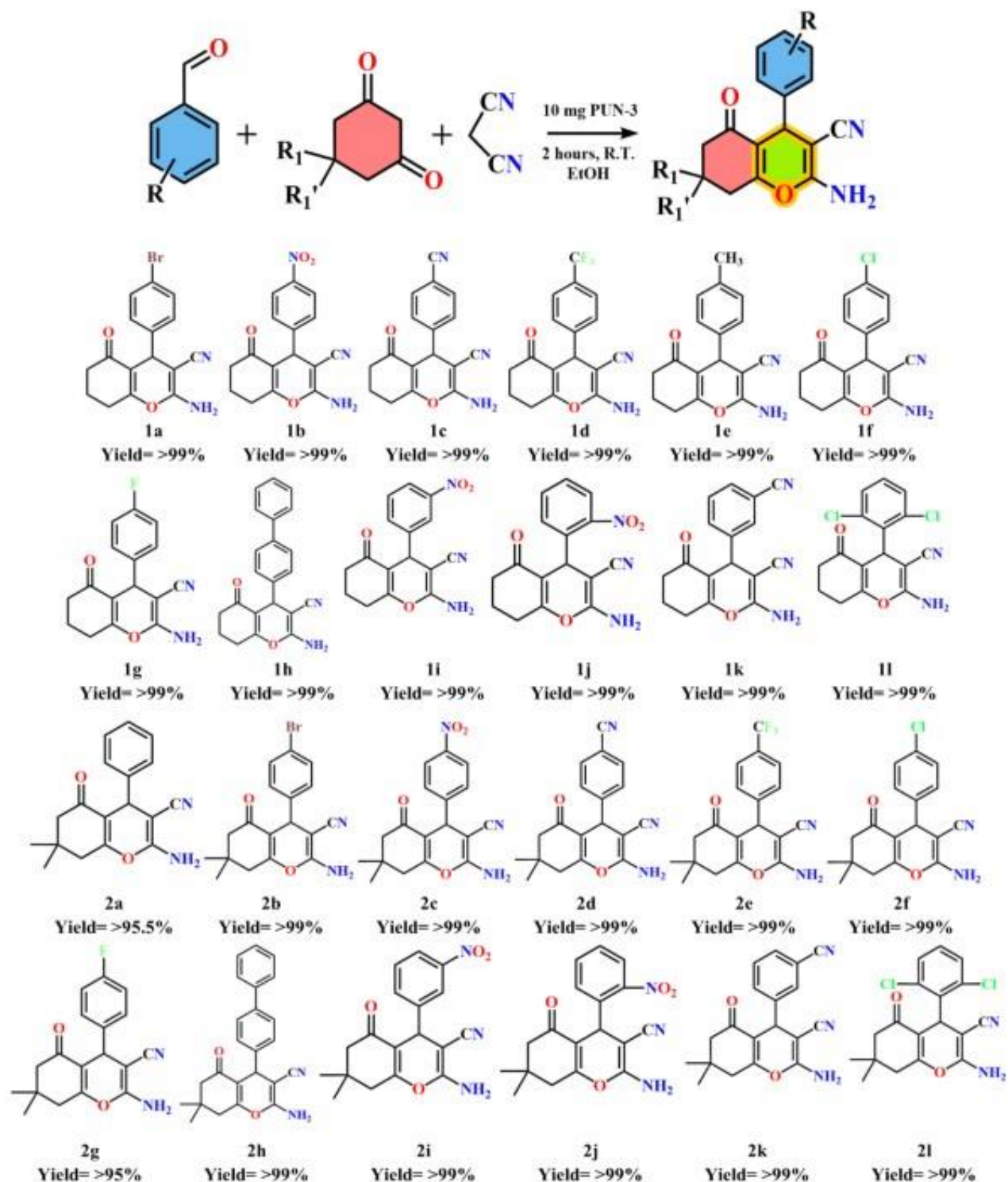


Appendix Figure 2.23: Recyclability of IPpop-1 catalysed cyanosilylation reaction

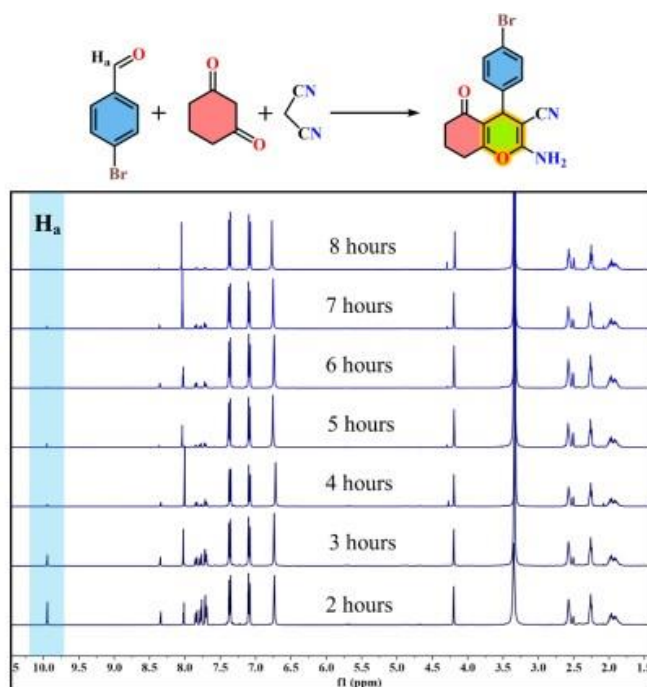


Entry	Cat. Amount	Solvent	Time (hour)	Temp (°C)	Yield (%)
1.	1 mg	Ethanol	8	R.T.	77
2.	2 mg	Ethanol	8	R.T.	79.3
3.	3 mg	Ethanol	8	R.T.	80.7
4.	4 mg	Ethanol	8	R.T.	81
5.	5 mg	Ethanol	8	R.T.	83
6.	10 mg	Ethanol	2	R.T.	73
7.	10 mg	Ethanol	4	R.T.	84.5
8.	10 mg	Ethanol	5	R.T.	94.7
9.	10 mg	Ethanol	6	R.T.	95.6
10.	10 mg	Ethanol	7	R.T.	98.5
11.	10 mg	Ethanol	8	R.T.	>99
12.	10 mg	Methanol	8	R.T.	>99
13.	10 mg	MeCN	8	R.T.	46.5
14.	10 mg	THF	8	R.T.	50
15.	10 mg	Toluene	8	R.T.	0
16.	0 mg	Ethanol	8	R.T.	0

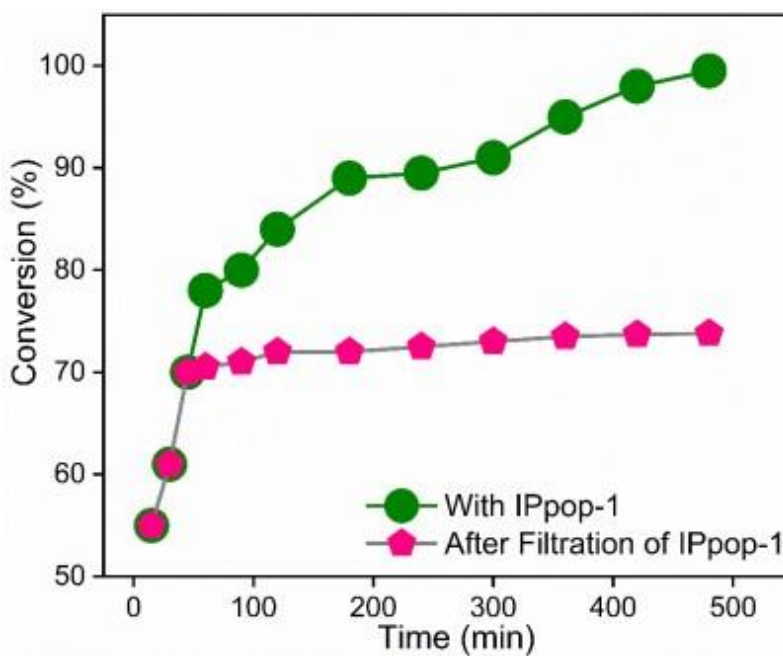
Appendix Table 2.3: Optimization table of IPpop-1 catalysed Three component reaction



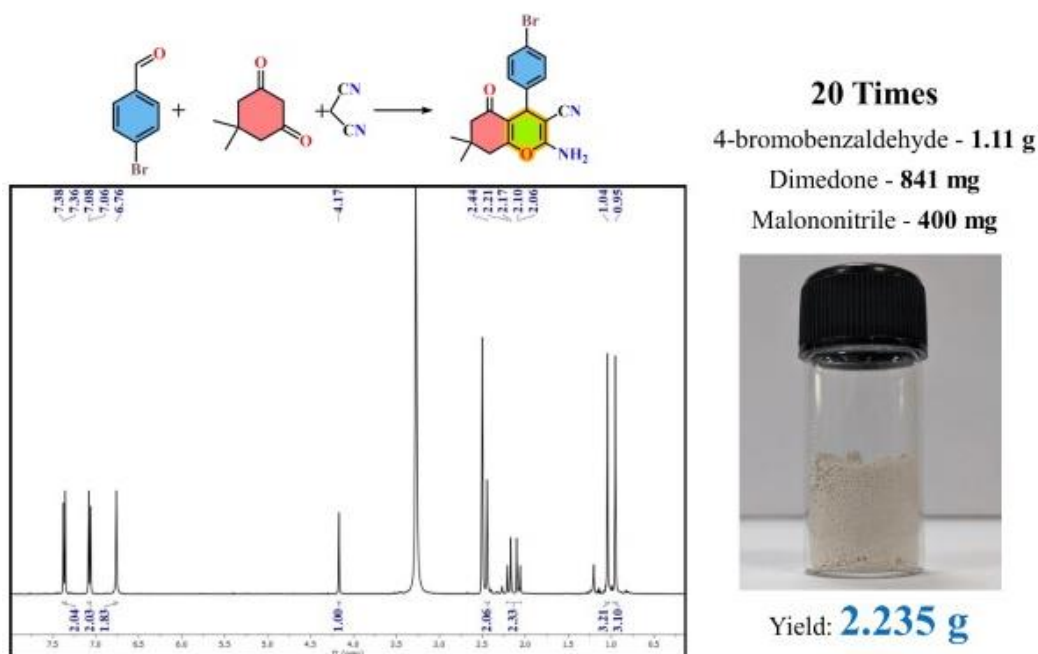
Appendix Table 2.4: Product list of IPPOP-1 catalysed three components reaction



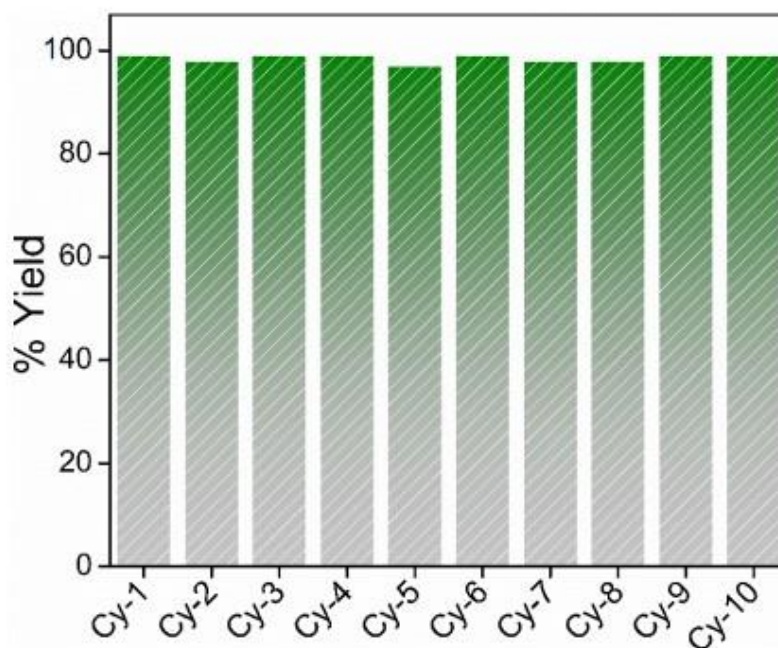
Appendix Figure 2.24: Time dependent ¹H NMR spectra of IPpop-1 catalysed three component reaction



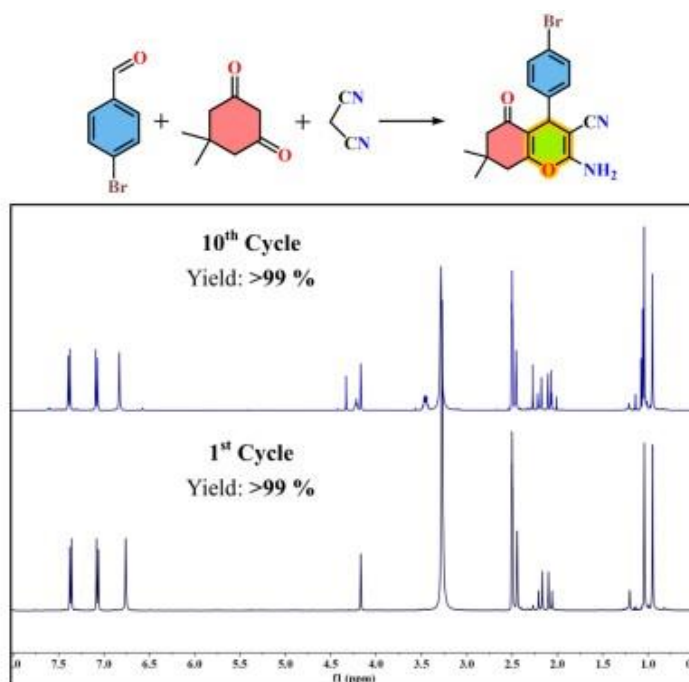
Appendix Figure 2.25: Hot filtration test of IPpop-1 catalysed three component reaction



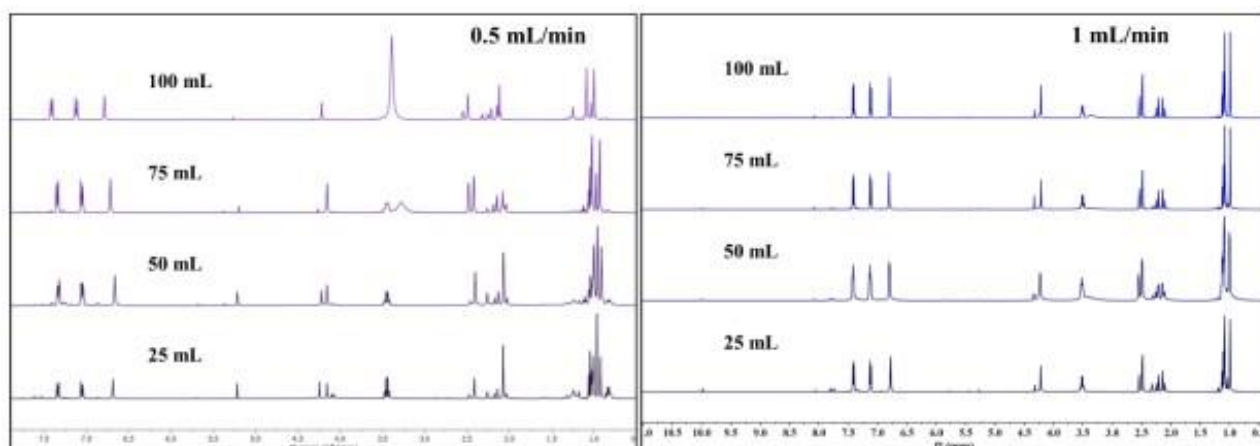
Appendix Figure 2.26: Large scale base catalysed multi-component reaction by IPpop-1



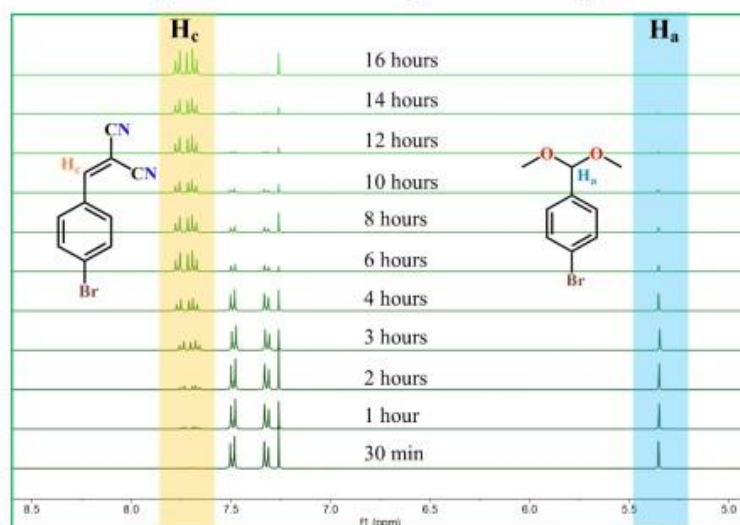
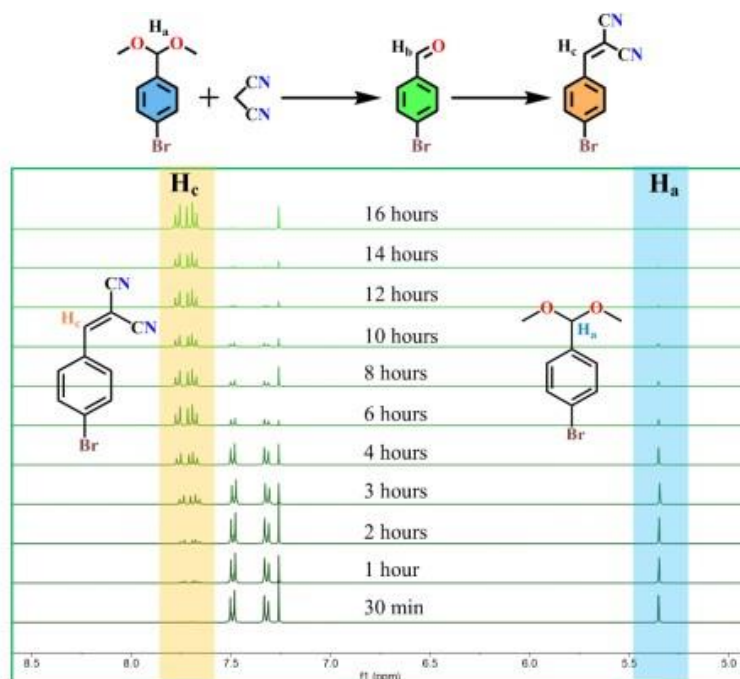
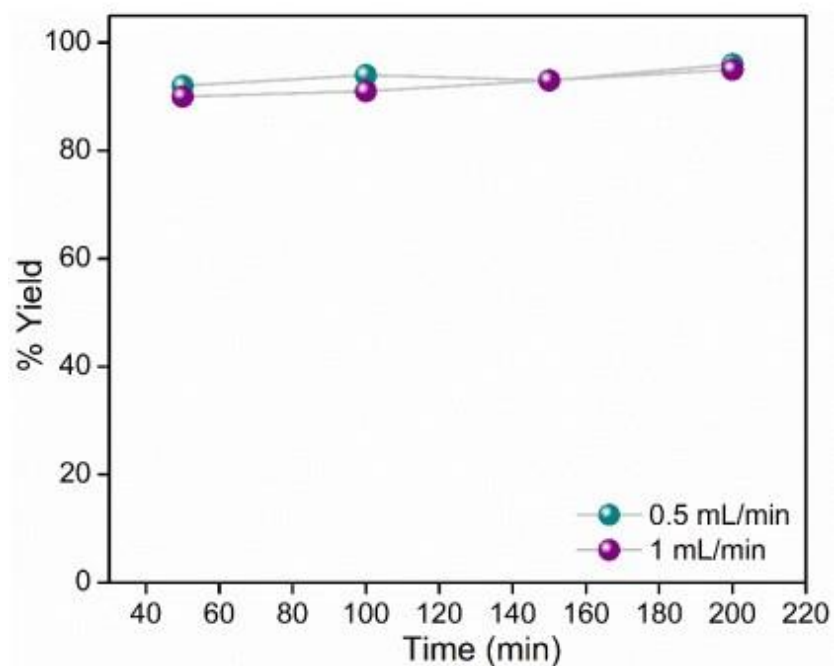
Appendix Figure 2.27: Recyclability of IPpop-1 catalysed three component reaction

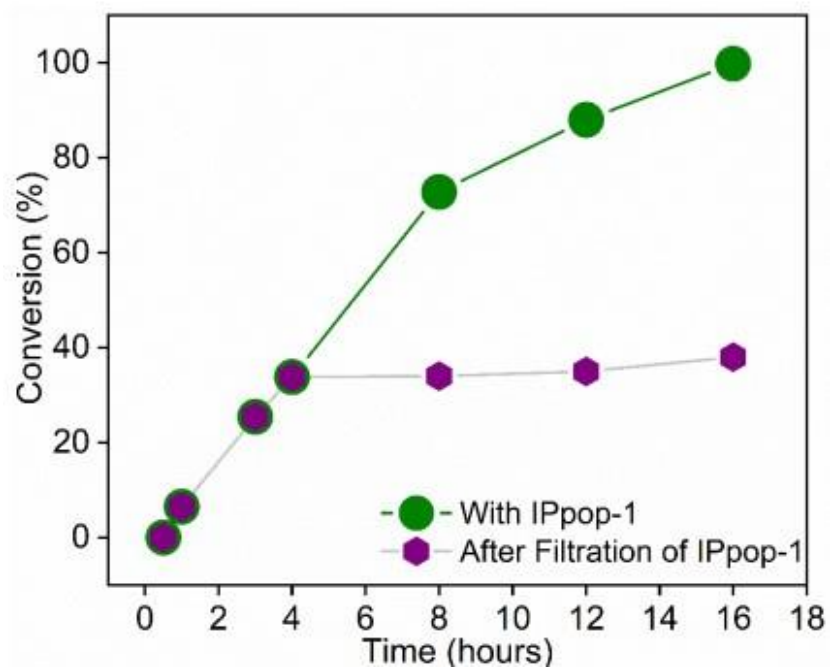


Appendix Figure 2.28 ¹H NMR spectra of recycled multi-component product catalysed by IPpop-1

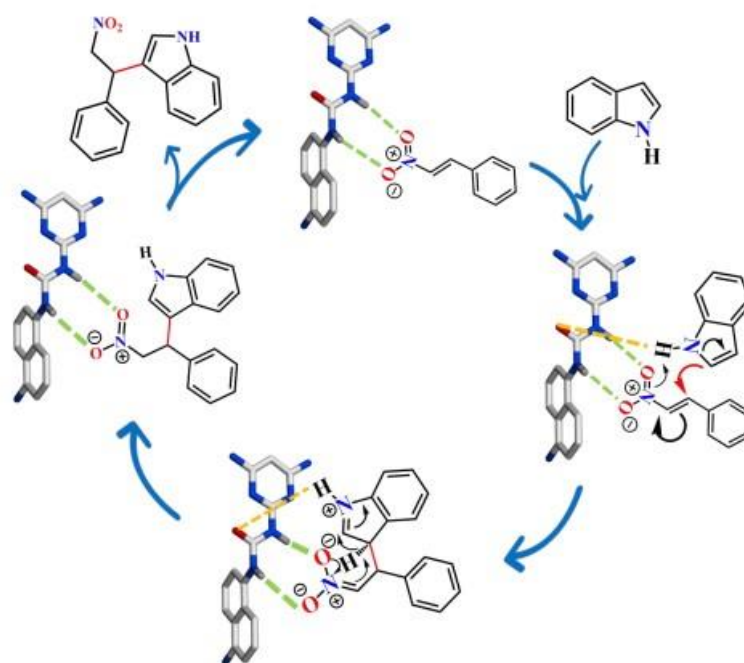


Appendix Figure 2.29: ¹H NMR spectra of continuous flow reaction in different volume interval with different flow rate

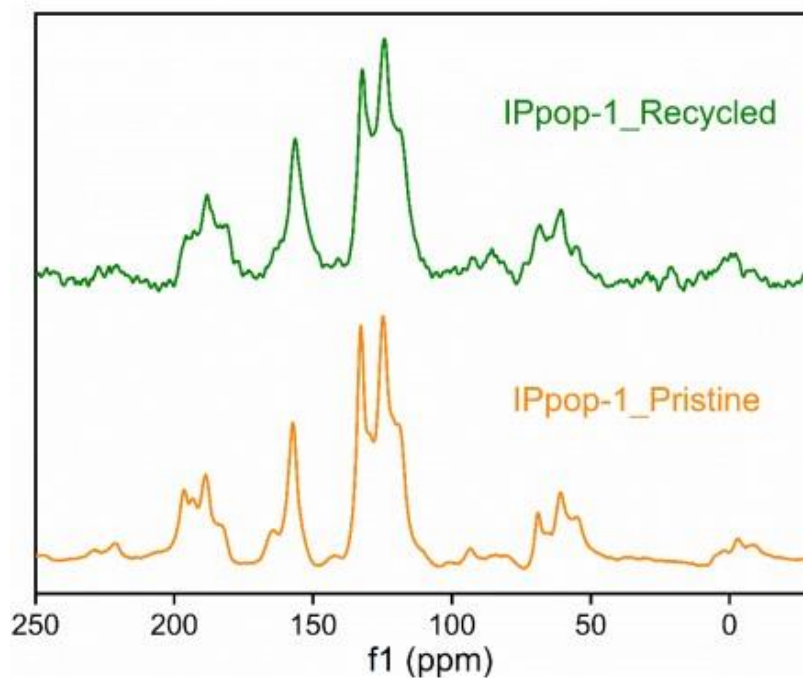




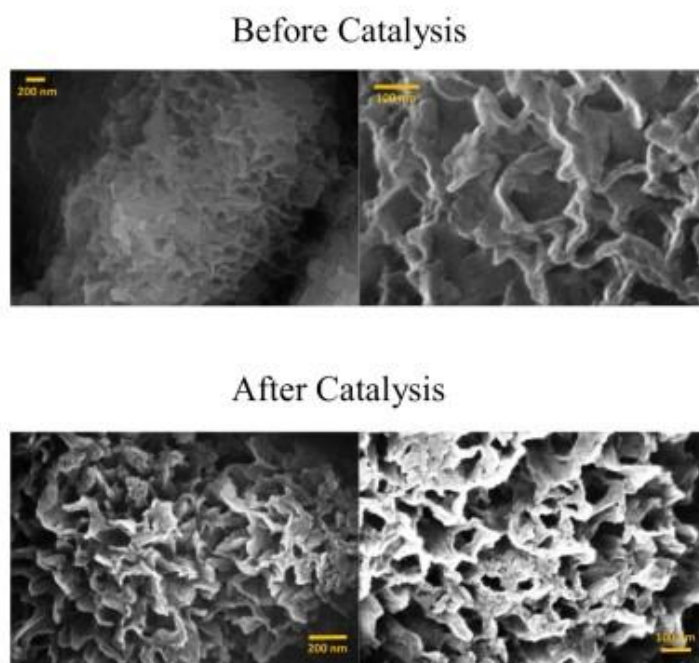
Appendix Figure 2.32: Time dependent NMR spectra of IPpop-1 catalysed cascade reaction



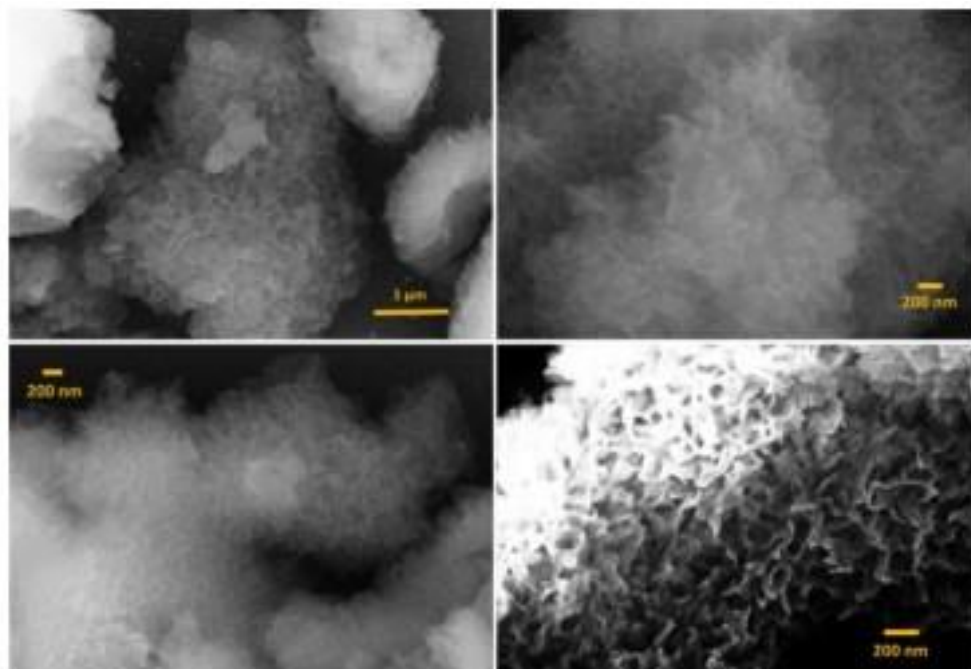
Appendix Figure 2.33: Plausible mechanistic cycle of IPpop-1 catalysed FC Reaction



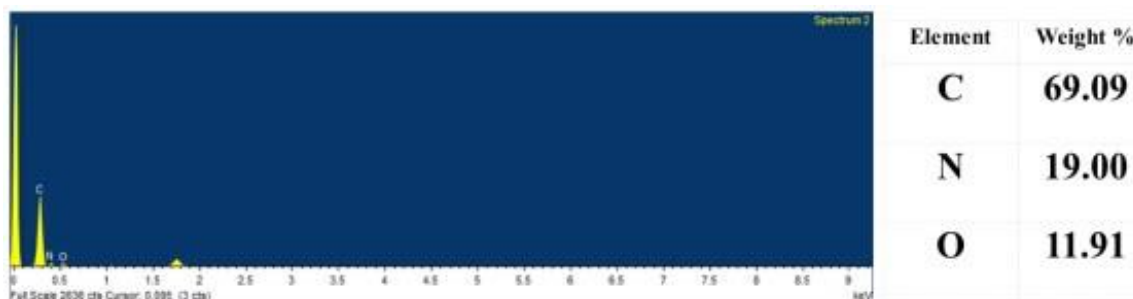
Appendix Figure 2.34: ^{13}C -CP-MAS NMR of IPpop-1 before and after catalysis



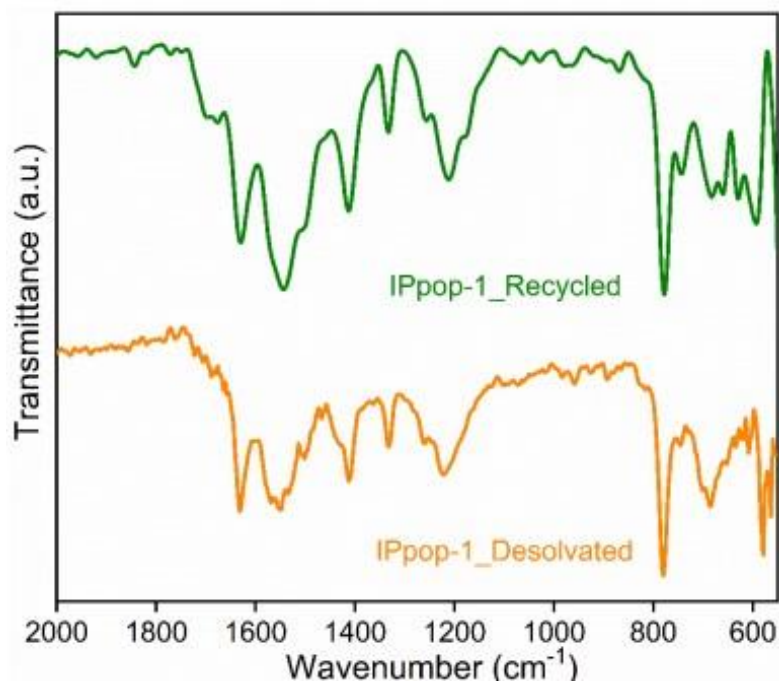
Appendix Figure 2.35: FESEM images of IPpop-1 before and after catalysis



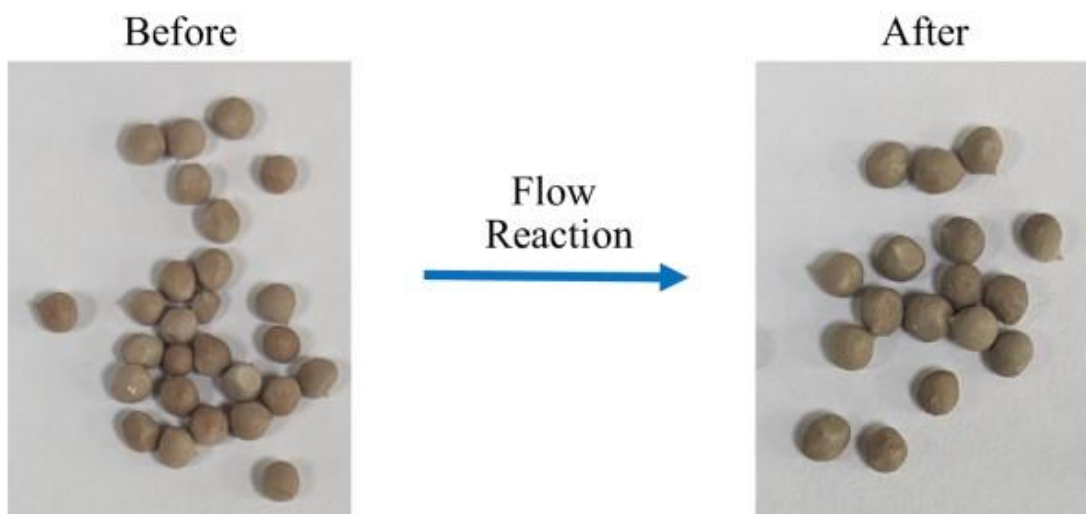
Appendix Figure 2.36: FESEM images of IPpop-1 after catalysis



Appendix Figure 2.37: EDX of IPpop-1 after catalysis



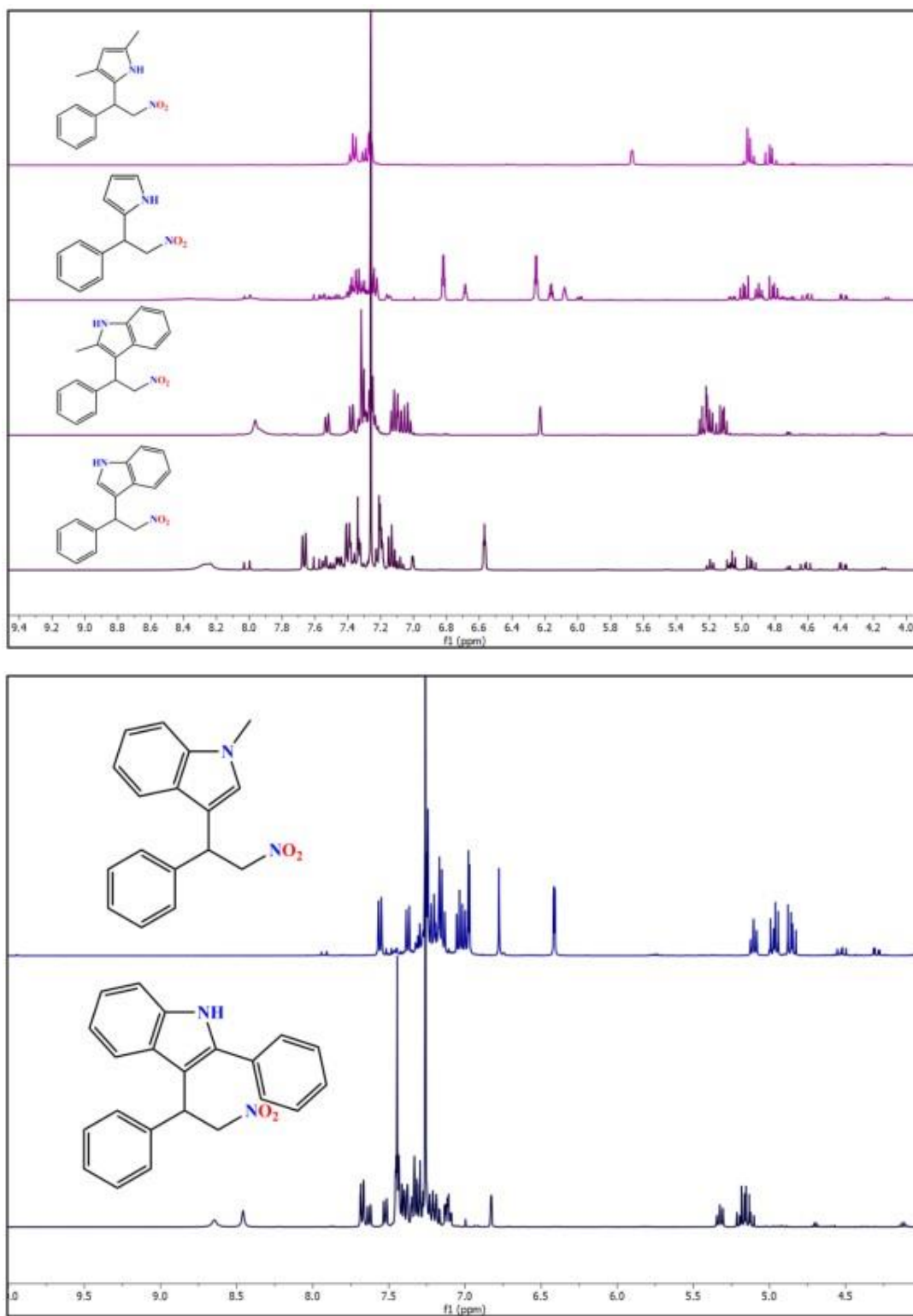
Appendix Figure 2.38: FT-IR of IPpop-1 before and after catalysis

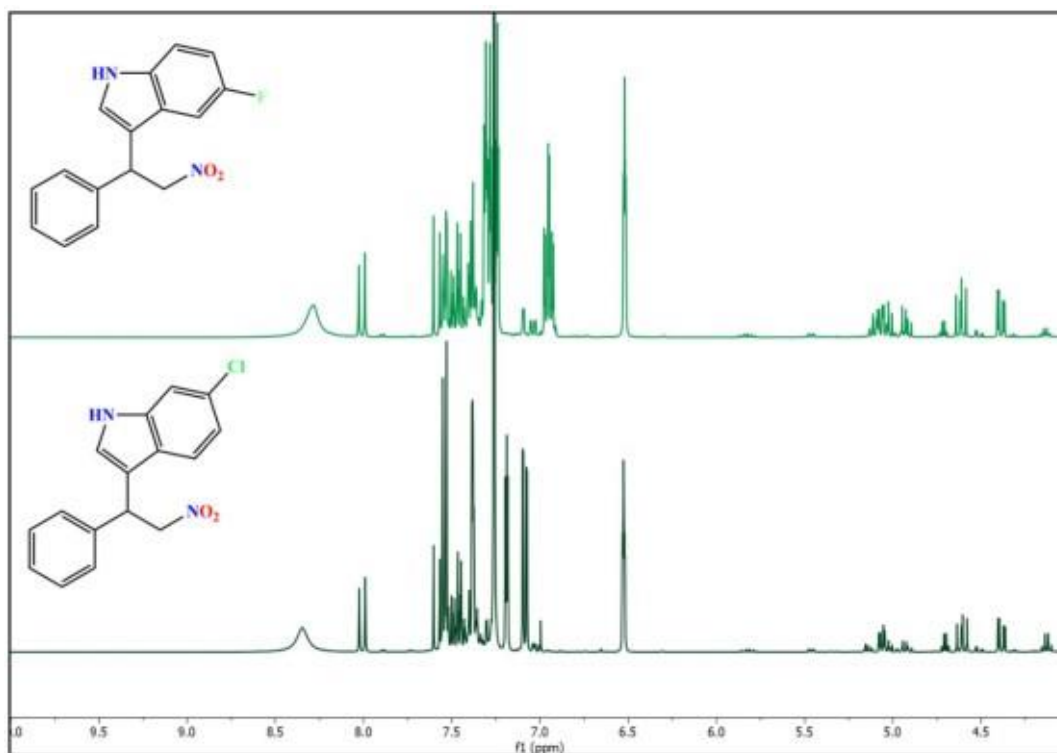


Appendix Figure 2.39: Digital picture of composite bead of IPpop-1 before and after catalysis

2.5.1. ^1H NMR Spectra of Products

2.5.1.1. ^1H NMR Spectra of Product of Friedel-Crafts Reaction

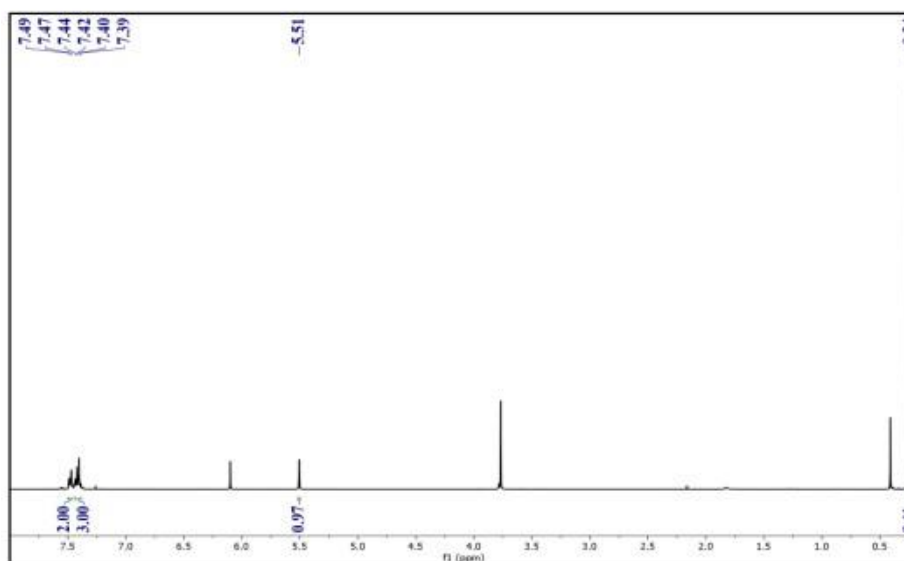


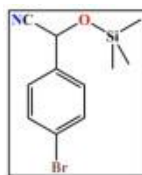


2.5.1.1. ^1H NMR Spectra of Product of Cyanosilylation Reaction



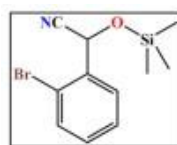
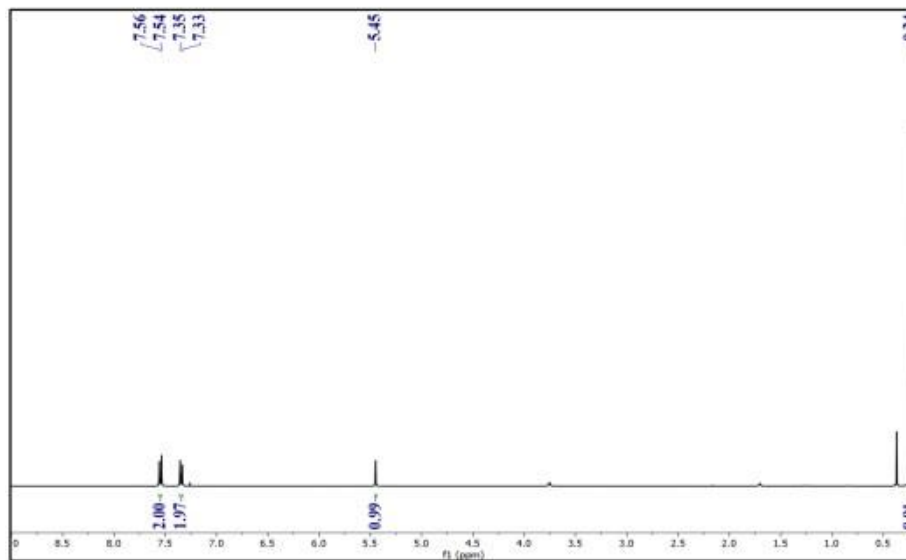
(Z)-3-phenyl-2-((trimethylsilyl)oxy)acrylonitrile:
 ^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.48 (d, 2H, $J = 8$ Hz, ArH), 7.41 (m, 3H, $J = 8$ Hz, ArH), 5.51 (s, 1H, AliH), 0.24 (s, 9H, Ali-H)





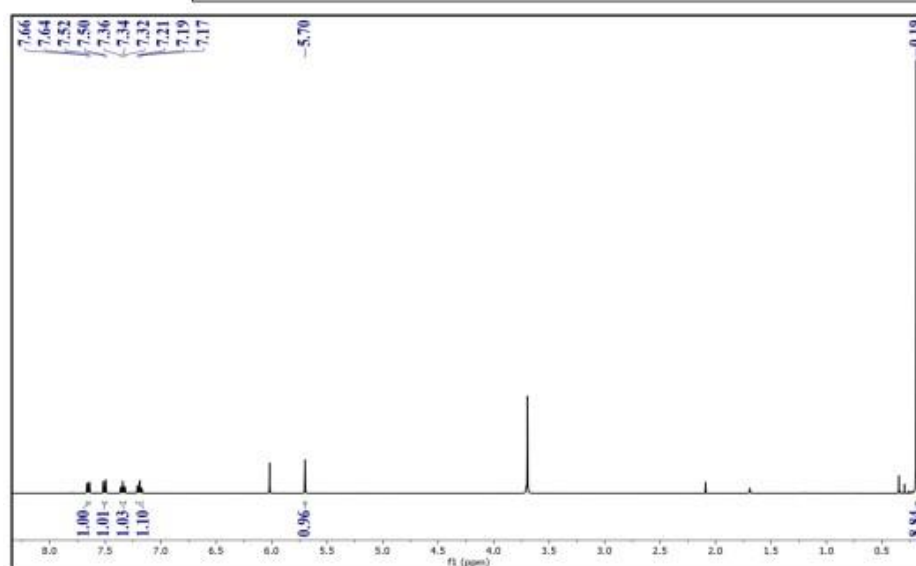
(Z)-3-(4-bromophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:

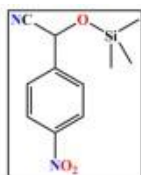
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.55 (d, 2H, $J = 8$ Hz, ArH), 7.34 (d, 2H, $J = 8$ Hz, ArH), 5.45 (s, 1H, AliH), 0.24 (s, 9H, Ali-H)



(Z)-3-(2-bromophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:

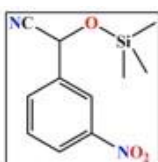
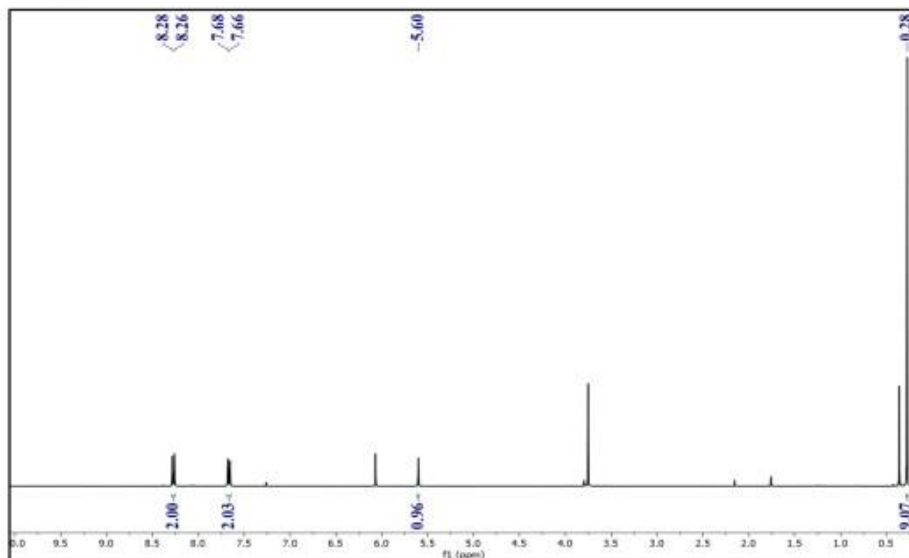
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.65 (d, 1H, $J = 8$ Hz, ArH), 7.51 (d, 1H, $J = 8$ Hz, ArH), 7.34 (t, 1H, $J = 8$ Hz, ArH), 7.19 (t, 1H, $J = 8$ Hz, ArH), 5.70 (s, 1H, AliH), 0.19 (s, 9H, Ali-H)





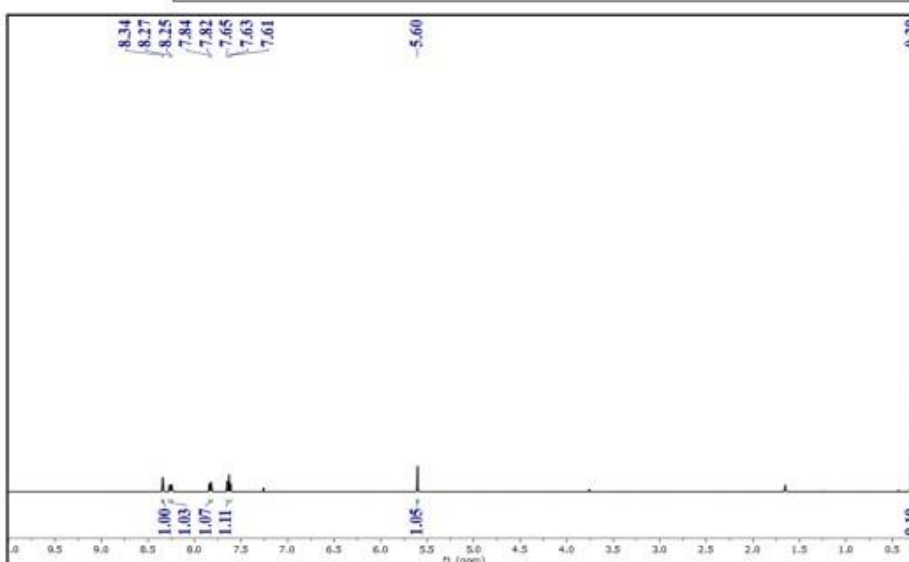
(Z)-3-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:

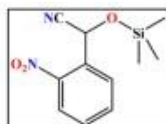
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.27 (d, 2H, $J = 8$ Hz, ArH), 7.67 (d, 2H, $J = 8$ Hz, ArH), 5.60 (s, 1H, AliH), 0.28 (s, 9H, Ali-H)



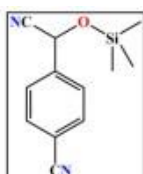
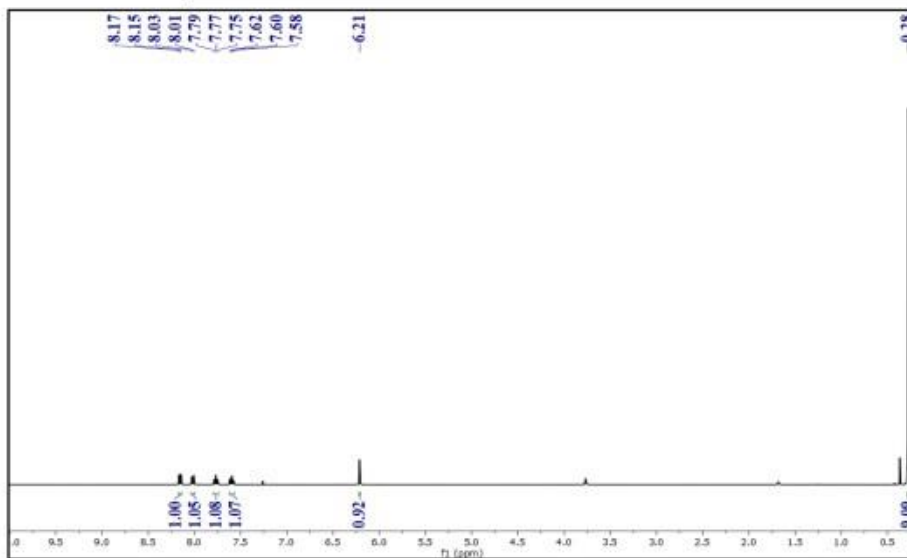
(Z)-3-(3-nitrophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.34 (s, 1H, $J = 8$ Hz, ArH), 8.26 (d, 1H, $J = 8$ Hz, ArH), 7.83 (d, 1H, $J = 8$ Hz, ArH), 7.63 (t, 1H, $J = 8$ Hz, ArH), 5.60 (s, 1H, AliH), 0.29 (s, 9H, Ali-H)

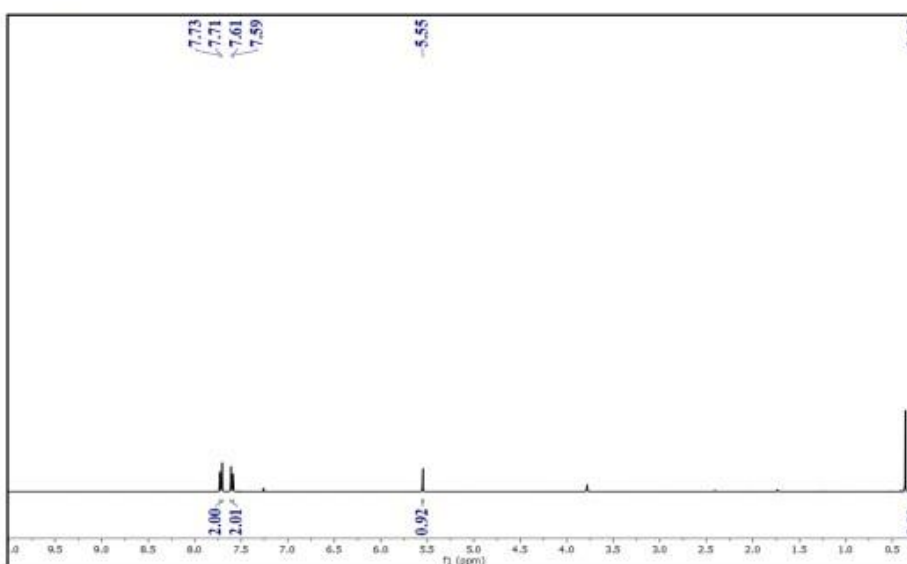


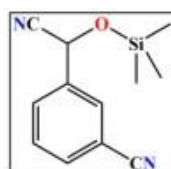


(Z)-3-(2-nitrophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.16 (d, 1H, $J = 8$ Hz, ArH), 8.02 (d, 1H, $J = 8$ Hz, ArH), 7.77 (t, 1H, $J = 8$ Hz, ArH), 7.60 (t, 1H, $J = 8$ Hz, ArH), 6.21 (s, 1H, AliH), 0.28 (s, 9H, Ali-H)

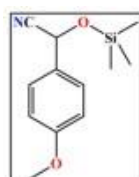
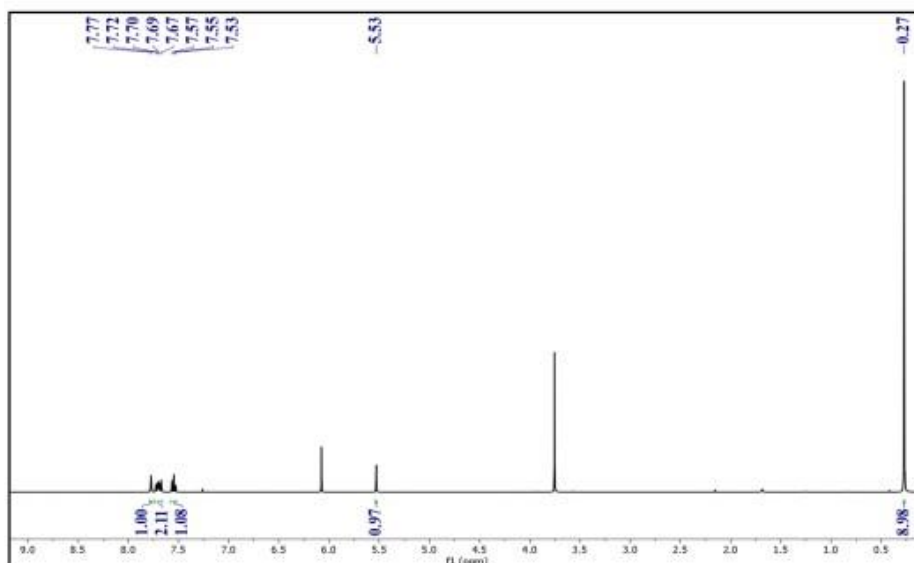


(Z)-4-(2-cyano-2-((trimethylsilyl)oxy)vinyl)benzonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.72 (d, 2H, $J = 8$ Hz, ArH), 7.60 (d, 2H, $J = 8$ Hz, ArH), 5.55 (s, 1H, AliH), 0.26 (s, 9H, Ali-H)

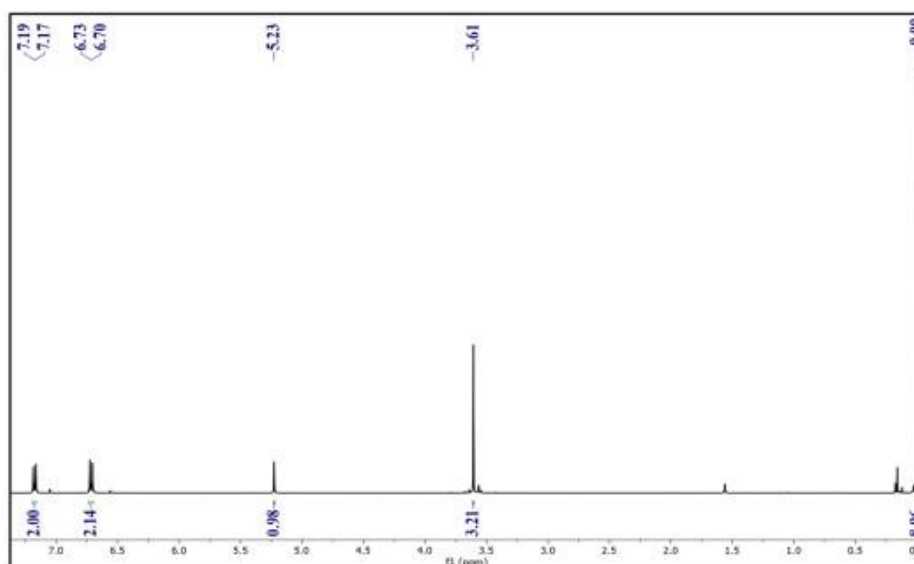


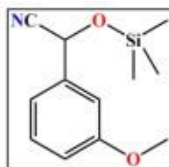


(Z)-3-(2-cyano-2-((trimethylsilyl)oxy)vinyl)benzonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.77 (s, 1H, $J = 8$ Hz, ArH), 7.70 (m, 2H, $J = 8$ Hz, ArH), 7.55 (t, 1H, $J = 8$ Hz, ArH), 5.53 (s, 1H, AliH), 0.27 (s, 9H, Ali-H)



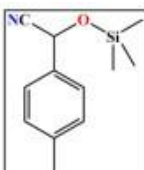
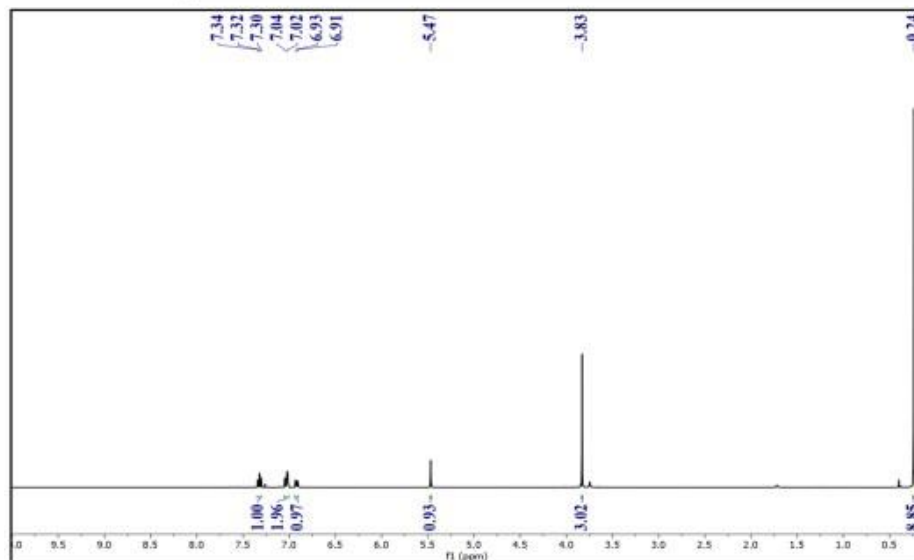
(Z)-3-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.18 (d, 2H, $J = 8$ Hz, ArH), 6.71 (d, 2H, $J = 8$ Hz, ArH), 5.23 (s, 1H, AliH), 3.61 (s, 3H, AliH), 0.00 (s, 9H, Ali-H)





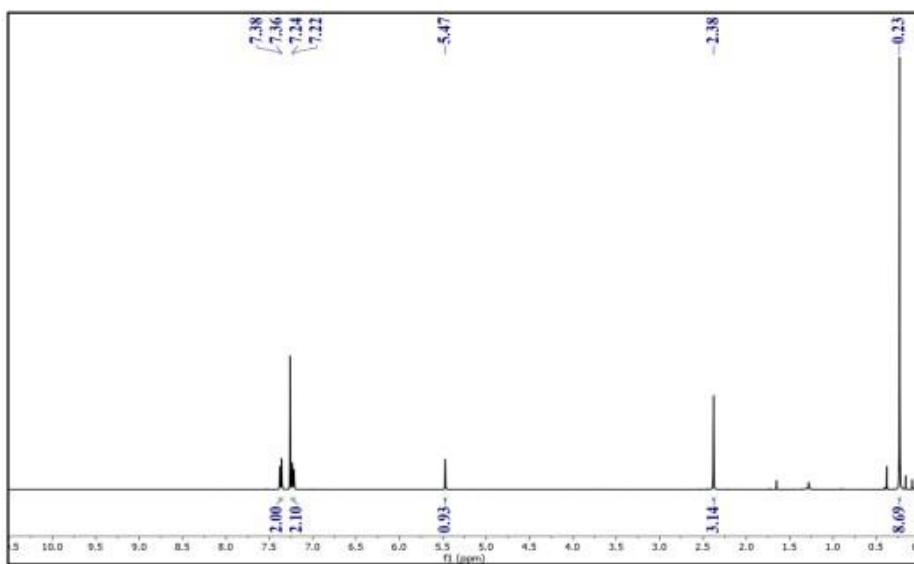
(Z)-3-(3-methoxyphenyl)-2-((trimethylsilyl)oxy)acrylonitrile:

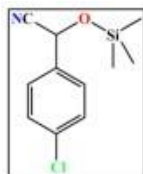
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.32 (t, 1H, $J = 8$ Hz, ArH), 7.02 (t, 2H, $J = 8$ Hz, ArH), 6.93 (d, 1H, $J = 8$ Hz, ArH), 5.47 (s, 1H, AliH), 3.83 (s, 3H, Ali-H), 0.24 (s, 9H, Ali-H)



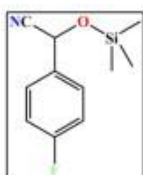
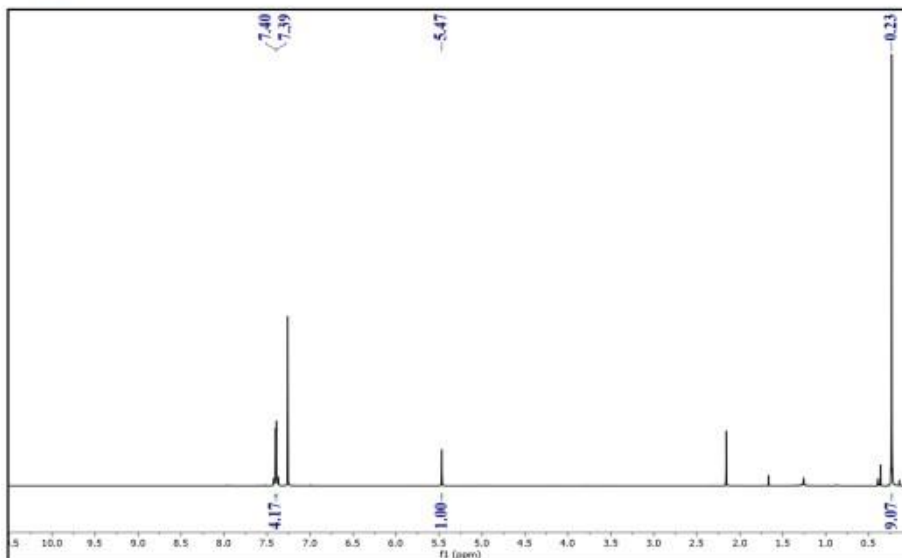
(Z)-3-(p-tolyl)-2-((trimethylsilyl)oxy)acrylonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.37 (d, 2H, $J = 8$ Hz, ArH), 7.23 (d, 2H, $J = 8$ Hz, ArH), 5.47 (s, 1H, AliH), 2.38 (s, 3H, AliH), 0.23 (s, 9H, Ali-H)

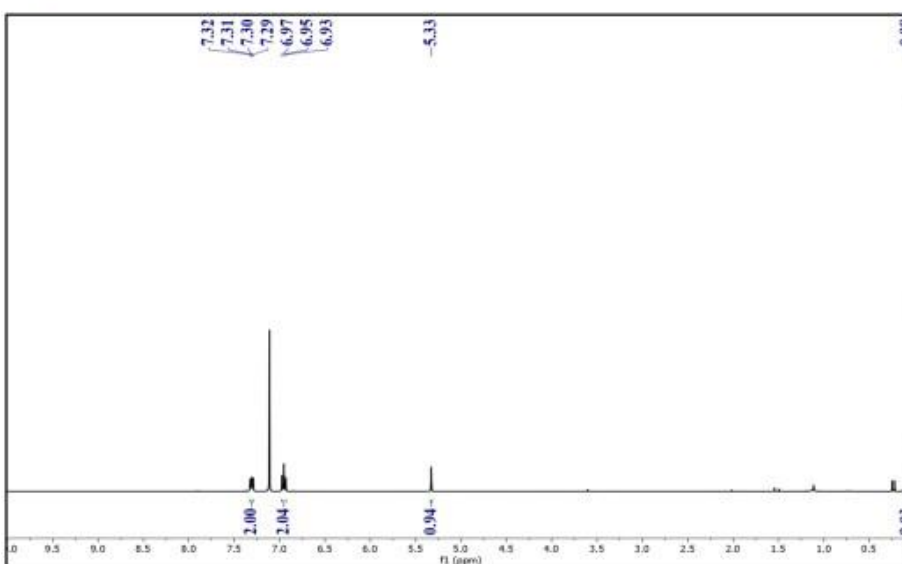


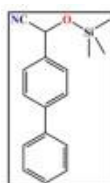


(Z)-3-(4-chlorophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C , TMS), δ (in ppm):
 7.40 (m, 4H, $J = 8$ Hz, ArH), 5.47 (s, 1H, Ali-H), 0.23 (s, 9H, Ali-H)

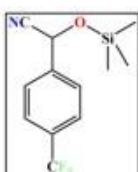
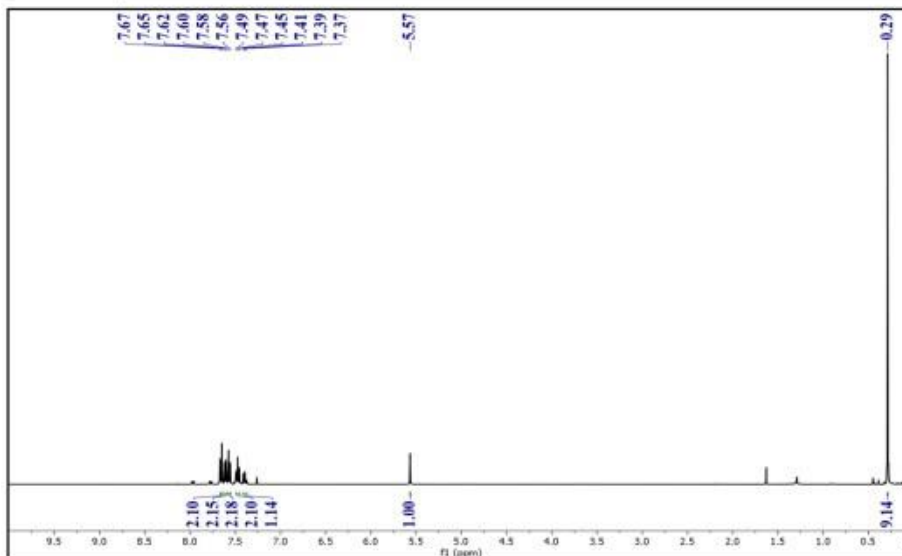


(Z)-3-(4-fluorophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.30 (m, 2H, $J = 8$ Hz, ArH), 6.95 (t, 2H, $J = 8$ Hz, ArH), 5.33 (s, 1H, AliH), 0.08 (s, 9H, Ali-H)

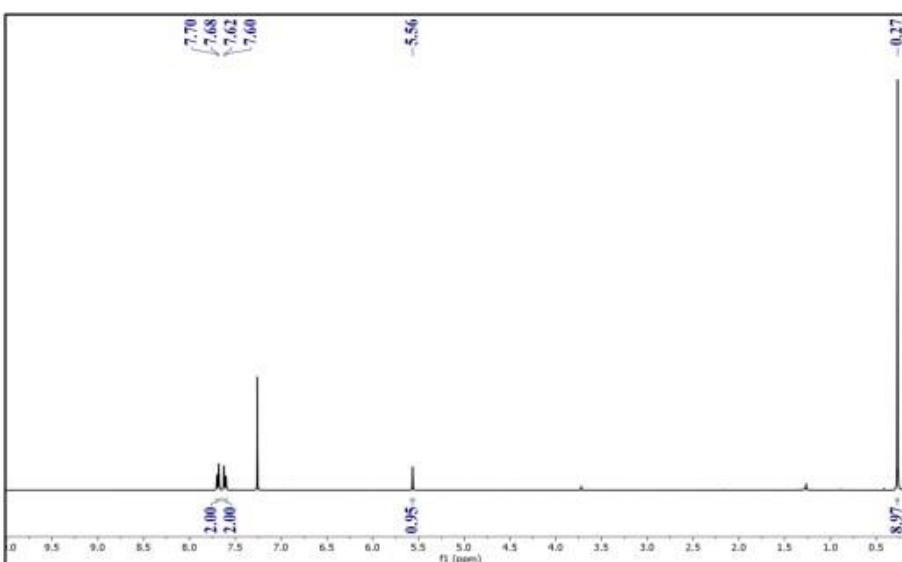


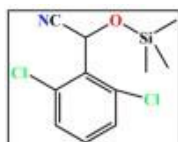


(Z)-3-([1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.66 (m, 2H, J = 8 Hz, ArH), 7.59 (m, 2H, J = 8 Hz, ArH), 7.47 (t, 2H, J = 8 Hz, ArH), 7.39 (t, 1H, J = 8 Hz, ArH), 5.57 (s, 1H, AliH), 0.29 (s, 9H, Ali-H)

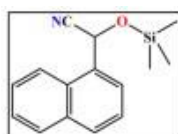
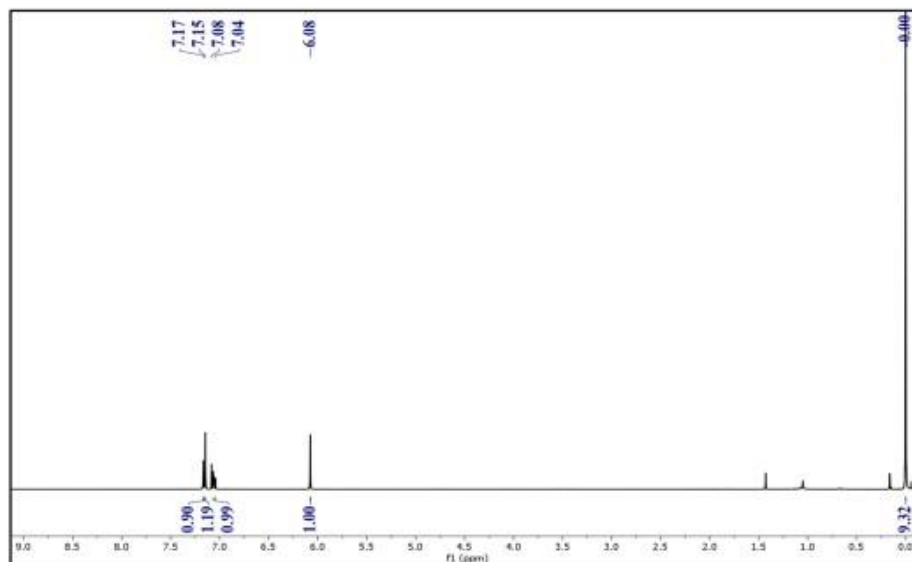


(Z)-3-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.69 (d, 2H, J = 8 Hz, ArH), 7.61 (d, 2H, J = 8 Hz, ArH), 5.56 (s, 1H, AliH), 0.27 (s, 9H, Ali-H)

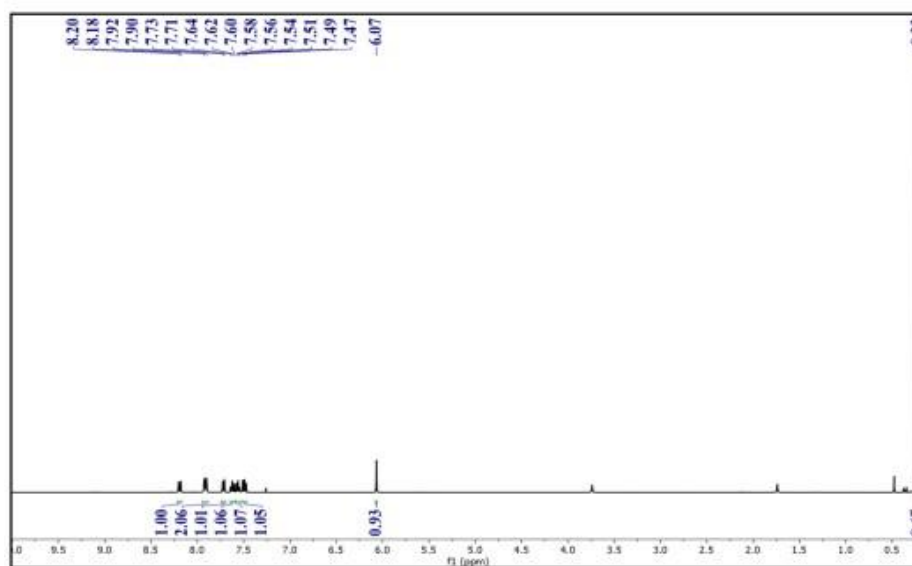


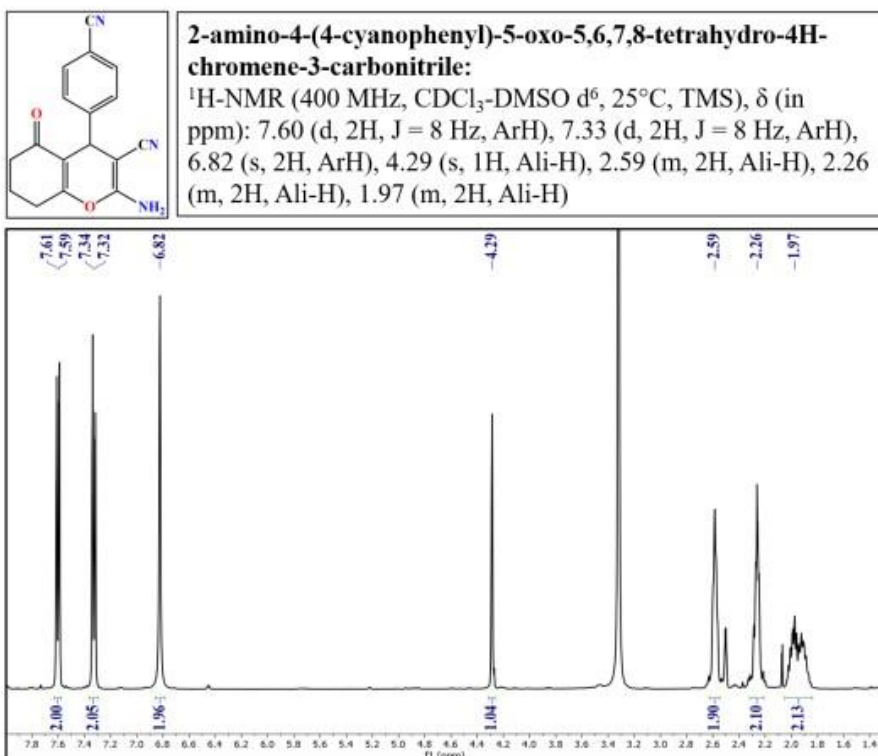
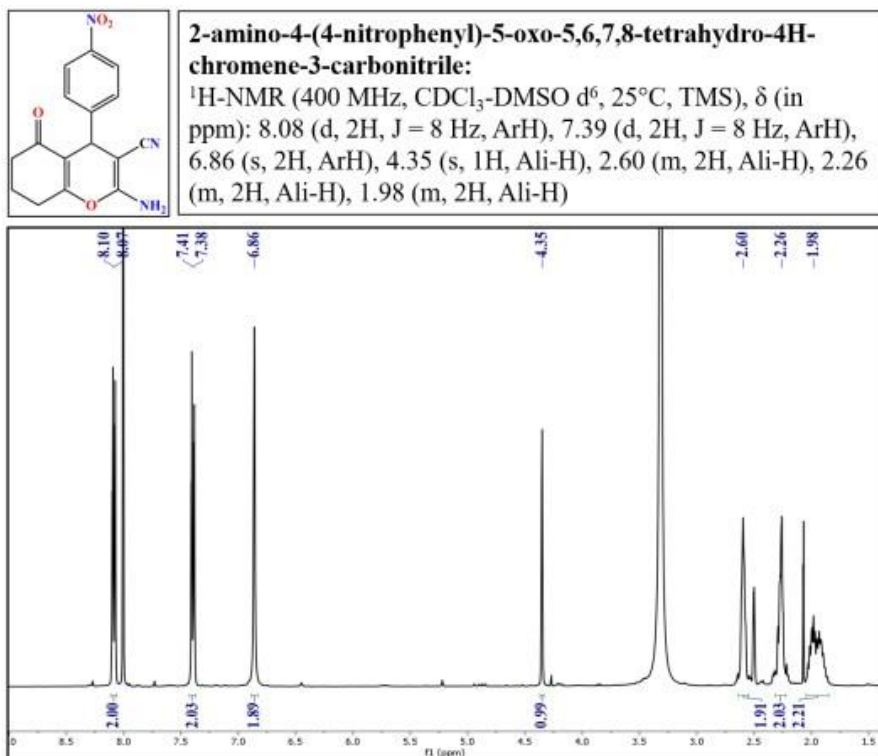


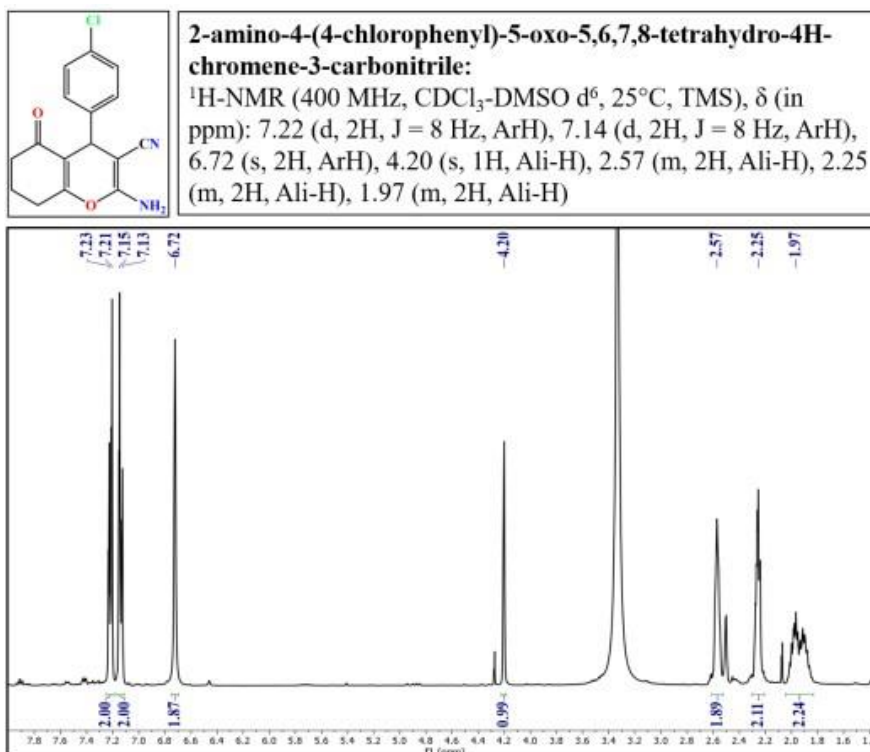
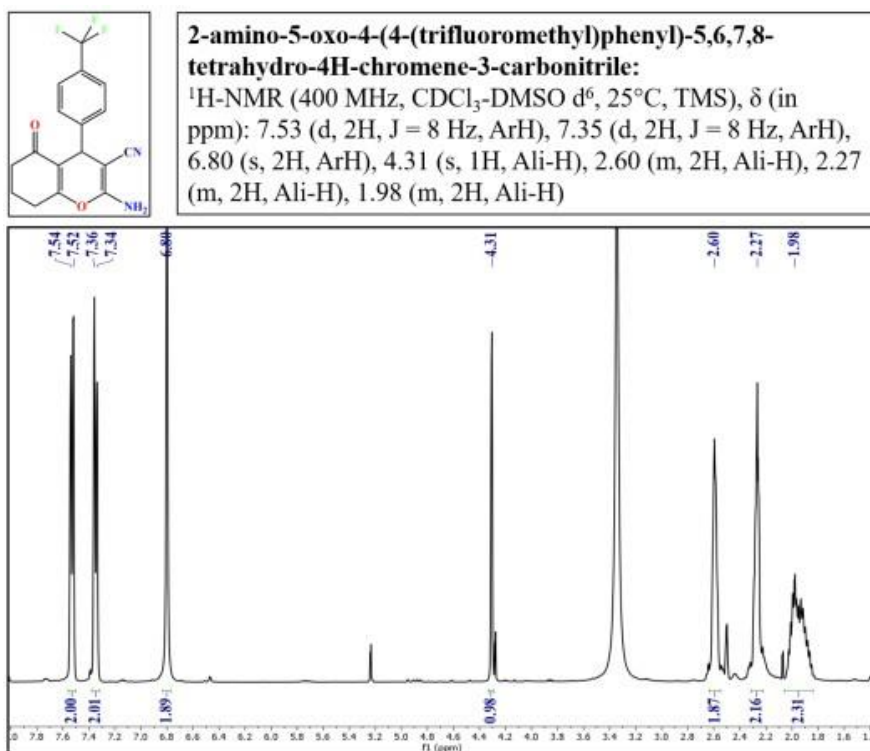
(Z)-3-(2,6-dichlorophenyl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.17 (m, 1H, $J = 8$ Hz, ArH), 7.08 (m, 3H, $J = 8$ Hz, ArH), 6.08 (s, 1H, AliH), 0.00 (s, 9H, Ali-H)

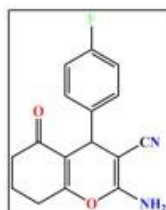


(Z)-3-(naphthalen-1-yl)-2-((trimethylsilyl)oxy)acrylonitrile:
 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.19 (d, 1H, $J = 8$ Hz, ArH), 7.91 (d, 2H, $J = 8$ Hz, ArH), 7.72 (d, 1H, $J = 8$ Hz, ArH), 7.62 (t, 1H, $J = 8$ Hz, ArH), 7.56 (t, 1H, $J = 8$ Hz, ArH), 7.49 (t, 1H, $J = 8$ Hz, ArH), 6.07 (s, 1H, AliH), 0.22 (s, 9H, Ali-H)



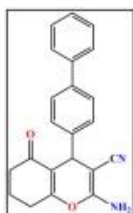
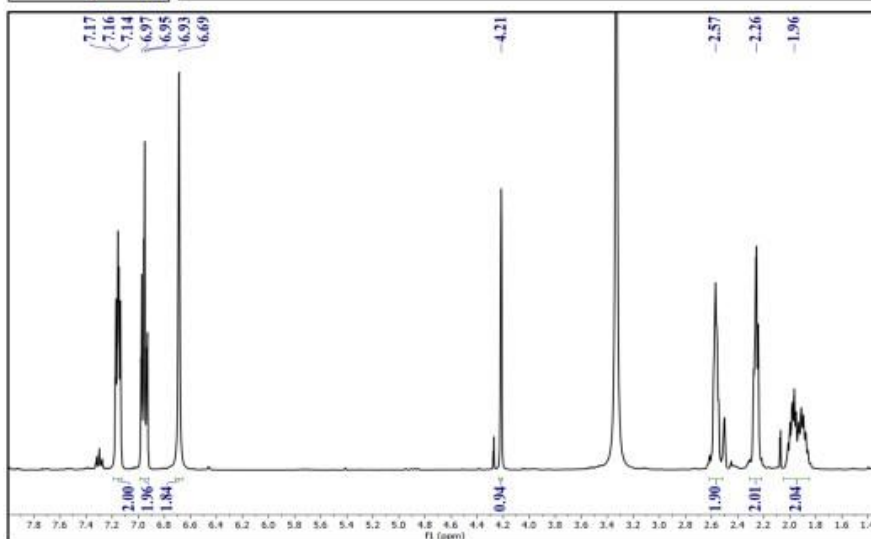
2.5.1.3. ^1H NMR Spectra of Product of Three Component Reaction





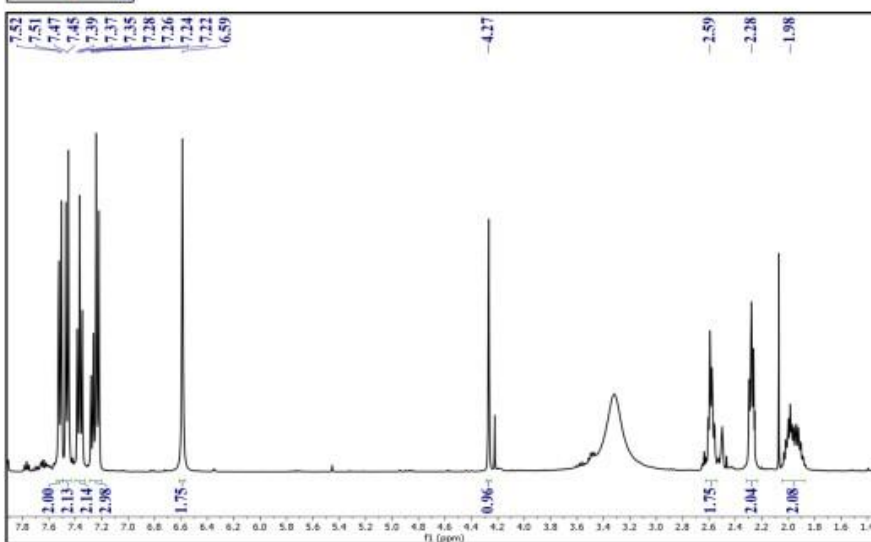
2-amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

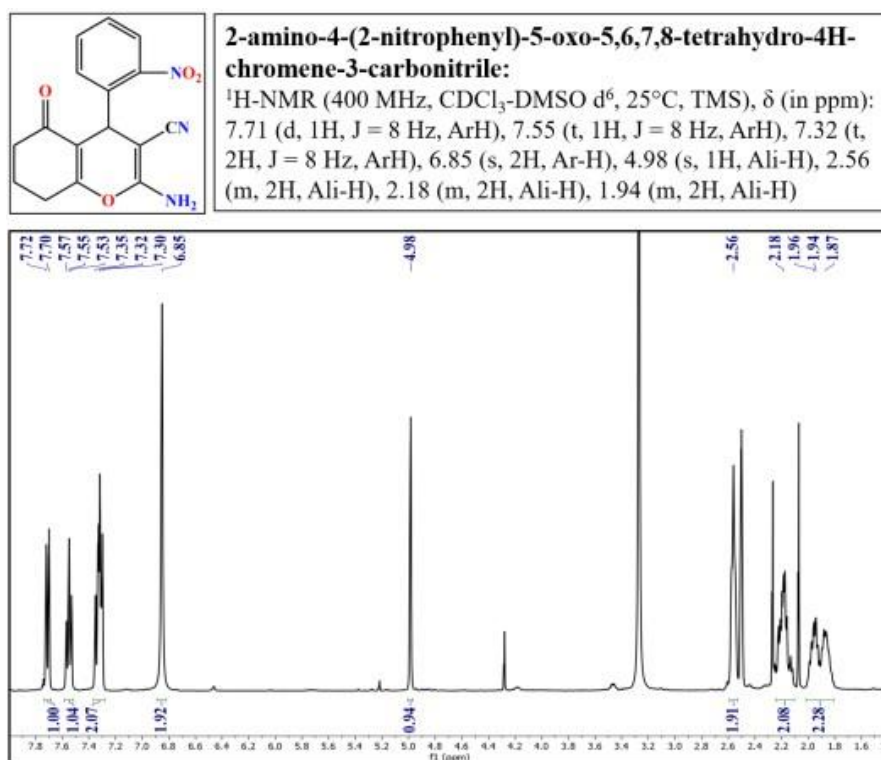
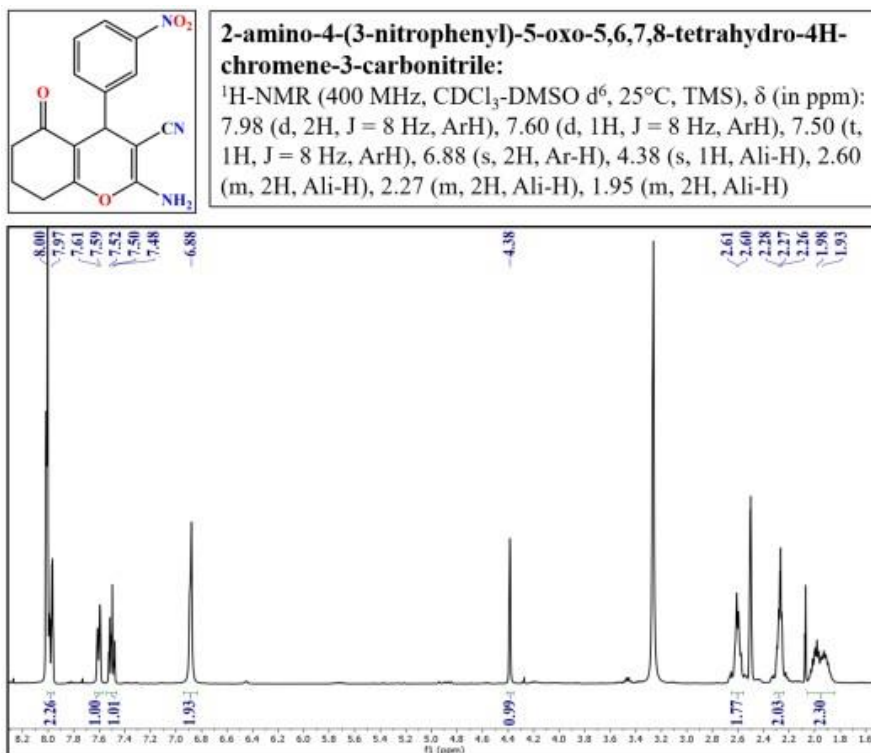
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C , TMS), δ (in ppm): 7.16 (t, 2H, $J = 8$ Hz, ArH), 6.95 (t, 2H, $J = 8$ Hz, ArH), 6.69 (s, 2H, ArH), 4.21 (s, 1H, Ali-H), 2.57 (m, 2H, Ali-H), 2.26 (m, 2H, Ali-H), 1.96 (m, 2H, Ali-H)



4-([1,1'-biphenyl]-4-yl)-2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C , TMS), δ (in ppm): 7.51 (d, 2H, $J = 8$ Hz, ArH), 7.46 (d, 2H, $J = 8$ Hz, ArH), 7.37 (t, 2H, $J = 8$ Hz, ArH), 7.23 (m, 3H, $J = 8$ Hz, ArH), 6.59 (s, 2H, ArH), 4.27 (s, 1H, Ali-H), 2.59 (m, 2H, Ali-H), 2.28 (m, 2H, Ali-H), 1.98 (m, 2H, Ali-H)

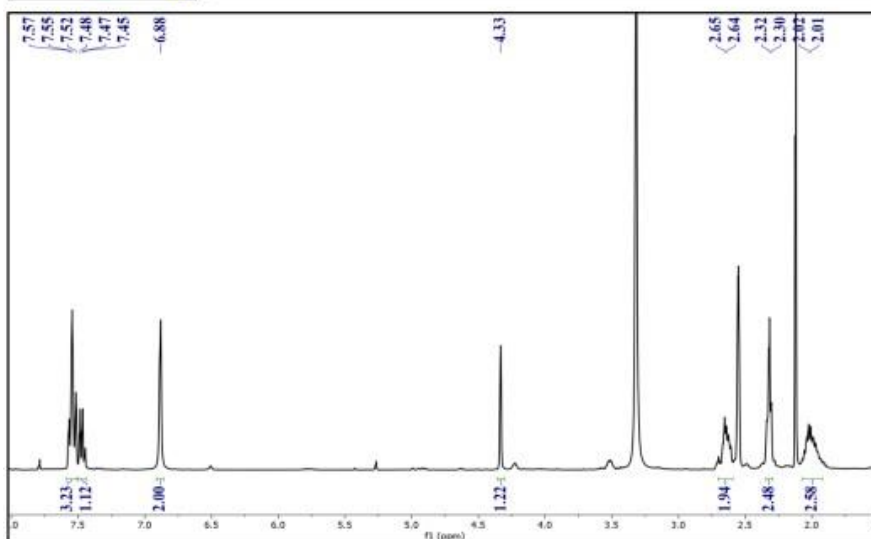






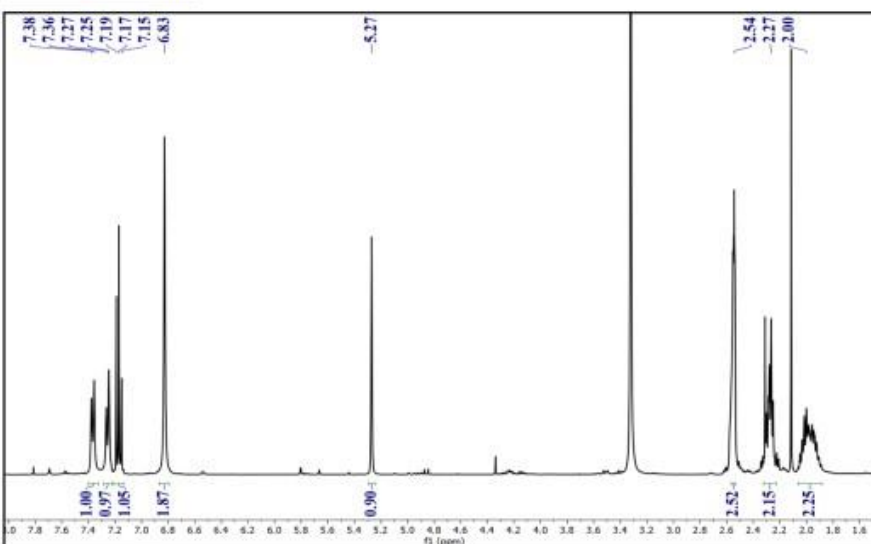
2-amino-4-(3-cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

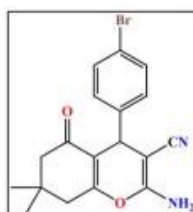
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 7.49 (m, 4H, $J = 8$ Hz, ArH), 6.88 (s, 2H, Ar-H), 4.33 (s, 1H, Ali-H), 2.64 (m, 2H, Ali-H), 2.31 (m, 2H, Ali-H), 2.01 (m, 2H, Ali-H)



2-amino-4-(2,6-dichlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

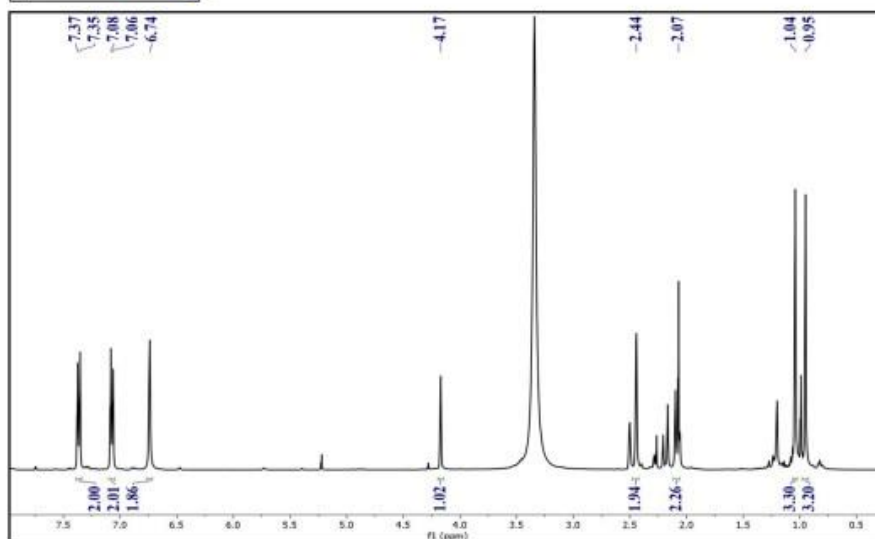
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 7.37 (d, 1H, $J = 8$ Hz, ArH), 7.26 (d, 1H, $J = 8$ Hz, ArH), 7.17 (t, 1H, $J = 8$ Hz, ArH), 6.83 (s, 2H, Ar-H), 5.27 (s, 1H, Ali-H), 2.54 (m, 2H, Ali-H), 2.27 (m, 2H, Ali-H), 2.00 (m, 2H, Ali-H)





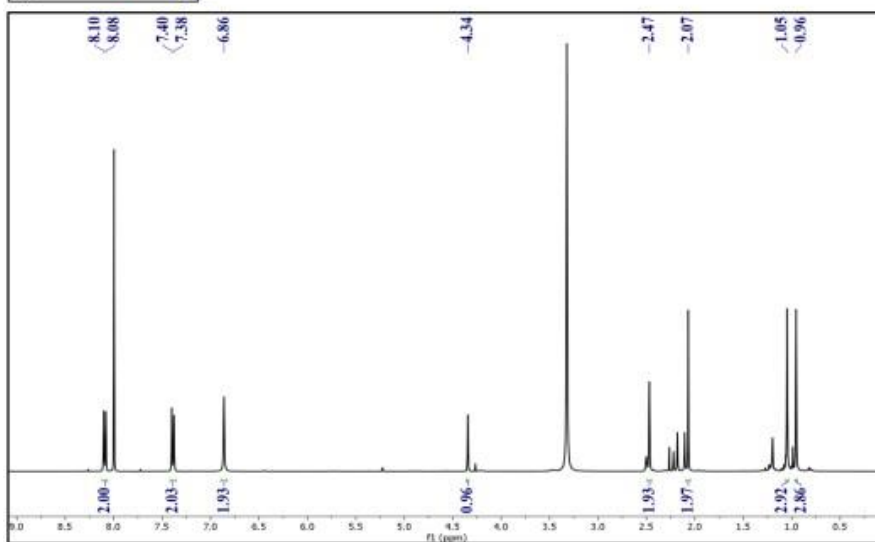
2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

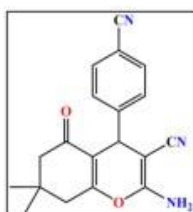
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 7.36 (d, 2H, $J = 8$ Hz, ArH), 7.07 (d, 2H, $J = 8$ Hz, ArH), 6.74 (s, 2H, ArH), 4.17 (s, 1H, Ali-H), 2.44 (s, 2H, Ali-H), 2.07 (s, 2H, Ali-H), 1.04 (s, 3H, Ali-H), 0.95 (s, 3H, Ali-H)



2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

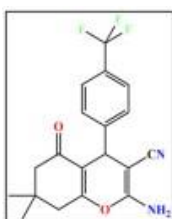
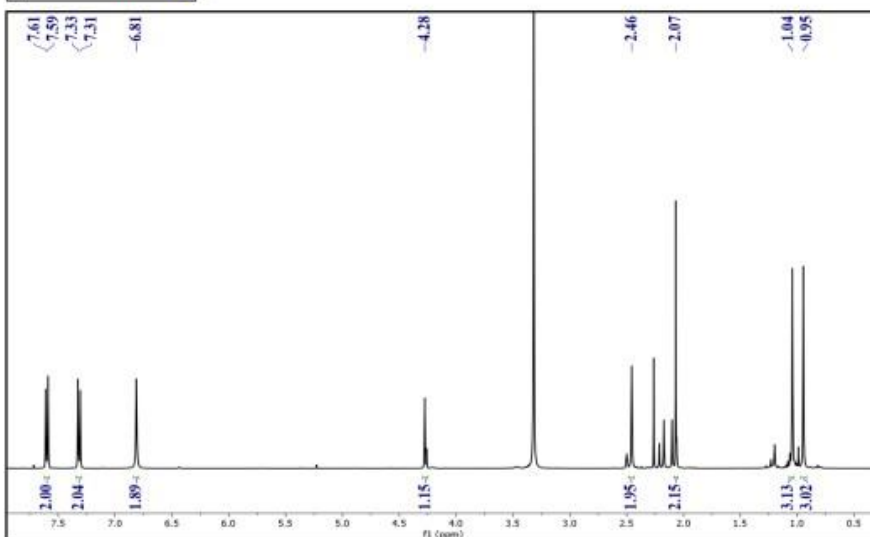
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 8.09 (d, 2H, $J = 8$ Hz, ArH), 7.39 (d, 2H, $J = 8$ Hz, ArH), 6.86 (s, 2H, ArH), 4.34 (s, 1H, Ali-H), 2.47 (s, 2H, Ali-H), 1.97 (s, 2H, Ali-H), 1.05 (s, 3H, Ali-H), 0.96 (s, 3H, Ali-H)





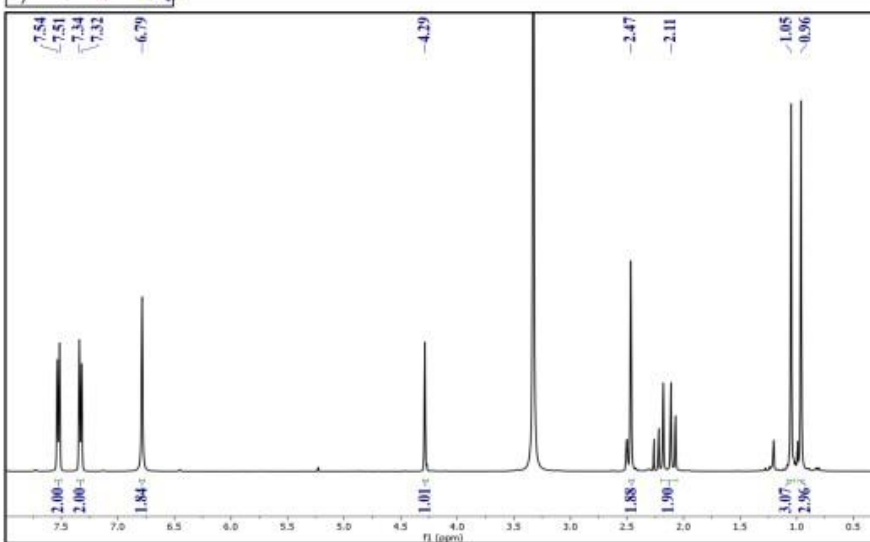
2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

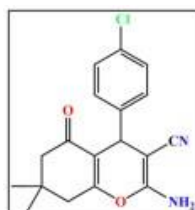
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 7.60 (d, 2H, $J = 8$ Hz, ArH), 7.32 (d, 2H, $J = 8$ Hz, ArH), 6.81 (s, 2H, ArH), 4.28 (s, 1H, Ali-H), 2.46 (s, 2H, Ali-H), 2.07 (s, 2H, Ali-H), 1.04 (s, 3H, Ali-H), 0.95 (s, 3H, Ali-H)



2-amino-7,7-dimethyl-5-oxo-4-(4-(trifluoromethyl)phenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

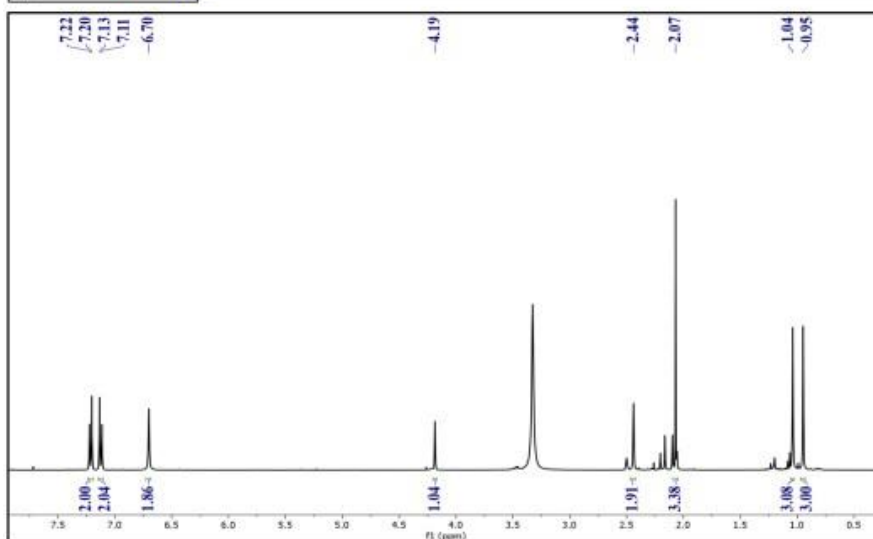
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C, TMS), δ (in ppm): 7.52 (d, 2H, $J = 8$ Hz, ArH), 7.33 (d, 2H, $J = 8$ Hz, ArH), 6.79 (s, 2H, ArH), 4.29 (s, 1H, Ali-H), 2.47 (s, 2H, Ali-H), 2.11 (m, 2H, Ali-H), 1.05 (s, 3H, Ali-H), 0.96 (s, 3H, Ali-H)





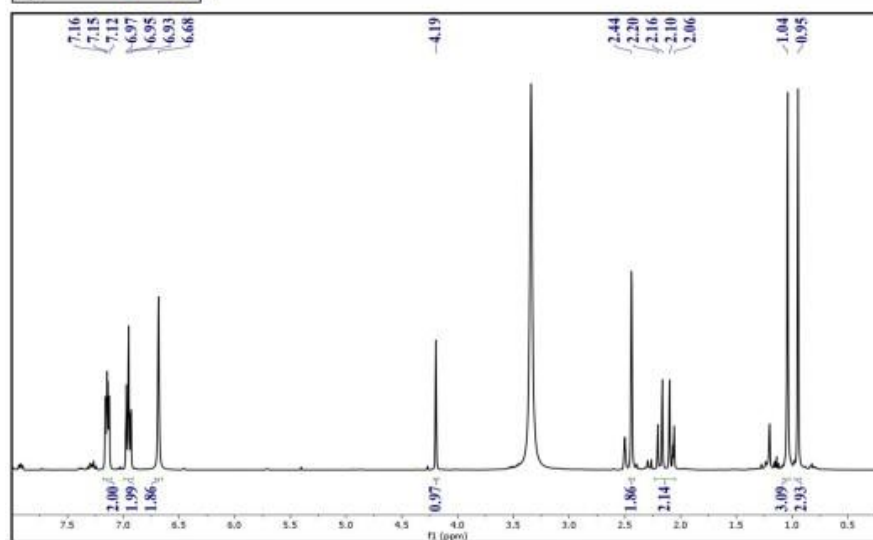
2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

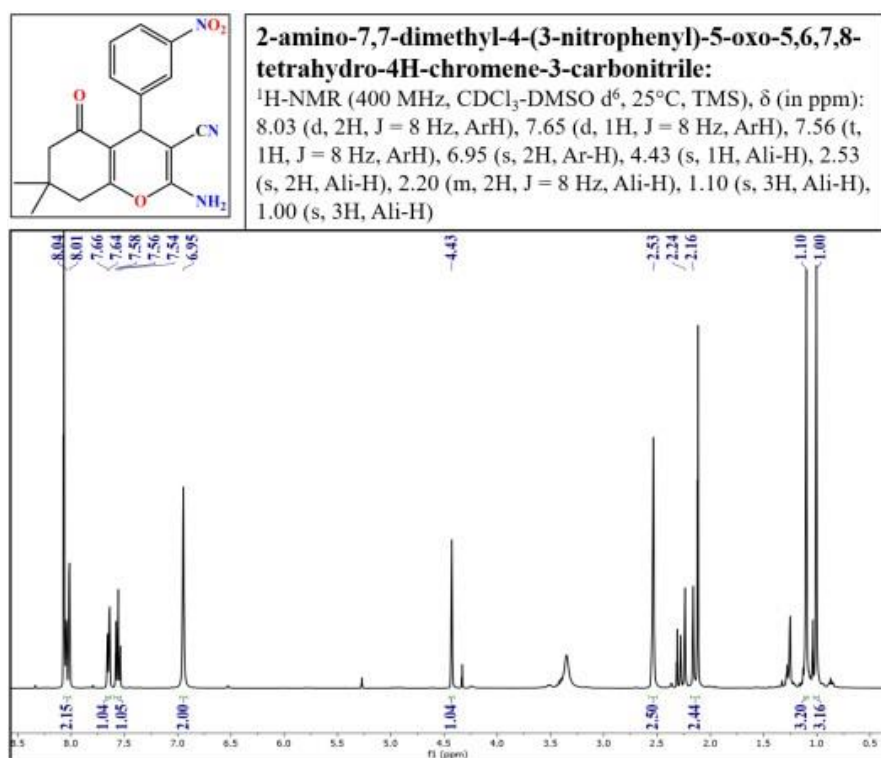
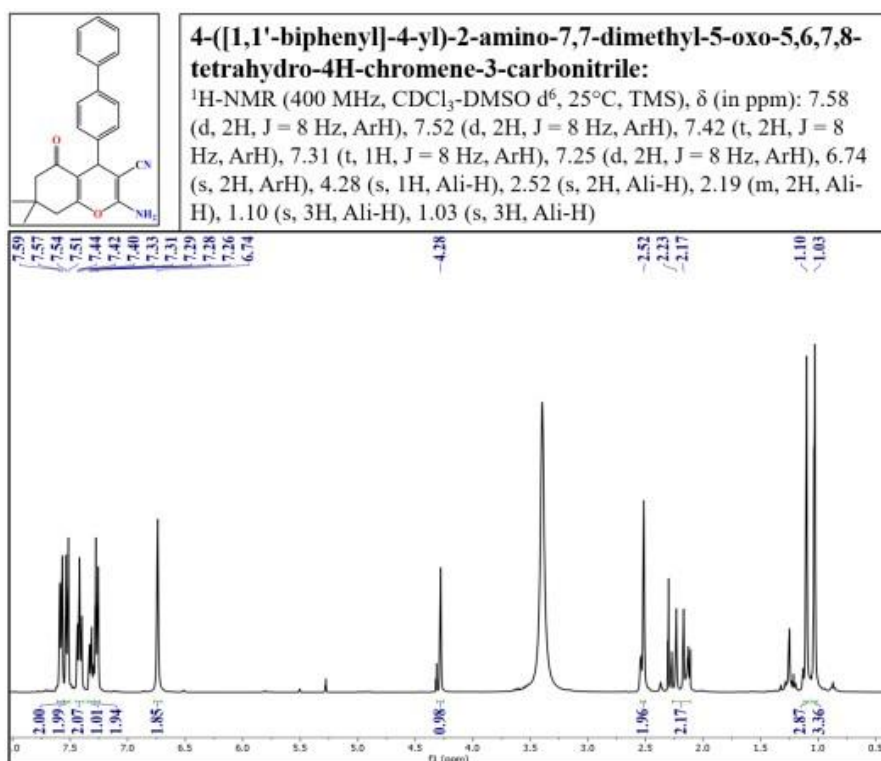
$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C , TMS), δ (in ppm): 7.21 (d, 2H, $J = 8$ Hz, ArH), 7.12 (d, 2H, $J = 8$ Hz, ArH), 6.70 (s, 2H, ArH), 4.19 (s, 1H, Ali-H), 2.44 (s, 2H, Ali-H), 2.07 (m, 2H, Ali-H), 1.04 (s, 3H, Ali-H), 0.95 (s, 3H, Ali-H)

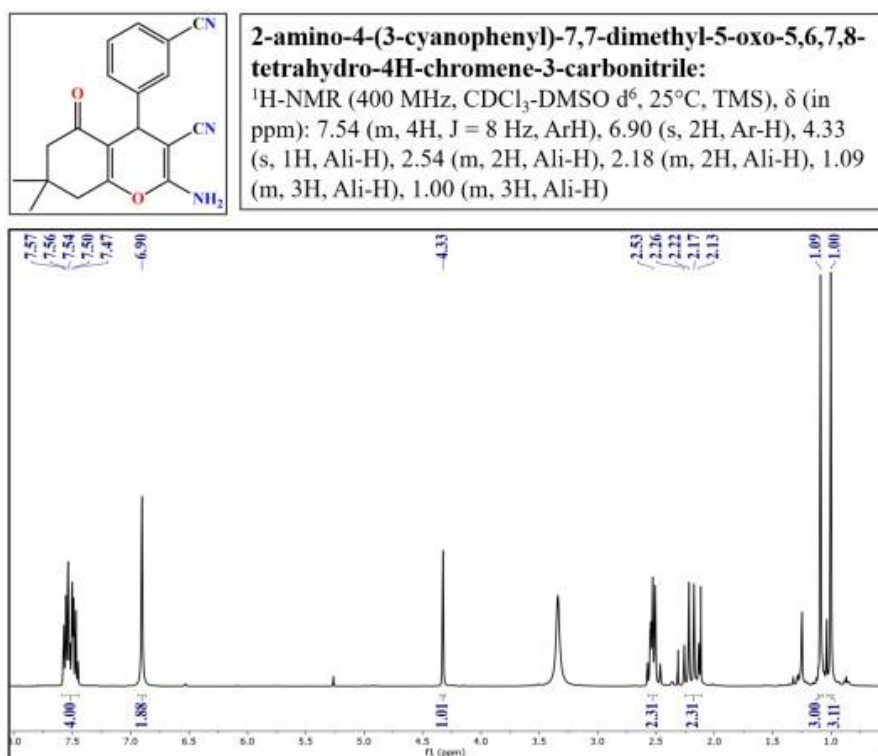
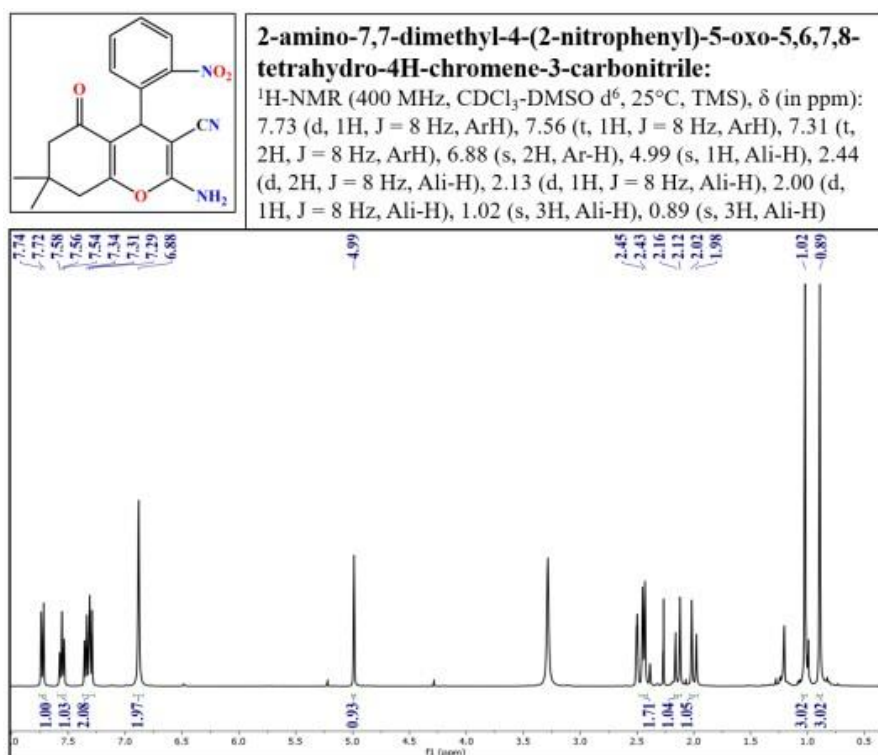


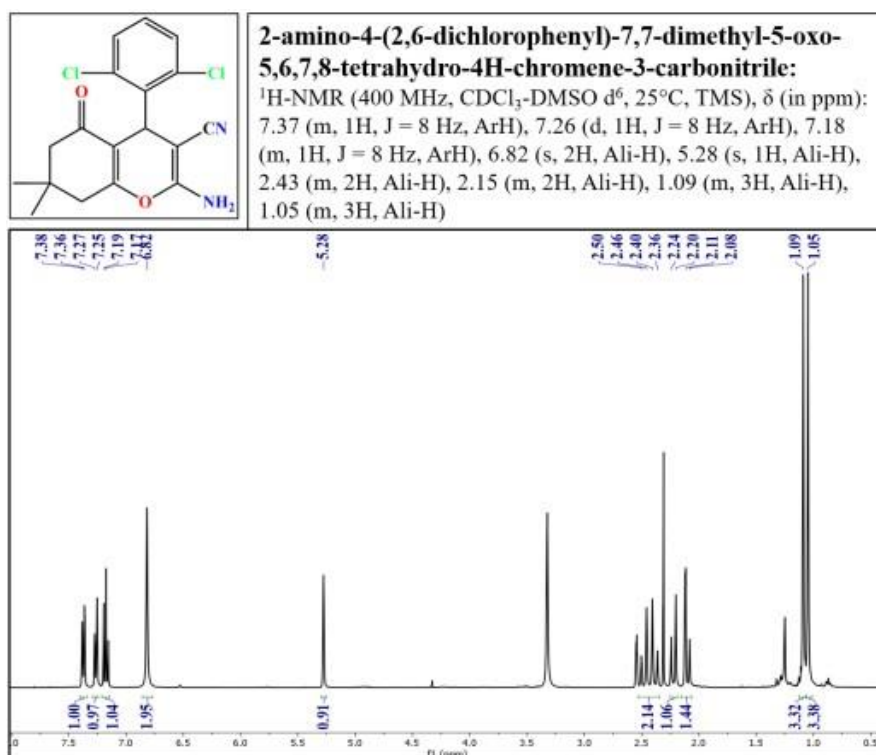
2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 -DMSO d_6 , 25°C , TMS), δ (in ppm): 7.14 (t, 2H, $J = 8$ Hz, ArH), 6.95 (t, 2H, $J = 8$ Hz, ArH), 6.68 (s, 2H, ArH), 4.19 (s, 1H, Ali-H), 2.44 (s, 2H, Ali-H), 2.13 (m, 2H, Ali-H), 1.04 (s, 3H, Ali-H), 0.95 (s, 3H, Ali-H)

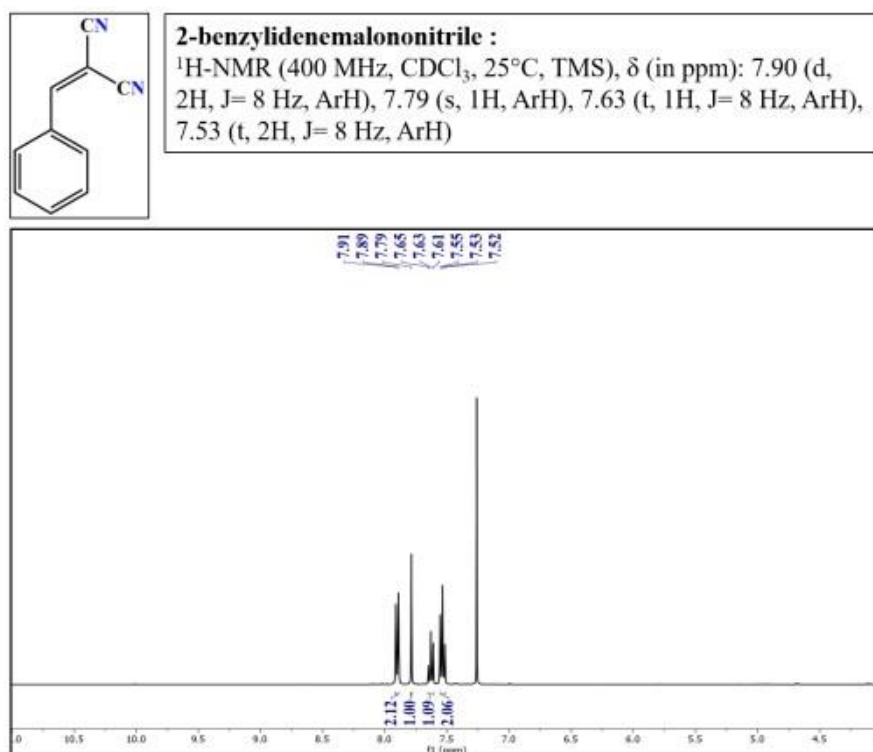


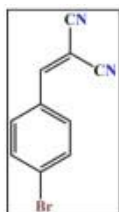




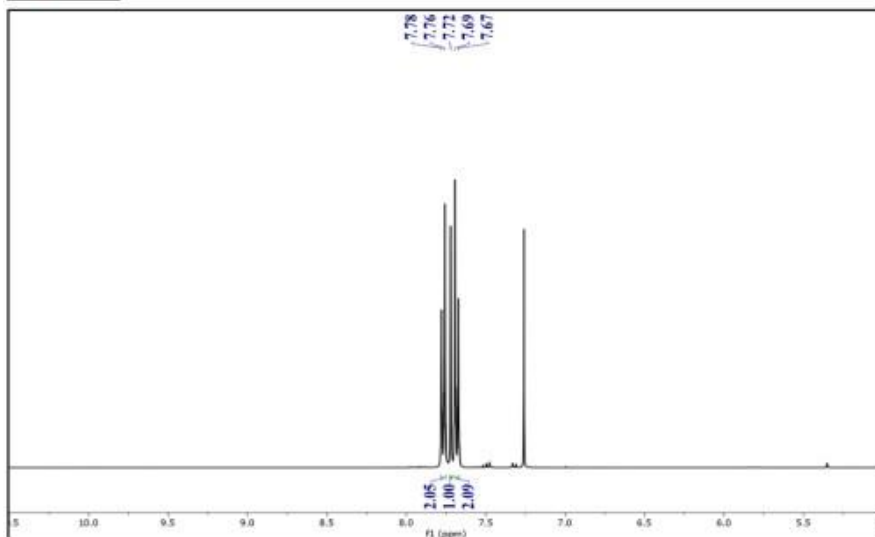


2.5.1.4. ¹H NMR Spectra of Product of Cascade Reaction



**2-(naphthalen-1-ylmethylene)malononitrile:**

^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.77 (d, 2H, ArH), 7.72 (s, 1H, ArH), 7.68 (d, 2H, $J = 8$ Hz, ArH)



Material Name	Functional Group.	Catalytic Reaction	Solvent	Temp. (°C)	Continuous Flow	Reference
Pd@UPOPs	Urea	Suzuki-Miyaura	H ₂ O	R.T.	No	3
Pd@UPOP	Urea	Suzuki-Miyaura	H ₂ O	R.T.	No	4
UOF-1 UOF-2	Urea	Suzuki-Miyaura	H ₂ O	R.T.	No	5
POP-TU	Thio-Urea	Michael Reaction	Mesitylene	R.T.	No	6
COF-TpTU	Thio-Urea	Methanolysis	MeOH	50	No	7
[Fe(dtp)(H ₂ O) ₃](H ₂ O) _{0.5} (2)	Coordination Complex	Friedel-Crafts reaction	DCM	R.T.	No	8
MNP-A, MNP-B	Nanoparticles	Friedel-Crafts reaction	DCM	R.T.	No	9
Zn-MOF (1)	Urea	Friedel-Crafts reaction	Toluene	60	No	10
Cu-MOF (1)	Urea	Friedel-Crafts reaction	CH ₃ CN	60	No	11
Zn-MOF (1)	Primary Amide	Friedel-Crafts reaction	DCM	35	No	12
NU-101	Urea	Friedel-Crafts reaction	THF/MeN O ₂	60	No	13
NU-GRH-1	Urea	Friedel-Crafts reaction	Toluene	60	No	14
UiO-67-Urea	Urea	Friedel-Crafts reaction	Toluene	70	No	15
CSMCRI-21	Carboxylic Acid	Friedel-Crafts reaction	Toluene	60	No	16
Calix[6]arene TSA F	Calix[6]arene	Friedel-Crafts reaction	H ₂ O	37	No	17
IPpop-1	Urea	Friedel-Crafts reaction/ Multi Component Reaction	EtOH	50 / R.T.	Yes	This Work

Appendix Table 2.5: Different catalytic reaction with the Urea / Thio-Urea group containing materials

2.6. References

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Chapter 3

Halide Ion Tuning in a Imidazoline Porous Organic Polymer for Photosynthesis of H_2O_2 from Sunlight, Air, and Seawater

3.1. Introduction

In the century of “energy crisis”, demand of renewable energy escalating due to restricted source of fossils fuels and conventional hydrothermal electricity production. Solar energy stands out as the most crucial candidate among clean and renewable energy sources on earth. Artificial photosynthesis of hydrogen peroxide (H_2O_2) directly from air and water in sunlight, has attracted considerable attention due to its rapidly growing demand in modern energy and environmental applications. In recent years, H_2O_2 has gained attention as a potential energy carrier in terms of storage and transportation due to its comparable energy density with compressed H_2 . In particular H_2O_2 can be used in single-chamber fuel cells as its output potential (1.09 V) is much lower to that of hydrogen (1.23 V) or methanol (1.21 V) fuel cells.¹ Hydrogen peroxide (H_2O_2) is a highly versatile oxidizing agent widely utilized as an environmentally benign disinfectant for the inactivation of pathogenic microorganisms and pollutants, as well as in personal care products, due to its higher oxidative properties in mild conditions and water and oxygen as green by-products.^{2,3} The global demand for H_2O_2 has been rising significantly, projected to approximately US\$15.4 billion by 2030.⁴ Production volumes have also expanded, from 4.4 million tons in 2022 to 7.8 million tons by 2032,⁵ yet there remains a considerable gap to be addressed through the development of more sustainable and cost-effective production techniques. Current methods for H_2O_2 production include persulfate electrolysis, electrochemical oxygen reduction, isopropanol oxidation, direct synthesis from hydrogen and oxygen, and the widely employed anthraquinone (AQ) oxidation process. However, the AQ process presents several challenges, including the use of large quantities of organic solvents (e.g., heavy aromatics and trioctyl phosphate), the reliance on expensive palladium-based catalysts, the degradation of anthraquinone molecules, and complex reaction steps such as catalyst hydrogenation and oxidation.

In this aspect, photocatalytic H_2O_2 generation offers the advantages of energy efficiency, mild reaction conditions, high selectivity to minimize waste by-products, avoidance of hazardous precursors and potential for continuous production. As with general photocatalysis, a problematic issue is the quick recombination of photogenerated electrons and holes, which dissipates the excitation energy as heat, resulting in a low catalytic efficiency even when facilitated by sacrificial reagents. Photocatalytic oxygen reduction reactions (ORR) and water oxidation reactions (WOR) are extremely promising green approaches for future massive H_2O_2 production. However, the light-driven 2e^- WOR pathway is not easy to achieve due to the uphill thermodynamics (1.76 V versus normalized hydrogen electrode, NHE) when compared with that of ORR. In general, the balance between WOR and ORR is very important for the production of H_2O_2 as they can synergistically determine the catalytic kinetics and efficiency. In order to adjust the challenge issues of WOR, the sacrificial agent oxidation method has been developed to replace WOR and most of sacrificial agents are based on alcohols (e.g., methanol, ethanol, isopropanol and benzyl alcohol, etc.).

In this regard researchers developed the photoredox active materials to tackle these challenges from last few years but most of the studied materials are mostly includes the conventional semiconductor such as TiO_2 , ZnO and CdS which generally have wide bandgaps with narrow absorption region limited their efficiency.⁶ In contrast, metal organic framework consists of metal nodes and organic moieties present tunable band gap but face the stability issue in harsh condition as well as the metal leaching.⁷ Comparatively, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is a popular metal-free photocatalyst but suffers from problems such as poor dispersibility, narrow absorption range and rapid electron-hole recombination.⁸ Resorcinol–formaldehyde resins have also garnered attention for their relatively straightforward synthesis and low-cost precursors, but are often associated with low exposed catalytic site surface area and difficulty in structural modification.⁹ Interestingly most of the work were conducted using covalent-organic framework which offer several advantages as photocatalytic materials, such as versatility, tailored energy gaps, high surface area, and selective catalysis^{10–16} but restrict due to high cost of monomers, difficult synthetic process, long term structural stability.

Porous organic polymers (POPs),^{17, 18} class of advanced functional porous materials, are stepping ahead than other materials due to their ease of synthesis, long term stability in harsh chemical conditions, cost effectiveness and applicable to real-time condition in the field catalysis,^{19–25} water remediation,^{26–31} gas separation^{32–37} along with other several applications. In this work we synthesized and characterized three imidazoline porous organic polymer, IPM-402F, IPM-402Cl and IPM-402Br, tuning the halide ions during the in-situ synthetic process. The imidazoline functionalized POP contains cationic backbone of the polymeric network with halide ion (F^- , Cl^- , Br^-) as counter anions inside the pores. These polymers are extremely chemically stable in different harsh conditions and possess the light harvesting property makes them photoactive catalyst. The photochemical H_2O_2 production was found in very high value with $535133 \mu\text{Mh}^{-1}\text{g}^{-1}$ in case of IPM-402F in the H_2O -EtOH (9:1) mixture under blue light (450 nm) irradiation which outperformed all the reported values in the field of photocatalytic H_2O_2 production. The production trend follows the order as IPM-402F > IPM-402Br > IPM-402Cl. Also, in only water medium the production rate was found to $384475 \mu\text{Mh}^{-1}\text{g}^{-1}$. In the real-world scenario, in sunlight, air, seawater, the impressive production rate of $58654 \mu\text{Mh}^{-1}\text{g}^{-1}$ for IPM-402F. The apparent quantum yield (AQY %) was found to be 26.36 and Solar to chemical conversion (SCC %) was calculated 1.233. Scavenging test suggested that the photocatalytic H_2O_2 production follows the direct 2e^- ORR pathway, also supported by the electrochemical process in 0.1M KOH. Mechanistic pathway was further investigated via DFT calculation and showed the dependency of water and the role of the halide anion in the process of H_2O_2 production.

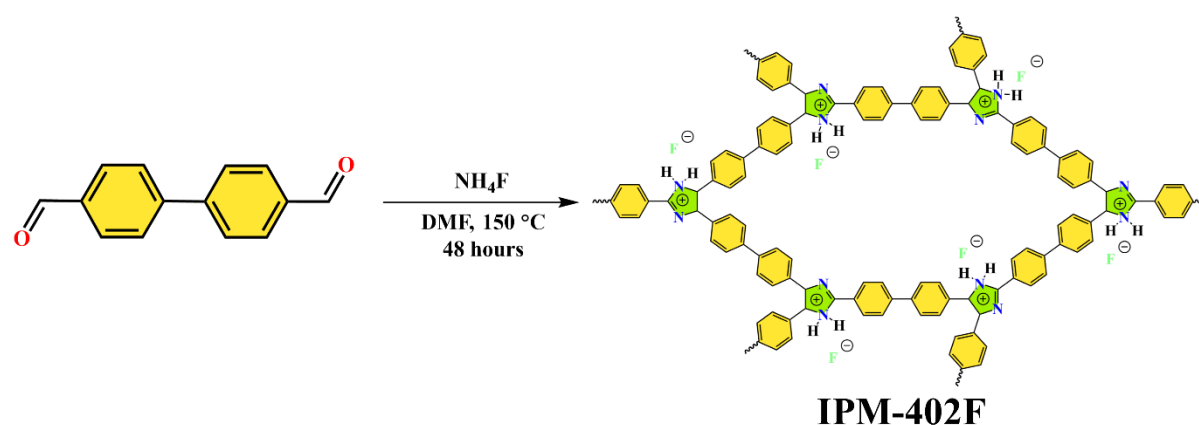
3.2. Experimental

3.2.1. Materials

Chemicals and materials used in this work as followings: 4,4'-Biphenyldicarboxaldehyde, N,N-dimethylformamide (DMF), Ammonium fluoride (NH_4F), Ammonium chloride (NH_4Cl), Ammonium bromide (NH_4Br), Titanium(IV) oxysulfate-sulfuric acid hydrate, Silver nitrate (AgNO_3), Sodium iodate (NaIO_3), Ethylenediaminetetraacetic acid disodium salt (2K-EDTA), Triethanolamine, Sodium azide (NaN_3), 1,4-Diazabicyclo[2.2.2]octane (DABCO), Hydroquinone (HQ), N-tert-butyl- α -Phenylnitron (PBN), Disodium 4,5-dihydroxy-1,3-benzenedisulfonate (Tiron), Ascorbic Acid (AA), para-Benzoquinone (p-BQ), tert-Butanol, Mannitol, Peroxide strip, Nitro blue tetrazolium chloride (NBT). All the reagents, starting materials and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals, BLD Pharm, Spectrochem, Rankem Chemicals depending on their availability and used without further purification.

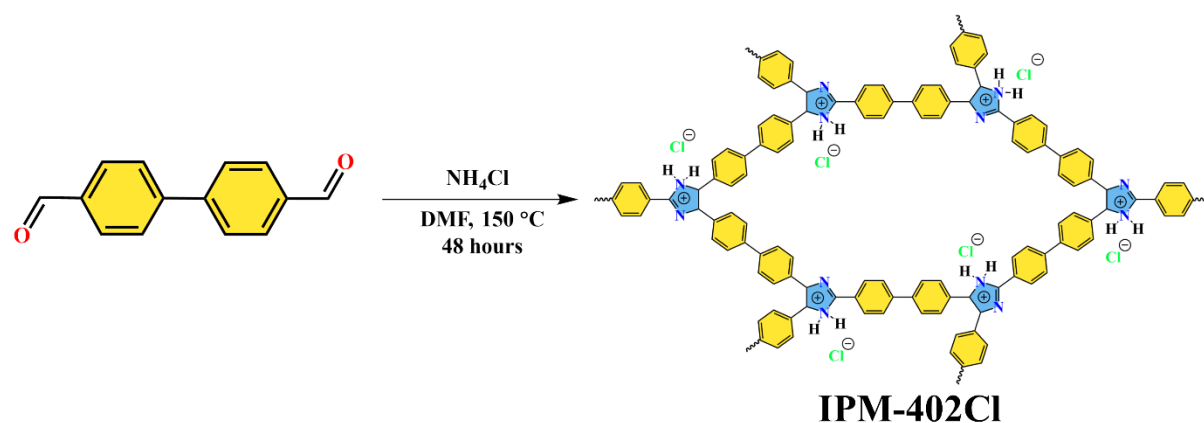
3.2.2. Synthesis

3.2.2.1. Synthesis of IPM-402F:



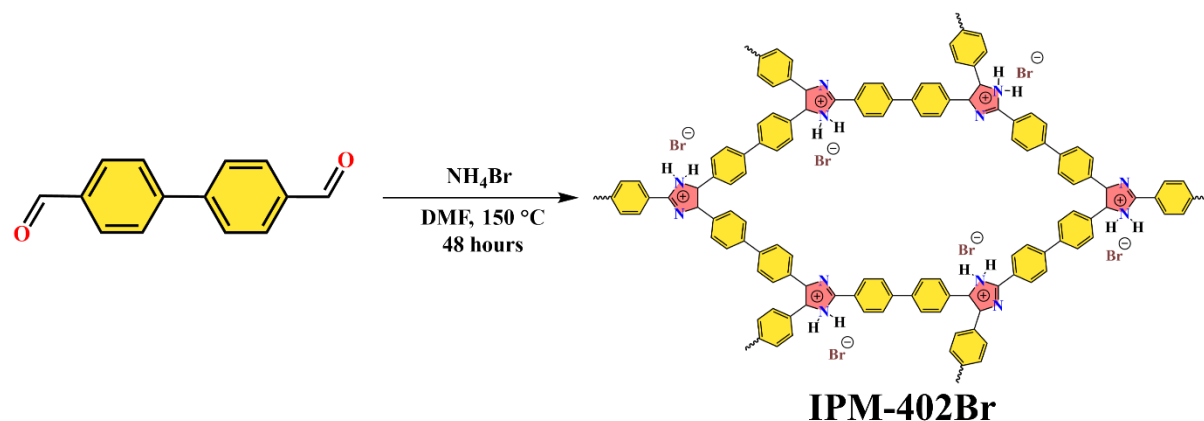
IPM-402F system was synthesized from cost-effective starting materials through a one-pot reaction with slightly modified reported protocol. A 20 mL Teflon capped glass vial was charged with 4,4'-Biphenyldicarboxaldehyde (3.5 mM) and ammonium fluoride (15 mM) and 10 mL anhydrous DMF. The mixture was then allowed to heat at 150 °C for 48 h in the hot air oven. The pale-yellow precipitate was collected, filtered and washed repeatedly with water, methanol, and then by acetone and chloroform. The resulting powder was dried at 80 °C under vacuum for overnight.

3.2.2.2. Synthesis of IPM-402Cl:



IPM-402Cl was synthesized as the same procedure as IPM-402F. Instead of NH_4F , 15 mM of ammonium chloride (NH_4Cl) was used.

3.2.2.3. Synthesis of IPM-402Br:



IPM-402Br was synthesized as the same procedure as IPM-402F and IPM-402Cl. Instead of NH_4F and NH_4Cl , 15 mM of ammonium bromide (NH_4Br) was used.

3.2.3. Material Stability and Methods:

3.2.3.1. Structural stability in acid and base conditions: To investigate the structural stability of IPM-402Xs in acid and base conditions, 50 mg of IPM-402Xs powder was submerged into 10 mL of 1 M HCl or NaOH aqueous solutions for 48 h at room temperature. Then, the mixture was filtrated and washed with water several times. The filtered powder was collected and submerged in water and MeOH, which were changed three times respectively. Finally, the solid was dried under vacuum at 80 °C overnight.

3.2.3.2. Photocatalytic H₂O₂ production: The IPM-402Xs (5 mg) was added to a 5 mL of water in glass Schlenk tube (10 mL), and then ultrasonicated for 10 min to disperse the IPM-402Xs after the vial was left uncapped under air. To make the oxygen-saturated atmosphere, the water in the Schlenk tube was bubbled with O₂ via a gas line. The system remained stirring at 500 rpm during the reaction period and was irradiated by different LED monochromatic lights. The distance between the light source and the Schlenk tube was 5.0 cm.

3.2.3.3. H₂O₂ detection methods: 2 mL 0.5mM titanium oxysulfate (TiOSO₄) aqueous solution added with sulfuric acid aqueous solution was added to 1 mL reaction solution to obtain solution, which was then kept for 30 min. H₂O₂ molecules react with titanium oxysulfate under acidic conditions to form titanium complexes (with strong absorption near 407 nm). The absorbance of titanium complexes at 407 nm is measured by UV-Vis spectrometer (Shimadzu UV-3600i), and then the amount of H₂O₂ generated by each reaction can be calculated.

3.2.3.4. Calibration for the measurements of H₂O₂ solutions: H₂O₂ solutions with different concentrations of 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mM were prepared. The TiOSO₄-H₂SO₄ solution was used as the color indicator. The mixture solution was shaken and then kept still for 30 minutes. UV-vis spectra of the solution were recorded by using a UV-vis spectrophotometer at 407 nm. The linear relationship between H₂O₂ concentration and the absorption intensity was established via calibration curve.

3.2.3.5. Cycling tests: After the reaction, the photocatalyst was centrifuged, washed with water and MeOH, and dried in a vacuum at 80 °C for 5 h. Then, the resulting photocatalyst was directly used for the subsequent runs.

3.2.3.6. Rotating ring disk electrode (RRDE) measurements (Hydrodynamic Technique): Rotating Ring Disk Electrode (RRDE) method with GC disk and Pt ring electrode was used to calculate the number of electrons and percentage of H₂O₂ production. Linear sweep voltammetry at a 10 mV/s scan rate was carried out on the disc electrode, whereas the ring was biased at H₂O₂ oxidation potential (0.7 V vs Ag/AgCl). These measurements were performed using a 0.1 M KOH (pH = 12) with various rotation rates (400, 625, 900, 1225, 1600, 2025 and 2500 rpm). Before each measurement, the electrolyte was saturated with O₂. The working electrocatalysts were prepared by taking 5 mg of the specific IPM-402X (X = -F, -Cl, -Br) in 1 mL IPA. 10 μ L Nafion binder was added to the mixture. This mixture was sonicated for 1 hour to prepare electrocatalyst ink. This ink was coated on the disk electrode and well-dried before the RRDE experiments.

The number of electrons (n) is calculated by this equation.

$$n = \frac{4I_d}{I_d + \frac{I_r}{N_c}}$$

The % of peroxide (p) produced is calculated via this equation.

$$p = \frac{2\frac{I_r}{N_c}}{I_d + \frac{I_r}{N_c}}$$

Here, I_d = disk current, I_r = ring current, and N_c = collection efficiency.

N_c is found to be 0.424 at room temperature and pressure.

3.2.3.7. Apparent Quantum Yield (AQY) measurement H_2O_2 evolution: The apparent quantum yield (AQY) for H_2O_2 evolution was determined under monochromatic irradiation using LED lamp with different intensity. The irradiation area was controlled as 4.7 cm². Depending on the amount of H_2O_2 produced by the photocatalytic reaction in one hour, and the AQY was calculated as follow:

$$AQY (\%) = \frac{[Produced H_2O_2 (mol)] \times 2}{Photon Number Entered into the Reactor (mol)} \times 100 \%$$

$$AQY (\%) = \frac{[N_A \times h \times c] \times [H_2O_2 (mol)] \times 2}{I \times S \times t \times \lambda}$$

$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ (Avogadro's Number)

$h = 6.626 \times 10^{-34} \text{ Js}$ (Planck's Constant)

$c = 3 \times 10^8 \text{ ms}^{-1}$ (speed of light)

I = intensity of light (W.cm^{-2})

S = irradiation area

t = irradiation time (seconds)

λ = wavelength of irradiation light

3.2.3.8. Solar to Chemical Energy Conversion (SCC) measurement H_2O_2 evolution: The solar-to-chemical energy conversion (SCC) efficiency was determined by using LED light sources. The irradiation area was controlled as 4.7 cm². Catalysts (5 mg) and solvent (5 mL) were put in the sample vial and the

sample vial. The system remained stirring at 500 rpm during reaction period. The SCC efficiency was calculated via following equation:

$$SCC (\%) = \frac{\Delta G \text{ of } H_2O_2 \text{ generation (Jmol}^{-1}) \times H_2O_2 \text{ formed (mol)}}{\text{Total input power (W)} \times \text{Reaction time (s)}} \times 100 \%$$

ΔG (free energy for H_2O_2 production) = 117 kJ mol⁻¹

3.3. Results and Discussion

3.3.1. Synthesis and Structural Characterization of the Catalyst

Fully π -conjugated halide ion incorporated imidazoline porous organic polymer IPM-402X (X = F, Cl, Br) were obtained via solvothermal reaction yielding a yellowish color powder (Section 3.2). Following the successful synthesis, the structural integrity and chemical composition of IPM-402-Xs were extensively probed and characterized utilizing a diverse array of techniques. The structural elucidation of the IPM-402Xs was accomplished through ¹³C CP-MAS NMR spectroscopy. The signal at ~165 ppm (violet) is attributed to the imine bond (-C=N-) carbons; the signals at ~65 ppm (pink) and ~45 ppm (blue) is ascribed to the other two carbons of imidazole moiety. Furthermore, the distinct signals at ~138 ppm (yellow) and ~145 ppm (green) correspond to aromatic ring carbon connected to the imine carbon of imidazoline moiety and carbon of the aromatic ring connected with imidazoline moiety, respectively (Figure 3.1a-c, Appendix Figure 3.2-3.5). The presence of a prominent peak appearing at ~1665 cm⁻¹, denoting the stretching vibrations inherent to the imine (-C=N-) bonds, along with a broad peak centered around 3400 cm⁻¹, arising from N-H stretching signals (Appendix Figure 3.6-3.9) in the FT-IR spectrum of IPM-402Xs serves as compelling evidence affirming the successful synthesis. Furthermore, to unravel the intricate electronic state of IPM-402Xs, X-ray photoelectric spectroscopy (XPS) was employed. This unveiled distinctive peaks at ~285 eV, ~399 eV indicative of carbon (C1s) and nitrogen (N1s), present in the all the polymeric network from the survey scan of IPM-402X (Appendix Figure 3.10, 3.13, 3.16). The peaks for free counter

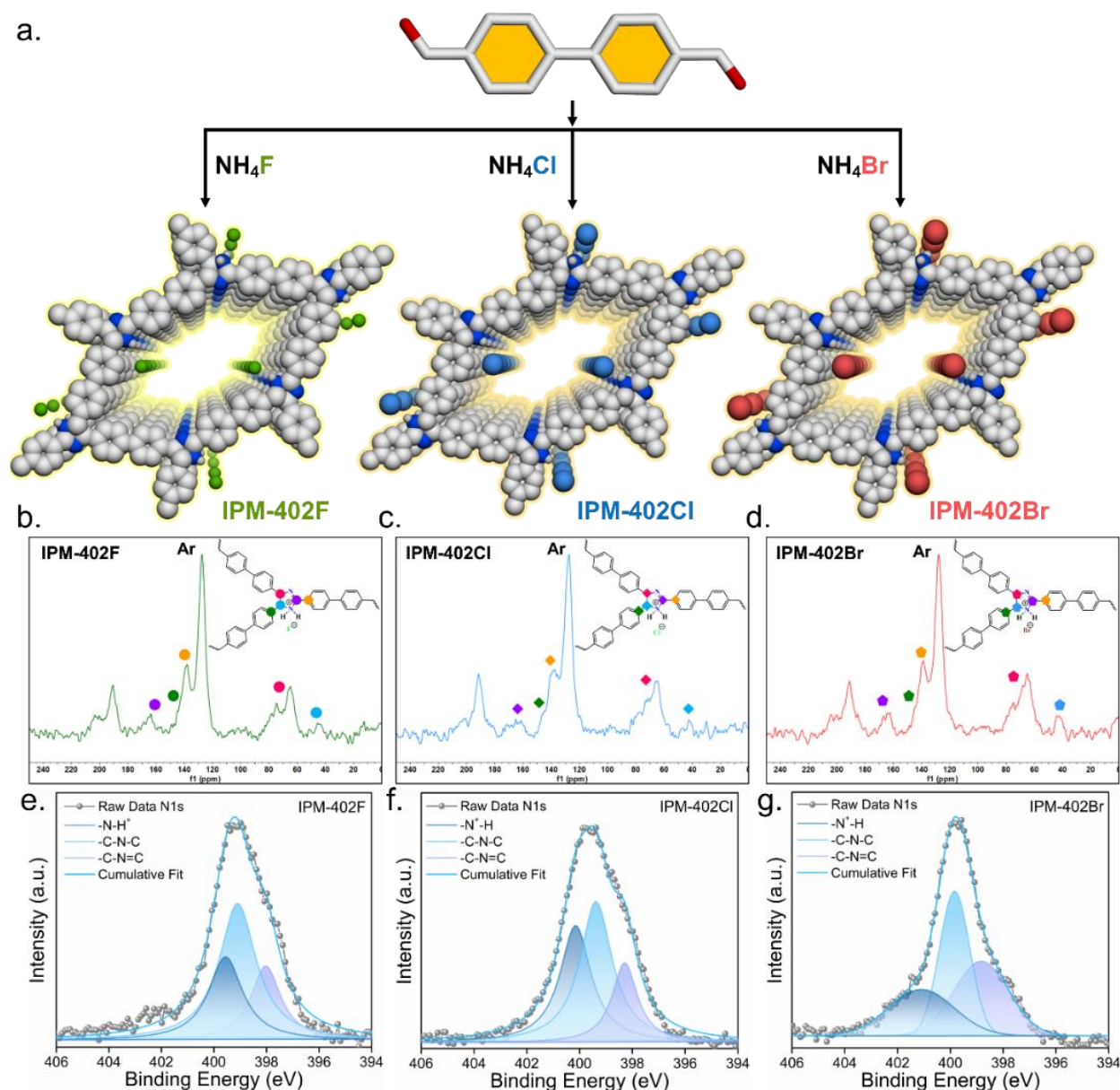


Figure 3.1. (a) Synthetic scheme of IPM-402Xs, (color code: grey-carbon, deep blue-nitrogen, green-fluorine, light blue-chlorine, brick red-bromine), (b, c, d) ^{13}C CP-MAS NMR of IPM-402Xs, and (e, f, g) deconvoluted N1s XPS spectra of IPM-402Xs.

halide anions are also observed in XPS survey spectra at ~ 685 eV for fluorine ($\text{F}1\text{s}$), ~ 197 eV for chlorine ($\text{Cl}2\text{p}$) and ~ 67 eV for bromine ($\text{Br}3\text{d}$) from IPM-402F, IPM-402Cl and IPM-402-Br respectively (Appendix Figure 3.12, 3.15, 3.18). The deconvolution of the $\text{C}1\text{s}$ peaks revealed four subpeaks with binding energies at 288.92, 286.37, 285.15, and 284.60 eV, which correspond to binding energies of -C=O , -C-N/C=N , -C-C/C-H , and -C=C , respectively (Appendix Figure 3.11, 3.14, 3.17). IPM-402Cl and IPM-

402Br also exhibit analogous binding energies. The chemical environment of nitrogen in IPM-402F was investigated by deconvoluting the N1s peak in a narrow scan. The peak could be split into three subpeaks assigned to the binding energies centered at 399.55, 399.09, and 398.02 eV, which correspond to the binding energies of N^+-H , $C-N-C$, and $C-N=C$ (imine), respectively (Figure 3.1e-g). The thermal stability of IPM-402X was thoroughly examined via Thermogravimetric Analysis (TGA). Notably, an initial weight decrement was observed below $\sim 100^\circ\text{C}$ across all polymers, attributed to the desorption of entrapped solvent molecules followed by a thermal resistance up to $\sim 250^\circ\text{C}$ for IPM-402F and $\sim 300^\circ\text{C}$ for IPM-402Cl and IPM-402-Br. Beyond this temperature, a gradual weight loss was observed, accounting for the decomposition of their organic frameworks (Appendix Figure 3.19). To elucidate the morphology of IPM-402Xs, FESEM and TEM analysis was performed. The FESEM analysis revealed an irregular spherical-morphology (Appendix Figure 3.20-3.22). Additionally, TEM analysis shows the layered structure of the IPM-402Xs (Appendix Figure 3.23, 3.25, 3.27) with elemental mapping confirms the homogenous presence of all the elements in IPM-402Xs (Appendix Figure 3.24, 3.26, 3.28). The porosity of IPM-402Xs was investigated using N_2 adsorption isotherms at 77K and CO_2 adsorption at 195K. The low N_2 uptake can be attributed to the densely packed network facilitated by hydrogen bonding and free halide counter ions (Appendix Figure 3.29). In contrast, IPM-402Xs demonstrate substantial CO_2 uptake owing to interaction-based adsorptions. The uptake amount follows the order of IPM-402F > IPM-402Cl > IPM-402Br as the size of anions follows the reverse trend of $Br^- > Cl^- > F^-$ (Appendix Figure 3.30). Zeta potential measurements revealed that the surface charges of IPM-402F, IPM-402Cl, and IPM-402Br are positive, with zeta potentials of 41.6 mV, 53.9 mV, and 32.6 mV, respectively (Appendix Figure 3.31). All these characterization techniques strongly suggest the formation of the polymeric network of the IPM-402Xs.

To enhance the relevance of these materials in real-time conditions, they must exhibit high chemical stability. Hence, the chemical stability of IPM-402Xs was assessed by subjecting them to 1M NaOH, 1M HCl, and 30% H_2O_2 solutions for 48 hours, followed by characterization using FT-IR and TGA (Appendix Figure 3.32-3.37). The FT-IR spectra of the treated IPM-402Xs exhibited no shifts in peak positions compared to the pristine materials, indicating identical chemical structures. Similarly, the TGA profiles resembled those of the pristine IPM-402Xs, confirming their chemical stability and robust nature under the harsh chemical conditions.

3.3.2. Photophysical Characterization:

The electrical band structures and photophysical properties of all the IPM-402Xs were further investigated. An UV-Vis Diffuse Reflectance spectroscopy (UV-Vis DRS) experiment reveals that all three IPM-402Xs exhibit a wide absorption range of 200 – 500 nm (Figure 3.2a, Appendix Figure 3.38-3.40), suggesting their light-harvesting behavior. For IPM-402F, IPM-402Cl, and IPM-402Br, the corresponding Tauc plot

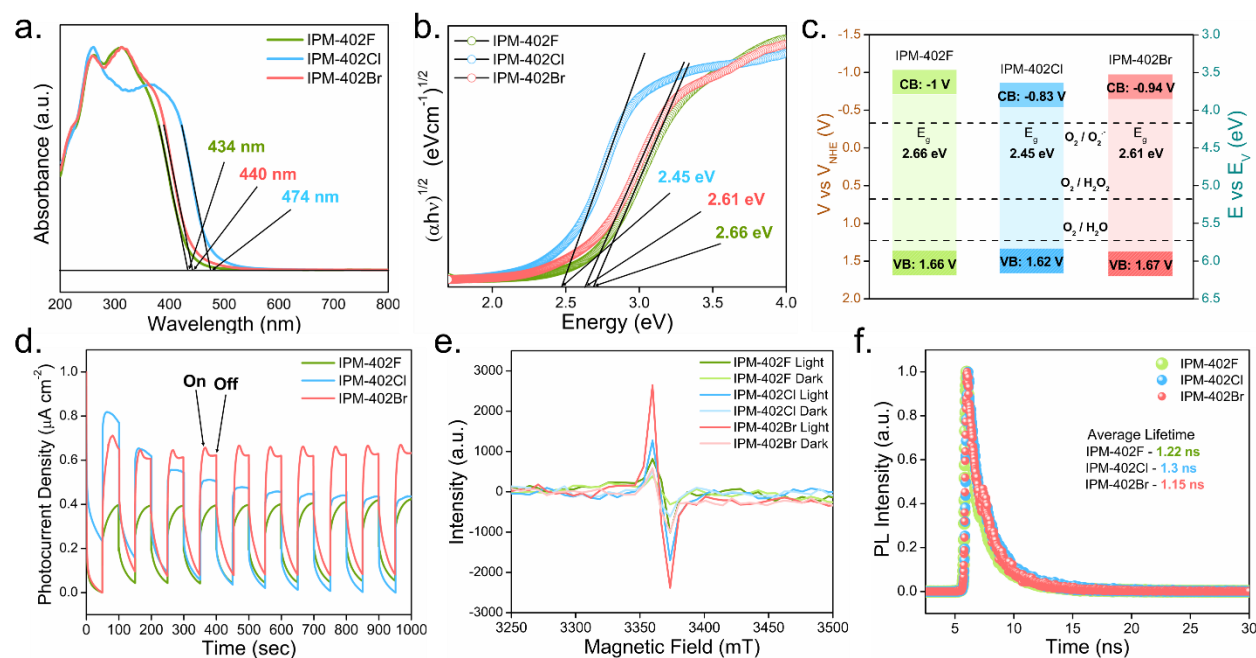


Figure 3.2. (a) Solid state UV-Vis spectra, (b) corresponding Tauc's plots, (c) band structure consists of valence band (VB) and conduction band (CB), (d) transient photo-current response, (e) solid state EPR spectra in presence of light and dark, and (f) time resolved fluorescence spectra of IPM-402Xs.

indicated optical band gaps of 2.66, 2.45, and 2.61 eV, respectively (Figure 3.2b, Appendix Figure 3.41-3.43). The VBM (vs. NHE) were determined to be 1.66 V, 1.62 V, and 1.67 V for IPM-402F, IPM-402Cl and IPM-402Br respectively from the UPS (Appendix Section 3.5.1, Appendix Figure 3.45-3.46). The electrochemical Mott-Schottky plots for these three IPM-402Xs have positive slopes, indicative of n-type semiconductor properties (Appendix Figure 3.47-3.49). The conduction band (CB) position was calculated to be -1 V, -0.83 V, and -0.94 V for three IPM-402Xs respectively, which are all more negative than the redox potentials for stepwise $2e^-$ oxygen reduction reaction (ORR, $E_{\text{NHE}} = 0.68$ V). These results indicate the thermodynamic feasibility of H_2O_2 photosynthesis by all three IPM-402Xs without using any sacrificial reagents. The detailed band structures of three IPM-402Xs are summarized in Figure 3.2c. The transient photocurrent measurement of these IPM-402Xs shows the effective charge separation for all the species with the value of current density of $0.41 \mu\text{A cm}^{-2}$ for IPM-402F, $0.44 \mu\text{A cm}^{-2}$ for IPM-402Cl and $0.62 \mu\text{A cm}^{-2}$ for IPM-402Br (Figure 3.2d). These results demonstrate that the formation of the imidazoline linkage significantly improves electron-hole separation and suppresses electron-hole recombination, likely due to the enhanced electron transfer facilitated by the cationic nature of the IPM-402Xs network. The trend of the photoinduced charges is IPM-402Br > IPM-402Cl > IPM-402F. Strong interactions between IPM-402F and the dissolved O_2 in the electrolyte solution may cause this phenomenon, depleting the photogenerated electrons and drastically reducing the photocurrent density. The electrochemical impedance spectroscopy

(EIS) also indicates the superior electronic conductivity of all IPM-402Xs (Appendix Figure 3.50-3.51). The solid-state electron paramagnetic resonance (EPR) shows the solid-state radical present in all the materials, but under visible light irradiation, all the IPM-402Xs can generate photoinduced free charges (Figure 3.2e). The fluorescence decay curves determine the average fluorescence lifetime of 1.22 ns for IPM-402F, 1.3 ns for IPM-402Cl and 1.15 ns for IPM-402Br (Figure 3.2f).

3.3.3. Photocatalytic H₂O₂ Production:

Photocatalytic H₂O₂ production by IPM-402Xs was then performed in an aqueous system in atmospheric conditions or O₂ saturated system under blue light (Appendix Figure 3.52-3.54, $\lambda \sim 450$ nm) irradiation. Without adding any electron sacrificial agent, IPM-402F can produce 1922 μM H₂O₂ in an oxygen-saturated system in 1 hour, showing a mass-specific production rate of $384475 \mu\text{Mh}^{-1}\text{g}^{-1}$. The production rate was found to be $313668 \mu\text{Mh}^{-1}\text{g}^{-1}$ and $349781 \mu\text{Mh}^{-1}\text{g}^{-1}$ for IPM-402Cl and IPM-402Br, respectively, under an O₂-saturated aqueous system (Figure 3.3a, Appendix Figure 3.55-3.59). It was noteworthy that IPM-402Xs outperformed all the porous materials-based systems, being the best photocatalyst to produce H₂O₂ in pure water to date (Figure 3.3g, Appendix Table 3.1). Under white light irradiation ($\lambda \sim 400 - 800$ nm) IPM-402Xs showed excellent photocatalytic behavior towards H₂O₂ production with $885 \mu\text{Mh}^{-1}$ for IPM-402F, $590 \mu\text{Mh}^{-1}$ for IPM-402Cl and $663 \mu\text{Mh}^{-1}$ for IPM-402Br (Appendix Figure 3.57). In the air, IPM-402F can produce $622 \mu\text{Mh}^{-1}$ H₂O₂, more than $414 \mu\text{Mh}^{-1}$ by IPM-402Cl, and $570 \mu\text{Mh}^{-1}$ by IPM-402Br (Appendix Figure 3.57) under blue light irradiation while under white light irradiation those values are 595, 344 and $533 \mu\text{Mh}^{-1}$ respectively (Appendix Figure 3.59). When ethanol introduced as an electron sacrificial agent (H₂O: EtOH = 9:1), the production rate increased to $535133 \mu\text{Mh}^{-1}\text{g}^{-1}$ for IPM-402F in O₂ saturated system, more than IPM-402Cl ($477759 \mu\text{Mh}^{-1}\text{g}^{-1}$) and IPM-402Br ($529058 \mu\text{Mh}^{-1}\text{g}^{-1}$) (Figure 3.3a). Under white light, irradiation H₂O₂ production rate was 913, 643, and $711 \mu\text{Mh}^{-1}$ for IPM-402F, IPM-402Cl, and IPM-402Br (Appendix Figure 3.60). In the open-air system, IPM-402F, IPM-402Cl, and IPM-402Br can produce 1839, 1184, and $1424 \mu\text{M h}^{-1}$ H₂O₂ when ethanol is used as an electron sacrificial agent (Appendix Figure 3.57).

In the context of *real-world scenarios*, photocatalytic H₂O₂ production was performed under sunlight and in seawater in atmospheric conditions. Under *sunlight, air and in pure water*, IPM-402F produced 268 μM in 1 hour, while IPM-402Cl and IPM-402Br produced 256 and 275 $\mu\text{M h}^{-1}$, respectively (Figure 3.3b). Also, in seawater (from the Arabian Sea of India), IPM-402Xs were found to have excellent photocatalytic production of H₂O₂ (Appendix Table 3.8). In the air and blue light irradiation, IPM-402F can produce $1634 \mu\text{M h}^{-1}$ H₂O₂, whereas IPM-402Cl and IPM-402Br can produce 712 and $1368 \mu\text{M h}^{-1}$, respectively (Figure 3.3c). In seawater presence of sunlight and air, *the most realistic condition*, the photocatalytic H₂O₂ production rate was found to be 58654, 45573, and $55070 \mu\text{M h}^{-1}\text{g}^{-1}$ (Figure 3.3c) for IPM-402F, Br, and

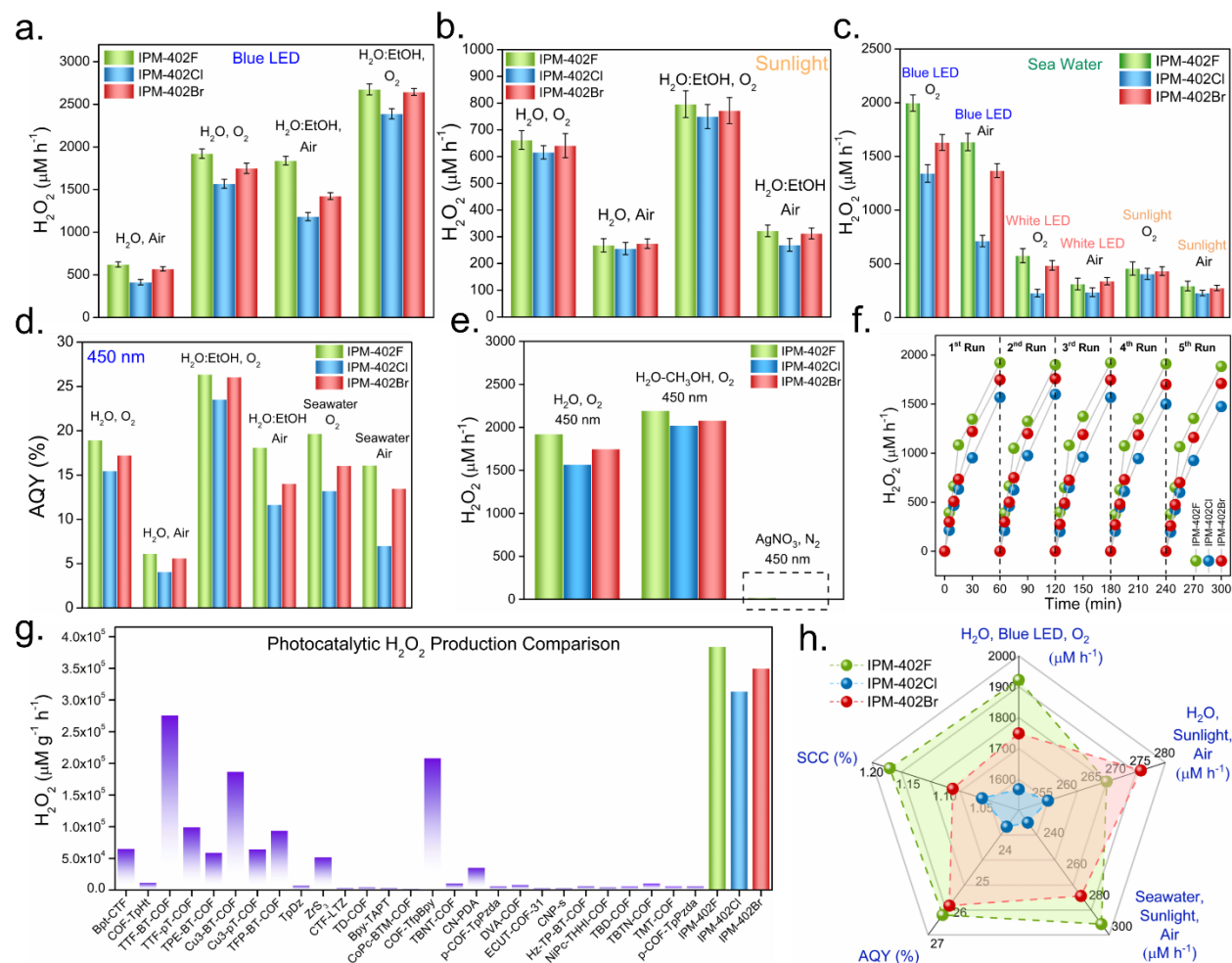


Figure 3.3. Photocatalytic H_2O_2 production by IPM-402Xs in (a) water and water-ethanol mixture under blue light irradiation, (b) water and water-ethanol mixture under sunlight, (c) seawater under different environment, (d) % AQY at 450 nm, (e) the half-redox reaction, (f) recyclability test for photocatalytic H_2O_2 production by IPM-402Xs, (g) comparison table for H_2O_2 production by porous materials with IPM-402Xs, and (h) radar plot of photocatalytic H_2O_2 production by IPM-402Xs.

Cl, respectively. Photocatalytic H_2O_2 production was also performed in different sacrificial agents, isopropyl alcohol (IPA), benzyl alcohol (BA), in different harsh chemical conditions in 1M acid and base, and in different LED sources and temperature Appendix Figure 3.61-3.63, Appendix Table 3.10-3.11). The apparent quantum yield (AQY %) was found 26.36, 23.53 and 26.06 for IPM-402F, Cl and Br in the $\text{H}_2\text{O:EtOH}$, outperforms all the porous materials (Figure 3.3d, Appendix Table 3.2, 3.13). Solar to chemical conversion (SCC %) was also calculated 1.233, 1.101 and 1.151 for IPM-402F, Cl and Br respectively in O_2 saturated $\text{H}_2\text{O:EtOH}$ system under sunlight irradiation which is much higher than plant photosynthesis (0.1%) (Appendix Table 3.3, 3.14).

The catalyst's role and mechanism of H_2O_2 production were investigated using control studies and scavenging reactions. The absence of O_2 , light, and catalyst led to little H_2O_2 generation, indicates these three are the main parameter. O_2 removal by N_2 results in negligible H_2O_2 generation, indicating that the ORR is the main route for photocatalytic H_2O_2 production using IPM-402Xs. Two Half redox reactions was performed using AgNO_3 (electron acceptor) and N_2 for WOR and MeOH and O_2 for ORR respectively. ORR reaction rate is little higher than standard condition suggesting MeOH act as electron sacrificial agent in ORR reaction, but there is no H_2O_2 production was noticed for WOR half reaction (Figure 3.3e), confirms the photocatalytic H_2O_2 production by IPM-402Xs is $2e^-$ transfer process. Different scavenging agent was introduced to reaction medium to analyze the reactive species involved in the reaction. In presence of AgNO_3 and NaIO_3 dramatically decreased H_2O_2 production was noticed. IPM-402F decreased H_2O_2 production in half, whereas IPM-402Cl and IPM-402Br had negligible production, indicating photogenerated electrons (e^-) participated in redox processes (Appendix Figure 3.69-3.70). No H_2O_2 was generated under anaerobic circumstances, validating the ORR route. There is no effect of h^+ and $^1\text{O}_2$ in the reaction path and also $\text{OH}^\bullet$ radical rules out the step-wise $1e^-$ WOR pathway (Appendix Figure 3.71).

In order to verify the two $2e^-$ H_2O_2 production by IPM-402Xs, oxygen reduction reaction (ORR) was investigated via electrochemical rotating ring disc electrode (RRDE) technique. The cyclic voltammetry (CV) of the modified RRDE electrode, conducted in N_2 -saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1} shows no reduction peak (Appendix Figure 3.79) under the potential range of 0.3 to 1.0 V vs RHE. However, when an electrolyte was saturated with O_2 , a cathodic peak at $\sim 0.46 \text{ V}$ vs RHE was observed for all IPM-402Xs (Appendix Figure 3.79) confirming that the redox process attributable to the reduction of O_2 . This is further confirmed by increase in current density on diffusion region while performing the linear swept voltammetry (LSV) with RRDE electrode under rotation speed ranging from 400-2500 rpm (Figure 3.4a-c, Appendix Figure 3.80-3.82). The comparative RRDE analysis conducted at 1600 rpm reveals that IPM-402F exhibits a lower onset potential and higher H_2O_2 production compared to IPM-402Br and IPM-402Cl (Figure 3.4d-e). This finding is consistent with the results observed under photocatalytic conditions. The average number of transferred electrons (n) and H_2O_2 selectivity for different catalysts, measured between 0.35 and 0.55 V vs RHE at 1600 rpm, are shown in Figure 3.4d-e. The results indicate that the n values of IPM-402F, IPM-402Cl, and IPM-402Br are 2.78, 2.89 and 2.81, respectively. Correspondingly, the H_2O_2 selectivity for these catalysts is 61.5%, 55.7%, and 59.6%. These findings suggest that the H_2O_2 production catalyzed by IPM-402Xs primarily occurs via a $2e^-$ ORR process.

After the catalytic process the structural stability of the polymeric network of IPM-402Xs by ^{13}C CP-MAS NMR, FT-IR, TGA, TEM, XPS discussed in the Appendix Section 3.5.4.

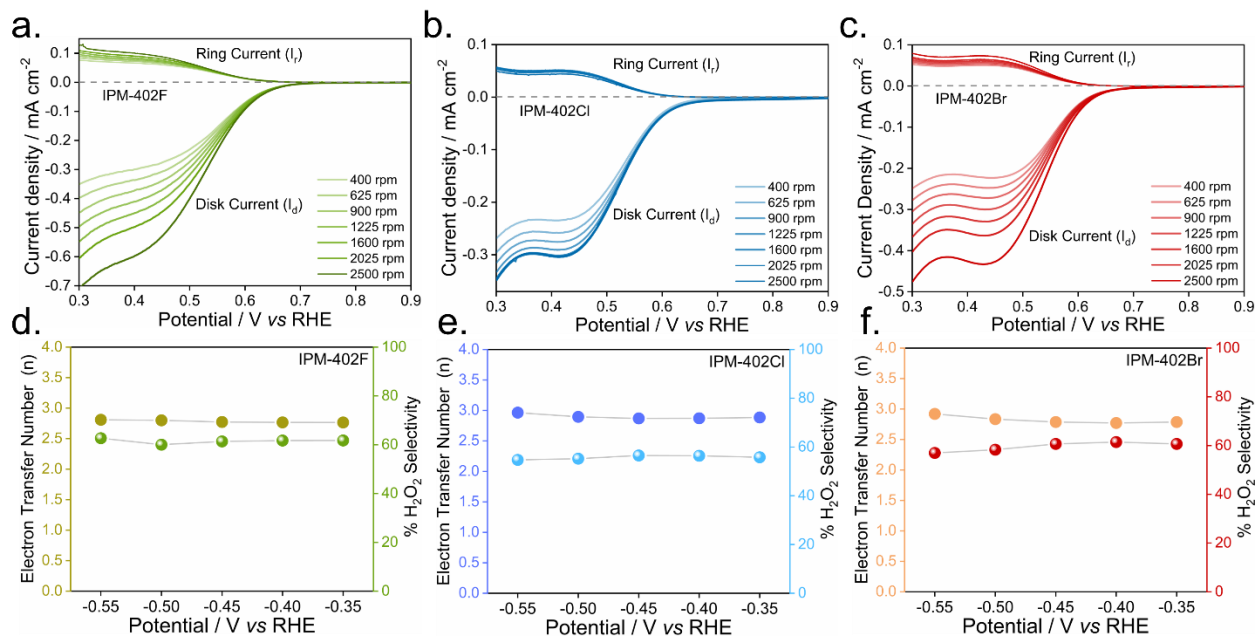


Figure 3.4. (a, b, c) LSV curves at different rotation speed of IPM-402Xs, and (d, e, f) electron transfer number and H₂O₂ selectivity from RRDE experiment in 0.1M KOH of IPM-402Xs.

3.3.4. Mechanistic Studies of Photocatalytic H₂O₂ Production:

The remarkably exciting structure-property correlations exhibited by IPM-402Xs spurred our investigation into the underlying reaction mechanism. Density functional theory (DFT) was employed to get mechanistic insights in the formation of H₂O₂ from O₂ catalyzed by IPM-402Xs. The molecular fragmentation approach was used to unravel reaction mechanism and structure activity relationship of different IPM-402Xs by considering the repeating units of IPM-402F, IPM-402Cl, and IPM-402Br and IPM-402 (Appendix Figure 3.99).

The IPM-402Xs series comprising IPM-402F, IPM-402Cl, and IPM-402Br displayed distinct structural features in IN1 (IN1-O). In IPM-402F, the H-F bond exhibited greater covalency, with a bond length of 0.98 Å forming HF and neutral polymer, while the other hydrogen displayed a strong hydrogen bonding (H-bond) with F (N-H = 1.10 Å; H-HF = 1.35 Å). IPM-402Cl and IPM-402Br depicted similar H-bonding, with H-Cl and H-Br bond lengths of 1.45 Å and 1.43 Å, respectively while, the N-H bond length of 2.18 Å and 1.41 Å were attributed to IPM-402Cl and IPM-402Br, respectively indicating hydrogen bonding between -NH and -X. Regarding H-bonding strength, IPM-402F showed the highest, followed by IPM-402Br, while IPM-402Cl exhibited the weakest (Appendix Figure 3.102, Appendix Section 3.5.6).

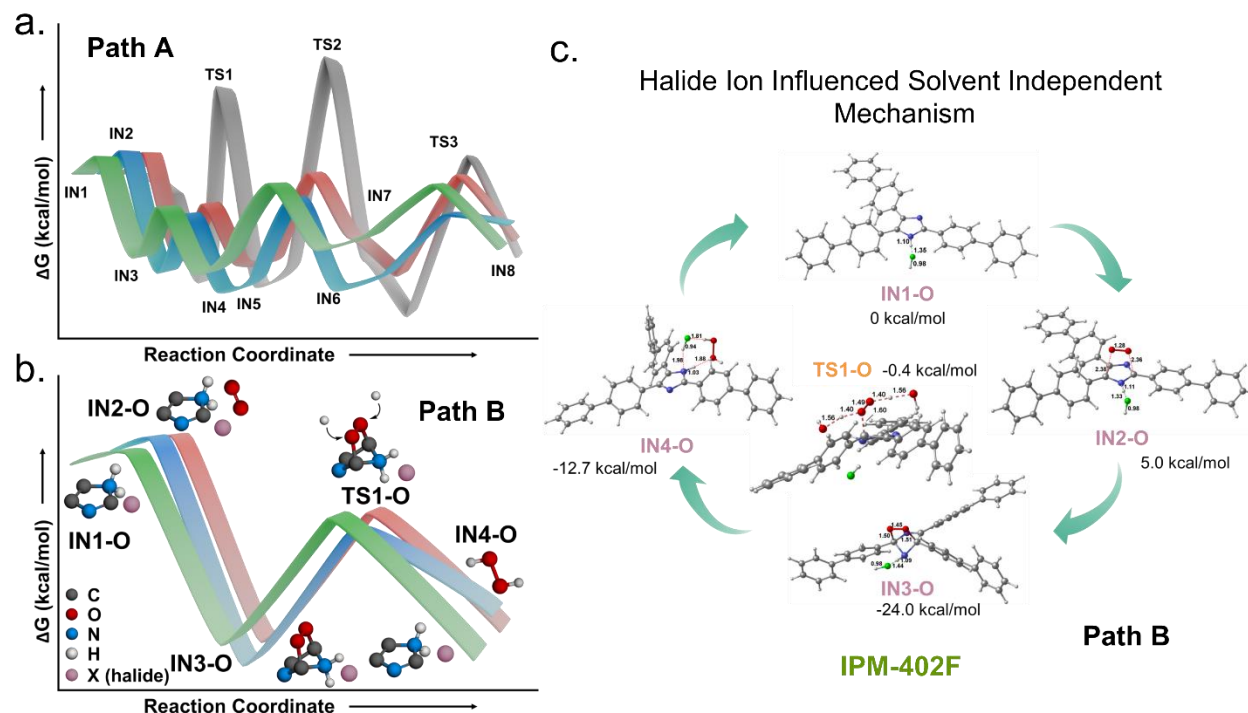


Figure 3.5. (a) halide ion influenced solvent dependent pathway, (b) halide ion influenced solvent independent pathway, and (c) halide ion influenced solvent independent pathway with energy value of IPM-402F.

We studied solvent dependent (path-A) (Figure 3.5a, Appendix Section 3.5.6) as well as the solvent independent (path-B) O_2 activation mechanistic route to understand the role of H_2O in the formation of photocatalytic H_2O_2 . In the solvent-independent pathway (Path-B), the insertion of oxygen in IN1-O leads to the formation of IN2-O, where the imidazolium- O_2 distance is 2.3 Å in IPM-402F, 3.3 Å in IPM-402Cl, and more than 3.5 Å in IPM-402Br. The formation of IN2-O from IN1-O is relatively straight-forward in the presence of oxygen atmosphere with Gibbs free energy of 5.0 kcal/mol, 6.7 kcal/mol and 6.9 kcal/mol for IPM-402F, IPM-402Br and IPM-402Cl, respectively. The decline in Gibbs free energy during the conversion of IN2-O to IN3-O signifies that the adsorption of O_2 on the IPM-402X is an exergonic process with Gibbs free energies of -24.0 kcal/mol (IPM-402F), -30.2 kcal/mol (IPM-402Cl), -27.9 kcal/mol (IPM-402Br), -36.8 kcal/mol (IPM-402) (Figure 3.5b). The protonation of adsorbed O_2 occurs aided by halide mediators, occurs through TS1-O (IPM-402F = -8.8 kcal/mol, IPM-402Cl = -11.4 kcal/mol, and IPM-402Br = -8.9 kcal/mol). O_2 adsorbed IN3-O (IN3 in path-A) species formed undergo direct reduction to form the product. This process takes place through a single transition state, TS1-O (ΔG = 0.4 kcal/mol for IPM-402F, ΔG = -2.8 kcal/mol for IPM-402Cl and ΔG = -1.1 kcal/mol for IPM-402Br, where addition of both protons to the adsorbed O_2 yields the H_2O_2 in IN4-O. IPM-402F gives the best results for this transformation

with an energy of 24.4 kcal/mol followed by IPM-402Br and IPM-402Cl with an activation energy of 26.8 and 27.4 kcal/mol, respectively. The presence of halide plays a huge role in stabilizing the material and tailoring the electron density on the polymers for efficient H_2O_2 production. This can be seen through the highly stabilized IN3A intermediate formation in IPM-402, which will require a minimum activation energy of 62.5 kcal/mol to overcome the TS4-O transition state. Thus, the halides, directly or indirectly, encourage the formation of H_2O_2 through TS1-O. The IN3-O remains the TDI (turn-over determining intermediate), while the only possible transition state, TS1-O, is the TDTS (turn-over determining transition state) for this transformation (Appendix Figure 3.107).

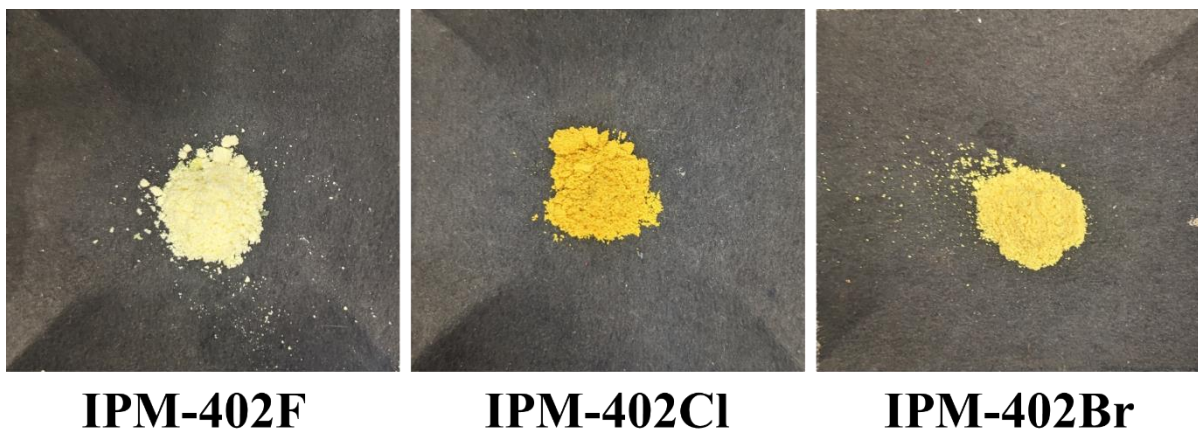
In comparison, Path B, the solvent-independent pathway, offers a more efficient mechanism for H_2O_2 formation catalyzed by IPM-402X compared to the solvent-dependent Path A. Path B consistently demonstrates lower activation barriers: 24.4 kcal/mol for IPM-402F, 26.8 kcal/mol for IPM-402Br, and 27.4 kcal/mol for IPM-402Cl, whereas Path A's barriers are higher: 24.3 kcal/mol for IPM-402F, 28.7 kcal/mol for IPM-402Cl, and 28.3 kcal/mol for IPM-402Br. These lower barriers indicate a more favorable and kinetically accessible pathway, enhancing H_2O_2 production efficiency. Although this minute difference in activation energies (ΔE) between Path A and Path B is not enough to eliminate any one of the pathways, the experimental results suggest the absence of water molecules directly interacting with the activated O_2 or the polymeric surface as shown in Path B. Thus, contributing to the viability of Path B, displaying the outer-sphere reduction process for the formation of O_2 , with IPM-402F being the most efficient, followed by IPM-402Br and IPM-402Cl. Additionally, Path B's single transition state (TS1-O) simplifies the reaction mechanism, contrasting with Path A's multiple transition states and intermediate steps, which introduce additional energy barriers. This streamlined process minimizes potential energy loss, contributing to a more direct and effective catalytic cycle. Thus, Path B emerges as a superior and more efficient route for H_2O_2 formation catalyzed by IPM-402X.

3.4. Conclusion

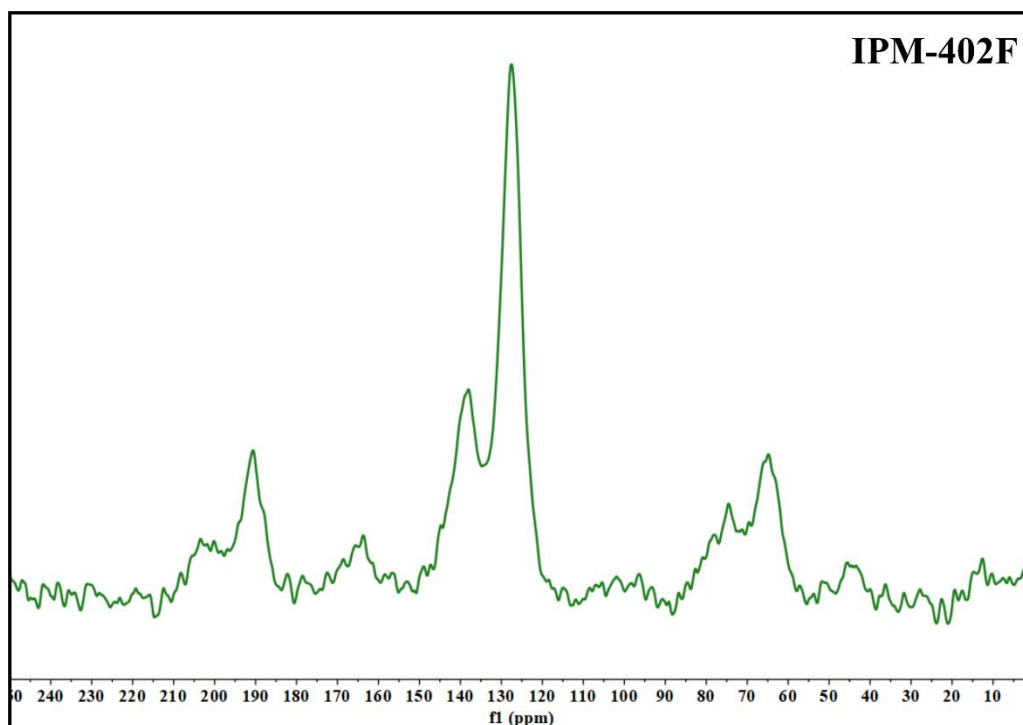
In this work we have synthesized three imidazole based cationic porous organic polymer with different halide ion inside the pores of the polymeric networks. The materials tested highly chemical stable in different harsh conditions. The highly conjugated imidazoline moiety makes the polymers extremely photoactive in the visible light region. The polymeric materials of IPM-402Xs shows excellent photocatalytic behavior towards H_2O_2 production from water and air. IPM-402Xs were performed extremely well in the real-world condition. In seawater and under sunlight and aerobic condition IPM-402Xs can produced significant amount of H_2O_2 , shows its real-time applicability. Photocatalytic H_2O_2 production follows direct $2e^-$ ORR pathway, confirmed by different scavenging test and the electrochemical

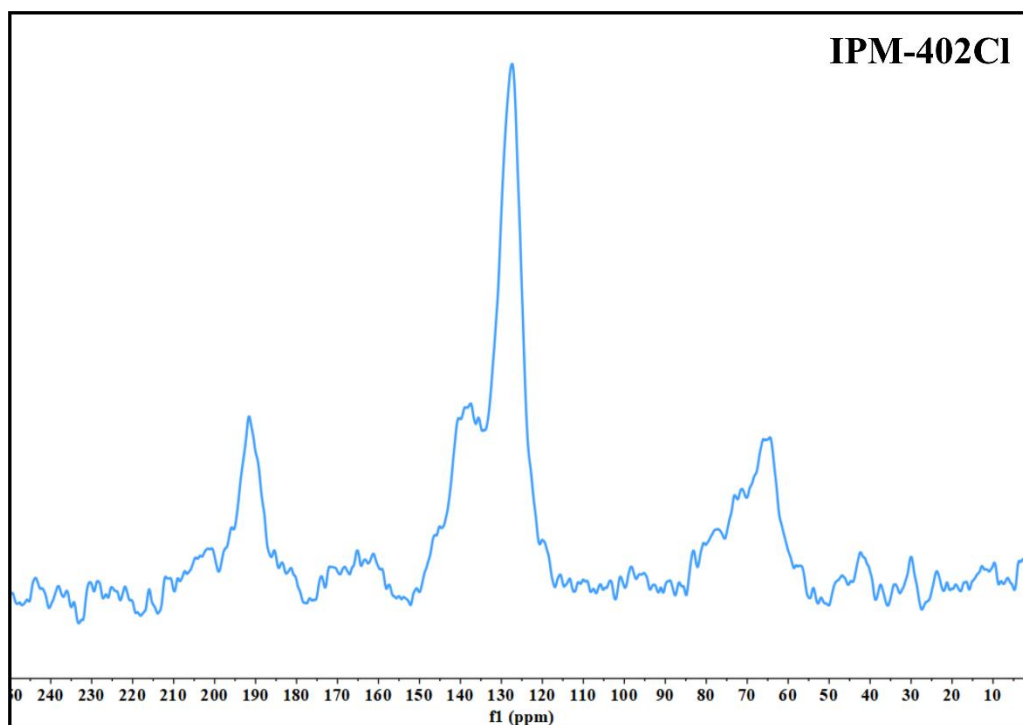
measurements. Finally, the mechanistic pathway was investigated via DFT calculations. We believe this work can significantly contribute towards the energy crisis in this world.

3.5. Appendix Section

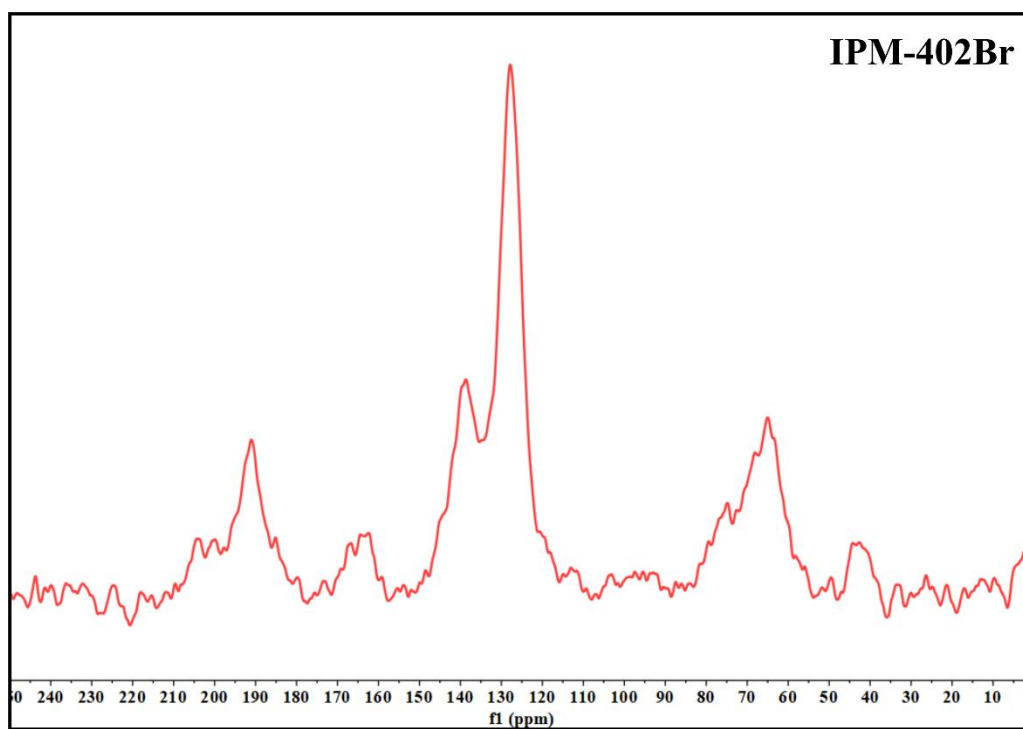


Appendix Figure 3.1: Digital photograph of powder samples of IPM-402Xs

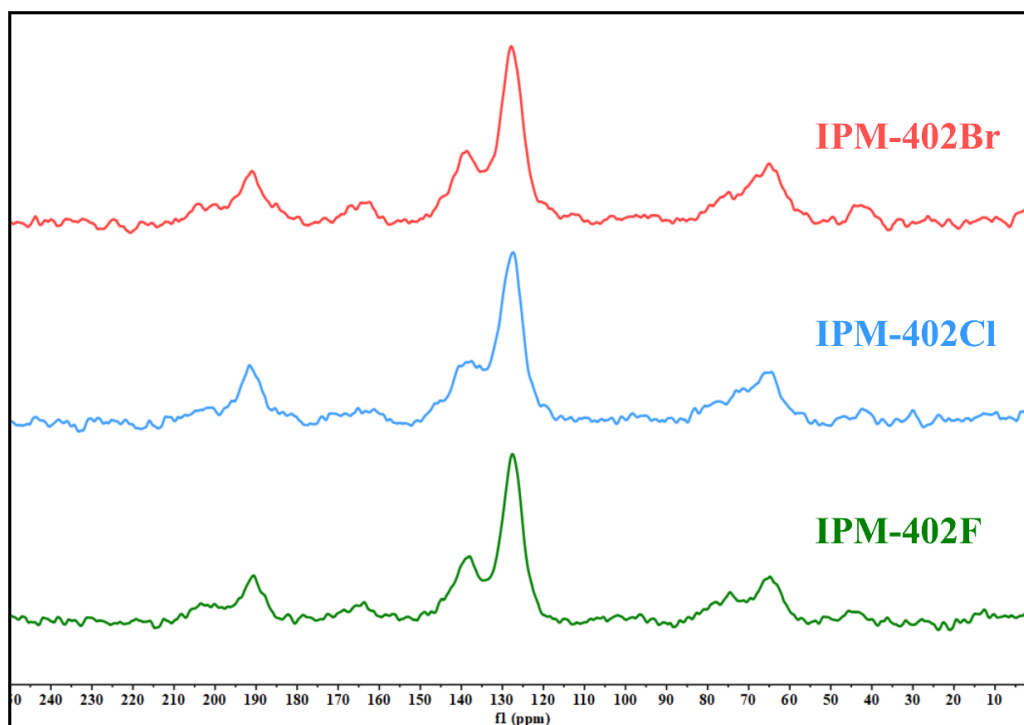
Appendix Figure 3.2: ^{13}C CP-MAS NMR spectra of IPM-402F



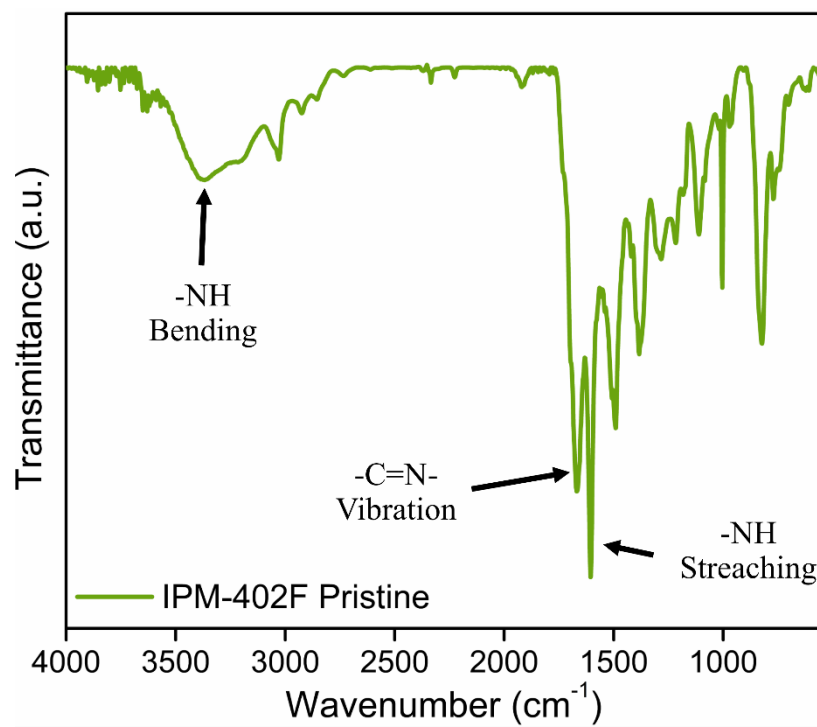
Appendix Figure 3.3: ^{13}C CP-MAS NMR spectra of IPM-402F



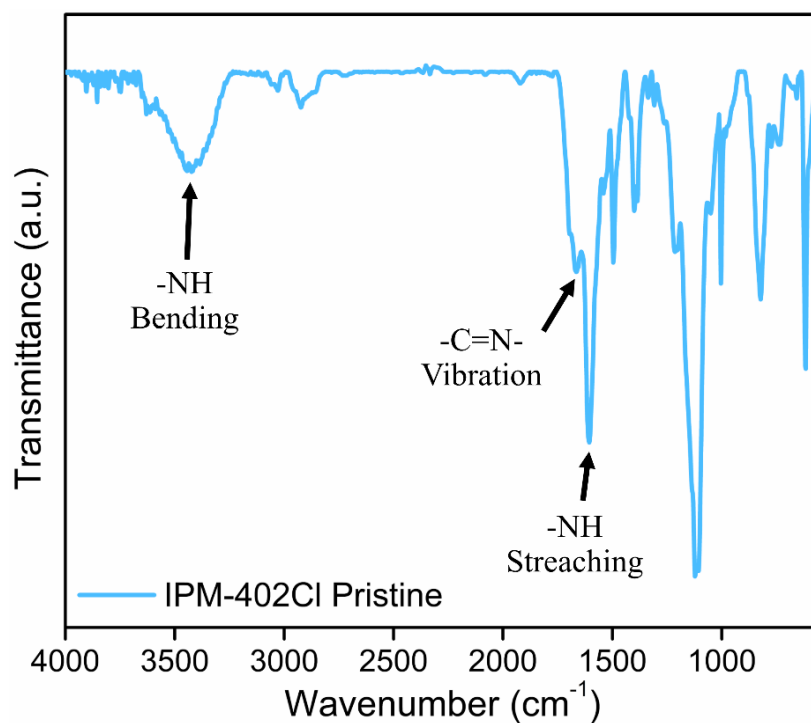
Appendix Figure 3.4: ^{13}C CP-MAS NMR spectra of IPM-402F



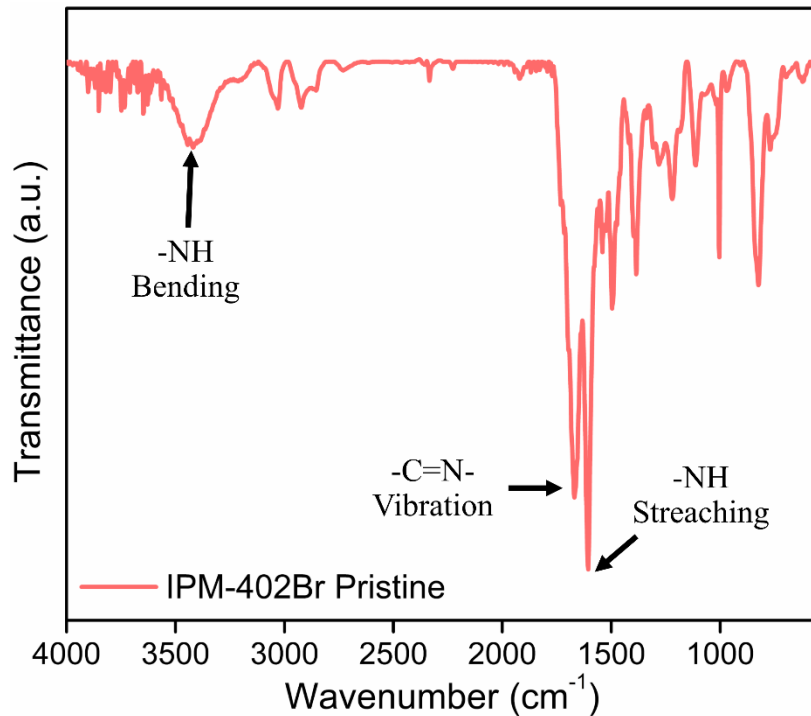
Appendix Figure 3.5: Comparison of ^{13}C CP-MAS NMR spectra of IPM-402Xs



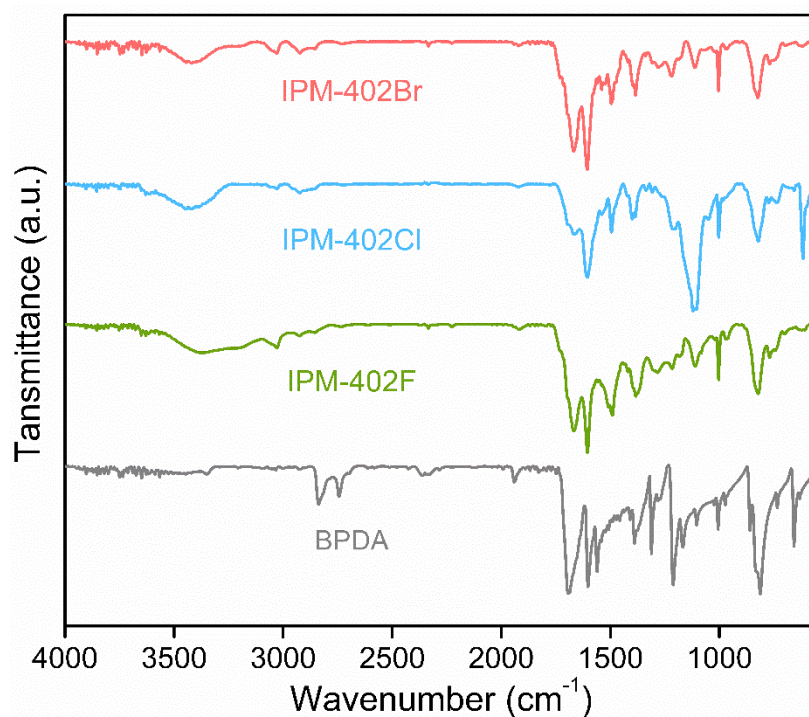
Appendix Figure 3.6: FT-IR spectra of IPM-402F



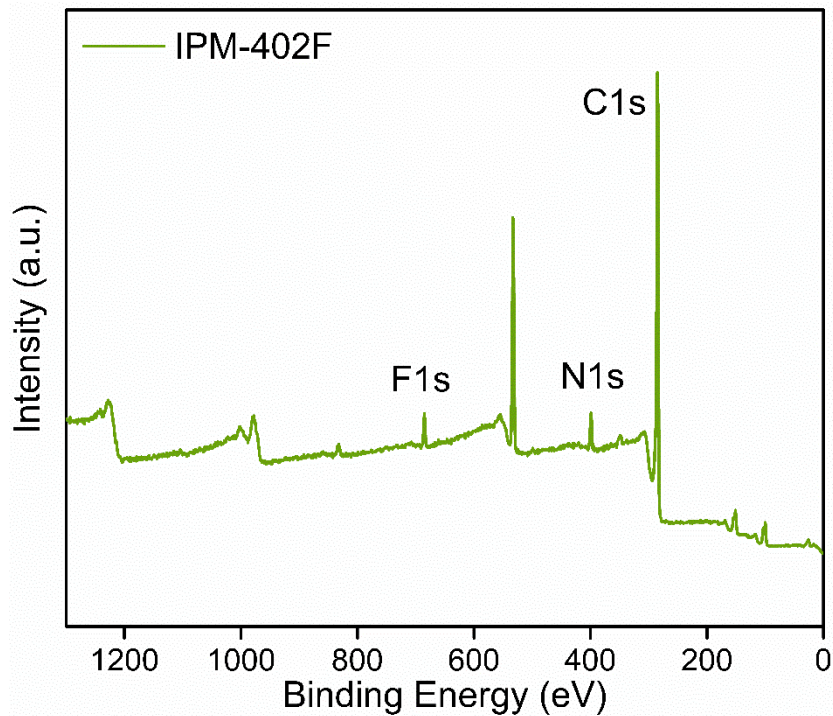
Appendix Figure 3.7: FT-IR spectra of IPM-402Cl



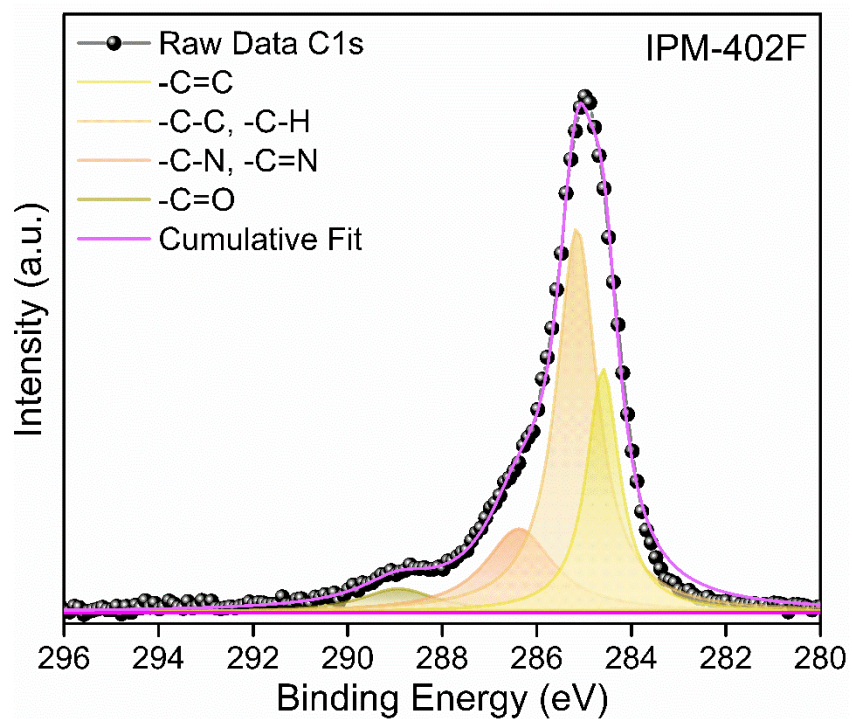
Appendix Figure 3.8: FT-IR spectra of IPM-402Br



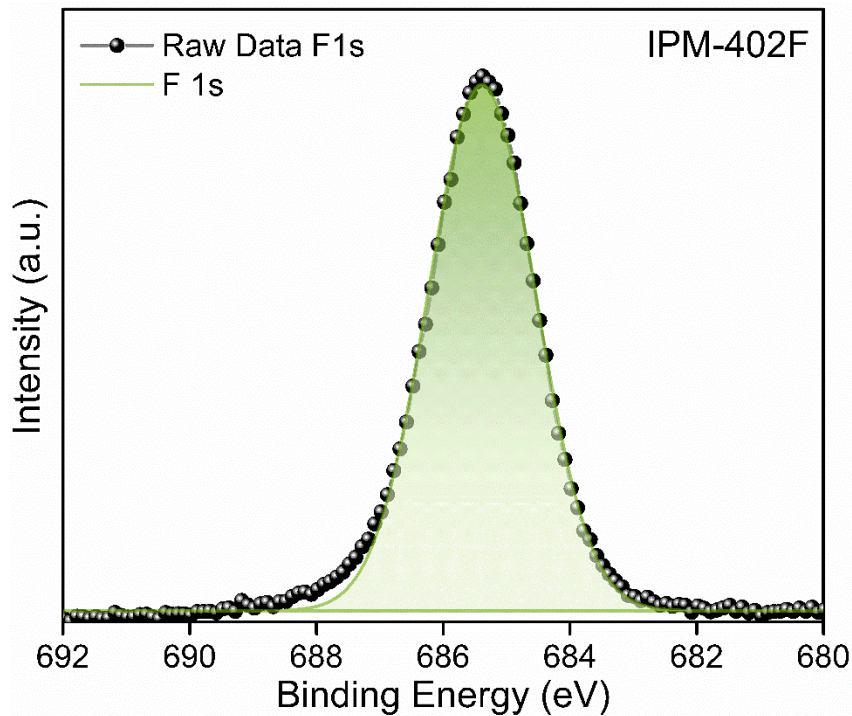
Appendix Figure 3.9: Stack FT-IR spectra of IPM-402Xs and the starting material



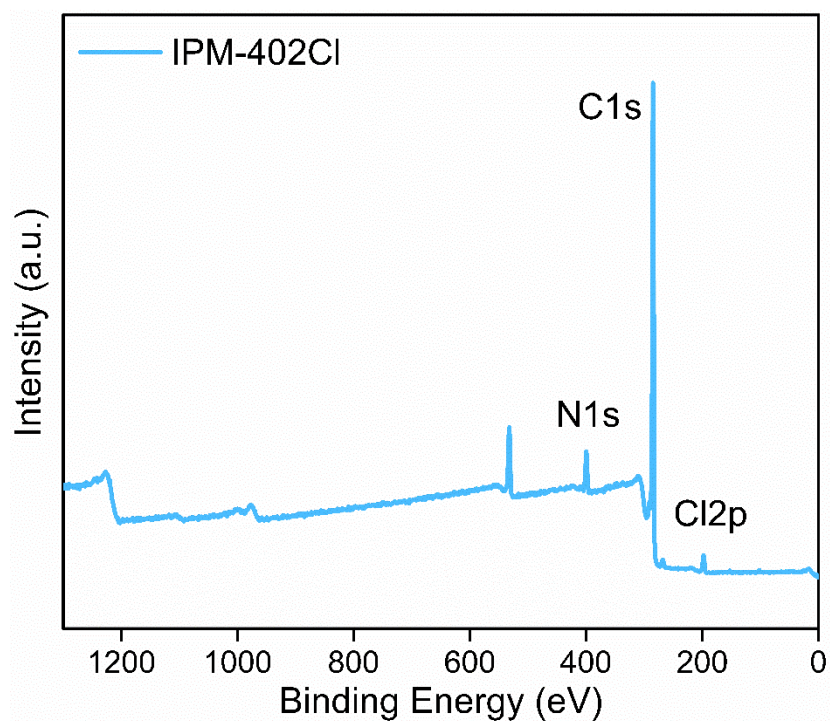
Appendix Figure 3.10: XPS Survey spectra of IPM-402F



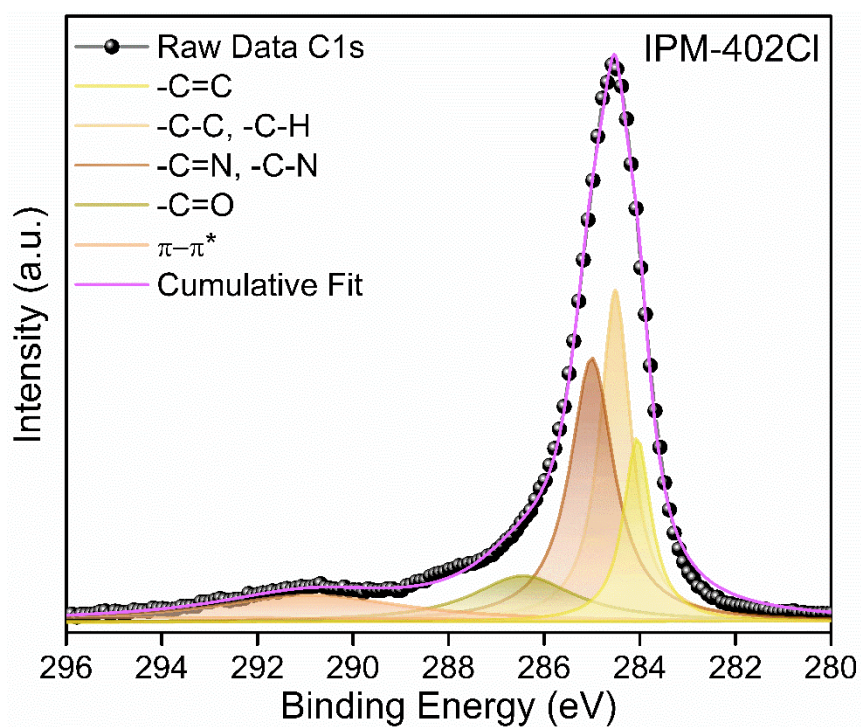
Appendix Figure 3.11: High resolution deconvoluted C1s spectra of IPM-402F



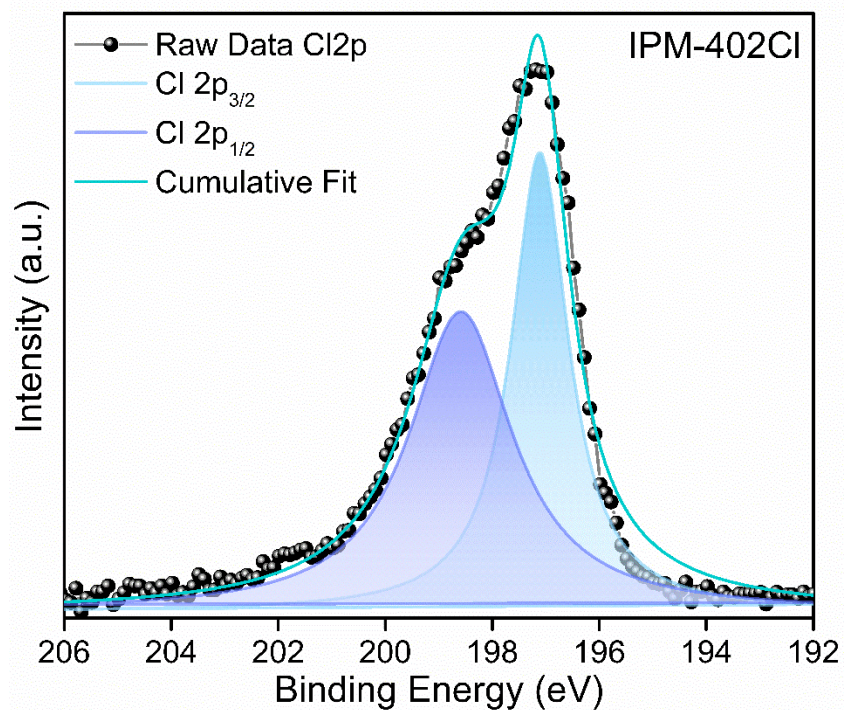
Appendix Figure 3.12: High resolution deconvoluted F1s spectra of IPM-402F



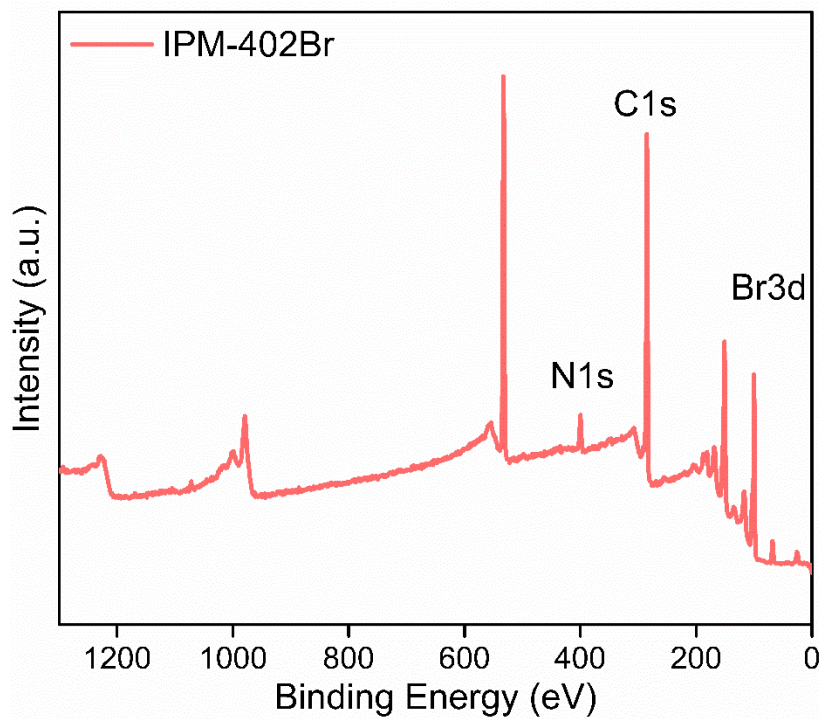
Appendix Figure 3.13: XPS Survey spectra of IPM-402Cl



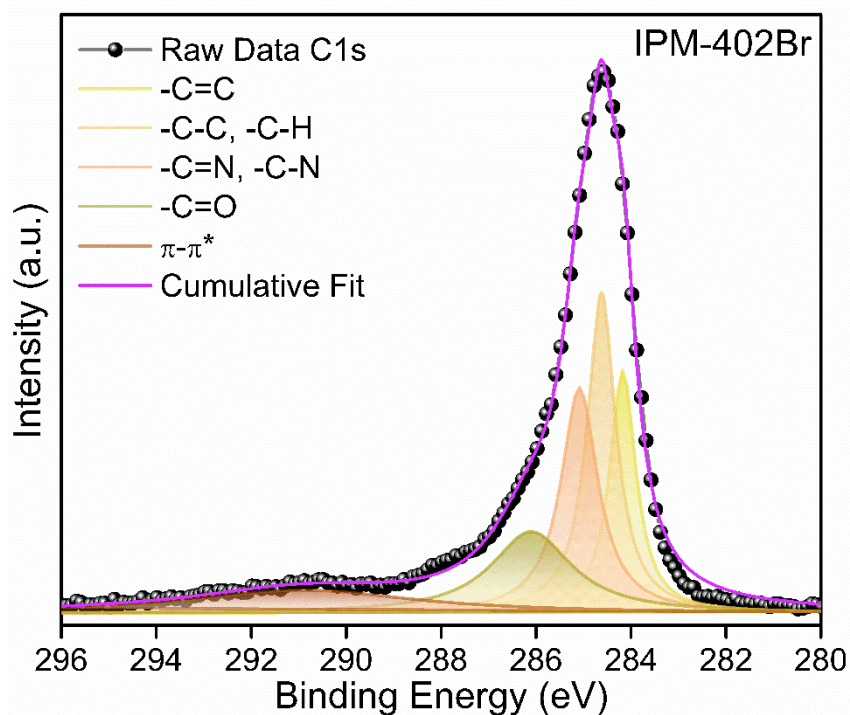
Appendix Figure 3.14: High resolution deconvoluted C1s spectra of IPM-402Cl



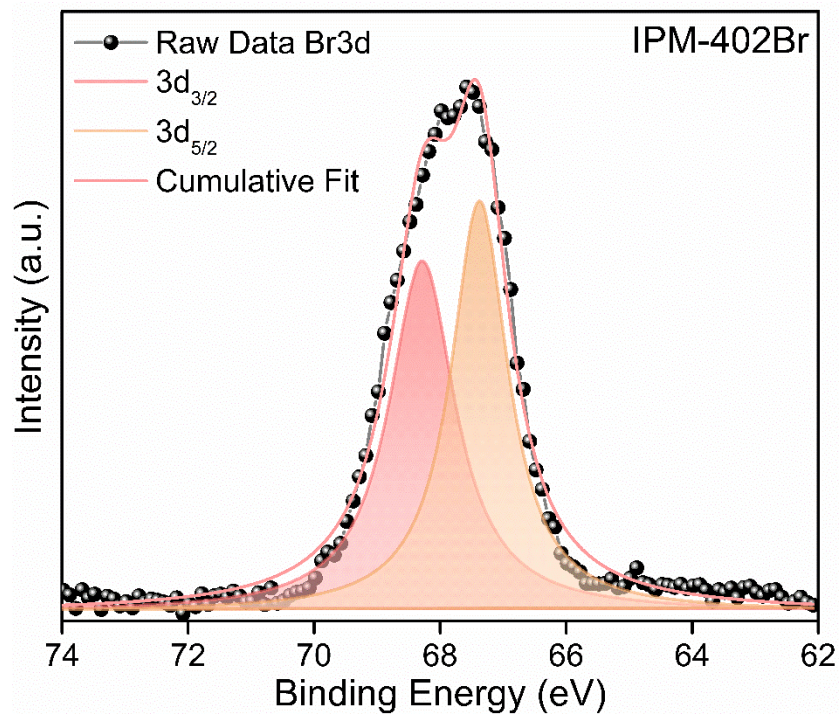
Appendix Figure 3.15: High resolution deconvoluted Cl2p spectra of IPM-402Cl



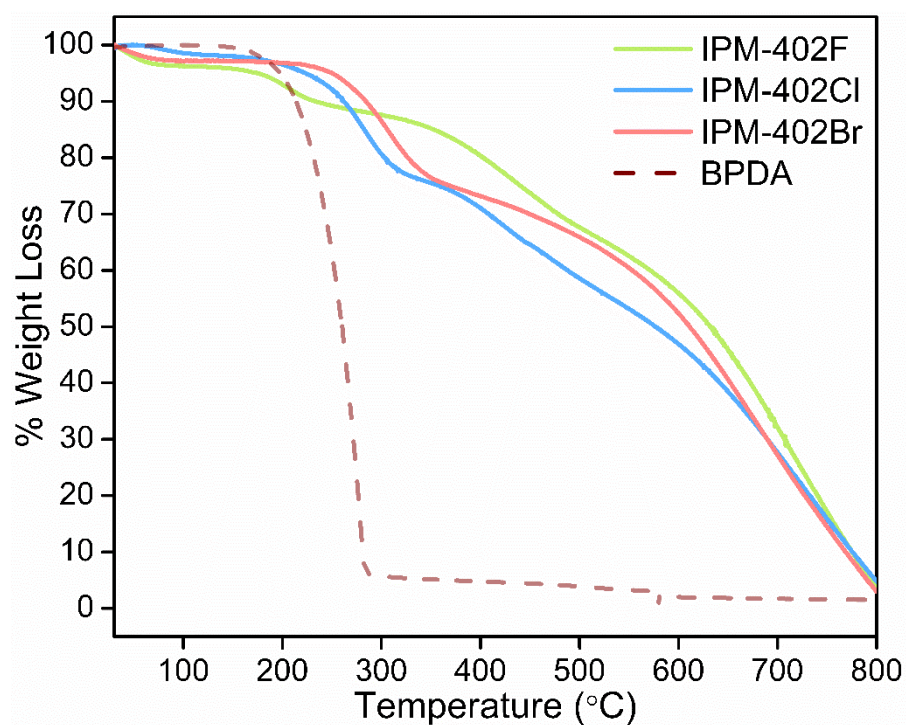
Appendix Figure 3.16: XPS Survey spectra of IPM-402Br



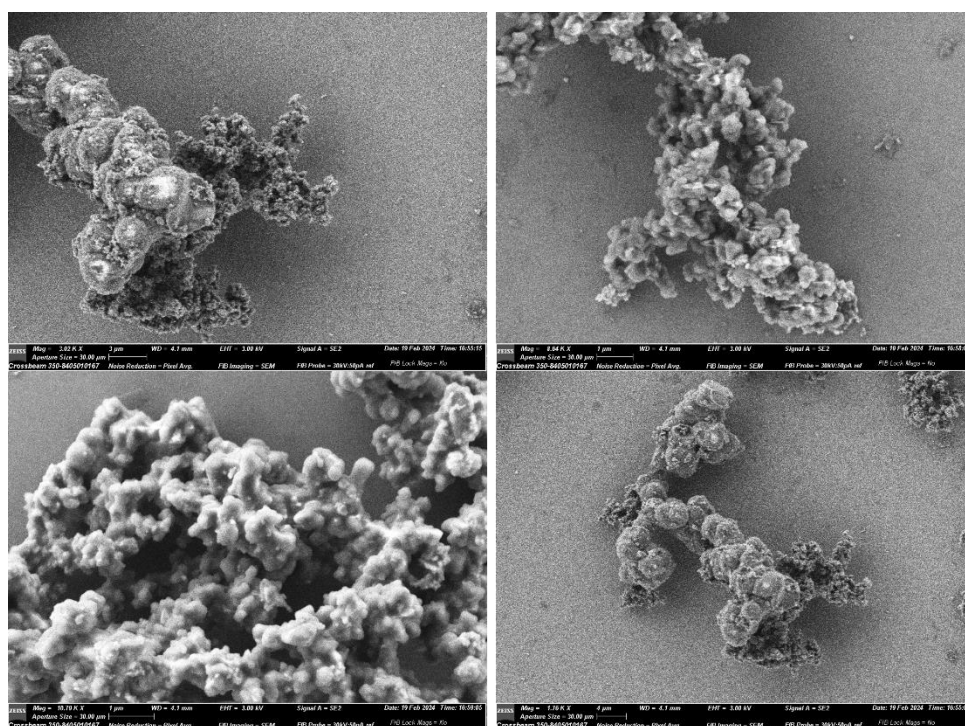
Appendix Figure 3.17: High resolution deconvoluted C1s spectra of IPM-402Br



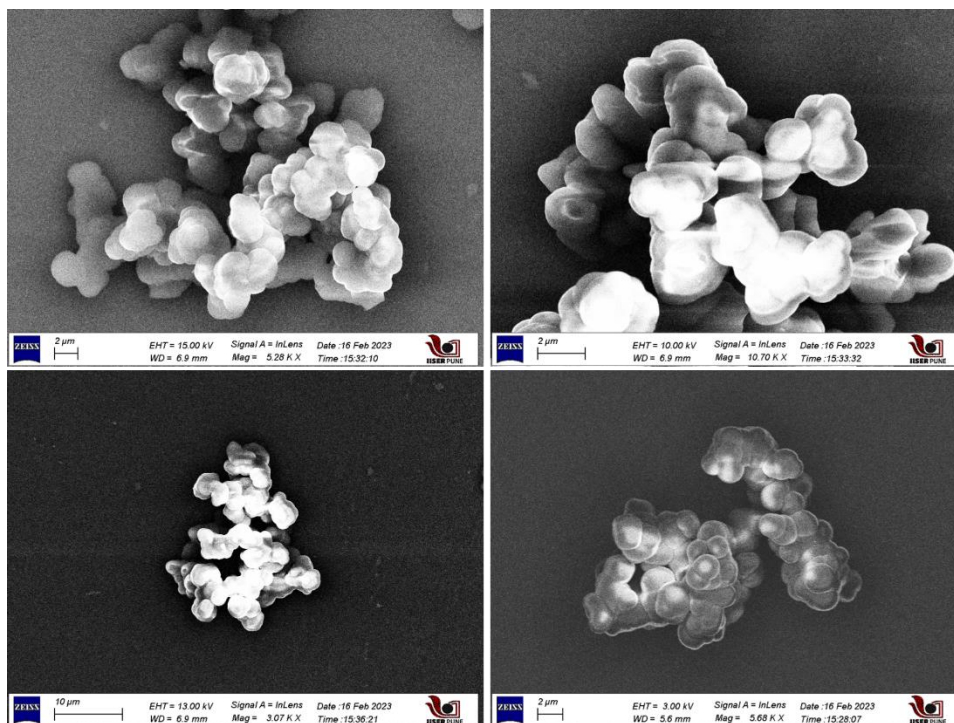
Appendix Figure 3.18: High resolution deconvoluted Br3d spectra of IPM-402Br



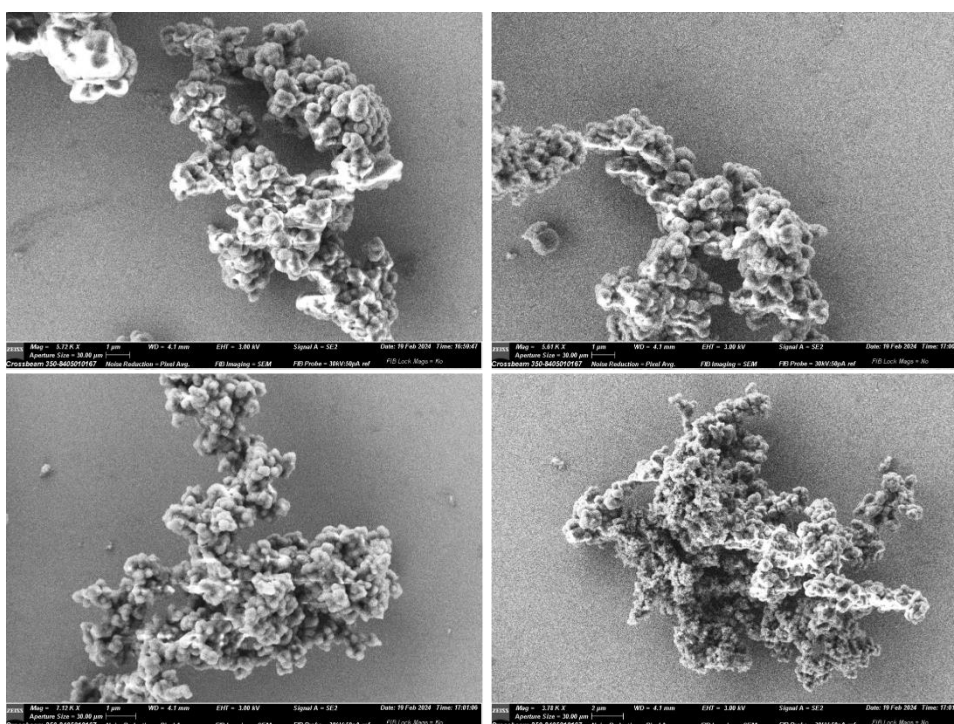
Appendix Figure 3.19: TGA spectra of IPM-402Xs and the starting material



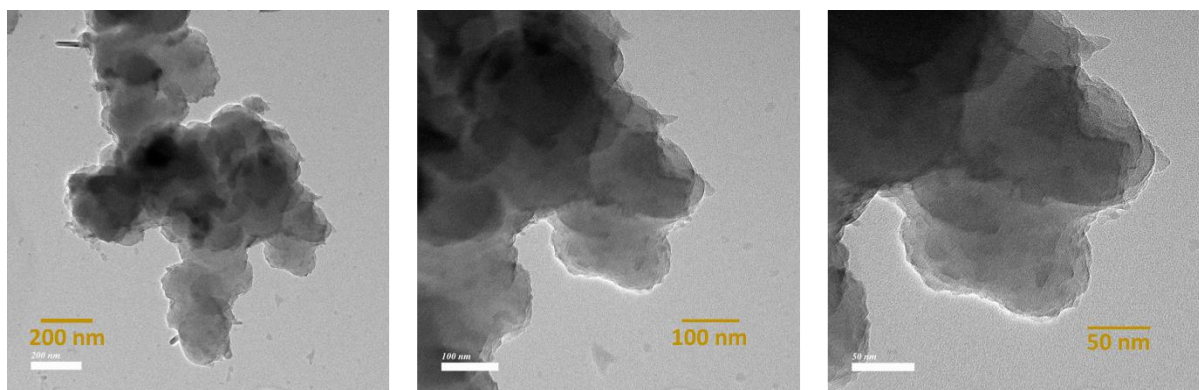
Appendix Figure 3.20: TEM images of IPM-402F



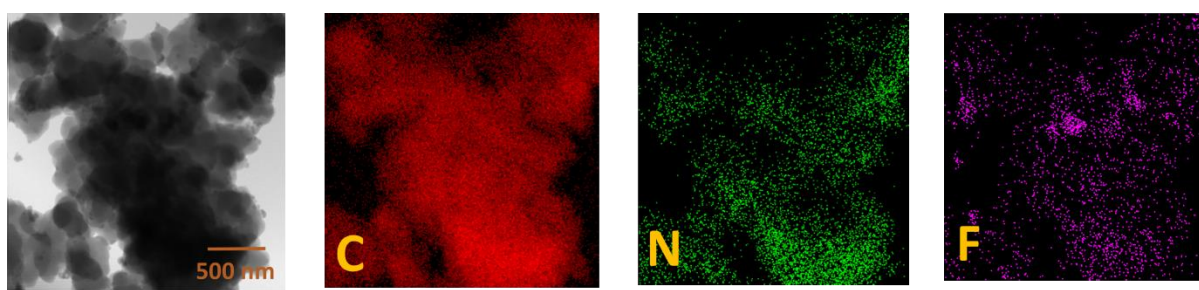
Appendix Figure 3.21: TEM images of IPM-402F



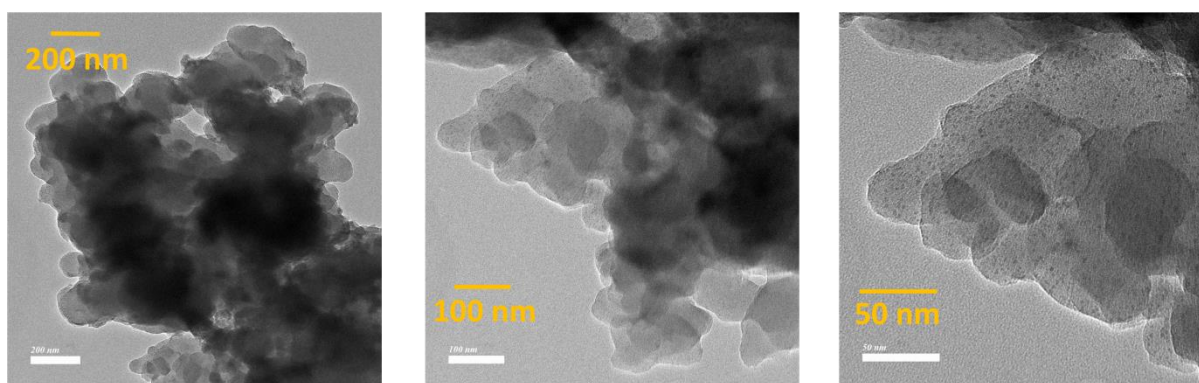
Appendix Figure 3.22: TEM images of IPM-402F



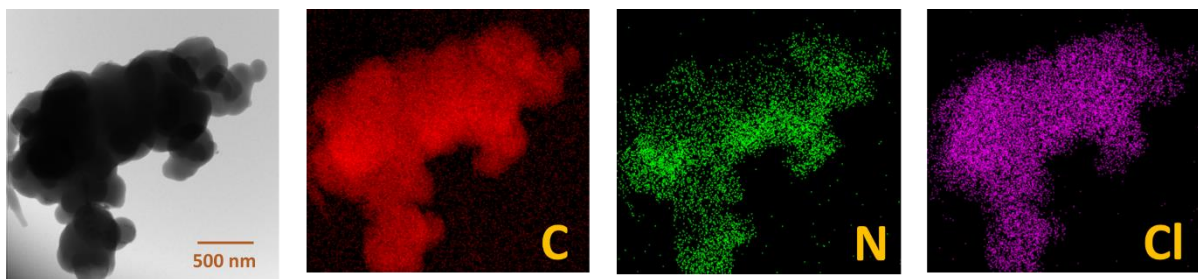
Appendix Figure 3.23: TEM images of IPM-402F



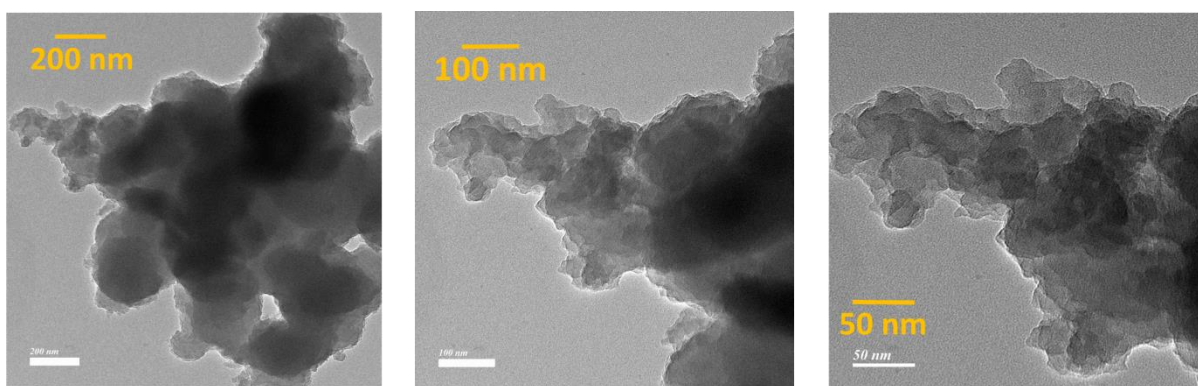
Appendix Figure 3.24: Elemental mapping of IPM-402F



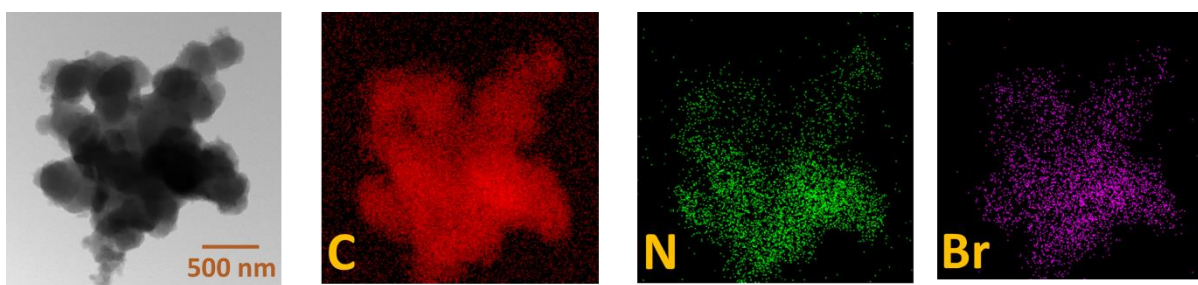
Appendix Figure 3.25: TEM images of IPM-402Cl



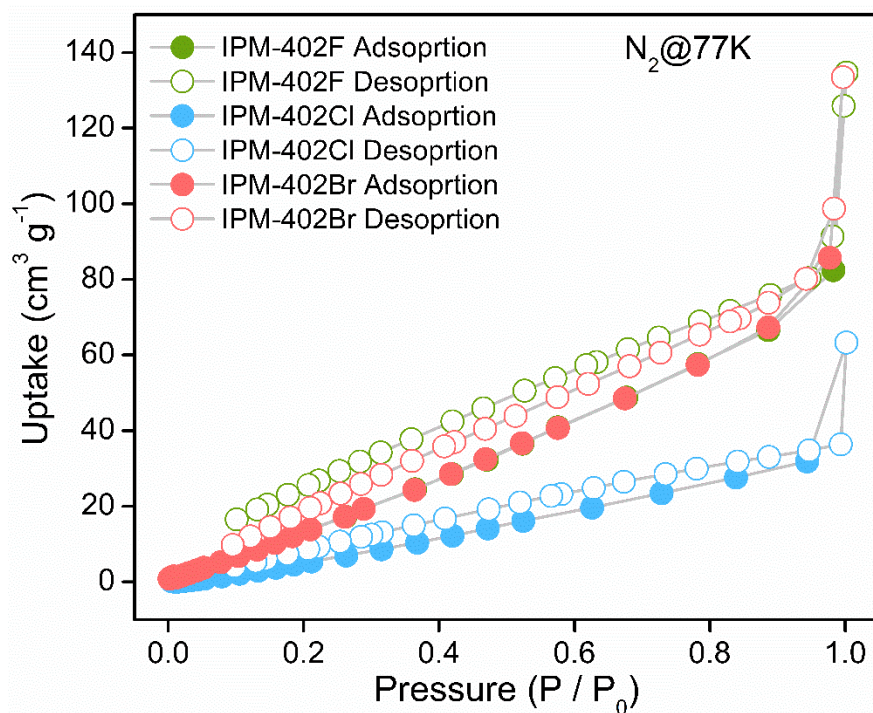
Appendix Figure 3.26: Elemental mapping of IPM-402Cl



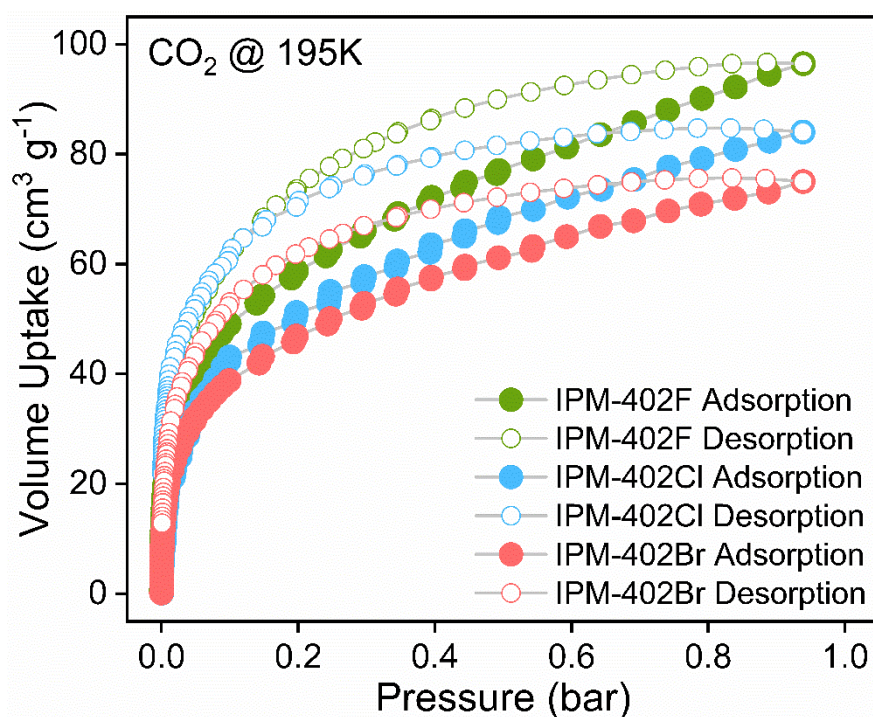
Appendix Figure 3.27: TEM images of IPM-402Br



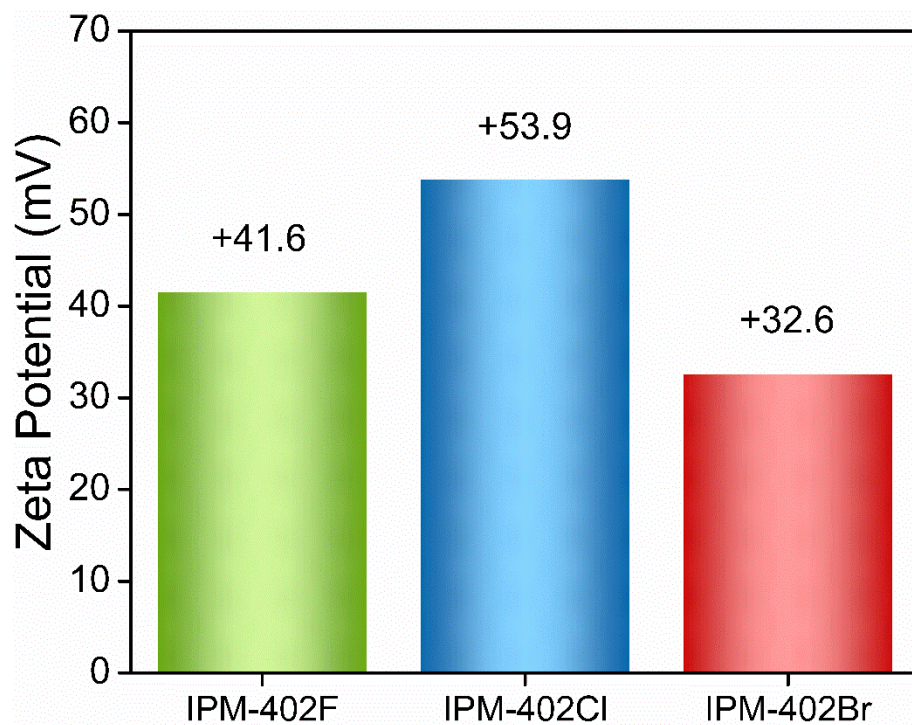
Appendix Figure 3.28: Elemental mapping of IPM-402Br



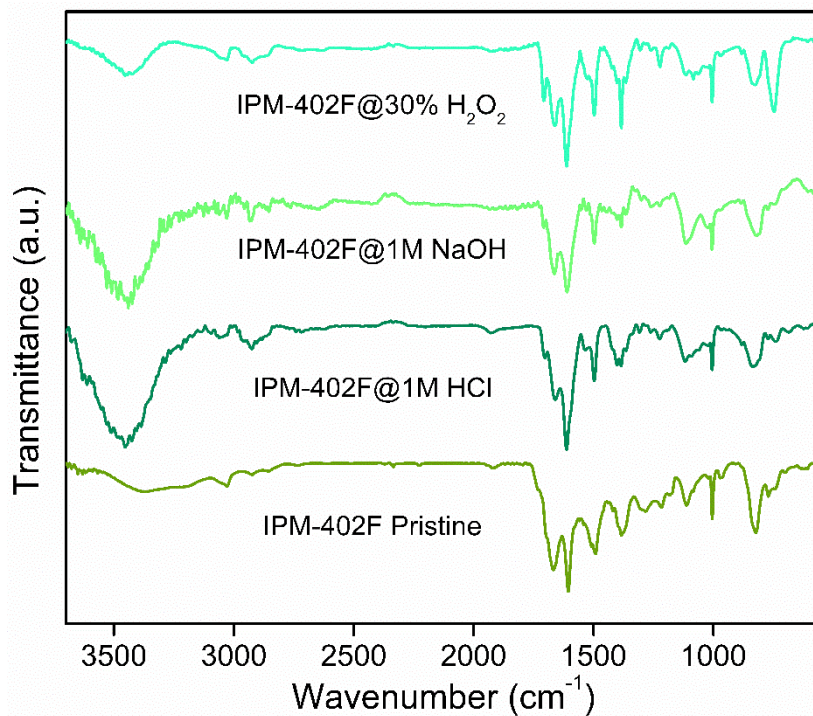
Appendix Figure 3.29: N₂ adsorption at 77K of IPM-402X



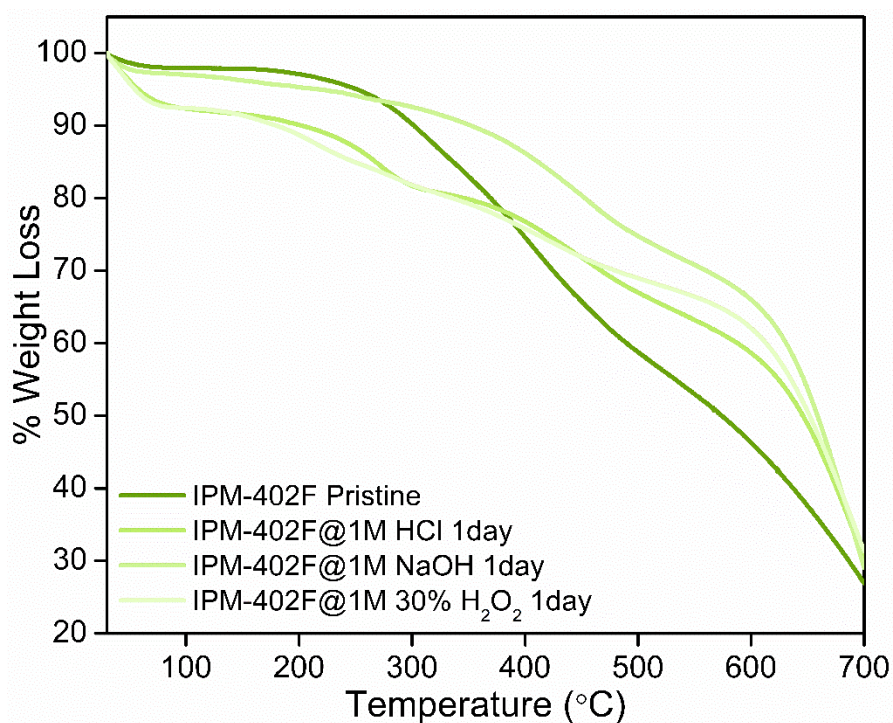
Appendix Figure 3.30: CO₂ adsorption at 195K of IPM-402Xs



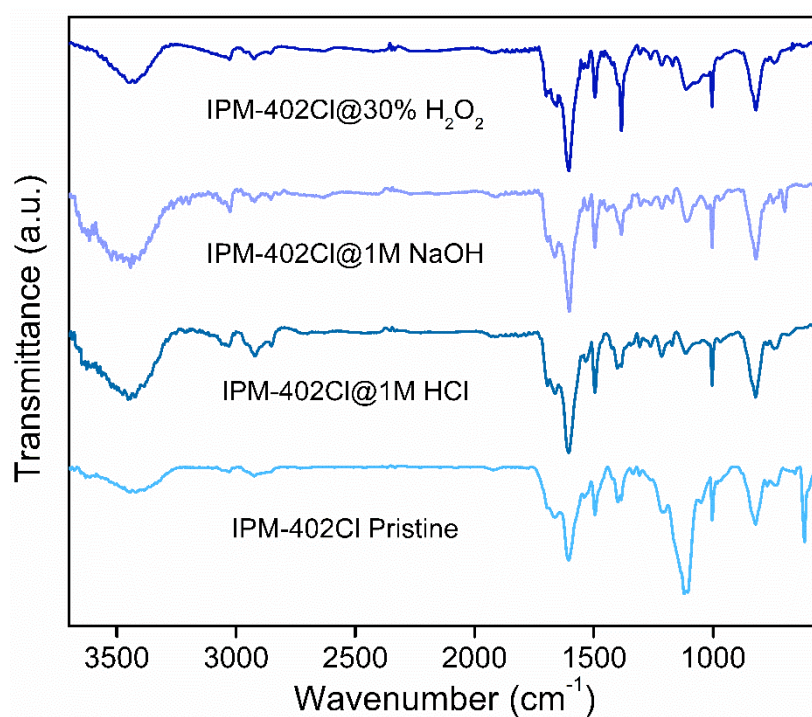
Appendix Figure 3.31: Zeta potential of IPM-402F shows cationic nature of polymeric network



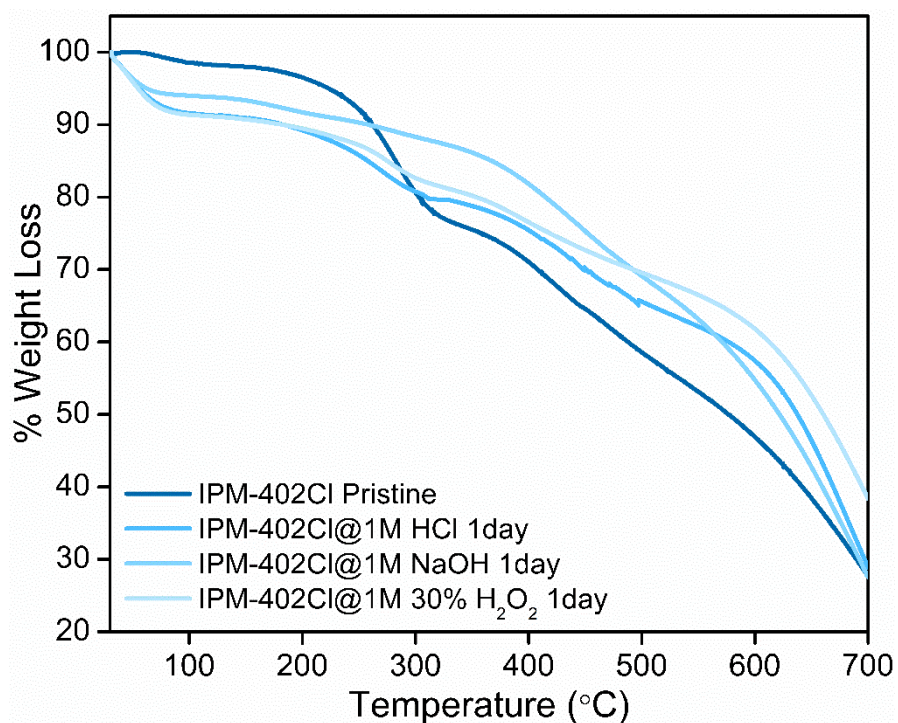
Appendix Figure 3.32: FT-IR spectra of IPM-402F after treatment in different chemical environment



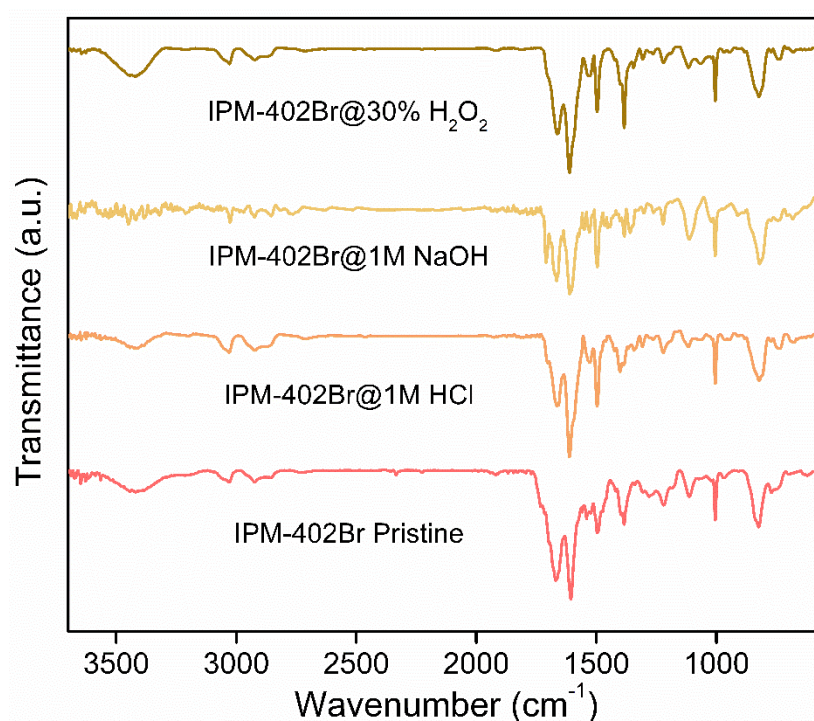
Appendix Figure 3.33: TGA spectra of IPM-402F after treatment in different chemical environment



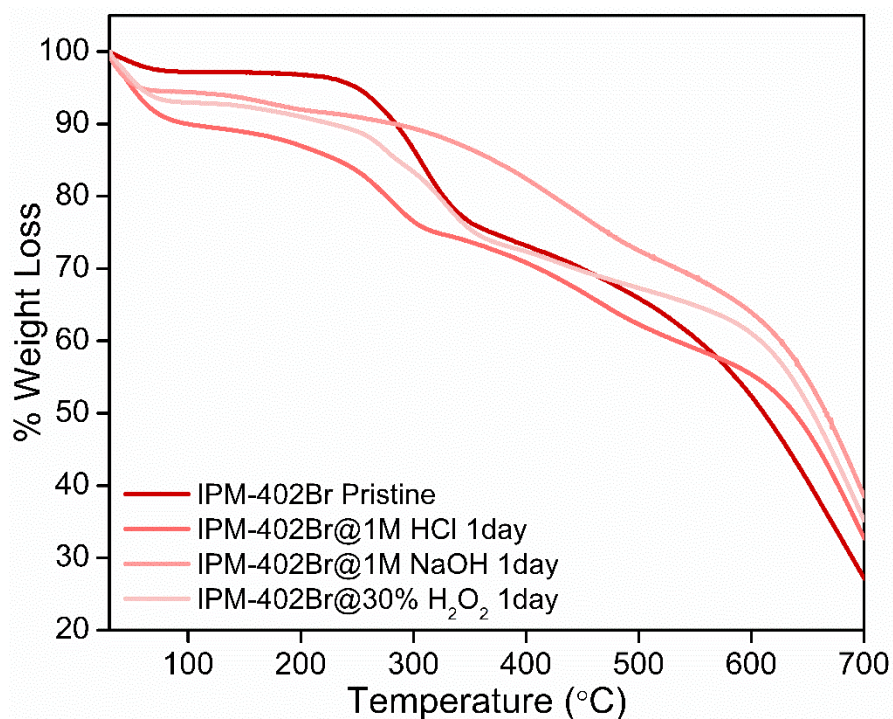
Appendix Figure 3.34: FT-IR spectra of IPM-402Cl after treatment in different chemical environment



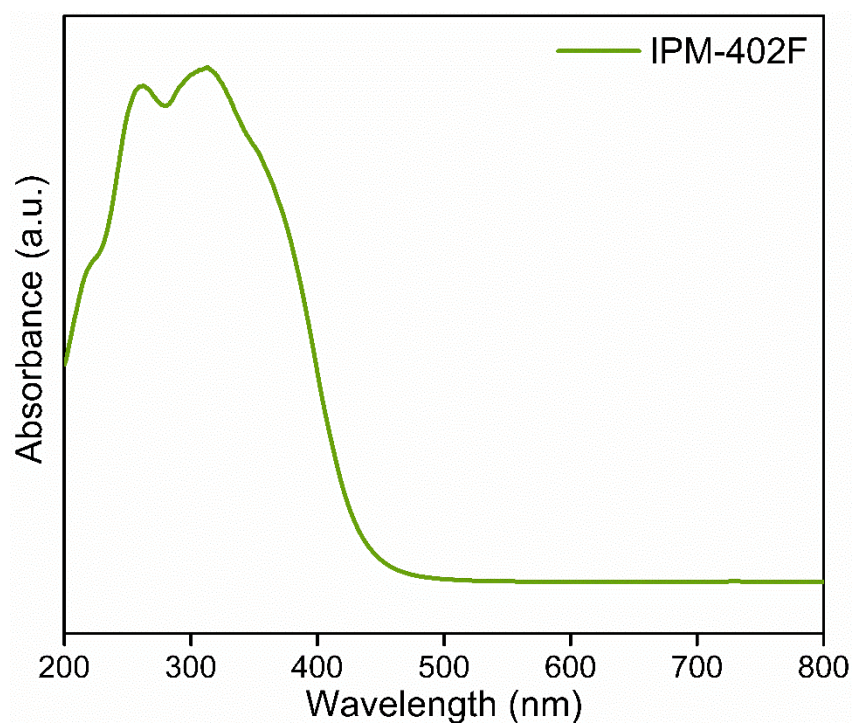
Appendix Figure 3.35: TGA spectra of IPM-402Cl after treatment in different chemical environment



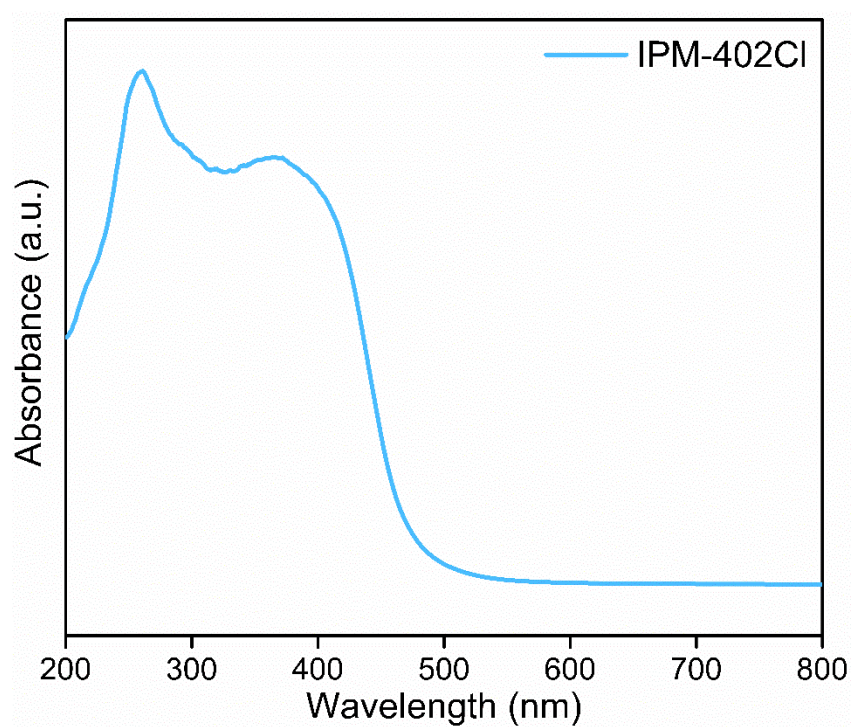
Appendix Figure 3.36: FT-IR spectra of IPM-402Br after treatment in different chemical environment



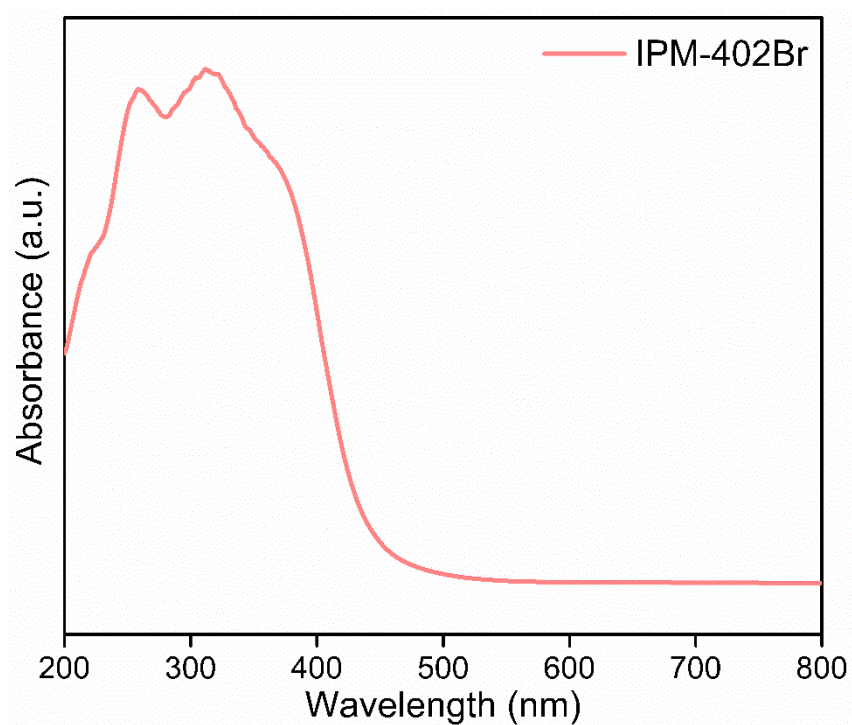
Appendix Figure 3.37: TGA spectra of IPM-402Br after treatment in different chemical environment



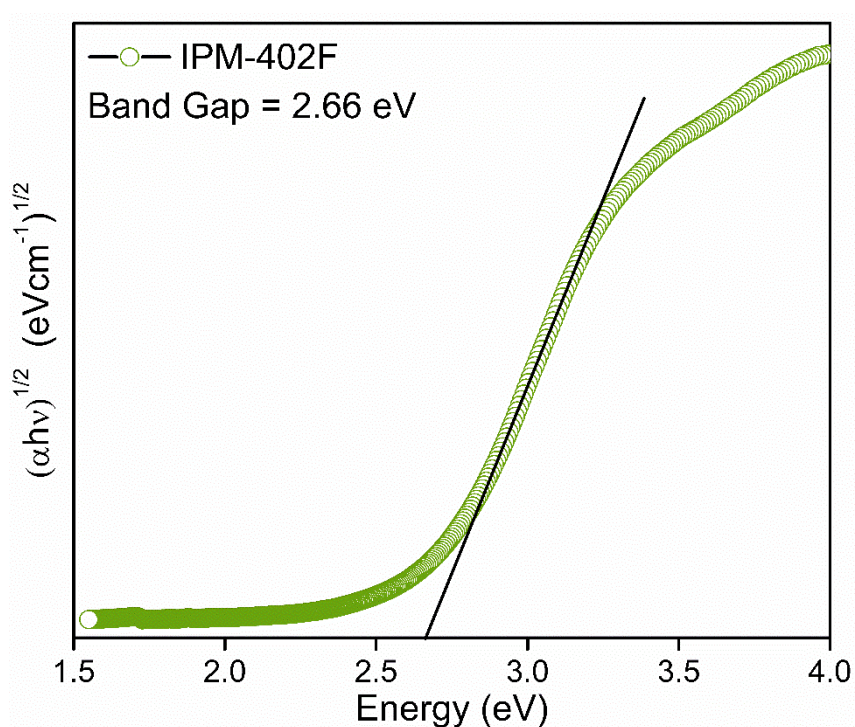
Appendix Figure 3.38: Solid state UV-Vis spectra of IPM-402F



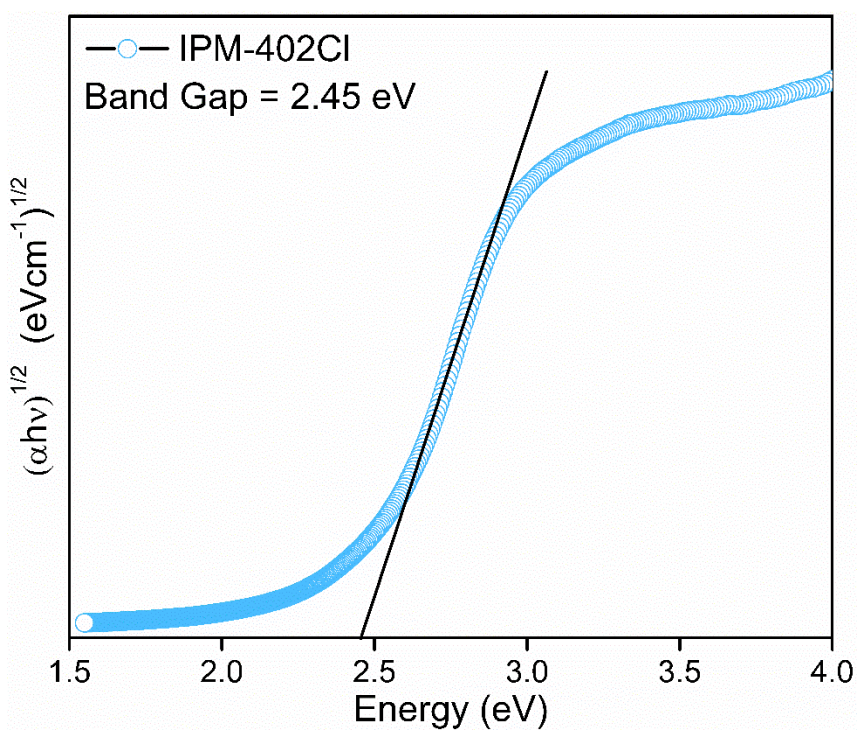
Appendix Figure 3.39: Solid state UV-Vis spectra of IPM-402Cl



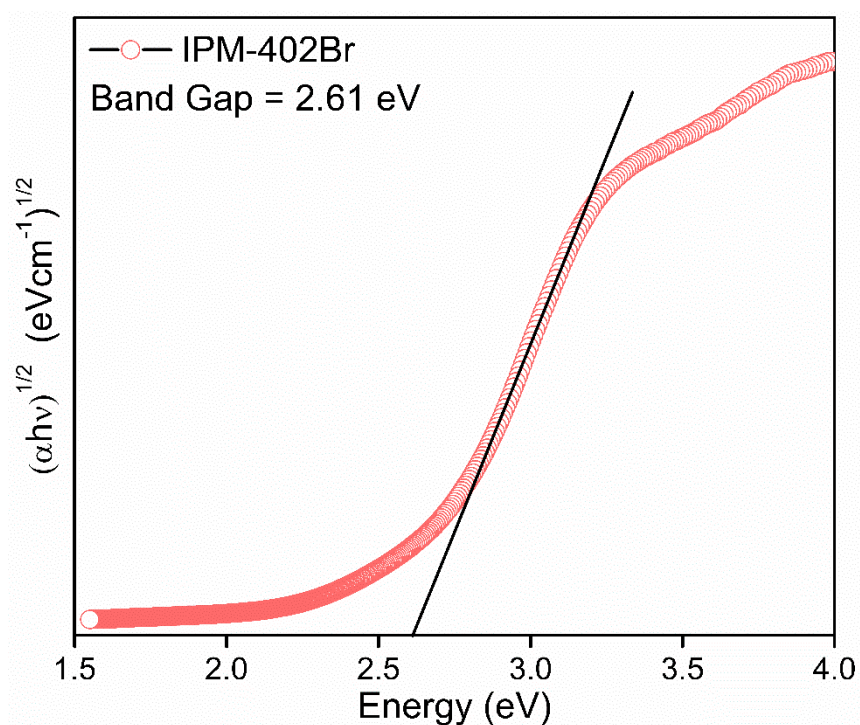
Appendix Figure 3.40: Solid state UV-Vis spectra of IPM-402Br



Appendix Figure 3.41: Tauc's plot of IPM-402F and corresponding band gap



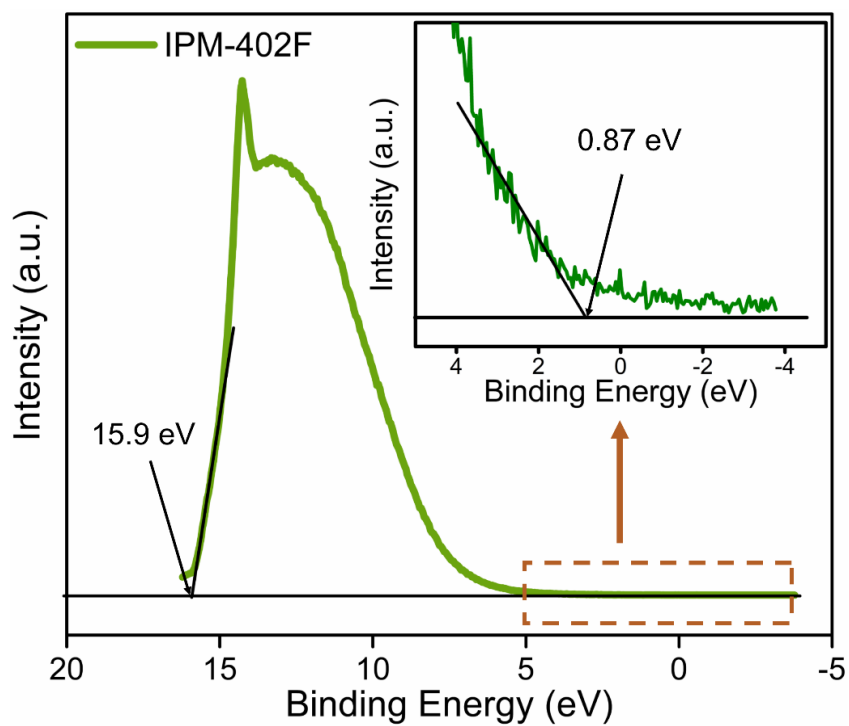
Appendix Figure 3.42: Tauc's plot of IPM-402Cl and corresponding band gap



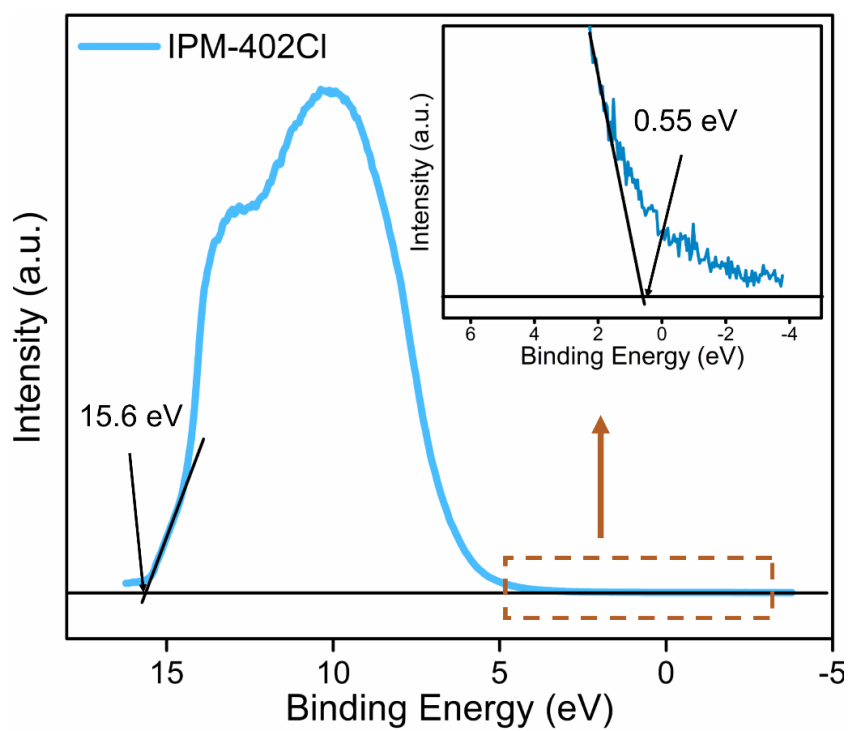
Appendix Figure 3.43: Tauc's plot of IPM-402Br and corresponding band gap

Appendix Section 3.5.1. Valence Band Energy Calculation from Ultraviolet Photoelectron Spectroscopy (UPS)

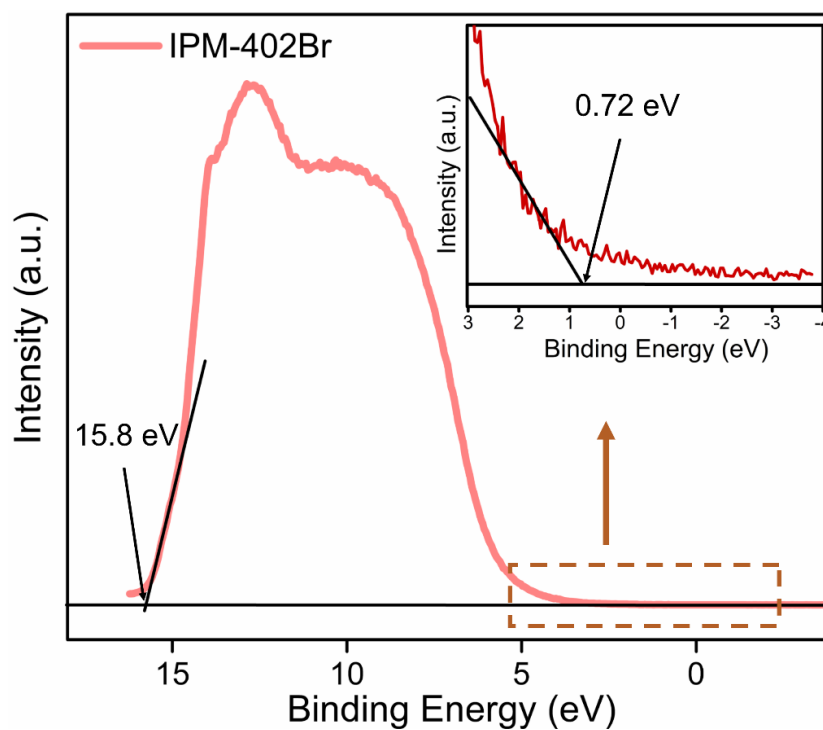
Ultraviolet photoelectron spectroscopy (UPS) reveals the valence band maxima (VBM) energy of all the IPM-402X. The valence band energy (E_{VB}) was obtained by subtracting the width of the UPS spectra peak from the excitation energy (21.22 eV) (Figure S48-S50) Followed by subtraction of 4.5 eV for conversion to electrochemical potential energy (Ref- M5).



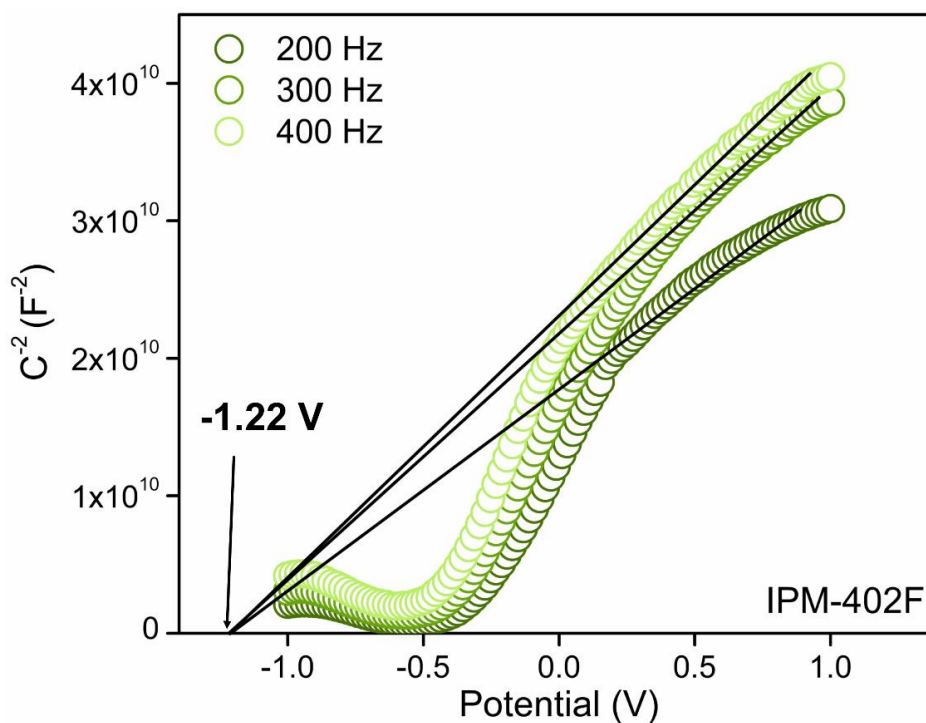
Appendix Figure 3.44: UPS spectra of IPM-402F



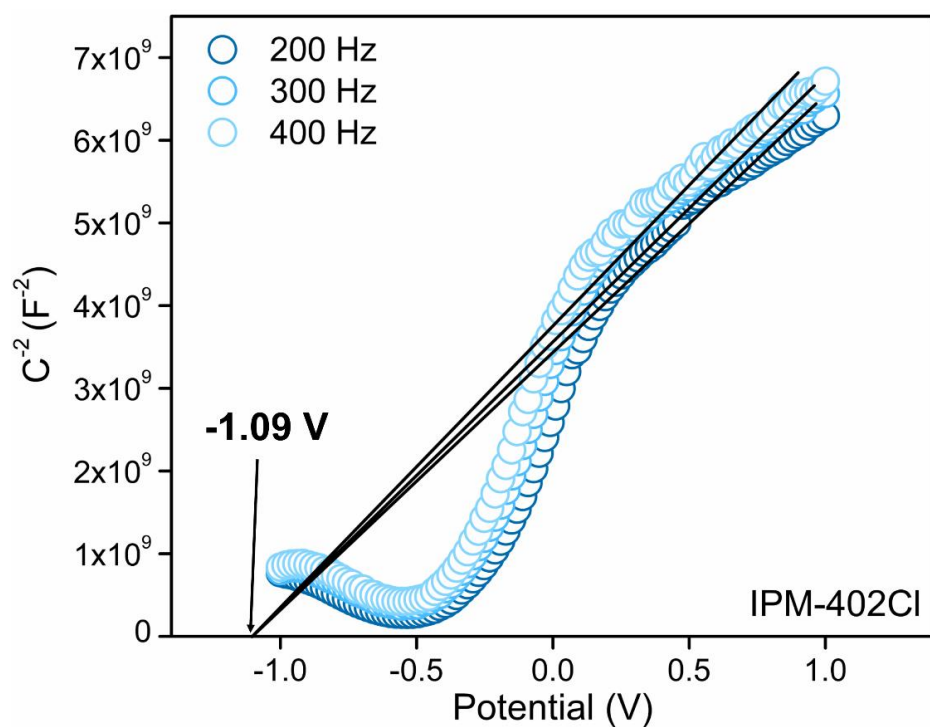
Appendix Figure 3.45: UPS spectra of IPM-402Cl



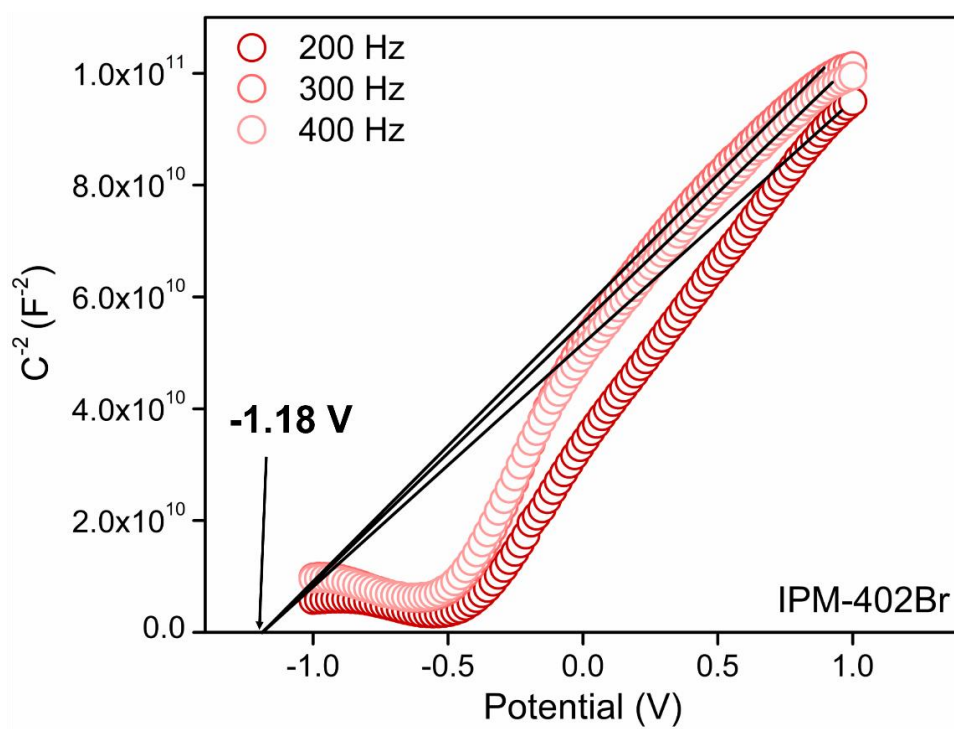
Appendix Figure 3.46: UPS spectra of IPM-402Br



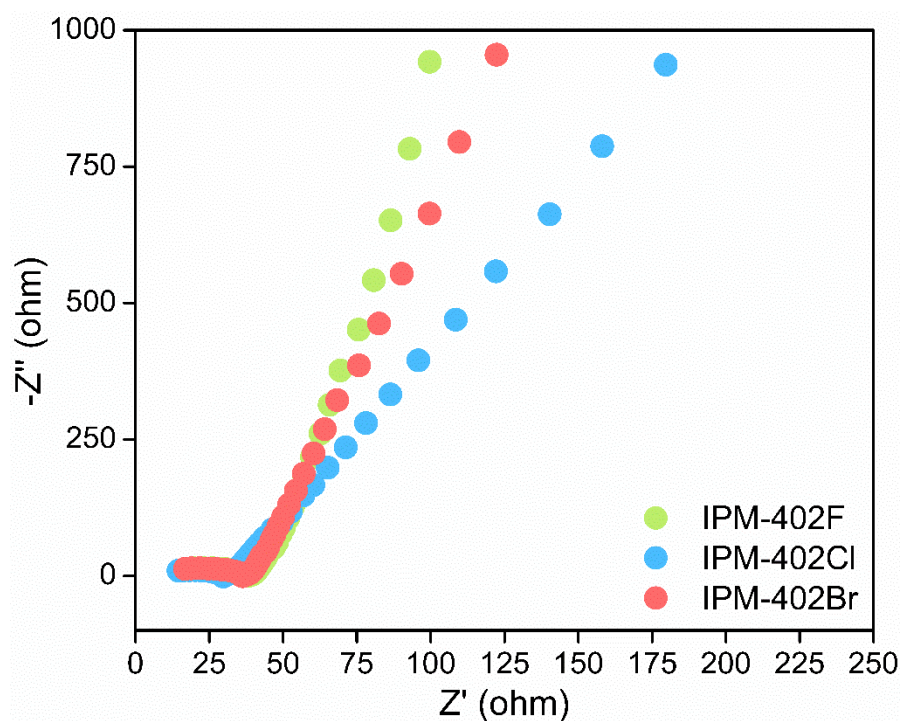
Appendix Figure 3.47: Mott-Schottky Plot of IPM-402F



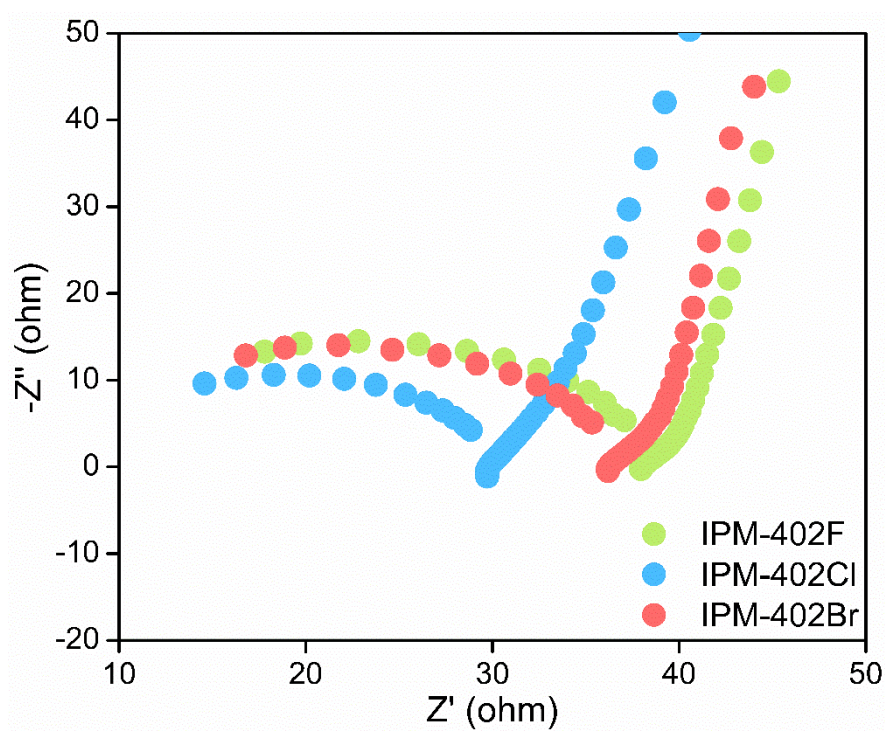
Appendix Figure 3.48: Mott-Schottky Plot of IPM-402Cl



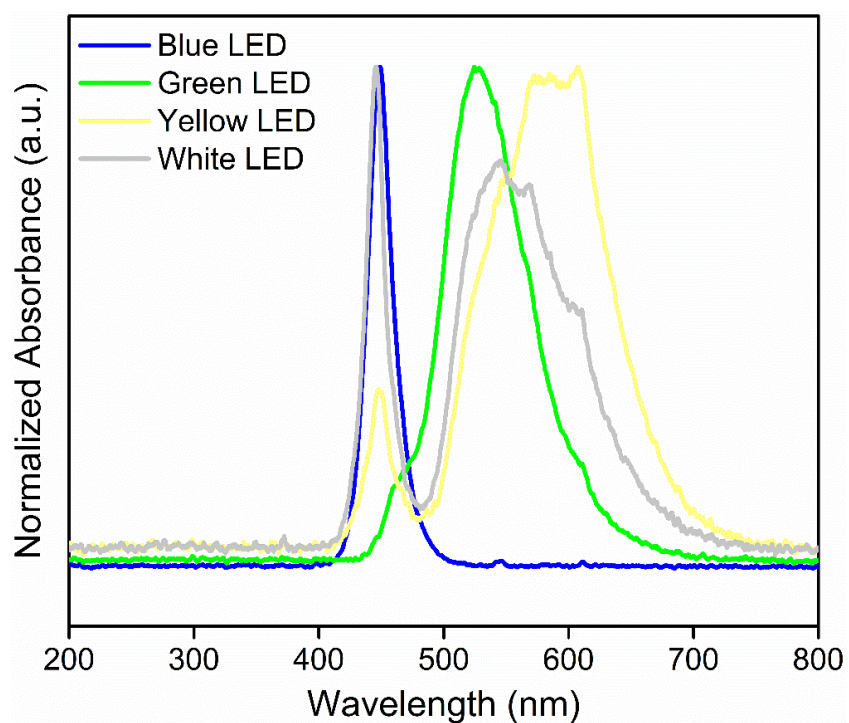
Appendix Figure 3.49: Mott-Schottky Plot of IPM-402Br



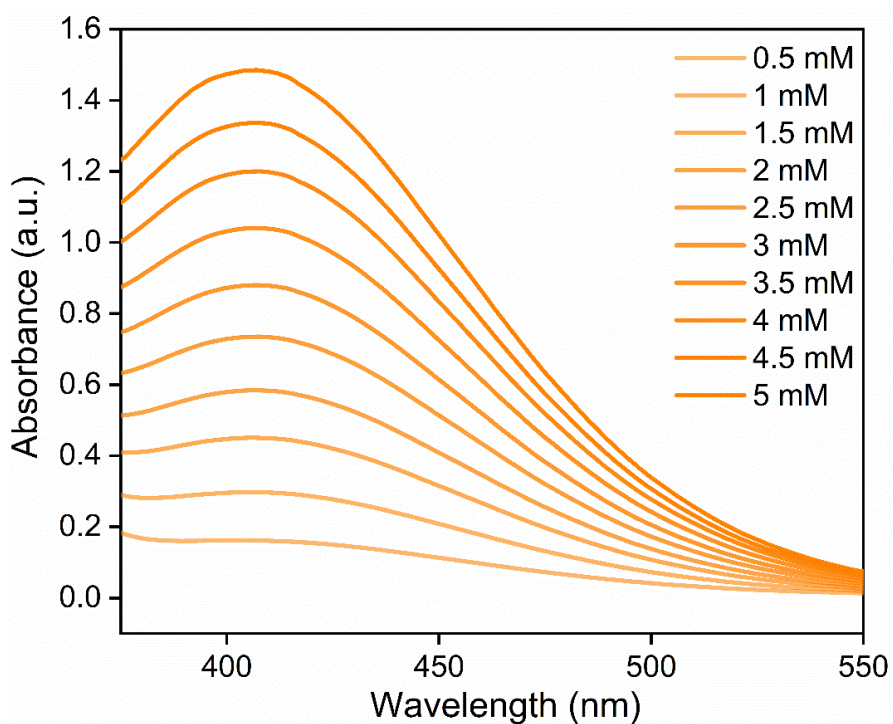
Appendix Figure 3.50: EIS Plot of IPM-402Xs

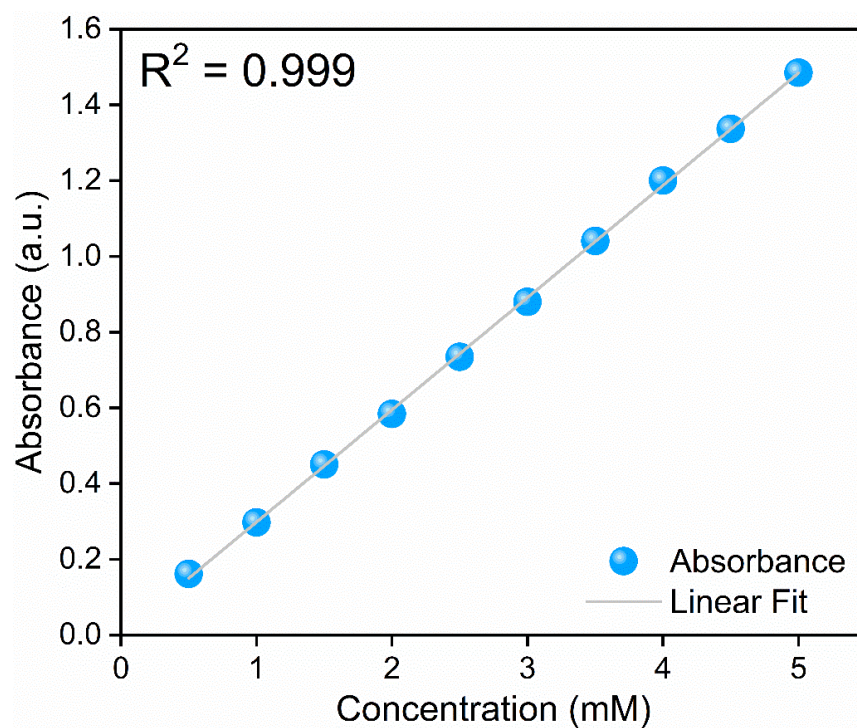


Appendix Figure 3.51: EIS Plot of IPM-402Xs

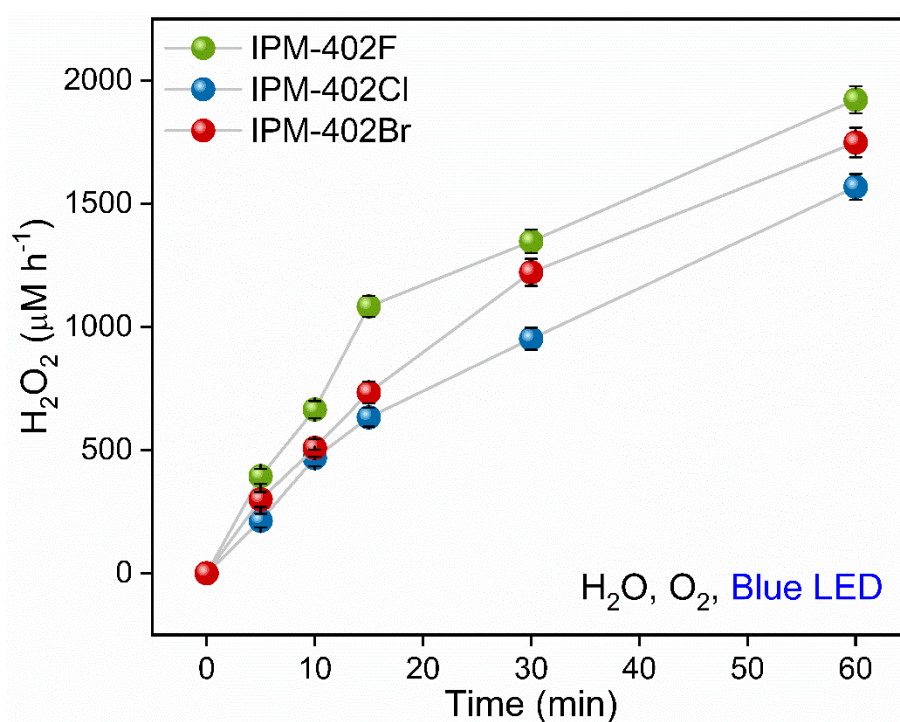
Appendix Section 3.5.2. Photocatalytic H₂O₂ Production

Appendix Figure 3.52: Absorbance profile of different LED's

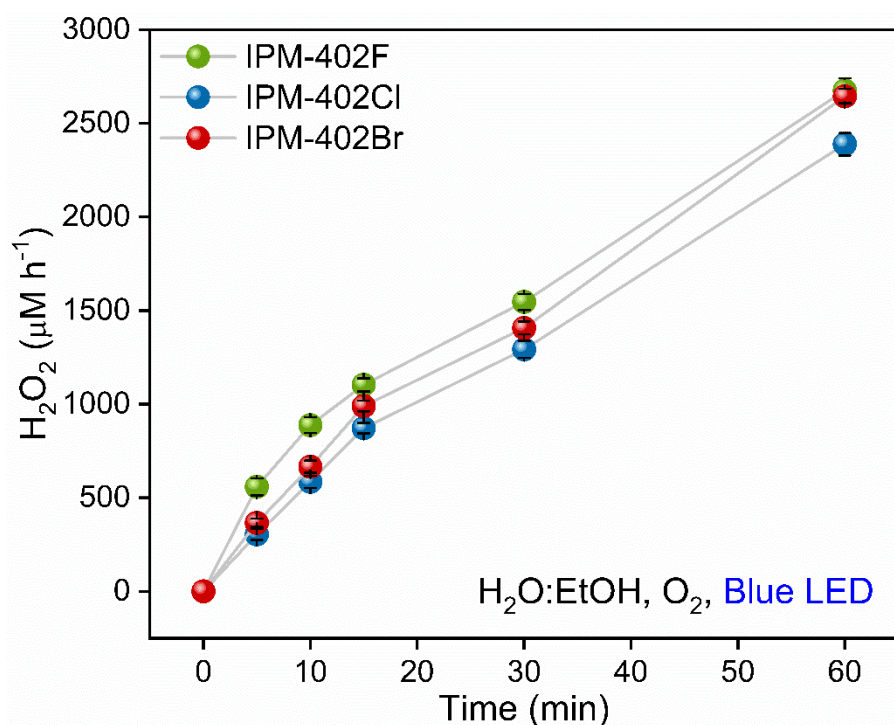
Appendix Figure 3.53: UV-Vis spectra of different concentration of H₂O₂ for calibration curve



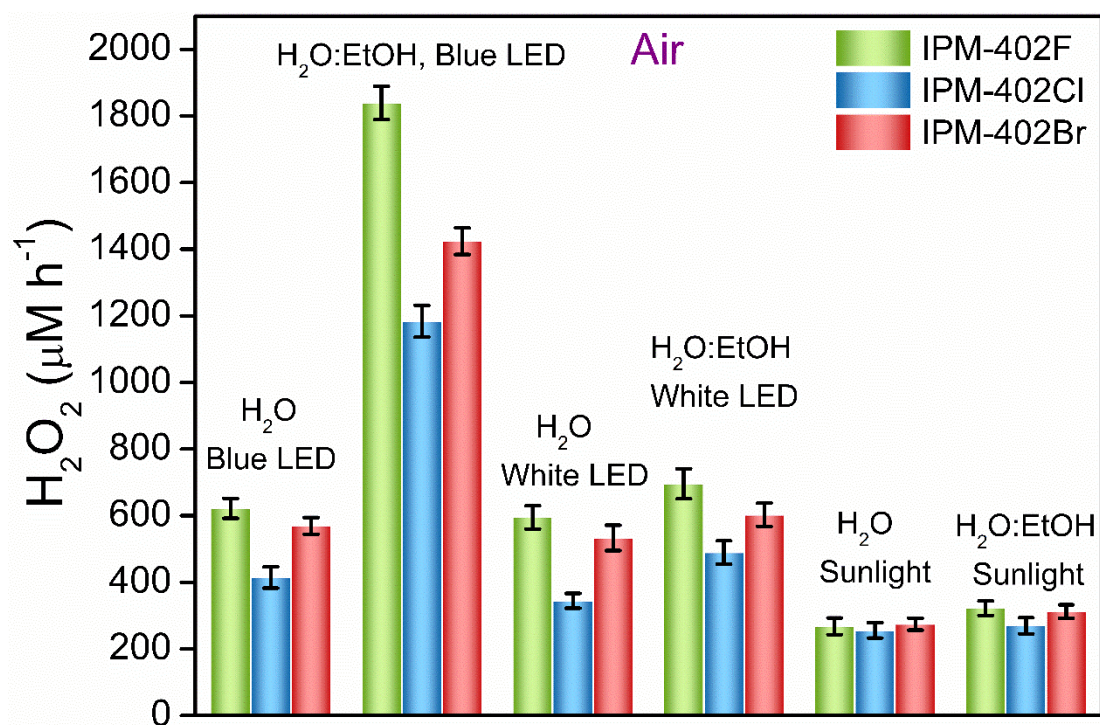
Appendix Figure 3.54: Linear fit of H_2O_2 calibration



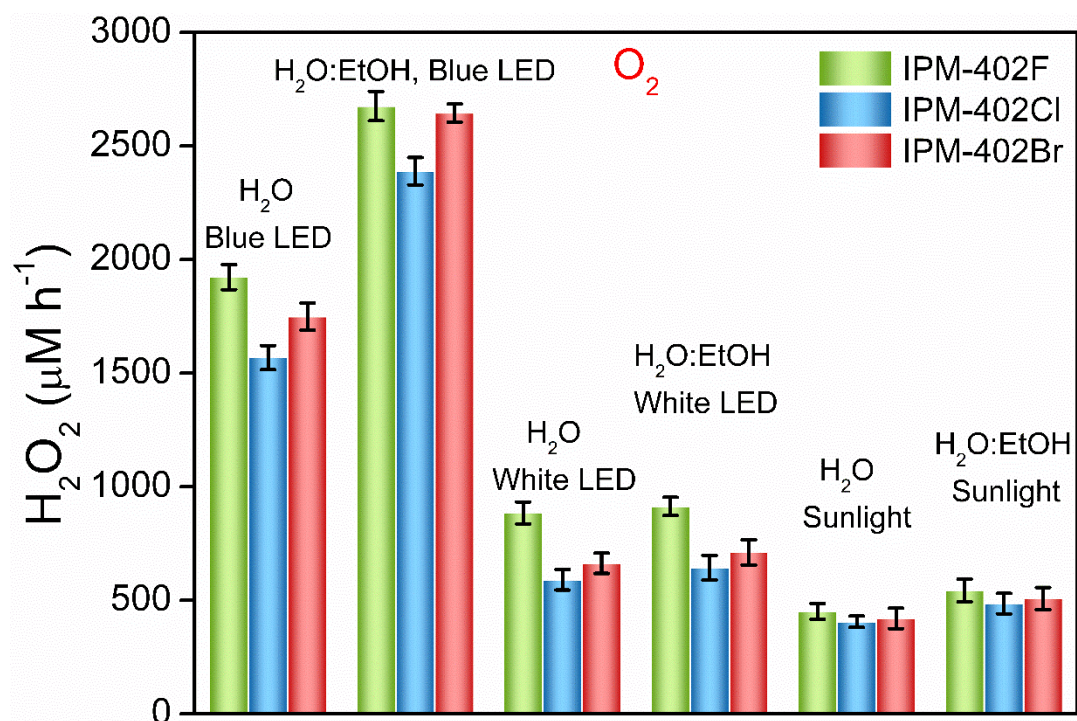
Appendix Figure 3.55: Time dependent H_2O_2 Production in O_2 saturated H_2O in Blue LED



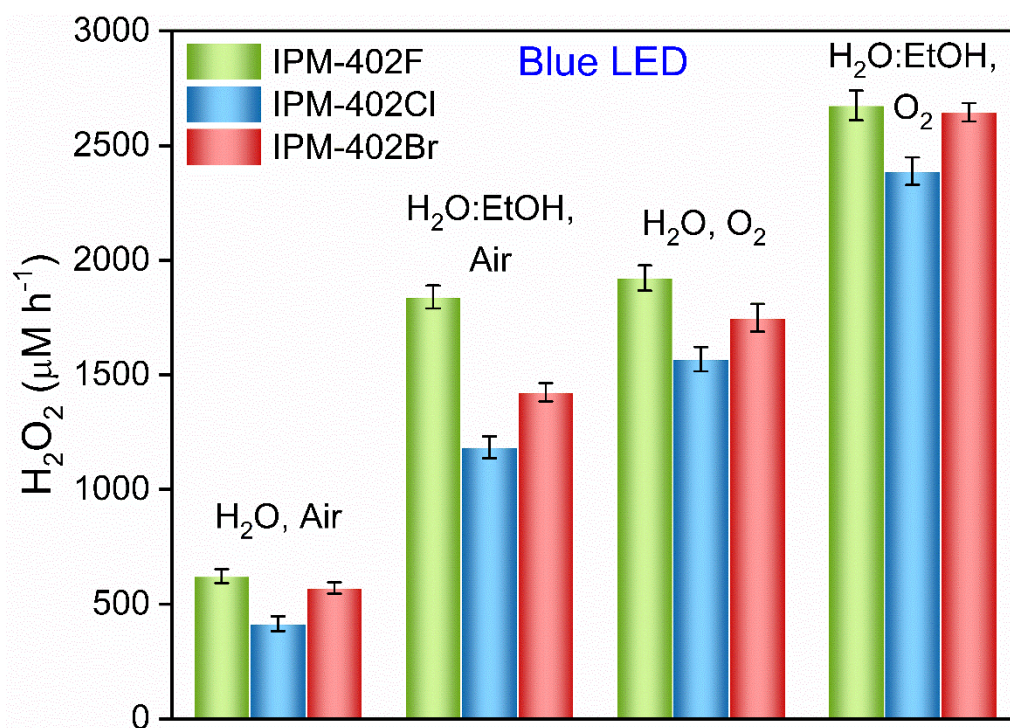
Appendix Figure 3.56: Time dependent H₂O₂ production in O₂ saturated H₂O:EtOH (9:1) in Blue LED



Appendix Figure 3.57: H₂O₂ production comparison in different condition in Air by IPM-402Xs



Appendix Figure 3.58: H₂O₂ production comparison in different condition in O₂ by IPM-402Xs

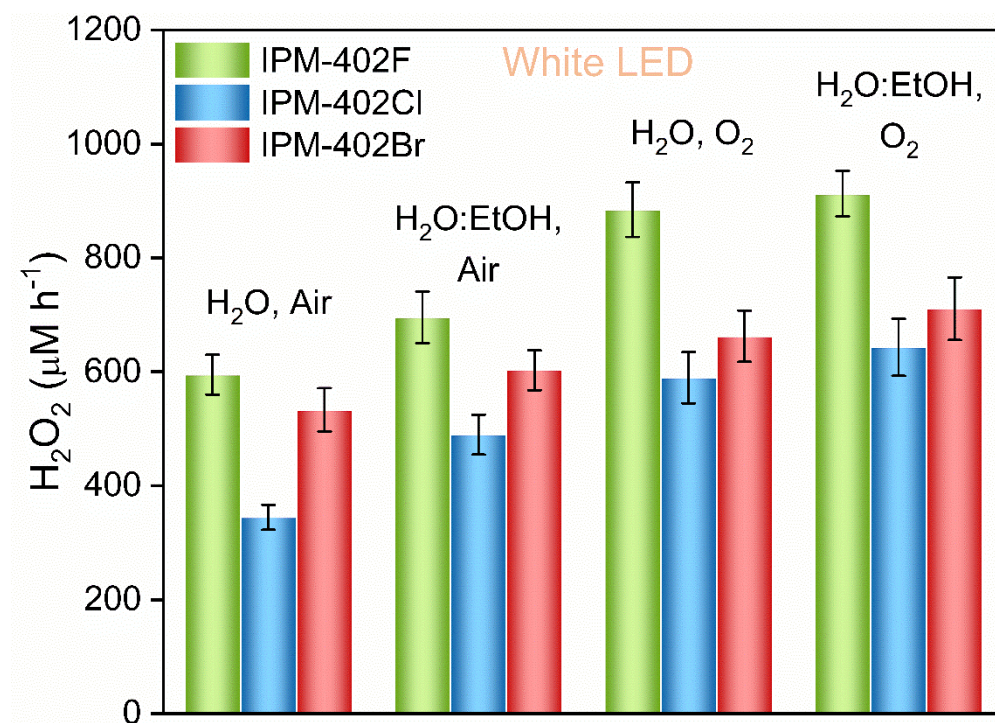


Appendix Figure 3.59: H₂O₂ production comparison in different conditions in blue LED by IPM-402Xs

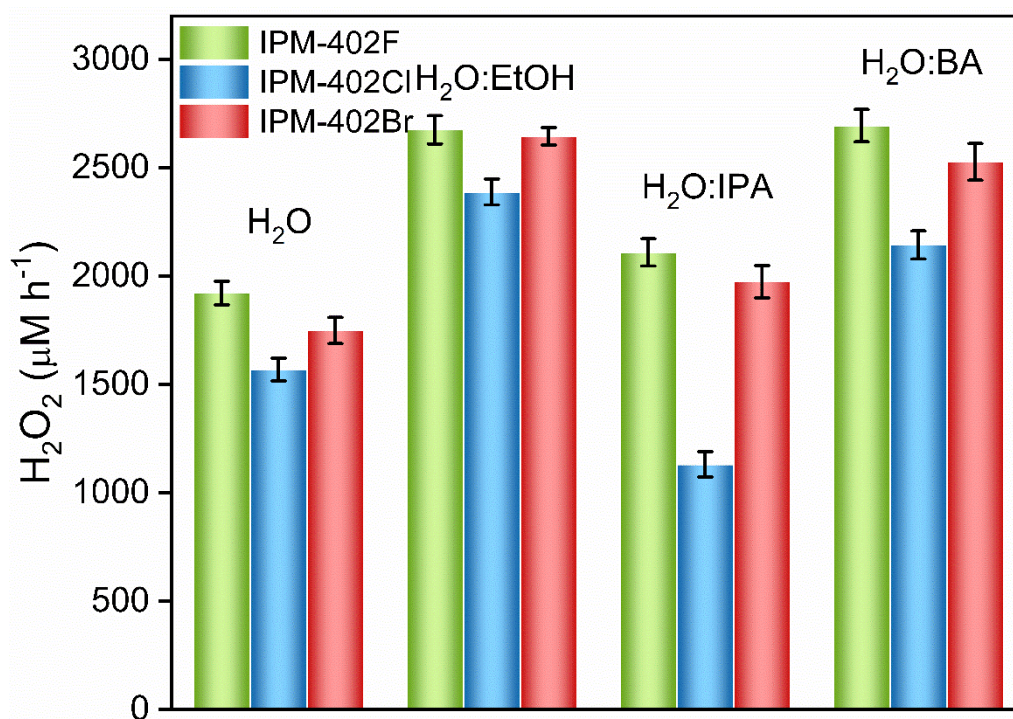
Appendix Table 3.1: Comparison Table of Photocatalytic H₂O₂ Production by Porous Materials

Sr. No.	Material	H ₂ O ₂ (microM g ⁻¹ h ⁻¹)	Reaction Medium	Wavelength (nm)	Reference
1.	IPM-402F	384475	H ₂ O-O ₂	450	<i>This Work</i>
2.	IPM-402Cl	313668			
3.	IPM-402Br	349780			
4.	Bpt-CTF	65362	H ₂ O-O ₂	350-780	S1
5.	COF-TpHt	11986		> 420	S2
6.	TTF-BT-COF	276000	H ₂ O-O ₂	> 420	S3
7.	TTF-pT-COF	99600			
8.	TPE-BT-COF	59200			
9.	Cu ₃ -BT-COF	187000	H ₂ O-O ₂ -FAA	> 420	S4
10.	Cu ₃ -pT-COF	64600			
11.	TFP-BT-COF	94000			
12.	TpDz	7327	H ₂ O-O ₂	> 420	S5
13.	ZrS3	52060	H ₂ O-BN	AM 1.5G	S6
14.	CTF-LTZ	4068	H ₂ O/EtOH-O ₂	300 W Xe Lamp	S7
15.	TD-COF	4620	H ₂ O-O ₂	400 - 700	S8
16.	Bpy-TAPT	4038	H ₂ O-O ₂		S9
17.	CoPc-BTM-COF	2096	H ₂ O/EtOH-O ₂	400	S10
18.	COF-TfpBpy	208400	H ₂ O	420 – 700	S11
19.	TBNT-COF	11013	H ₂ O-O ₂	400 (300 W Xe Lamp)	S12
20.	CN-PDA	35480	H ₂ O-O ₂	> 400	S13
21.	p-COF-TpPzda	6434	H ₂ O	> 420	S14
22.	DVA-COF	8450	H ₂ O/BnOH-O ₂	420	S15
23.	ECUT-COF-31	3229	H ₂ O/EtOH-O ₂	Xe Lamp	S16
24.	CNP-s	3200	H ₂ O	Solar Simulator	S17
25.	H ₂ -TP-BT-COF	6500	H ₂ O-O ₂	420 - 600	S18
26.	NiPc-THHI-COF	4589	H ₂ O-O ₂	> 400	S19
27.	TBD-COF	6085	H ₂ O-O ₂	400 - 700	S20
28.	TBTN-COF	11013	H ₂ O	>420	S21
29.	TMT-COF	6392			

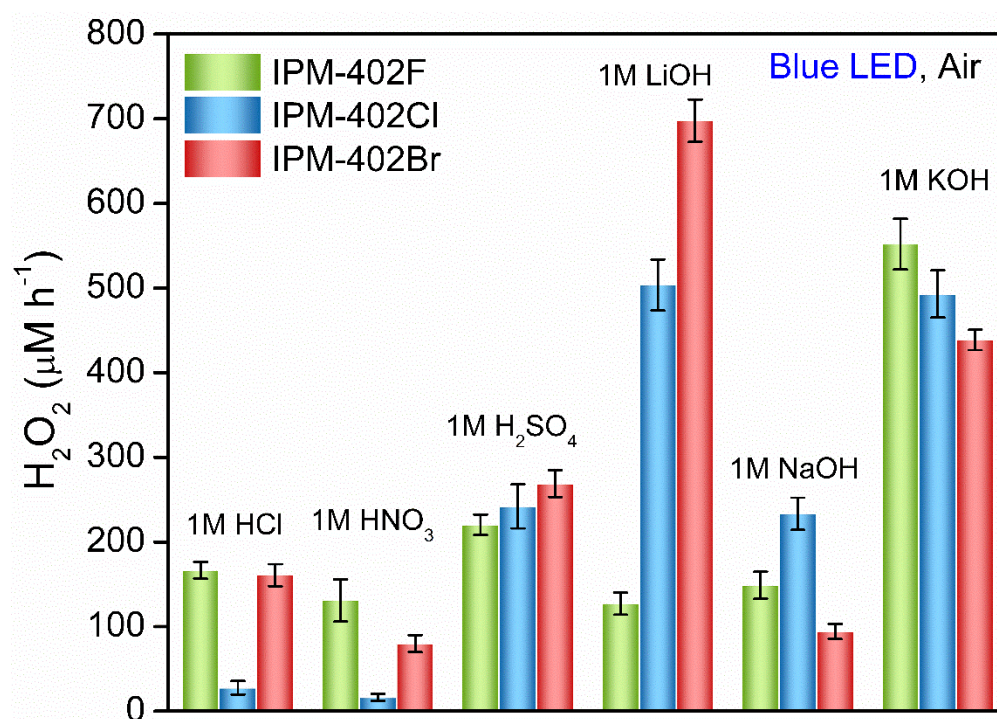
30.	p-COF-TpPzda	6434	H ₂ O	>420	S22
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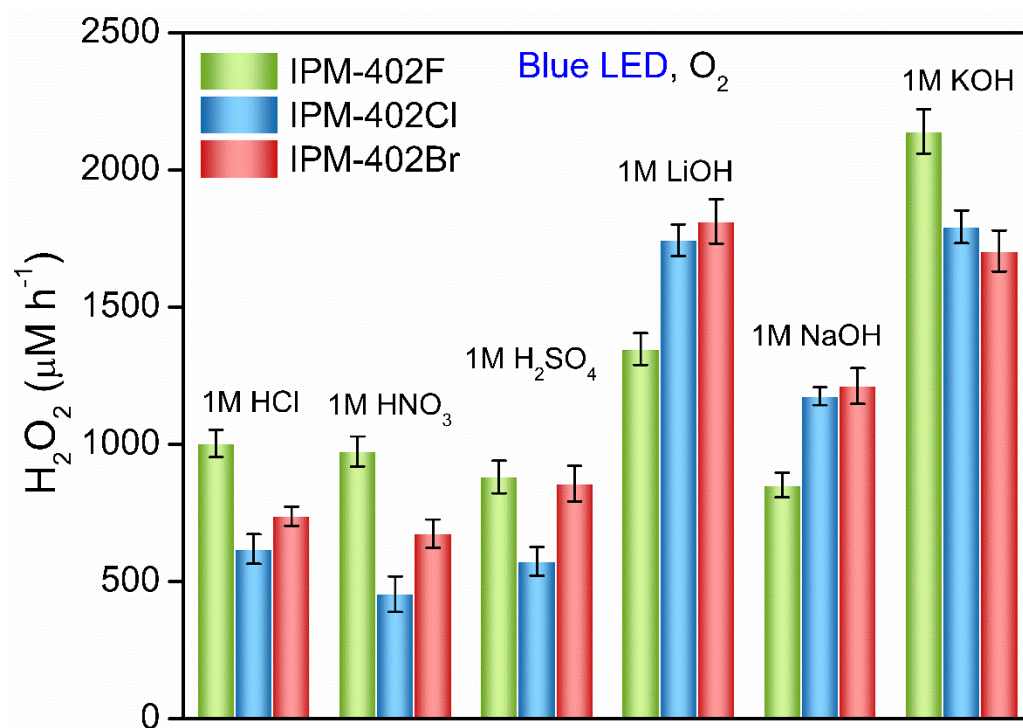
Appendix Figure 3.60: H₂O₂ production comparison in different condition in white LED by IPM-402Xs



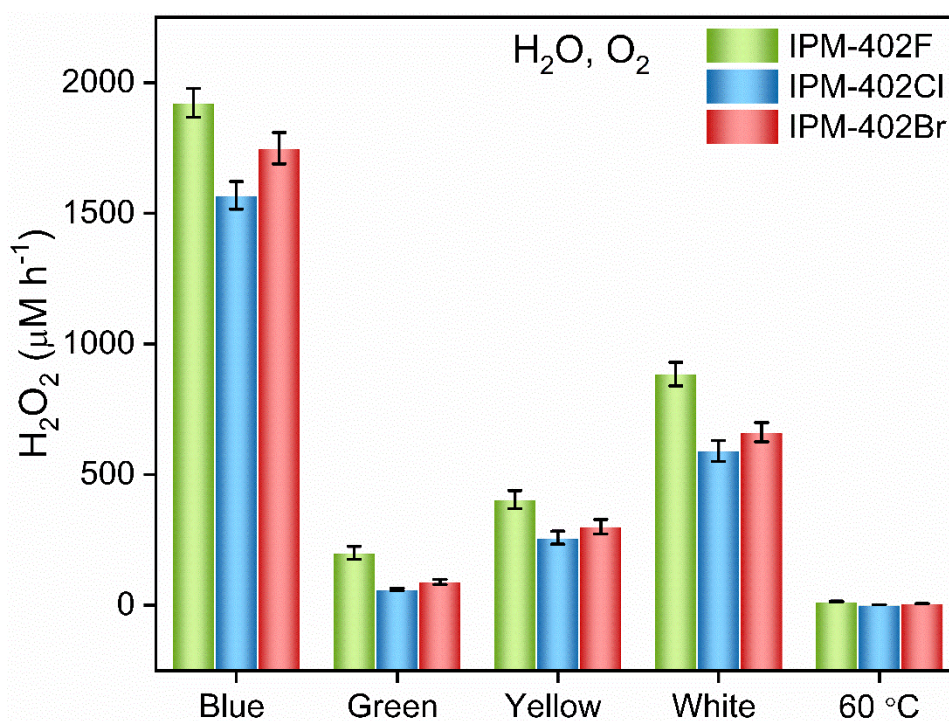
Appendix Figure 3.61: H_2O_2 production comparison in different electron sacrificial agents in blue LED and air by IPM-402Xs



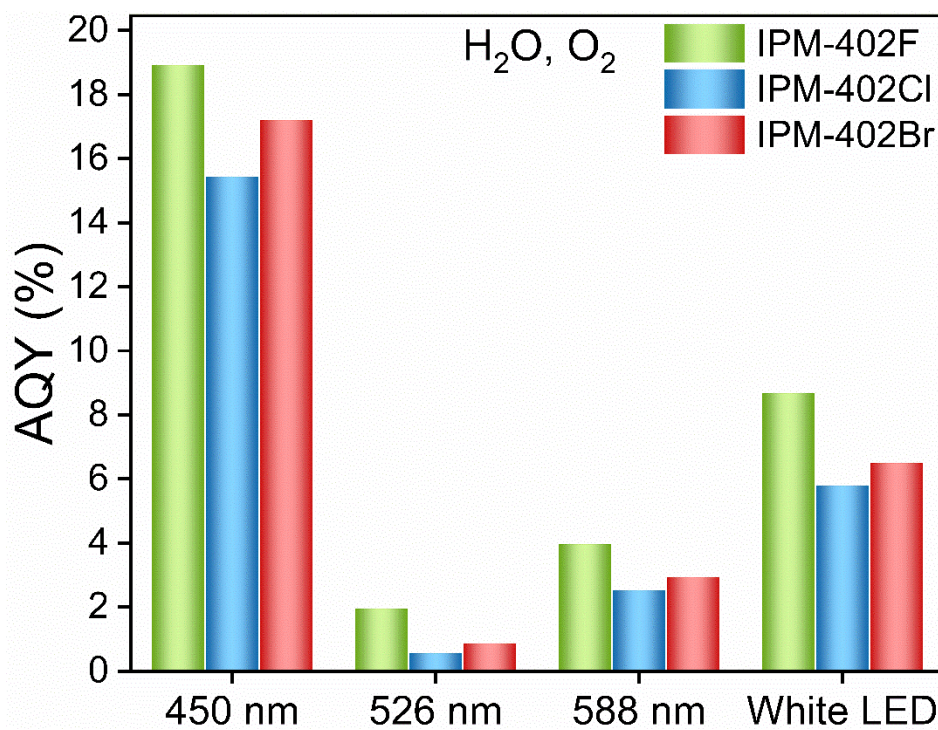
Appendix Figure 3.62: H_2O_2 production comparison in different chemical conditions in blue LED and air by IPM-402Xs



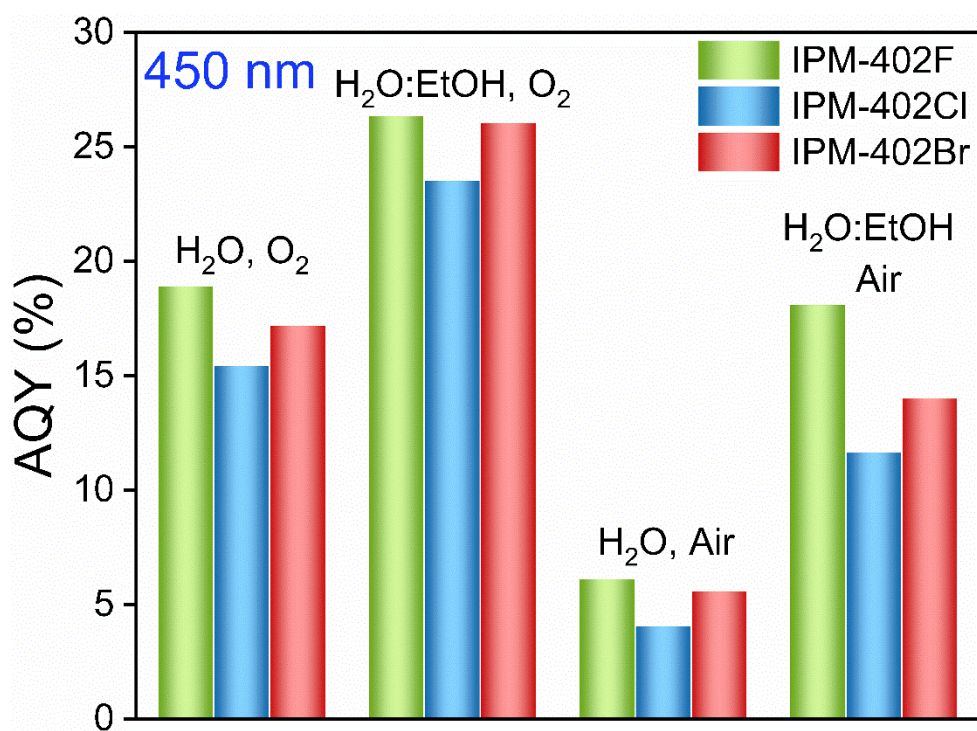
Appendix Figure 3.63: H_2O_2 production comparison in different chemical conditions in blue LED and O_2 by IPM-402Xs



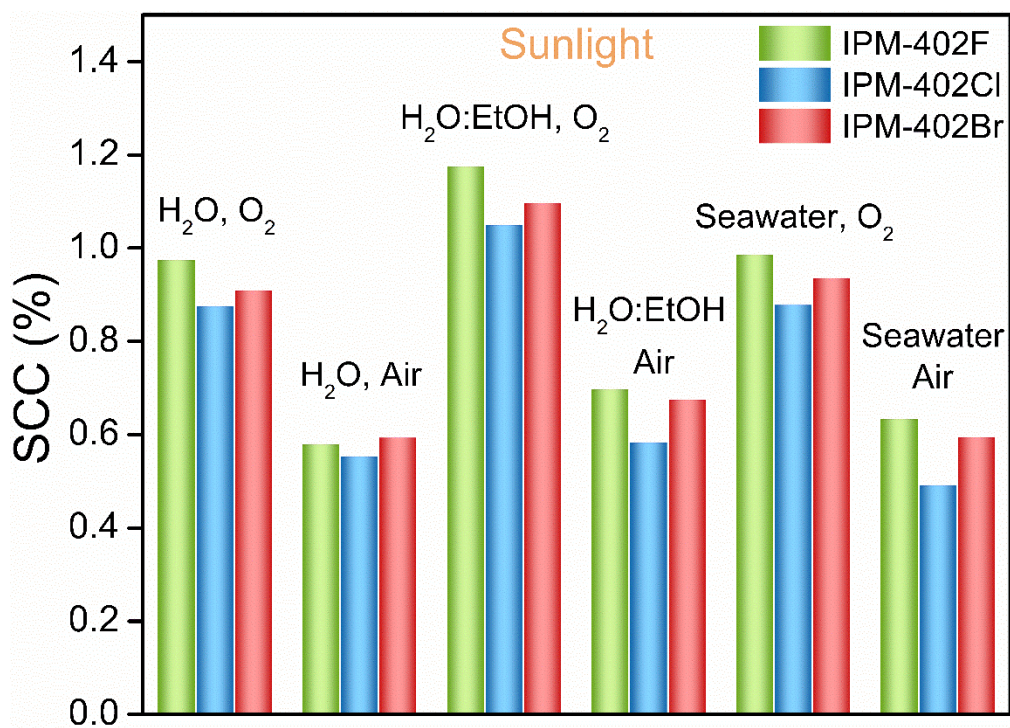
Appendix Figure 3.64: H_2O_2 production comparison in O_2 saturated H_2O in different LED and temperature by IPM-402Xs



Appendix Figure 3.65: AQY % in O_2 saturated H_2O in different wavelengths by IPM-402Xs



Appendix Figure 3.66: AQY % in different conditions at 450 nm IPM-402Xs



Appendix Figure 3.67: SCC % in different conditions in sunlight IPM-402Xs

Appendix Table 3.2: Comparison Table of % AQY for Photocatalytic H₂O₂ Production by Porous Materials

Sr. No.	Materials	Reaction Medium	AQY (%)	Wavelength (nm)	Reference
1.	IPM-402F	H ₂ O-O ₂	18.94	450	<i>This Work</i>
2.	IPM-402Cl	H ₂ O-O ₂	15.45		
3.		H ₂ O-O ₂	17.23		
4.	Sono-COF-F2	H ₂ O-O ₂	4.8	> 420	S23
5.	Bpt-CTF	H ₂ O-O ₂	8.6	400	S1
6.	CTF-NS-5BT	H ₂ O-O ₂	6.6	420	S24
7.	HEP-TAPT-COF	H ₂ O-O ₂	15.35	420	S25
8.	Tapt-Btt	H ₂ O-O ₂	4.6	450	S26
9.	TTF-BT-COF	H ₂ O-O ₂	11.9	420	S3
10.	FS-COFs	H ₂ O-O ₂	6.21	420	S27
11.	COF-N32	H ₂ O-O ₂	6.2	459	S28
12.	OCN-500	H ₂ O-O ₂	10.2	420	S29
13.	rGO@MRF-0.5	H ₂ O-O ₂	1.23	420	S30
14.	SA-TCPP	H ₂ O-O ₂	14.9	420	S31
15.	CHF-DPDA	H ₂ O-O ₂	16	420	S32
16.	TpDz	H ₂ O-O ₂	11.9	420	S5
17.	TPB-DMTP-COF	H ₂ O-O ₂	18.4	420	S33
18.	Bpy-TAPT	H ₂ O-O ₂	8.6		S9
19.	PTA@TTB-EB	H ₂ O-O ₂	6.6	420	S34
20.	TBNT-COF	H ₂ O-O ₂	7.59	400	S12
21.	COF-2CN	H ₂ O-O ₂	6.8	420	S35
22.	CN-PDA	H ₂ O-O ₂	5.1	400	S13
23.	DHAA-Tp COF	H ₂ O-O ₂	4.6	420	S36
24.	COF-Tfp-BpyDaaq	H ₂ O-O ₂	8.3	420	S37
25.	TBD-COF	H ₂ O-O ₂	5.67	400-700	S20
26.	EFB-MOF	H ₂ O-O ₂	1.03	410	S38

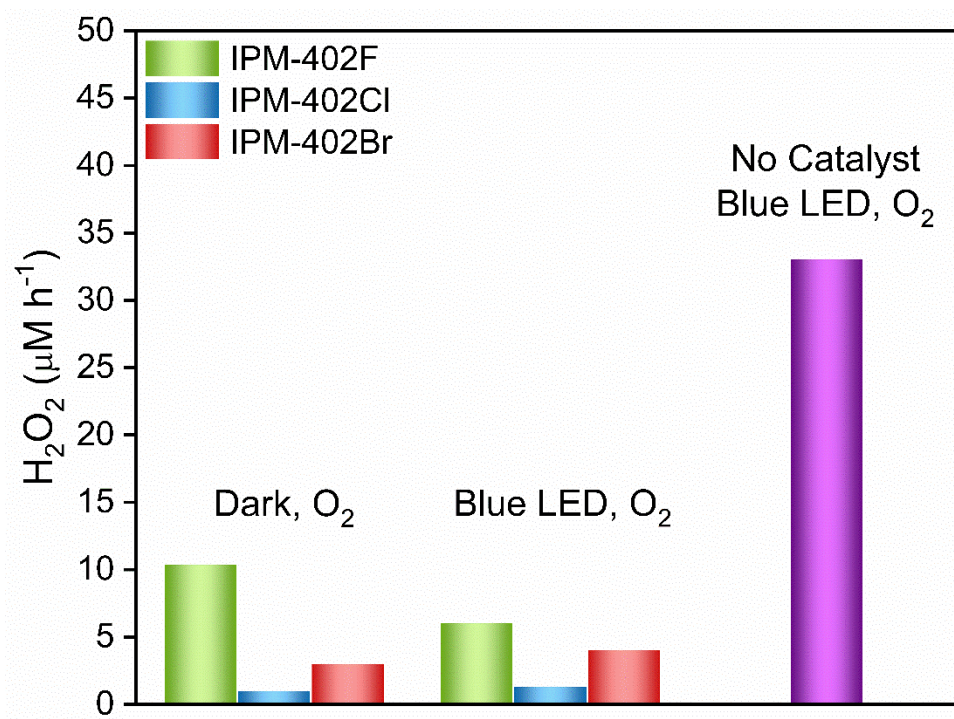
Appendix Table 3.3: Comparison Table of % SCC for Photocatalytic H₂O₂ Production by Porous Materials

Sr. No.	Materials	Reaction Medium	SCC (%)	Wavelength (nm)	Reference
1.	IPM-402F	H₂O-Air	0.58	Sunlight	<i>This Work</i>
2.					
3.	IPM-402Cl	H₂O-Air	0.55		
	IPM-402Br	H₂O-Air	0.59		
4.	CTF-BDDBN	H ₂ O-O ₂	0.14	> 420	S39
5.	Bpt-CTF	H ₂ O-O ₂	0.2	350 - 780	S1
6.	HEP-TAPT-COF	H ₂ O-O ₂	0.65	420	S25
7.	Tapt-Btt	H ₂ O-O ₂	0.296	450	S26
8.	Py-Da-COF	H ₂ O-O ₂	0.09	420 - 700	S40
9.	TZ-COF	H ₂ O	0.036	> 420	S41
10.	TTF-BT-COF	H ₂ O-O ₂	0.49	> 420	S3
11.	Cu ₃ -BT-COF	H ₂ O/O ₂ /FAA	0.62	> 420	S4
12.	COF-N32	H ₂ O-O ₂	0.31	420	S28
13.	TF ₅₀ -COF	H ₂ O/EtOH-O ₂	0.17	> 400	S42
14.	CHF-DPDA	H ₂ O-O ₂	0.78	> 420	S32
15.	TpDz	H ₂ O-O ₂	0.62	> 420	S5
16.	TPB-DMTP-COF	H ₂ O-O ₂	0.76	> 420	S33
17.	TD-COF	H ₂ O-O ₂	0.15	400 - 700	S8
18.	Bpy-TAPT	H ₂ O-O ₂	0.65		S9
19.	CTP-BD	H ₂ O-O ₂	0.31	>400	S43

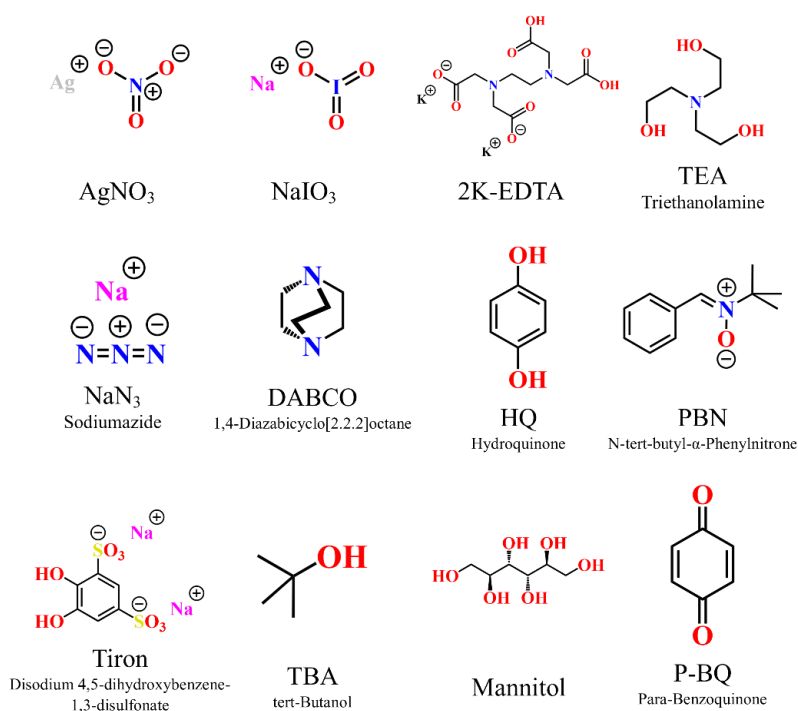
20.	CN-PDA	H ₂ O-O ₂	0.41	>400	S13
21.	CTP-TD	H ₂ O-O ₂	0.31	300W Xe Lamp	S44

Appendix Section 3.5.3. Photocatalytic Control and Scavenging Experiment

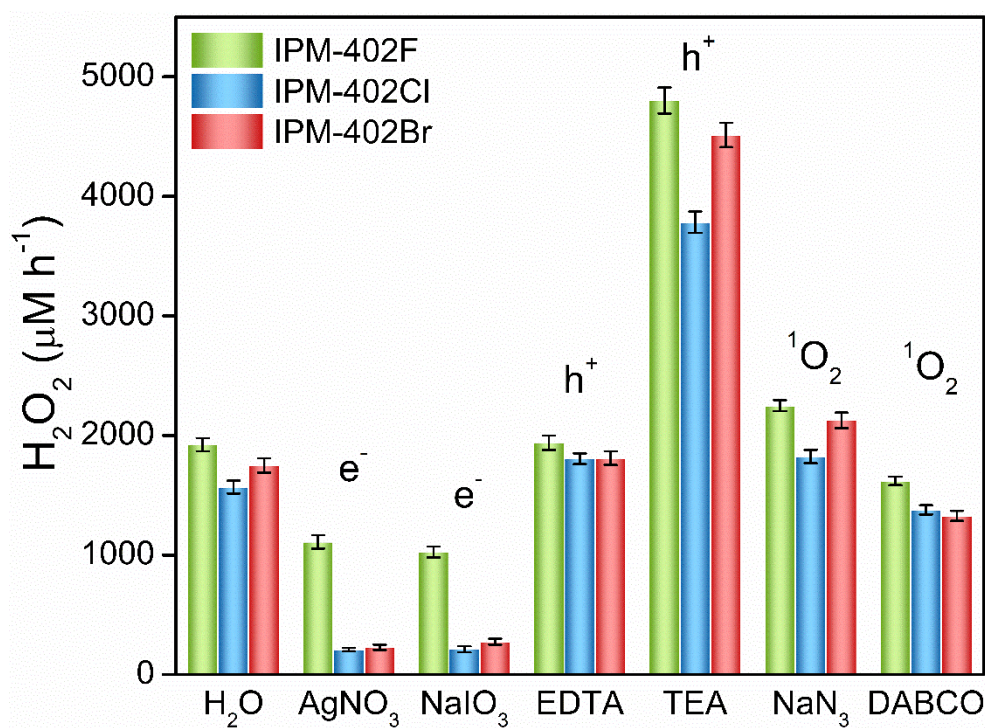
First the catalytic experiment was performed under dark condition in O₂ atmosphere then under blue light irradiation in N₂ atmosphere and lastly under standard catalytic condition but absence of catalyst. No significant production of H₂O₂ was found in each condition concludes that three main parameters of O₂, Light and catalyst is necessary for the H₂O₂ production. The scarce amount of production when dissolved O₂ was removed by N₂ indicates that ORR is the main pathway for photocatalytic H₂O₂ production by IPM-402Xs. Different scavenging agent AgNO₃, NaIO₃ (for electron), triethanolamine (TEA), EDTA (for h⁺), NaN₃, DABCO (for singlet oxygen, ¹O₂), hydroquinone (HQ, for radical), PBN, Tiron, Ascorbic acid (AA) (for superoxide radical, O₂^{•-}), and tert-butanol (TBA), mannitol (for hydroxide radical, OH[•]) was introduced to reaction medium to analyze the reactive species involved in the reaction (Figure- XX, SXX, Table SX). In presence of AgNO₃ and NaIO₃ the photocatalytic production of H₂O₂ reduced significantly. For IPM-402F, the H₂O₂ production became half but in case of IPM-402Cl and IPM-402Br, the production of H₂O₂ was insignificant (Figure- XX), validating that photogenerated electrons (e⁻) participated in the redox reaction. Also, in anaerobic condition, in presence of AgNO₃ and NaIO₃, IPM-402Xs cannot able to produce H₂O₂, confirming that H₂O₂ produced by ORR pathway. By adding EDTA, TEA, NaN₃, DABCO the H₂O₂ production did not effect, indicating that photogenerated h⁺ and ¹O₂ (Figure- XX) was not involved in the reaction pathway. Also, it was found that in presence of HQ, PBN, Tiron, AA, TBA, Mannitol, there was no significant decrease in the production of H₂O₂, indicates the there was no role of any photogenerated radicals and rules out the step-wise 1e⁻ WOR pathway (Figure- XX). Further, we tried to find the role of O₂^{•-} by using p-BQ (para-Benzoquinone) as scavenger and quantitative analysis by NBT degradation method. Peroxide strip test shows that in presence of p-BQ, IPM-402Xs are able to produce H₂O₂ (Figure- SXX) and also there was no change in UV-Vis absorption was found in NBT method (Figure- SXX), suggesting that there is absolutely no role of superoxide radical (O₂^{•-}) and rules out the step-wise 1e⁻ ORR process. According to the two-electron oxygen reduction (ORR) potential (O₂/H₂O₂ = 0.68 V vs NHE) (Ref- M14), which is in between in the E_{CB} and E_{VB} positions of all the IPM-402X, indicating that photocatalysts posses the favorable thermodynamic conditions for direct 2e⁻ ORR for H₂O₂ production.



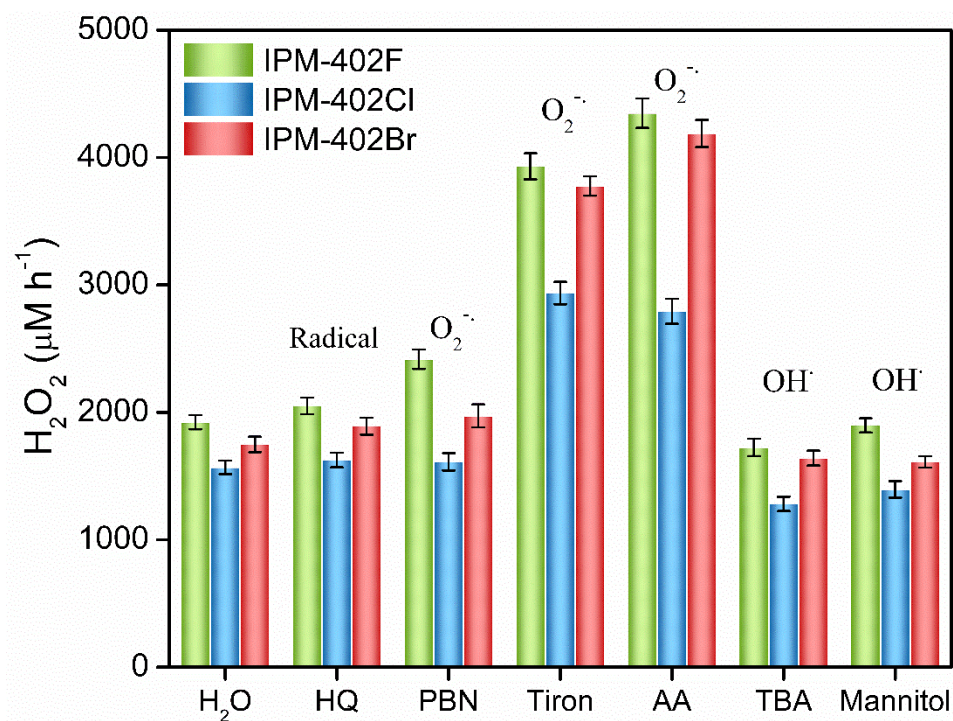
Appendix Figure 3.68: Control experiment in H₂O:EtOH (9:1) by IPM-402Xs



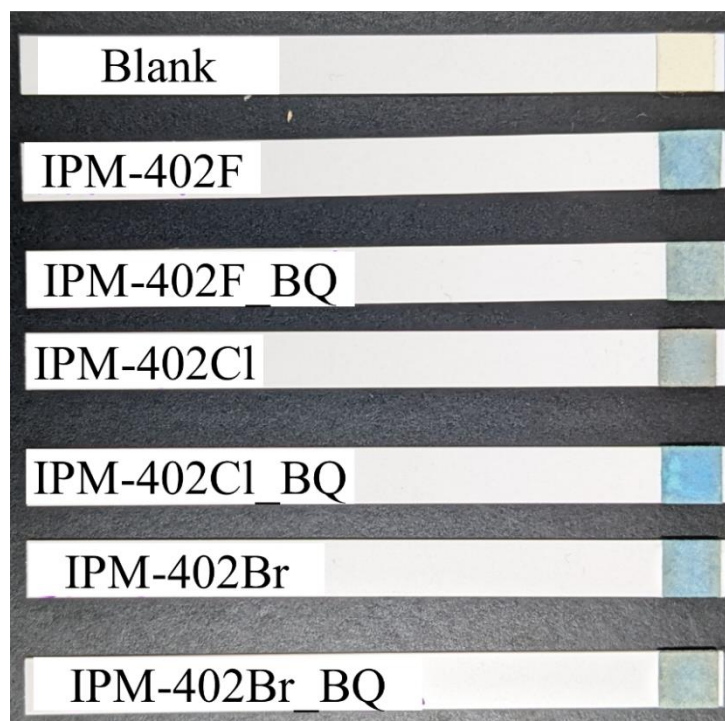
Appendix Figure 3.69: Chemical structure of different scavenger



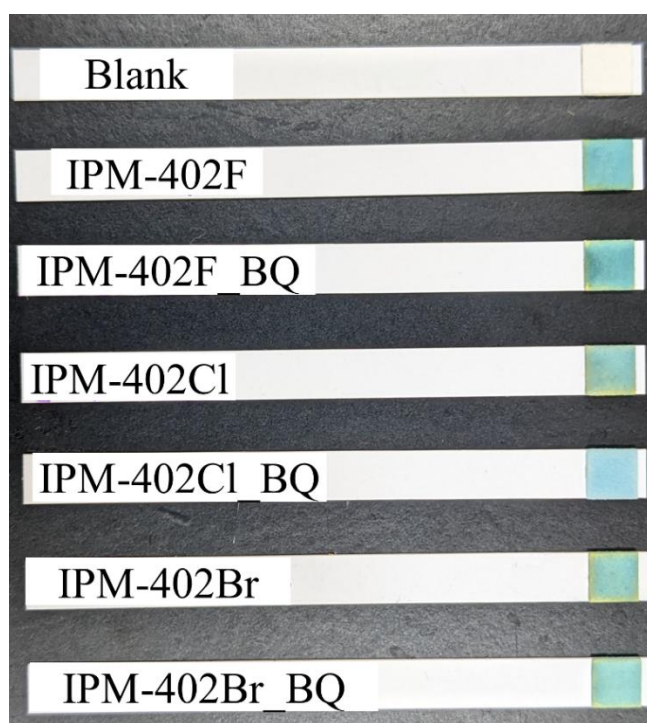
Appendix Figure 3.70: H₂O₂ production in presence of different sacrificial agents by IPM-402Xs



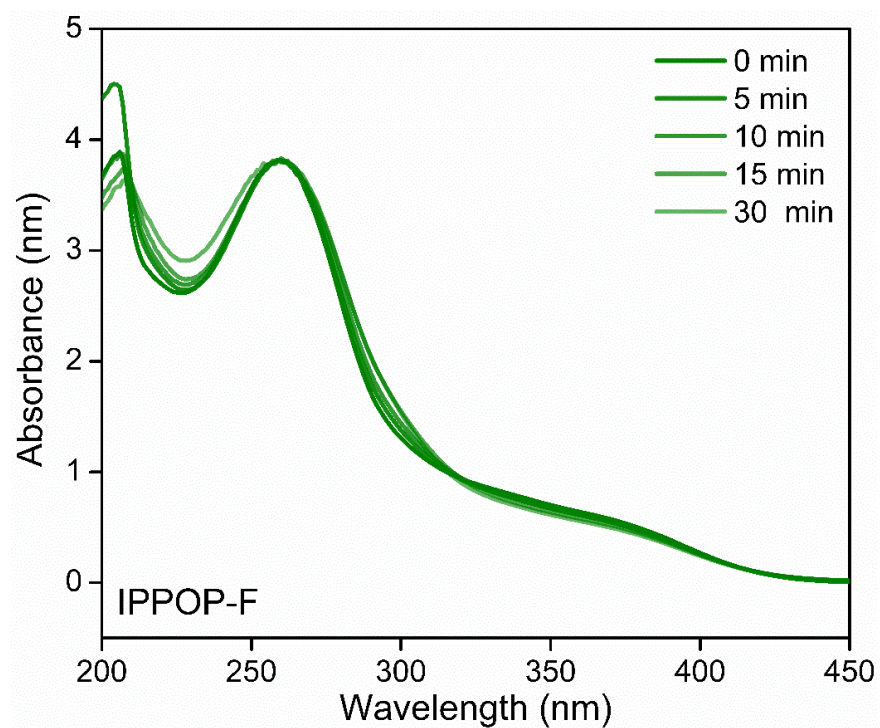
Appendix Figure 3.71: H₂O₂ production in presence of different sacrificial agents by IPM-402Xs



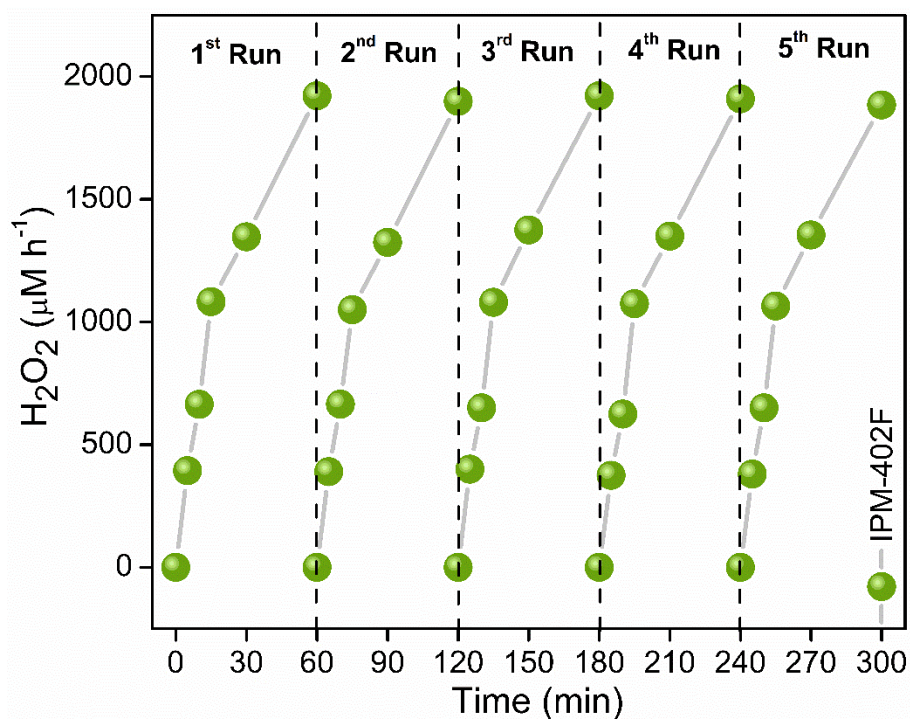
Appendix Figure 3.72: Peroxide strip (0-100 ppm) test in presence of p-benzoquinone as superoxide radical ($O_2^{\cdot-}$) scavenger



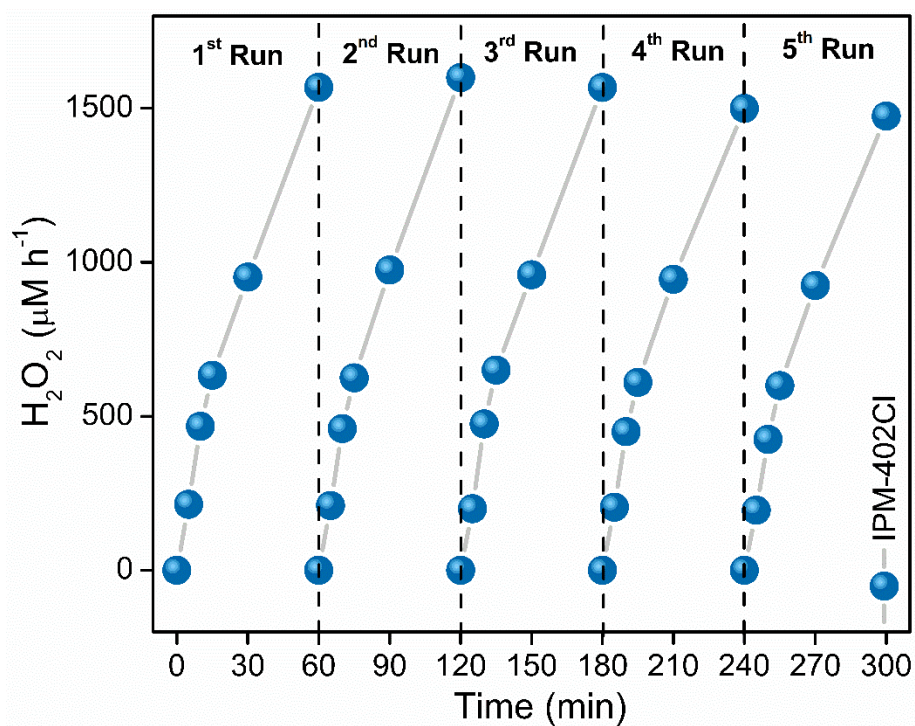
Appendix Figure 3.73: Peroxide strip (100-1000 ppm) test in presence of p-benzoquinone as superoxide radical ($O_2^{\cdot-}$) scavenger



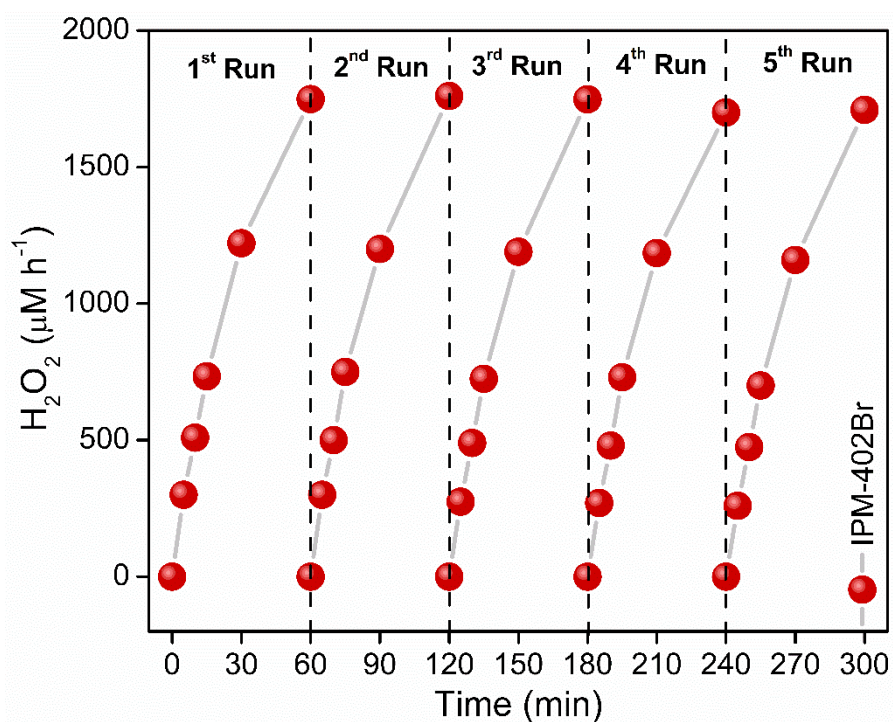
Appendix Figure 3.74: UV-Vis spectra of NBT test for superoxide radical ($\text{O}_2^{\bullet-}$) detection by IPM-402F



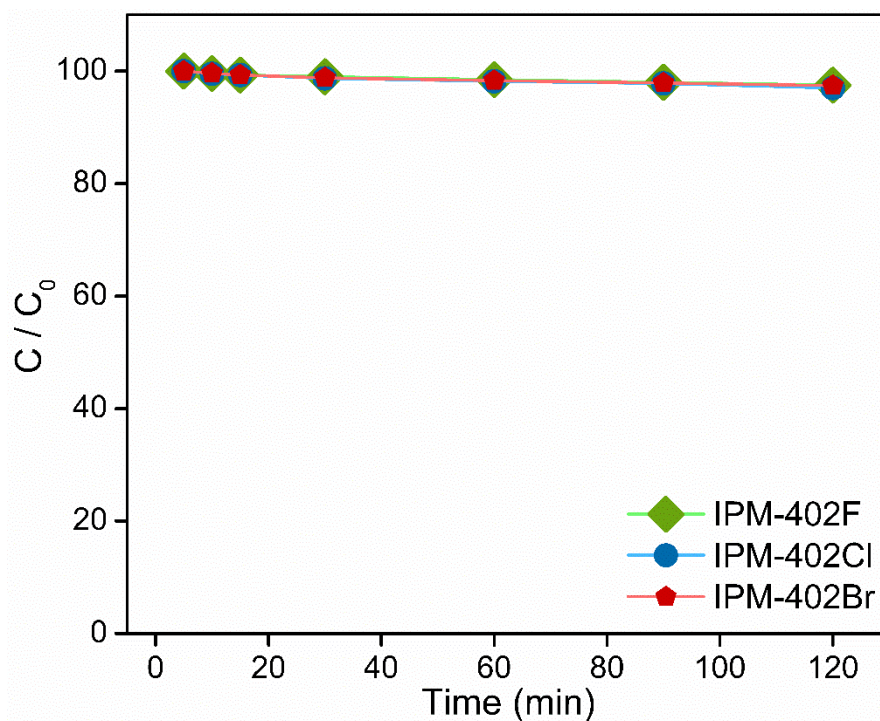
Appendix Figure 3.75: Recyclability in oxygen saturated H_2O in blue LED by IPM-402F



Appendix Figure 3.76: Recyclability in oxygen saturated H_2O in blue LED by IPM-402Cl



Appendix Figure 3.77: Recyclability in oxygen saturated H_2O in blue LED by IPM-402Br



Appendix Figure 3.78: H_2O_2 degradation test in presence of IPM-402Xs

Appendix Section 3.5.4. H_2O_2 production in different conditions

Appendix Table 3.4: In pure water

H_2O_2 ($\mu\text{mol h}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Air, Blue LED	622	414	570
O ₂ , Blue LED	1922	1568	1749
Air, White LED	595	344	533
O ₂ , White LED	885	590	663
Air, Sunlight	268	256	275
O ₂ , Sunlight	451	405	420

Appendix Table 3.5: H₂O₂ production rate in pure water

H₂O (μmol h⁻¹ g⁻¹)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Air, Blue LED	124401	82889	113938
O ₂ , Blue LED	384475	313668	349781
Air, White LED	119000	68916	106650
O ₂ , White LED	176915	117988	132500
Air, Sunlight	53661	51164	54944
O ₂ , Sunlight	90200	81000	84000

Appendix Table 3.6: In H₂O-EtOH mixture (H₂O : EtOH = 9:1)

H₂O:EtOH (μmol h⁻¹)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Air, Blue LED	1839	1184	1424
O ₂ , Blue LED	2676	2389	2645
Air, White LED	696	490	603
O ₂ , White LED	913	643	711
Air, Sunlight	322	270	313
O ₂ , Sunlight	543	485	507

Appendix Table 3.7: H₂O₂ production rate in H₂O-EtOH mixture

H₂O:EtOH ($\mu\text{mol h}^{-1} \text{g}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Air, Blue LED	367870	236787	284846
O ₂ , Blue LED	535133	477759	529058
Air, White LED	139116	97941	120553
O ₂ , White LED	182518	128586	142153
Air, Sunlight	64461	53931	62504
O ₂ , Sunlight	108600	97000	101400

Appendix Table 3.8: In Sea water (Arabian sea, 19°05'N, 72°49'E)

Sea Water ($\mu\text{mol h}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Air, Blue LED	1634	712	1368
O ₂ , Blue LED	1996	1341	1630
Air, White LED	312	236	339
O ₂ , White LED	576	227	485
Air, Sunlight	293	228	275
O ₂ , Sunlight	456	406	432

Appendix Table 3.9: Presence of different sacrificial agent

Sacrificial Agent, H₂O, O₂, Blue LED ($\mu\text{mol h}^{-1}$)			
Condition	IPPOP-F	IPPOP-Cl	IPPOP-Br
H ₂ O	1922	1568	1749
H ₂ O:EtOH (9:1)	2676	2389	2645
H ₂ O:IPA (9:1)	2110	1131	1974
H ₂ O:BenzyI Alcohol (9:1)	2695	2144	2527

Appendix Table 3.10: In different chemical condition

Acid-Base, Air, Blue LED ($\mu\text{mol h}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
1M HCl	167	27	160
1M HNO ₃	131	16	80
1M H ₂ SO ₄	220	242	269
1M LiOH	127	503	698
1M NaOH	149	223	94
1M KOH	552	493	439

Appendix Table 3.11: In different chemical condition

Acid-Base, O₂, Blue LED ($\mu\text{mol h}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
1M HCl	1002	618	738
1M HNO ₃	973	454	674
1M H ₂ SO ₄	881	573	856
1M LiOH	1347	1744	1812
1M NaOH	851	1175	1212
1M KOH	2140	1793	1704

Appendix Table 3.12: In different light source and heat

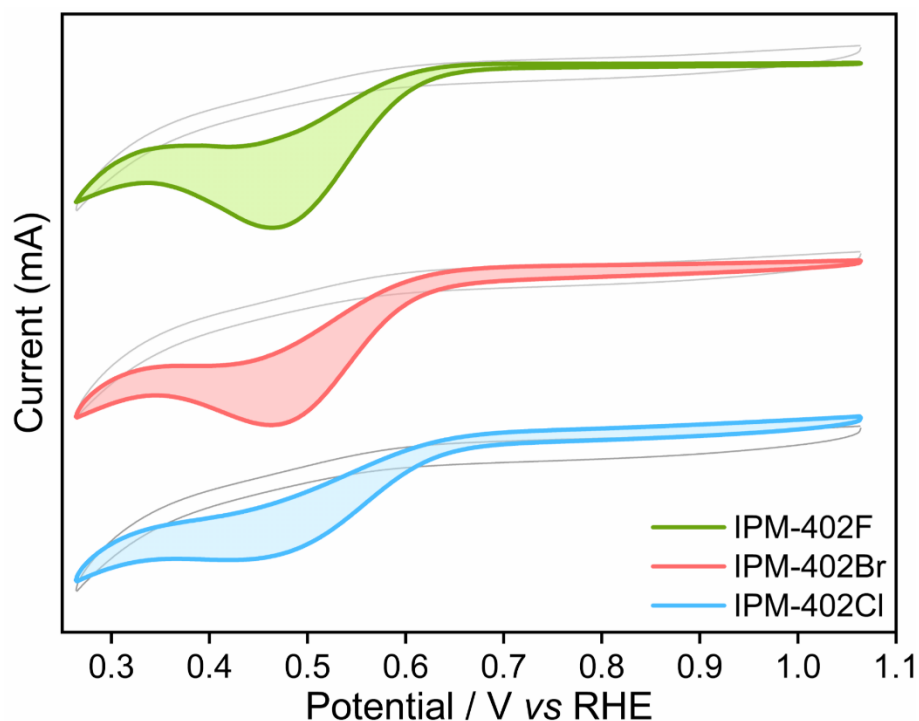
H₂O, O₂ ($\mu\text{mol h}^{-1}$)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
Blue LED	1922	1568	1749
Green LED	200	60	89
Yellow LED	404	258	300
White LED	885	590	663
60 °C	13	1	5

Appendix Table 3.13: Apparent Quantum Yield (%) at 450 nm

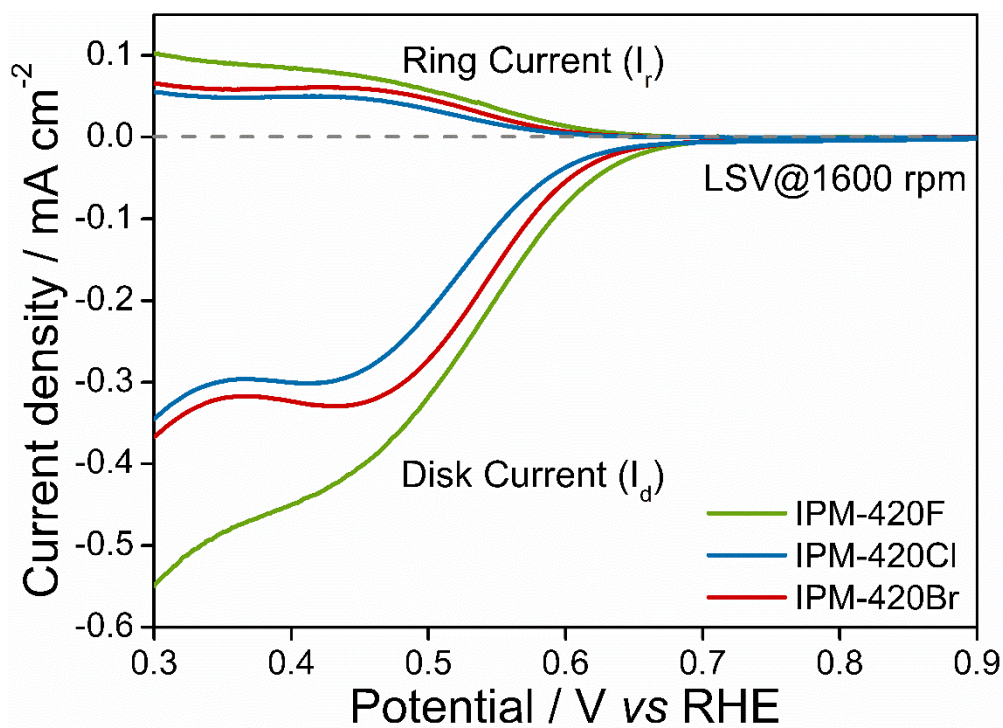
AQY (%)			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
H ₂ O, O ₂ , Blue LED	18.94	15.45	17.23
H ₂ O, Air, Blue LED	6.128	4.08	5.61
H ₂ O:EtOH, O ₂ , Blue LED	26.36	23.53	26.06
H ₂ O:EtOH, Air, Blue LED	18.123	11.66	14.03
Seawater, O ₂ , Blue LED	19.66	13.21	16.06
Seawater, Air, Blue LED	16.09	7.01	13.47

Appendix Table 3.14: Solar to Chemical Conversion (%)

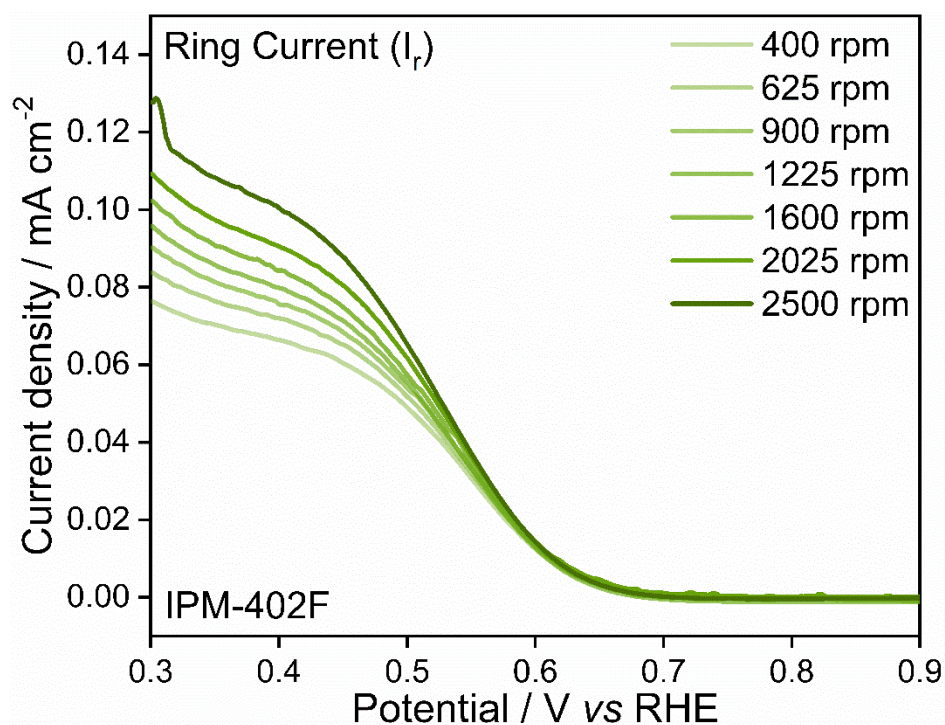
SCC (%) Sunlight			
Condition	IPM-402F	IPM-402Cl	IPM-402Br
H ₂ O, O ₂	1.024	0.919	0.953
H ₂ O, Air	0.609	0.581	0.623
H ₂ O:EtOH, O ₂	1.233	1.101	1.151
H ₂ O:EtOH, Air	0.732	0.612	0.709
Seawater, O ₂	1.035	0.922	0.981
Seawater, Air	0.666	0.517	0.625



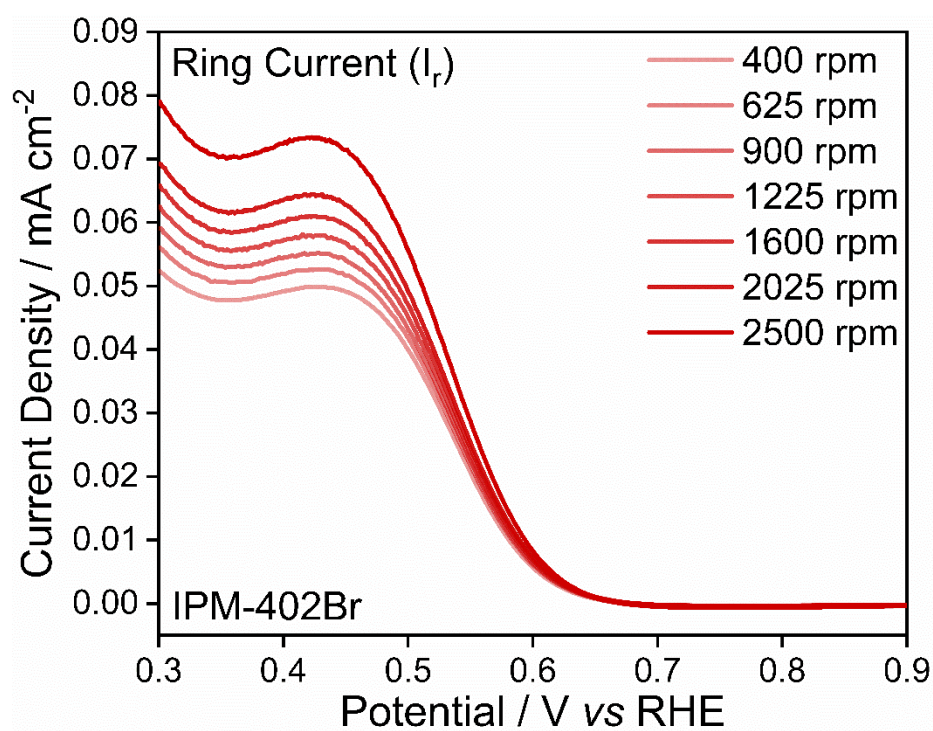
Appendix Figure 3.79: Cyclic voltammetry of IPM-402Xs in O_2 saturated electrolyte (in N_2 saturated system- ash color)



Appendix Figure 3.80: RRDE at 1600 rpm in 0.1M KOH of IPM-402Xs



Appendix Figure 3.81: Ring Current (I_r) at different rotation speed in 0.1M KOH of IPM-402F

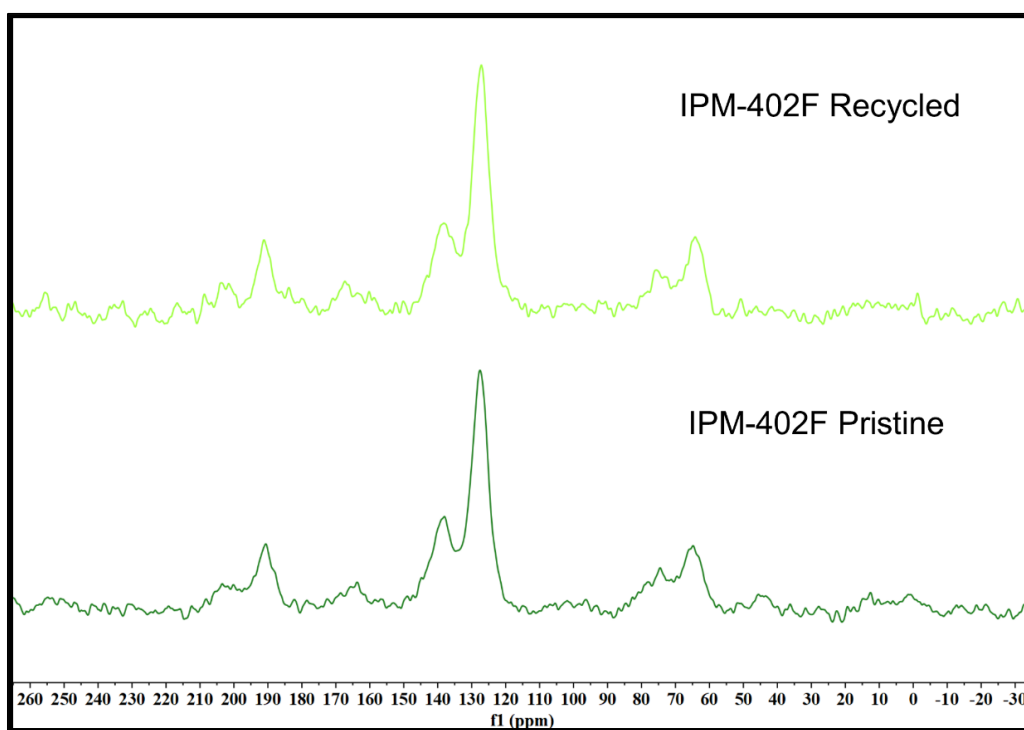


Appendix Figure 3.82: Ring Current (I_r) at different rotation speed in 0.1M KOH of IPM-402Br

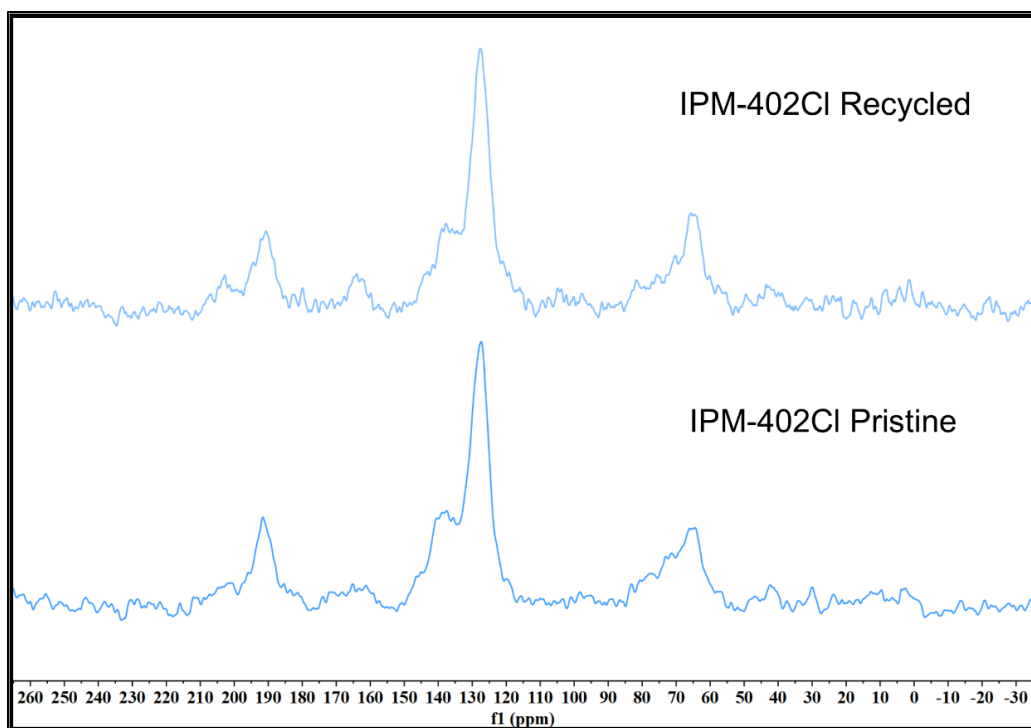
Appendix Section 3.5.4. Post Catalytic Characterization

After successful photocatalytic H_2O_2 production, we performed the post catalytic structural characterization to ensure that the structural stability of IPM-402Xs after photocatalysis process. ^{13}C CP-MAS NMR (Figure S) and FT-IR (Figure S) shows the all the characteristic peak present after the catalytic process. TGA profile (Figure S) also shows no change in the thermal stability of the materials. HRTEM images (Figure S) reveals the no change in the surface morphology and the elemental mapping (Figure S) also shows there is no change in the element present in the materials. The XPS survey spectra (Figure S) shows the all peaks related to the all the elements and also deconvoluted spectra (Figure S) confirms the same chemical environment as the pristine materials.

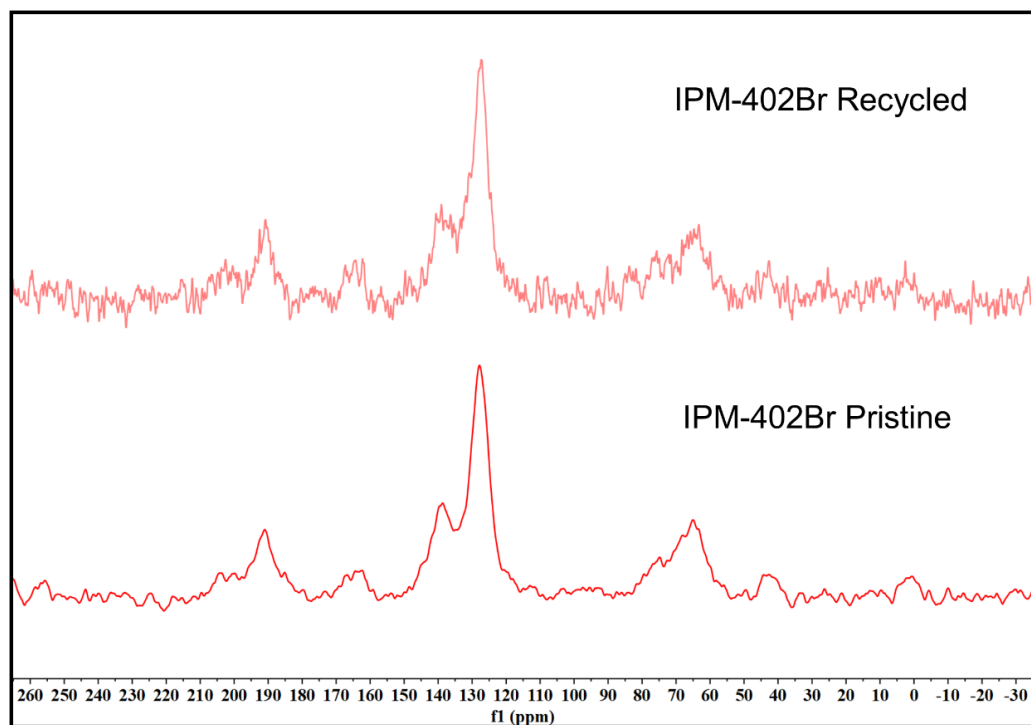
Also, we checked the DRS spectra (Figure S) for the absorbance properties of the materials, where we find there is no change in the absorbance profile of the IPM-402Xs.



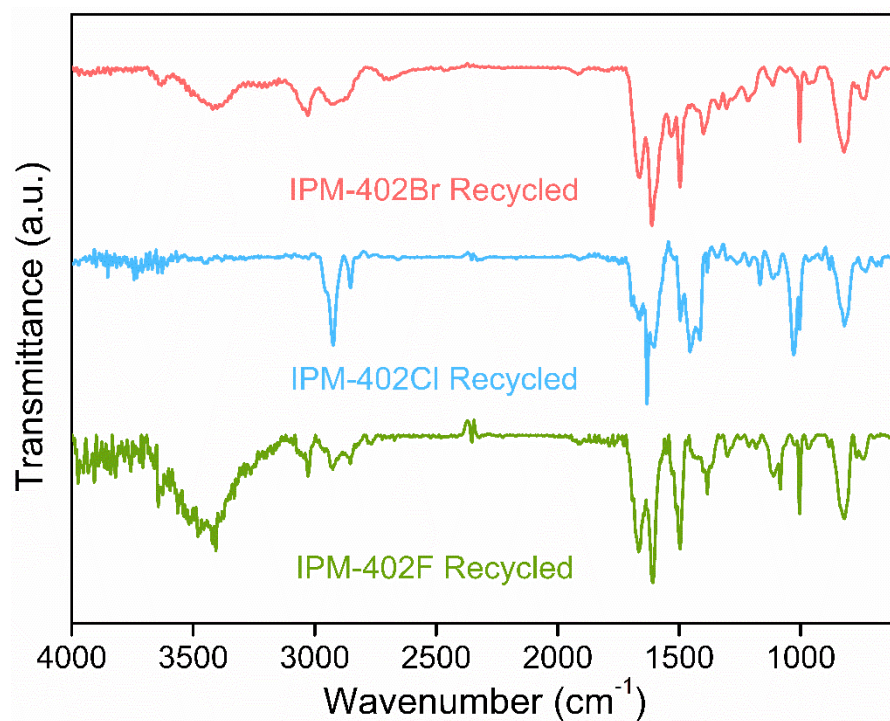
Appendix Figure 3.83. ^{13}C CP-MAS spectra of IPM-402F after catalytic cycles



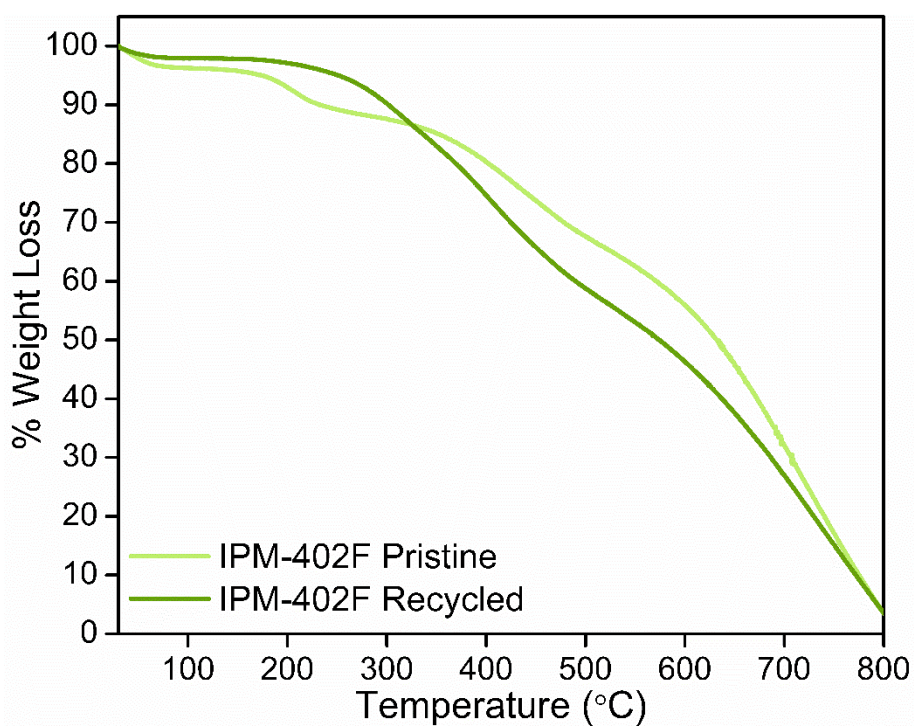
Appendix Figure 3.84: ^{13}C CP-MAS spectra of IPM-402Cl after catalytic cycles



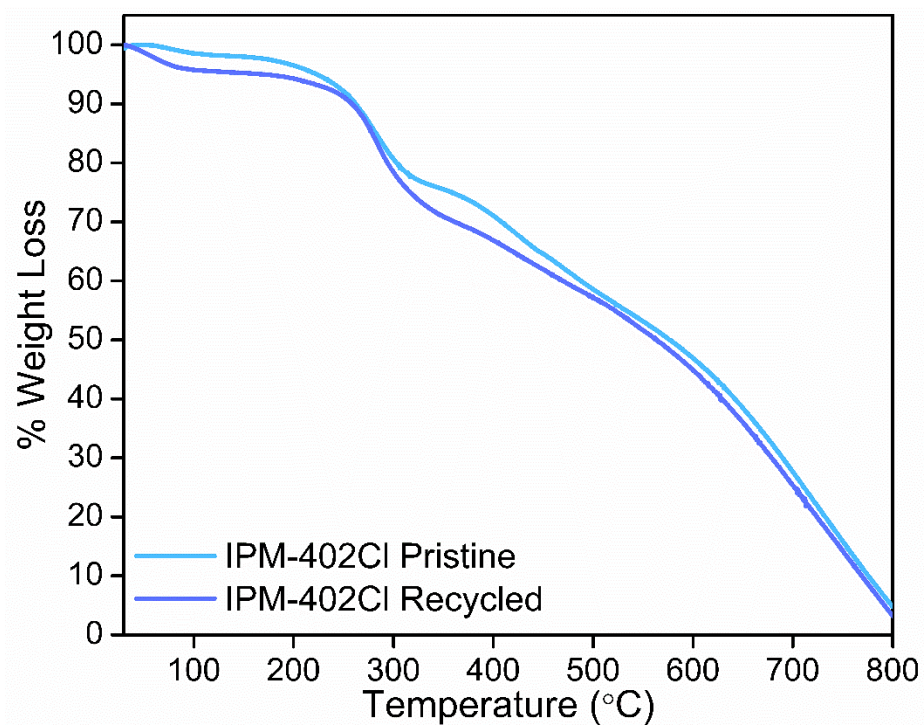
Appendix Figure 3.85: ^{13}C CP-MAS spectra of IPM-402Br after catalytic cycles



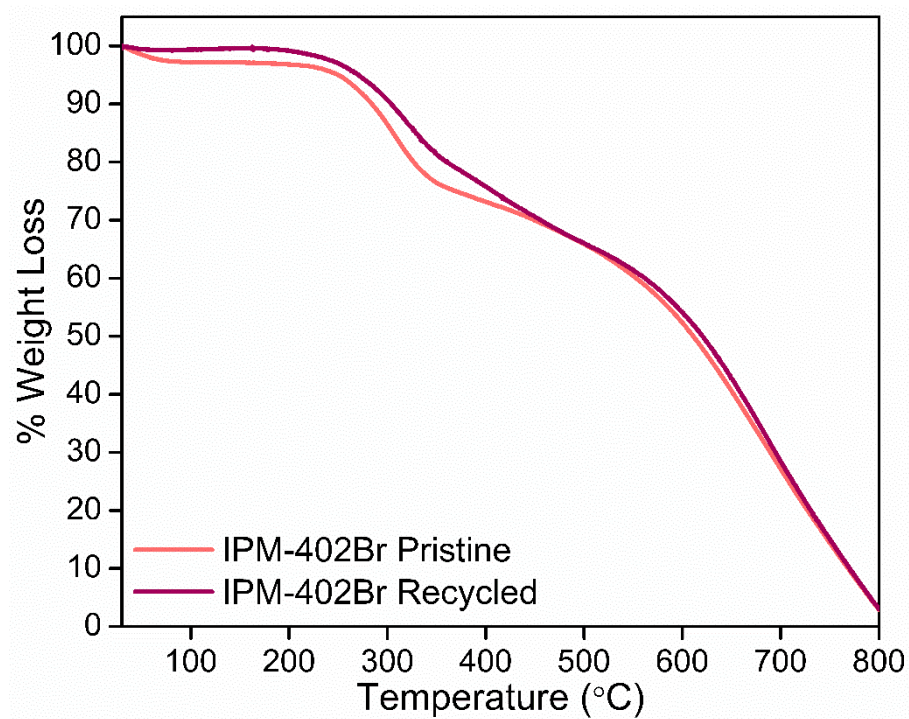
Appendix Figure 3.86: FT-IR spectra of IPM-402Xs after the catalytic cycles



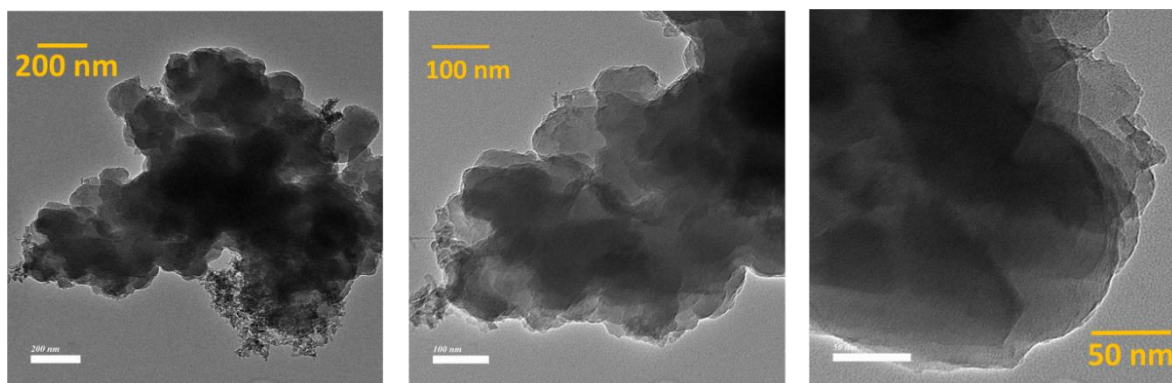
Appendix Figure 3.87: TGA profile of IPM-402F after the catalytic cycles



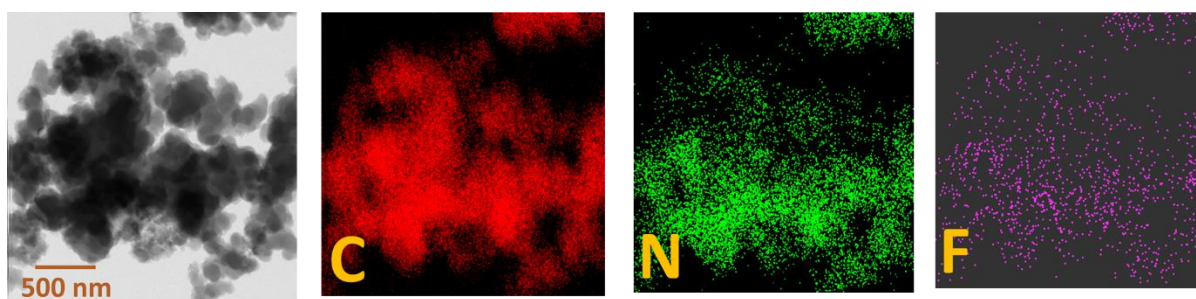
Appendix Figure 3.88: TGA profile of IPM-402Cl after the catalytic cycles



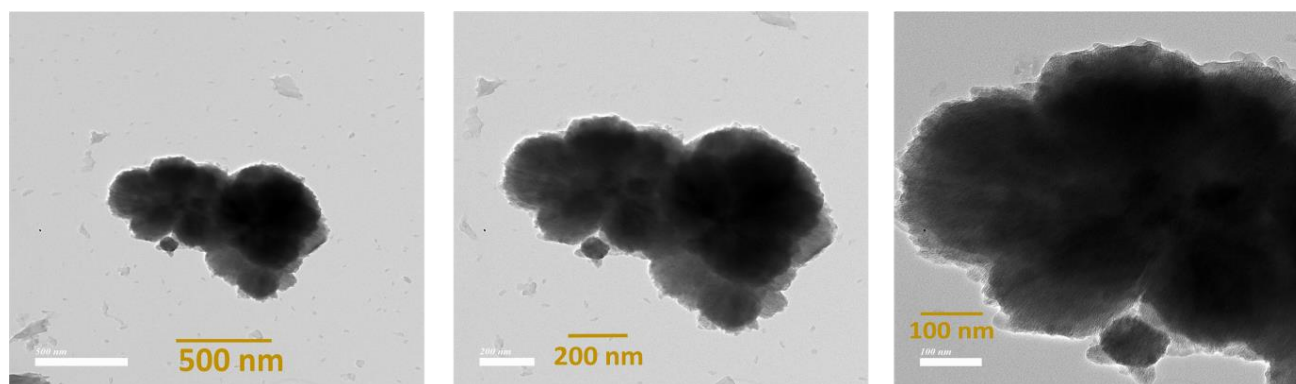
Appendix Figure 3.89: TGA profile of IPM-402Br after the catalytic cycles



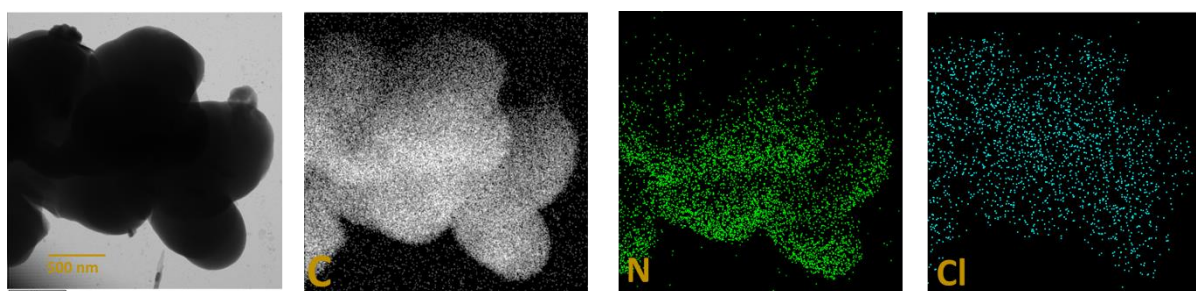
Appendix Figure 3.90: TEM images of IPM-402F after the catalytic cycles



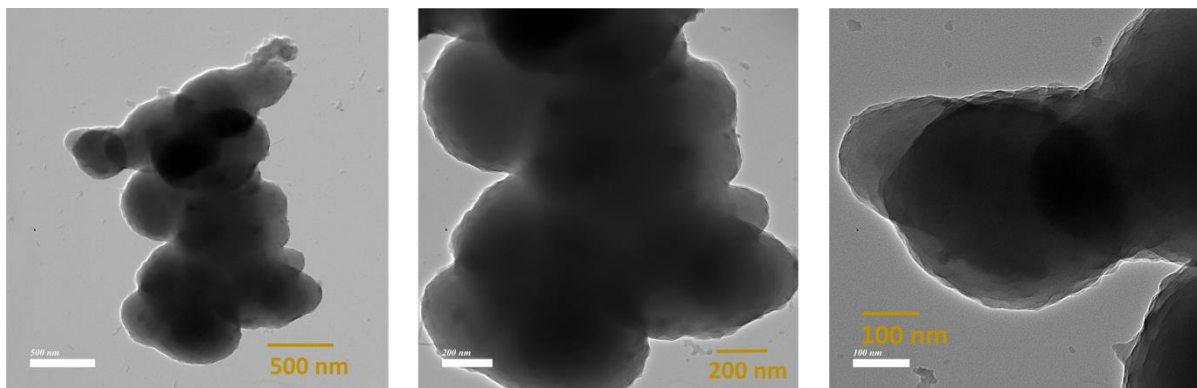
Appendix Figure 3.91: Elemental mapping of IPM-402F after the catalytic cycles



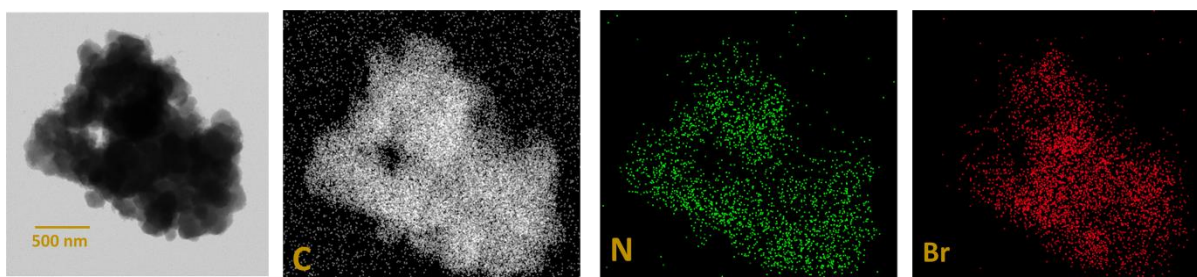
Appendix Figure 3.92: TEM images of IPM-402Cl after the catalytic cycles



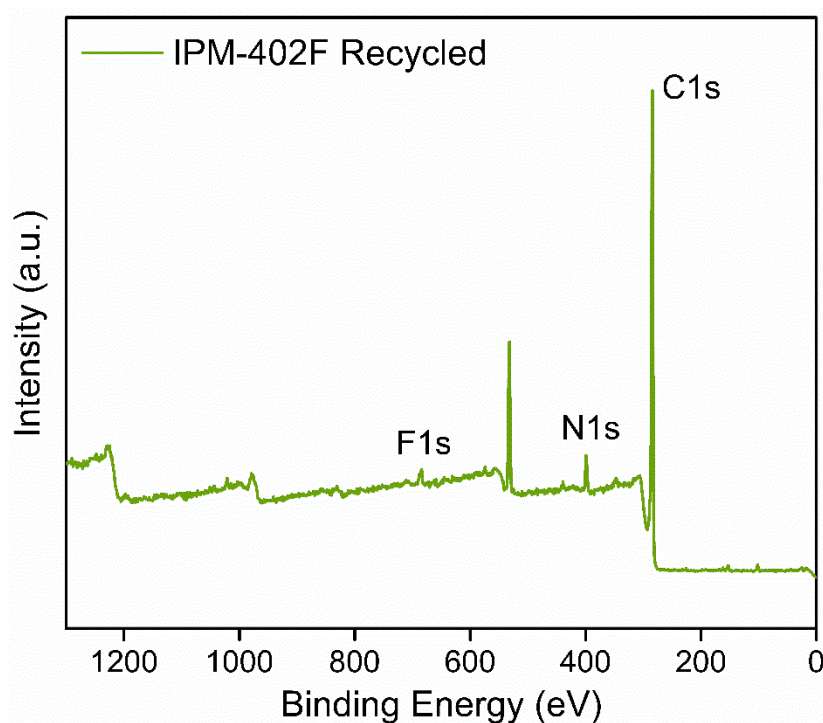
Appendix Figure 3.93: Elemental mapping of IPM-402Cl after the catalytic cycles



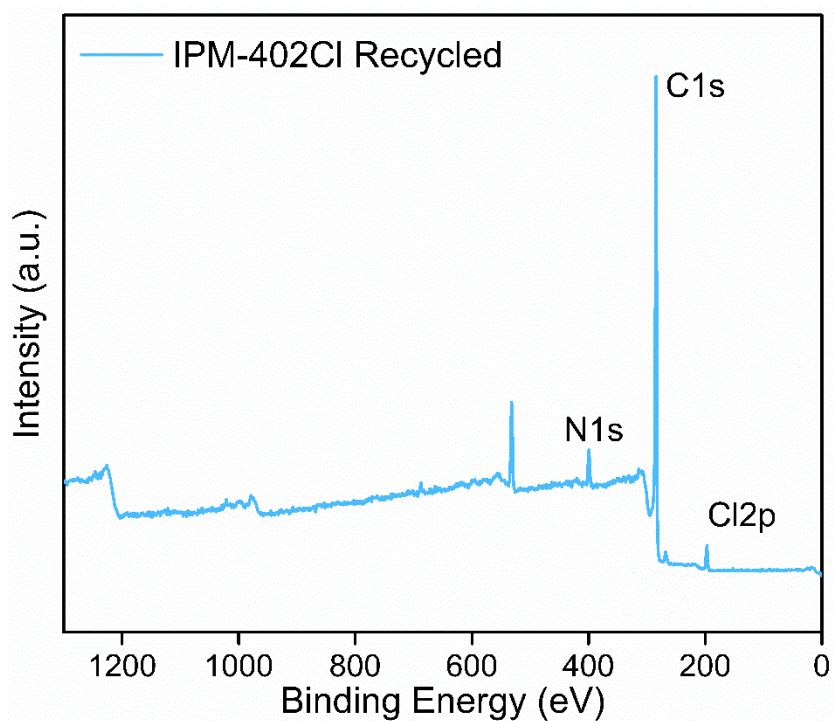
Appendix Figure 3.94: TEM images of IPM-402Br after the catalytic cycles



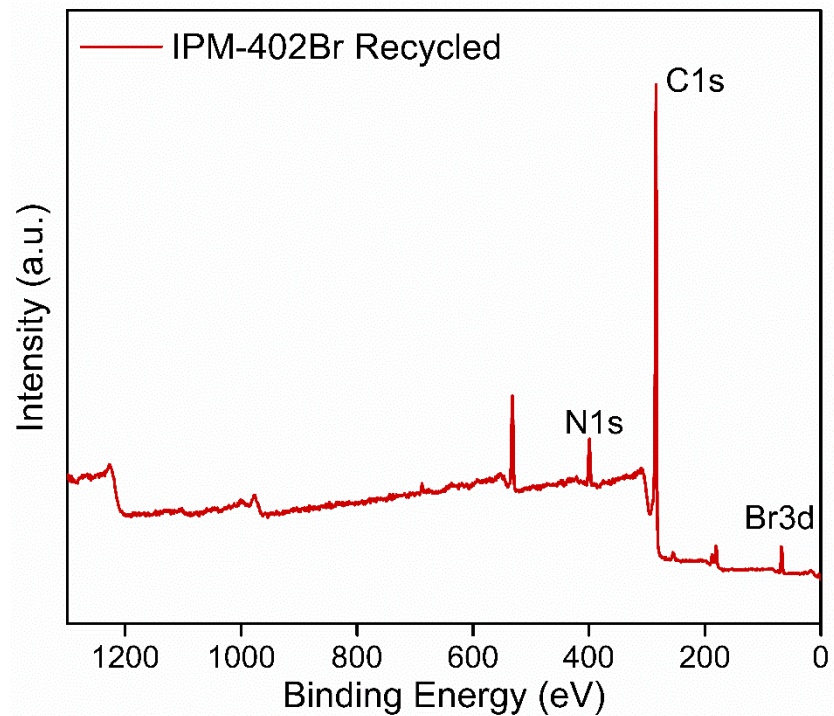
Appendix Figure 3.95: Elemental mapping of IPM-402Br after the catalytic cycles



Appendix Figure 3.96: XPS survey spectra of IPM-402F after the catalytic cycles



Appendix Figure 3.97: XPS survey spectra of IPM-402Cl after the catalytic cycles



Appendix Figure 3.98: XPS survey spectra of IPM-402Br after the catalytic cycles

Appendix Section 3.5.5. Computational Studies

3.5.5.1: Computational Details

All DFT calculations are carried out using the Gaussian-16 program^{S37} package and geometries are optimized using B3LYP-D3^{S38-S40} hybrid DFT functional and Pople's 6-31+G(d,p)^{S41-S43} basis set at temperature 298.15 K and 1 atm pressure with Self Consistent Field (SCF=tight) with energy cut-off of 10^{-8} Hartree.^{S44} All transition states are confirmed to be first order saddle point and optimized at the same level of theory.^{S45} Intrinsic reaction coordinate (IRC) calculations were also carried out for the transition state to connect the reactant and product adducts, as well as obtain the minimum energy path.^{S46, 47} The single point calculations were completed for all intermediates and transition states at M06-2X^{S48, 49} functional and 6-311++G(d,p) basis set.^{S50, 51} CYLview software was used to visualize all optimized transition states and intermediates.^{S52}

3.5.5.2. Solvent dependent IPM-402X catalyzed O₂ Activation

We studied solvent dependent (path-A) as well as the solvent independent (path-B) O₂ activation mechanistic route to understand the role of H₂O in the formation of photocatalytic H₂O₂. Further, to investigate the influence of the counter anion on the reactivity of IPM-402Xs and to elucidate the significance of H-X interactions in IPM-402Xs, a supportive study was conducted, omitting the counter ions in IPM-402. A thorough examination of two distinct catalytic cycles for IPM-402Xs and IPM-402 aimed to comprehend the role of halide ions in the respective H₂O₂ formation reactions (Figure SXX)

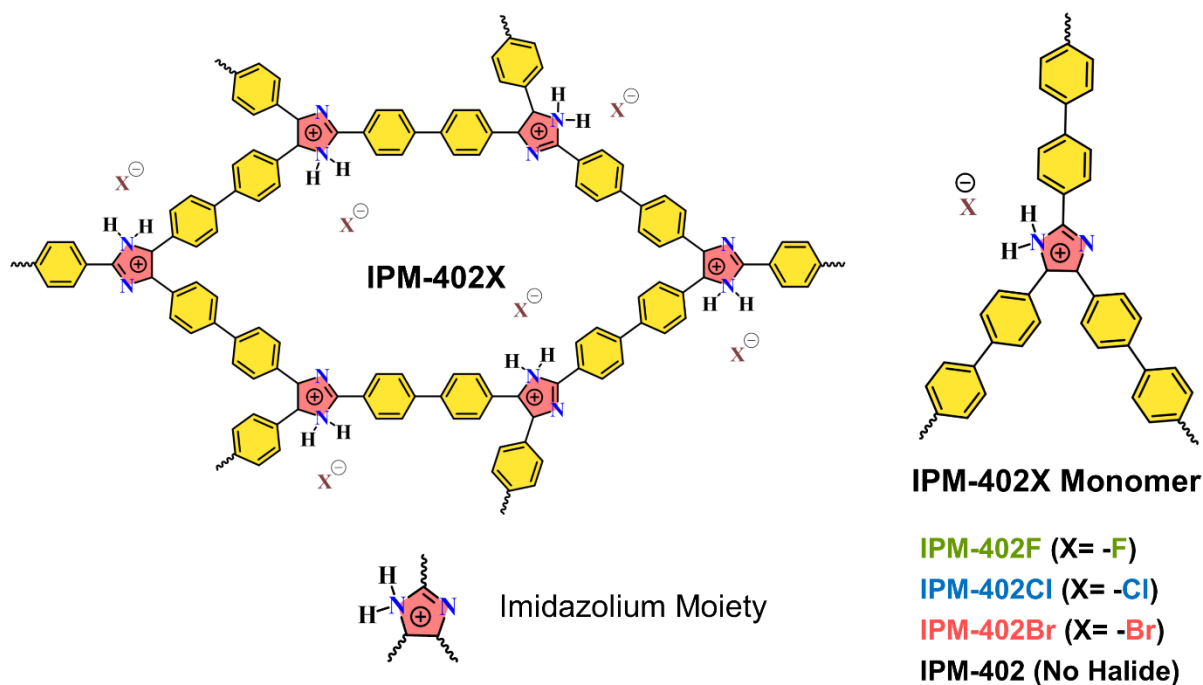
The insertion of oxygen in IN1 leads to the formation of IN2, where the imidazolium-O₂ distance is 2.3 Å in IPM-402F, 3.3 Å in IPM-402Cl, and more than 3.5 Å in IPM-402Br. The formation of IN2 from IN1 is relatively straight-forward in the presence of oxygen atmosphere with Gibbs free energy of 5.0 kcal/mol, 6.7 kcal/mol and 6.9 kcal/mol for IPM-402F, IPM-402Br and IPM-402Cl, respectively. The decline in Gibbs free energy during the conversion of IN2 to IN3 signifies that the adsorption of O₂ on the IPM-402X is an exergonic process with Gibbs free energies of -24.0 kcal/mol (IPM-402F), -30.2 kcal/mol (IPM-402Cl), -27.9 kcal/mol (IPM-402Br), -36.8 kcal/mol (IPM-402) (Figure 3). In IN3, strong H-bonding is observed between the oxygen and -NH proton in IPM-402Cl (1.3 Å), which is absent in the other IPM-402X. The protonation of absorbed O₂ occurs aided by halide mediators, occurs through TS1 (IPM-402F = -8.8 kcal/mol, IPM-402Cl = -11.4 kcal/mol, and IPM-402Br = -8.9 kcal/mol), resulting in the formation of -OOH in IN4. The energy barriers for IPM-402Xs are 15.2 kcal/mol for IPM-402F, 18.8 kcal/mol for IPM-402Cl and 19.0 kcal/mol for IPM-402Br (see SI Figure S1). The extent of hydrogen bonding varied among the different IPM-402Xs in IN4, with distances ranging from 1.3 to 1.5 Å. This bonding weakened further upon the formation of IN5, where distances extended from 1.6 to 1.9 Å with a substantial increase in the Gibbs free energy (IPM-402F displayed an energy increase of 9.3 kcal/mol, while IPM-402Cl and IPM-402Br display increase of 6.4 and 3.7 kcal/mol, respectively). The subsequent step involves the formation of the first molecule of H₂O₂ in IN6 through the transition state TS2

with energy barriers of 14.7, 20.8, and 23.2 kcal/mol for IPM-402F, IPM-402Cl, and IPM-402Br, respectively. This transition state displays a six-membered cyclic transition where O-O bond formation and proton transfer takes place simultaneously. The introduction of an additional water molecule initiates the formation of IN7 by following a mechanism involved in the conversion from IN4 to IN7. This step further enables the generation of the second molecule of H₂O₂ in IN8 through a cyclic transition state TS3 with energy barriers of 9.8, 17.7, and 23.6 kcal/mol for IPM-402F, IPM-402Cl, and IPM-402Br, respectively.

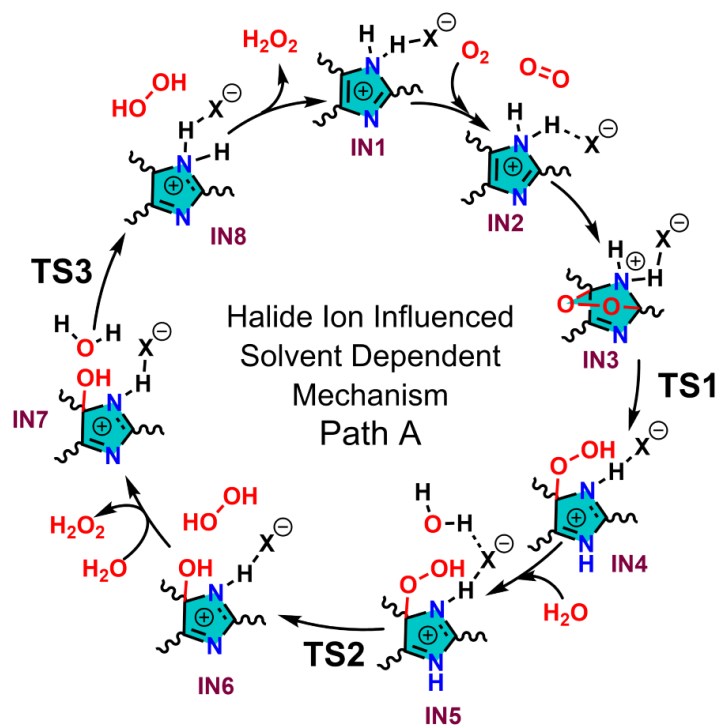
As discussed earlier, studying the catalytic performance of IPM-402 is important to understand the effect of absence of counter-ions. This IPM-402 (IN1A) was used for catalytic conversion of O₂ to H₂O₂. The formation of IN2A is stabilizing, $\Delta G = -7.0$ kcal/mol (Figure 3). The adsorption of O₂ on the imidazolium ring stabilizes the structure further to IN3A, $\Delta G = -36.8$ kcal/mol with the C-O bond length of 1.47 Å which is much shorter than C-O bond length in IN3 of IPM-402X (1.50-1.57 Å). Due to the absence of halide ions, there are no mediators for proton transfer from N-H to O, thus the TS1A displays high energy barrier of 62.6 kcal/mol for the formation of -OOH in IN4A. This energy barrier is not feasible under the given experimental conditions, leading to no -OOH formation.

Continuing further with the mechanism, the introduction of water molecule in IN4A leads to the formation of IN5A with increase in Gibbs free energy by 8.5 kcal/mol which is a trend in all COPs. Formation of the first H₂O₂ molecule takes place in IN6A through TS2A. Although the Gibbs free energy of IN6A is comparable to IN6 of other IPM-402Xs, the TS2A lies at 29.7 kcal/mol which is higher than the previous transition state, TS1A. Thus, the high energy barriers of TS1A and TS2A proves the inefficiency of IPM-402 in H₂O₂ formation and importance of halide in the formation of -OOH. The next transition state, TS3A depicts the formation of second H₂O₂ molecule from IN7A. The associated energy barriers for forming IN8A through TS3A is 40.5 kcal/mol which is much less than the previous two transition states but, still extremely high for the given reaction conditions.

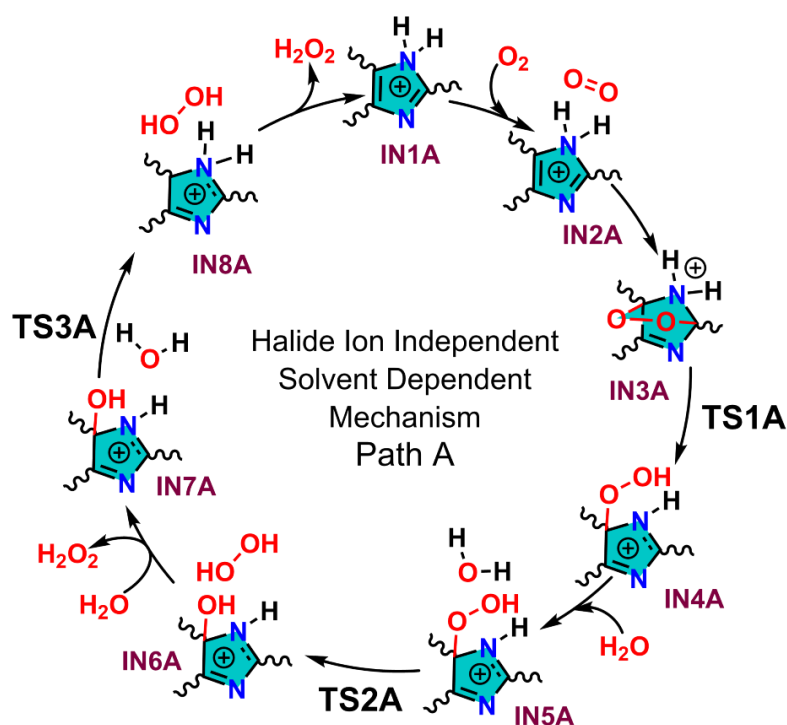
The overall activation energy barrier for the entire reaction pathway is calculated as 24.3 kcal/mol for IPM-402F, 28.7 kcal/mol for IPM-402Cl, 28.3 kcal/mol for IPM-402Br, and notably high at 66.6 kcal/mol for IPM-402A. This trend suggests that IPM-402F catalyzes H₂O₂ production most efficiently, followed by IPM-402Br and IPM-402Cl, aligning well with the experimental findings. The study underscores the critical influence of the counter-ion of IPM-402X on H₂O₂ production.



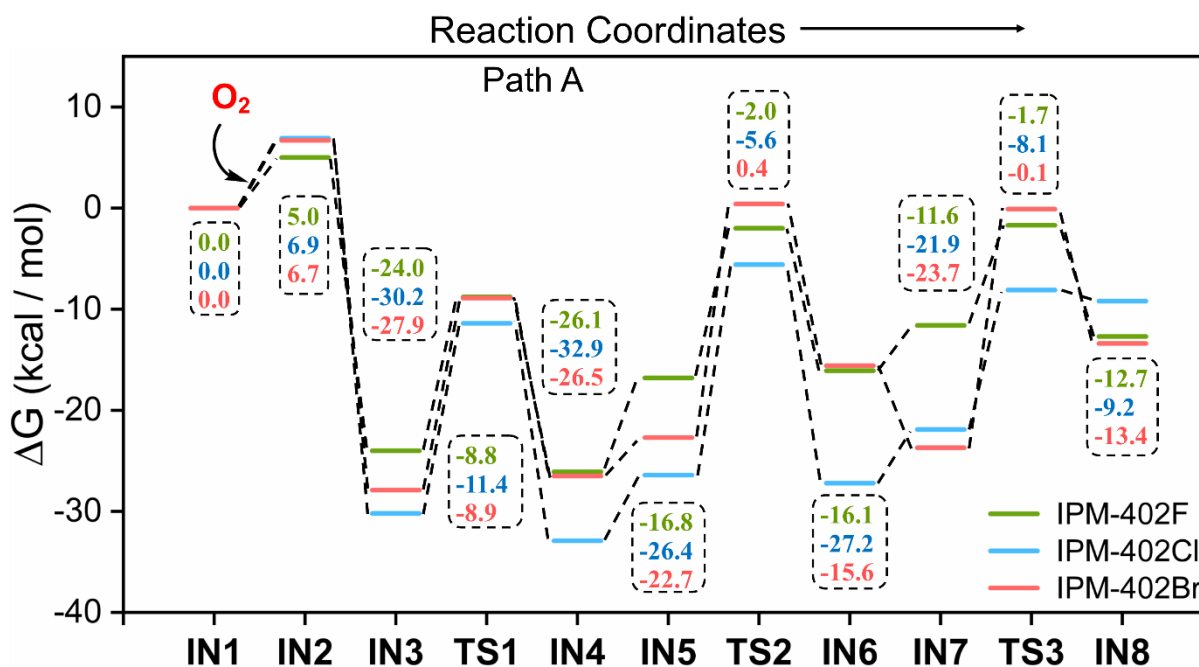
Appendix Figure 3.99: Structures of Polymeric network and monomeric unit of IPM-402Xs



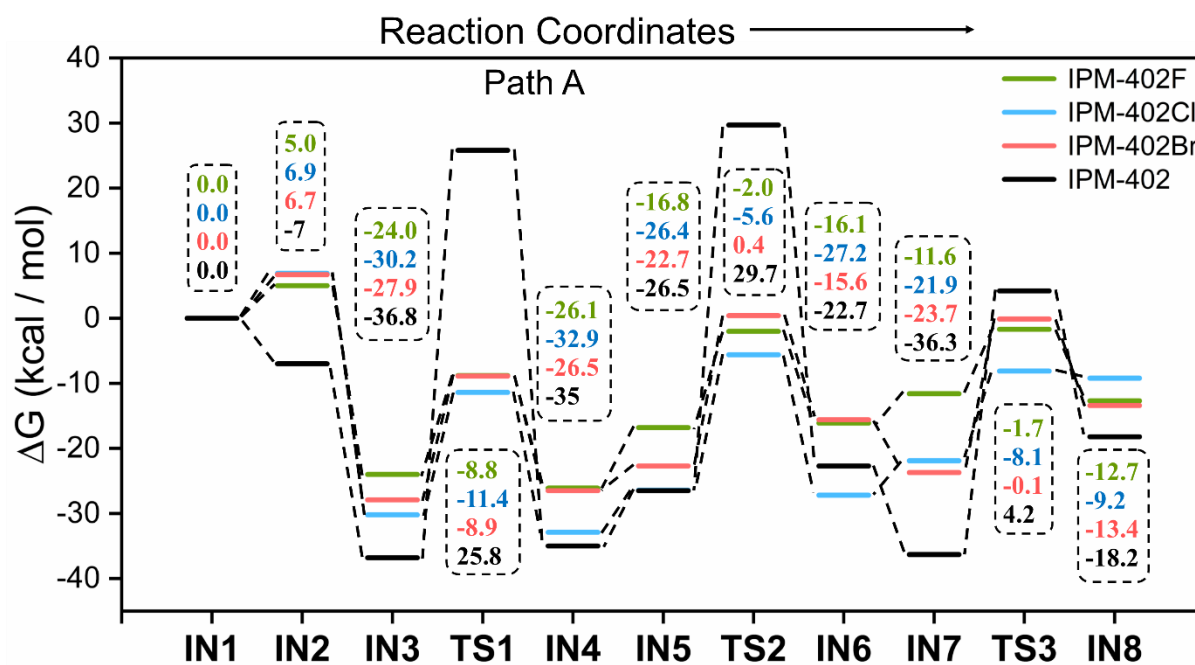
Appendix Figure 3.100: Halide ion influenced and solvent (H_2O) dependent mechanism of photocatalytic production of H_2O_2 by IPM-402Xs



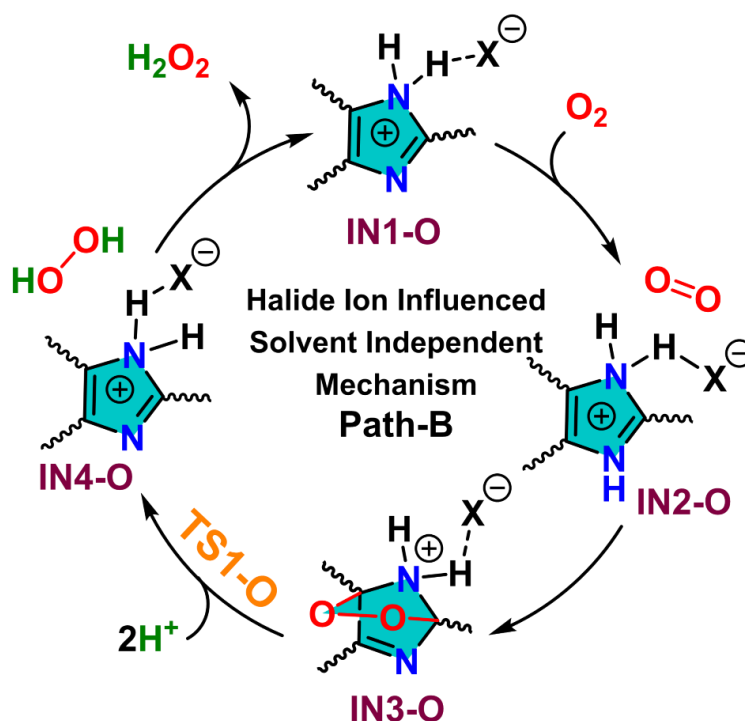
Appendix Figure 3.101: Halide ion independent and solvent (H_2O) dependent mechanism of photocatalytic production of H_2O_2 by IPM-402Xs



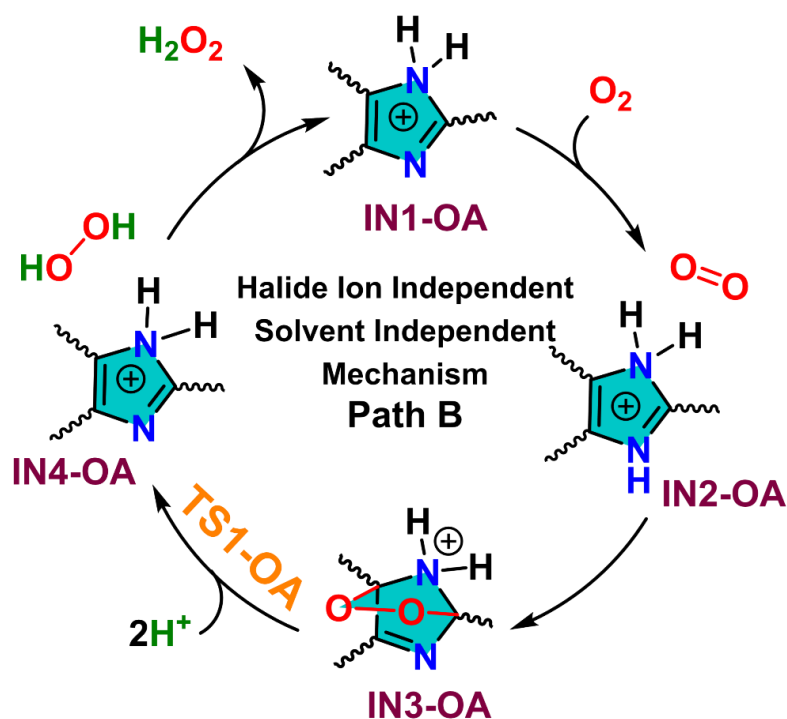
Appendix Figure 3.102: Energy diagram of Halide ion influenced and solvent (H_2O) dependent photocatalytic production of H_2O_2 by IPM-402Xs



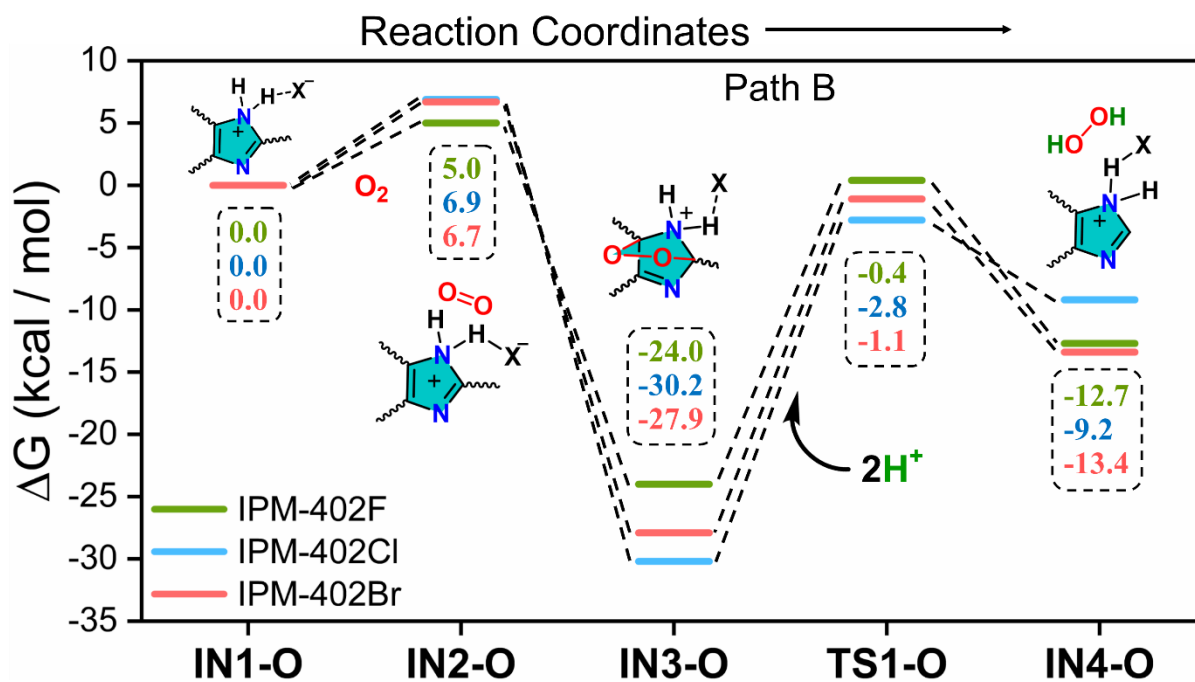
Appendix Figure 3.103: Energy diagram of Halide ion independent and solvent (H_2O) dependent photocatalytic production of H_2O_2 by IPM-402Xs



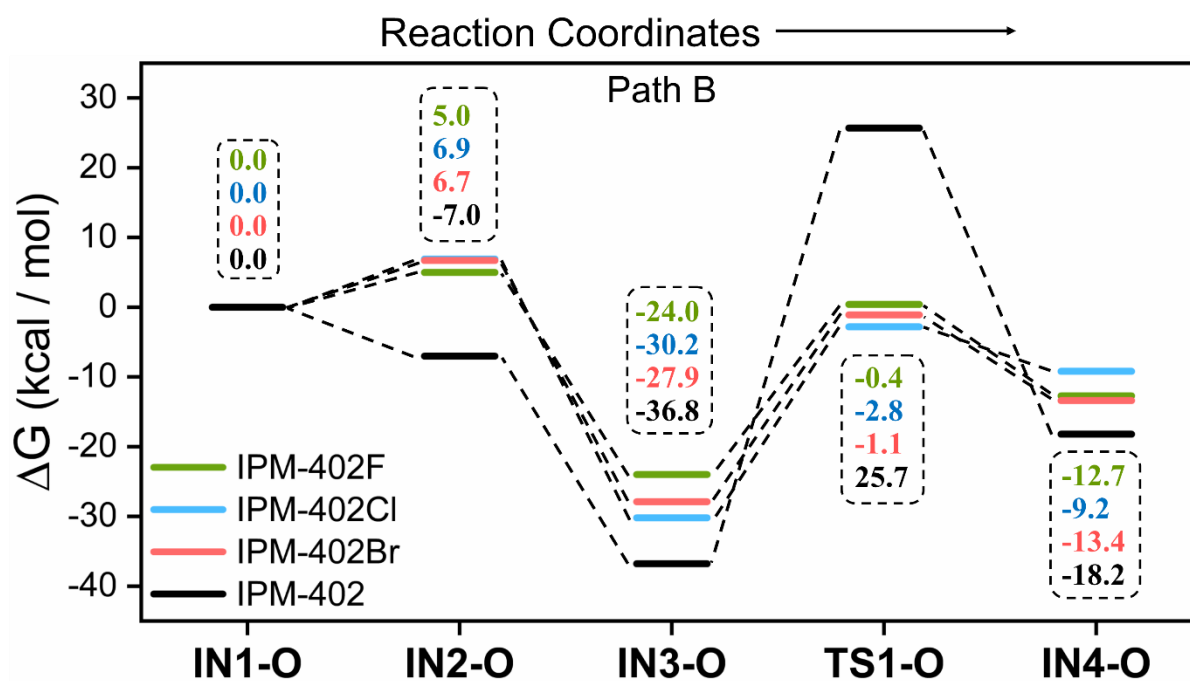
Appendix Figure 3.104: Halide ion influenced and solvent (H_2O) independent photocatalytic production of H_2O_2 by IPM-402Xs



Appendix Figure 3.105: Halide ion independent and solvent (H_2O) independent photocatalytic production of H_2O_2 by IPM-402Xs



Appendix Figure 3.106: Energy diagram of Halide ion influenced and solvent (H_2O) independent photocatalytic production of H_2O_2 by IPM-402Xs



Appendix Figure 3.107: Energy diagram of Halide ion independent and solvent (H_2O) independent photocatalytic production of H_2O_2 by IPM-402Xs

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Part - II

Fabrication of Task Specific Porous Materials Towards Detection and Remediation of Toxic Organic Arsenic in Water for Safe Drinking Water

The expansion of industry is an integral component of the development of contemporary civilization and urbanization. However, the direct discharge of their hazardous waste, produced by these companies, into widely used water sources has led to a significant rise in environmental contamination.¹ With the growth of population and water contamination, freshwater resources are becoming scarcer worldwide.² United Nations projections indicate that the world population may treble to 10 billion individuals by 2050, and up to one billion people may encounter severe challenges in obtaining clean water even by 2025.³ Due to the growing risks to living systems, much focus has been in the targeted and highly sensitive detection⁴ and remediation⁵ of harmful water contaminants. Among the pollutants Arsenic (As) poisoning is a curse to the humanity as As contamination is a major deadly problem all over world, specially Asia and Europe. Organic Arsenics (OA) are one of the less known from of Arsenic containing drugs but effective pollutants use in the poultry industry as a feed additive. Organic arsenic released in the environment through poultry litter and can convert into inorganic arsenic via different aerobic pathway.⁶ So, Organic arsenic simply increase the As pollution not only in the ground water as well as natural water sources as inorganic arsenic is more mobile and soluble in the water than organic arsenic. Advanced Functional Porous Materials (AFPMs) have become a promising material for an advanced sequestration and detection of environmental pollutants. Their additional functionalities can be adjusted by modifying the functional group in porous organic polymers and the counter anions within the pore of cationic Metal organic framework. This has revolutionized the selective sensing and capture of environmental pollutants.

This section contains two chapters, i.e. chapter 4 and chapter 5. In chapter 4, a highly luminescent water stable aromatic sulfonic acid decorated Zn-metal organic framework was synthesized towards selective detection of organic arsenic in water. In chapter 5, a urea functionalized size adaptable ionic porous organic polymer was synthesized and characterized for organic and inorganic arsenic decontamination from water. Additionally, mechanistic insight was studied via EXAFS, DFT and MD Simulation.

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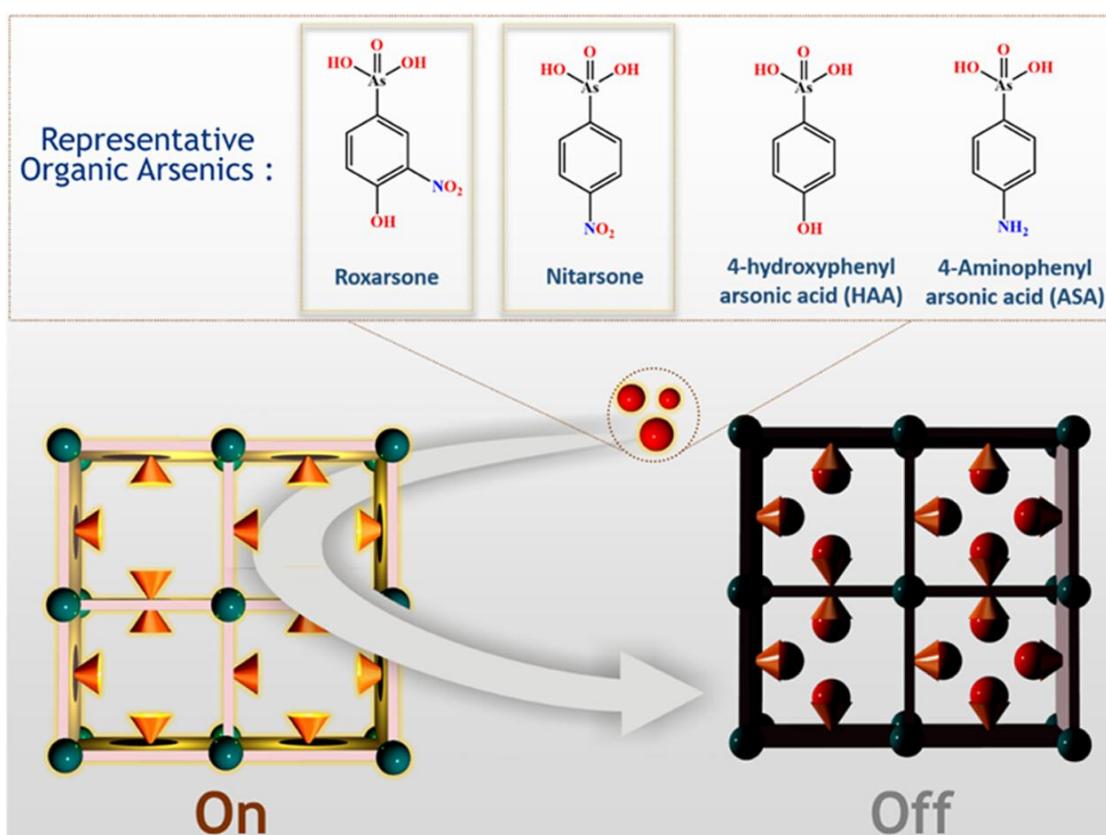
Chapter 4

Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water

4.1 Introduction

The poultry industry plays an indispensable role in the food industry, producing ~102 million metric tons of broiler meat per year globally as of 2021.¹ United States (US) produced an estimated 20.4 million metric tons of poultry meat, while India produced 4.2 million metric tons. The poultry industry uses several drugs including organic arsenic,² which inhibits diseases, accelerates growth, increases the feed efficacy, and enhances meat pigmentation in the poultry birds. Drugs such as 4-hydroxy-3-nitrophenylarsonic acid (roxarsone, ROX) and 4-nitrophenyl arsenic acid (nitarosone, NIT) are the two most extensively used arsenic-containing drugs in the poultry industry to accelerate growth³ and prevent blackhead disease (histomoniasis),² respectively, elevating the arsenic concentration in the broiler meat.⁴ Statistically, more than 90% of the organic arsenic fed to the poultry birds is excreted as unchanged drugs,^{5,6} resulting in serious contamination in the soil and water bodies. Survey shows that a geographical domain manufacturing 100 million poultry birds that consume 70% ROX would release ~4300 kg of arsenic per year to the environment, mostly in the agriculture field, as poultry manure is used as an effective fertilizer.² The discharge of such enormous amount of arsenic has escalated its concentration to 1000 $\mu\text{g/kg}$, which is much greater than the safety limit (10 ppb) determined by the World Health Organization (WHO).⁷ Additionally, in aerobic and anerobic environmental conditions, these organic arsenics are converted to dimethylarsonic acid (DMA), monomethylarsonic acid (MMA), and inorganic arsenics ($\text{As}^{5+}/\text{As}^{3+}$),^{8,9} which are not only highly toxic but also more soluble and mobile than the organic arsenic in water.¹⁰ Elemental arsenic (As), also called the slow-death poison, features prominently among the lethal and carcinogenic elements,¹¹ and can reach the human body from ground water as well as from chicken intake as food. In the human body, arsenic mainly accumulates in keratin-rich tissues^{12,13} and disrupts the energy transduction reactions, retarding ATP production alongside causing endothelial damage.¹⁴ Keeping in mind the severe toxicity of organic arsenics, it is necessary to develop potential sensors toward recognition of these contaminants in water. Till date, the detection of organic arsenics, particularly ROX and NIT, has depended on cumbersome instrumentation techniques, including gas chromatography (GC),¹⁵ inductively coupled plasma mass spectrometry (ICP-MS),^{16,17} high-performance liquid chromatography (HPLC),¹⁸ GC-atomic emission spectroscopy,¹⁹ and so on. Although these methods are efficient, they have pitfalls such as the need for intensive operational time, sophisticated equipment, and pretreatment of the sample, adding to the complexity of the measurement. In comparison with the abovementioned techniques, fluorogenic and colorimetric methods are advantageous owing to their fast response time, sensitivity, and very less sample pretreatment, making them viable. Constructed from a combination of metal ions/nodes and organic linkers held together periodically, metal-organic frameworks (MOFs) have attracted global research attention pertaining to their wide spectrum of applications, especially toward environmental issues on account of

bearing potential voids, functional linkers etc. With a strategic choice of the organic ligand and metal center, MOFs could be made ionic; in terms of their utilization toward fluorescence sensing, cationic MOFs^{20,21} are yet to be explored well. By taking leverage of π -rich organic linkers along with metal ions, MOFs can exhibit exceptional luminescence properties.²²⁻³⁶ Luminescent MOFs (L-MOFs) have come forth as competent sensory materials toward toxic small molecules,³⁷⁻⁴⁴ oxo-anions,⁴⁵ heavy metal ions,⁴⁶ and anions,⁴⁷ along with noxious gases.⁴⁸ Hitherto, the L-MOFs fabricated for organic arsenic detection have been rarely explored. Also, to the best of our knowledge, in the domain of porous materials, very few reports of organic arsenic sensing have been documented in the literature.⁴⁹⁻⁵² This provides a great scope toward developing novel sensory materials toward these toxic



Scheme 4.1. Schematic Representation of “Turn-Off” Sensing in iMOF-12C in the Presence of Toxic Organic Arsenics

organic arsenic drugs. It is worth mentioning that most of the reported MOF-based pollutant detection materials are in powder form.⁵³ However, the problems with the powder form are its processability and the real-time application. These obstacles can be overcome to fabricate MOF-based mixed-matrix membranes (MMMs), which provide the superior properties of MOF along with those of the adaptable and facile polymers. However, their detection applications are still being developed.⁵⁴

Toward fabricating a suitable sensory probe, we have chosen a π -electron-rich N-donor linker bearing a conjugated aromatic skeleton, making the MOF highly emissive in nature by virtue of ligand-centered emission. The organic sulfonic acid as a counter-anion gives extra framework functionality as well electronically contributes toward increasing the luminescent property and structural integrity.^{55,56} Precise selection of d^{10} metal ions in synergy with an extended conjugated organic ligand produced a positively charged chemically robust luminous framework furnished with multiple interacting sites for guest analyte molecules. Here, in this report, for the first time, a highly luminescent water-stable cationic iMOF-12C was constructed from an N-donor-based linker Tris(4-(1H-imidazol-1-yl)phenyl)amine and d^{10} metal ion Zn^{2+} for precise and sensitive recognition of the organic arsenic molecule roxarsone (ROX) and nitarsonic acid (NIT) from water (Scheme 4.1). Thus developed MOF-based sensor displayed selective and sensitive recognition of ROX and NIT via a turn-off fluorescence output signal with very swift response time. Additionally, the limit of detection (LOD) for these analytes was determined as the lowest among MOF-based sensors.

4.2 Experimental

4.2.1. Materials

All of the reagents and solvents used in this study were commercially available and used without further purification. Tris(4-bromophenyl)-amine, 4-hydroxy-3-nitrophenylarsonic acid (roxarsone, ROX), 4-hydroxyphenylarsonic acid (HAA), 4-aminophenylarsonic acid (ASA), Penicillin G potassium salt (PEN), and erythromycin (ERY) were purchased from Tokyo Chemical Industry (TCI). 1,5-Naphthalenedisulfonic acid (1,5-NDSA) and 4-nitrophenylarsonic acid (nitarsonic acid, NIT) were purchased from Sigma-Aldrich and Parshwamani metals, respectively, and used as received.

4.2.2. Synthesis

4.2.2.1. Synthesis of the Ligand Tris(4-(1H-imidazol-1-yl)phenyl)amine (TIPA): The ligand TIPA (L) was synthesized according to a reported protocol with slight modifications.⁵⁷ A mixture of Tris(4-bromophenyl)amine (500 mg, 1.04 mmol), imidazole (460 mg, 6.75 mmol), K_2CO_3 (610 mg, 4.41 mmol), and anhydrous $CuSO_4$ (6.5 mg, 0.041 mmol) was heated for 60 h at 160 °C under nitrogen atmosphere (Appendix Scheme 4.1, Appendix Figure 4.1). After that, the reaction mixture was cooled down to room temperature, dissolved in chloroform (50 mL), and washed with a copious amount of water. The organic layer was brought about to dryness to yield a pale-yellow-colored powder.

4.2.2.2. A combined mixture of ligand TIPA (L) (8.86 mg, 0.02 mmol), $Zn(NO_3)_2$ (5.95 mg, 0.02 mmol), 1,5-NDSA (11.00 mg, 0.03 mmol) in *N,N*-dimethylformamide (1 mL), and water (2 mL) was taken in a 5 mL glass vial and placed in a preheated oven at 90 °C for 48 h and slowly cooled down to room temperature

(Appendix Scheme 4.2). A suitable crystal was taken for the single-crystal X-ray diffraction data collection, and the remaining crystals of iMOF-12C were filtered and then washed with water and methanol several times. Single crystals of compound iMOF-12C were isolated with a yield of ~45%. To obtain the guest-free phase, these iMOF-12C crystals were immersed in MeOH for solvent exchange for 7 days and after separating, heated under vacuum overnight at 100 °C. Anal. (guest-free phase) found: C/N = 4.1315, C/H = 11.0532, N/S = 2.2088, C/S = 9.1256.

4.2.3. X-ray Structural Studies

X-ray diffraction data on single crystals of iMOF-12C was collected on a Bruker D8 Venture Duo X-ray diffractometer equipped with a Microfocus X-ray source (operated at 50 W; 50 kV/1 mA) and graded multilayer optics for monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) with a focused X-ray beam and a Photon 100 CMOS chip based detector system at 150 K. The crystal was mounted on nylon Cryo Loops (Hampton Research) with Paratone-N (Hampton Research). The data integration and reduction were processed with SAINT software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by a direct method using SHELXTL and was refined on F² with a full-matrix least squares technique using the SHELXL program package. All of the hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The BUMP command was used to avoid short contacts. The structures were examined using the Adsym subroutine in PLATON to assure that no additional symmetries could be applied to the model. CCDC number: 2177845 for iMOF-12C contains the supplementary crystallographic data for this paper.

4.2.4. Methods

4.2.4.1. Analyte preparation: Stock solutions of all analytes were prepared by dissolving 3 mg compound in 10 mL of water of concentration 300 ppm.

4.2.4.2. UV-Vis Studies: For every analyte, i.e., ROX, NIT, HAA, ASA, PEN, ERY and Cypermethrin (CYP), the UV-Vis spectra was recorded by taking their 0.5mM aqueous solution in a cuvette in 200-700 nm range.

4.2.4.3. Fluorescence Titration Study with iMOF-12C: 1 mg of desolvated iMOF-12C was placed in a quartz cuvette and 2 mL water was then added to obtain the dispersed phase. Initially photoluminescence spectra of iMOF-12C in water medium was recorded by exciting the dispersed iMOF-12C at 363 nm (spectra recorded in the range of 373-650 nm). After that, to the dispersed phase of MOF in water 300 ppm stock solution of ROX (4-Hydroxy-3-nitrophenylarsonic Acid, Roxarsone) and NIT (4-nitrophenylarsonic

Acid, Nitarsone) in water (20 μ L to 300 μ L) was added in-situ and spectras were recorded after each addition. With each incremental addition of ROX and NIT, quenching in the intensity of fluorescence emission of iMOF-12C was observed.

4.2.4.4. Competing Studies: We have taken HAA (4-hydroxyphenylarsonic Acid), ASA (4-aminophenylarsonic Ac-id), PEN (Penicillin G Potassium Salt), ERY (Erythromycin), CYP (Cypermethrin) in water. In a typical study, for initial investigation we have taken 1 mg of iMOF-12C in 2 mL of water. To the dispersed phase of iMOF-12C, 300 μ l (300 ppm) of the competing analyte was added from the stock solution and the corresponding spectra were recorded to check the response of MOF toward these analytes. For selectivity studies, to the dispersed MOF (1 mg) in water (2 ml) we added 300 μ l (300 ppm) of the competing analyte followed by the addition of 300 μ L (300 ppm) ROX and NIT solutions respectively from the stock as prepared earlier and recorded the fluorescence spectra after each addition.

4.2.4.5. Recyclability Study: 30 mg desolvated iMOF-12C was used for the recyclability studies. Firstly, luminescence spectra were recorded following a similar procedure mentioned above. Following this, fluorescence spectra was recorded after adding 300 μ l (300 ppm) ROX (for 1st Cycle). Rest of the iMOF-12C was dispersed in 60 mL water followed by adding 9 ml 300 ppm ROX solution. Then solution was shaken in a vortex shaker for 10 min and filtered, washed with methanol for several time to remove ROX. After that the compound was exchanged with methanol and desolvated before using for the next cycle. The sensitivity of iMOF-12C towards ROX were repeated for five cycles.

4.2.4.6. Detection Limit Calculation: For calculating detection limit ROX and NIT (20 – 200 μ L, 300 ppm stock solutions) were added to probe (desolvated iMOF-12C) (1mg in 2mL water) and fluorescent intensity was recorded. By plotting fluorescence intensity with increasing concentration of the organic arsenic acid, slope (m) of graph were calculated from there. Further, the standard deviation (σ) was calculated from five blank measurements of probe. Detection limit is calculated according to the formula:

Detection limit: (3σ /m)

4.2.4.7. Real Sample Analysis: We bought chicken from the local market. Then we dipped the raw chicken in the dispersed aqueous solution of iMOF-12C to fabricated MOF loaded chicken for the further experiment. For the quenching experiment with chicken extraction, we first dipped raw chicken into 300 ppm ROX solution and stirred for 2 hours and then extract the liquid out of chicken and fluorescence spectra of iMOF-12C were recorded after incremental addition of the extraction.

4.3 Results and Discussion

4.3.1. Synthesis and Structural Characterization

Single crystals of iMOF-12C were obtained by a solvothermal reaction of $\text{Zn}(\text{NO}_3)_2$, 1,5-naphthalenedisulfonic acid (1,5- NDSA), and ligand TIPA (L) in a solvent combination of water (2 mL) and *N,N*-dimethylformamide (1 mL) (Appendix Scheme 4.2). The iMOF-12C crystallized in monoclinic P_{21} space group, with the asymmetric unit of iMOF-12C comprising four Zn(II) atoms as the metal node, four units of ligand, three units of 1,5-NDSA, one coordinated water molecule, two μ_2 -hydroxo bridges, and two DMF molecules as guest molecules with the formula $\{[\text{Zn}_4\text{L}_4(\mu_2\text{-OH})_2(\text{H}_2\text{O})](1,5\text{-NDSA})_3(\text{DMF})_2 \cdot 11\text{H}_2\text{O}]\}_n$ (Figure 4.1a). A careful inspection of the coordination environment reveals an interesting coordination mode of the metal node. There are two types of Zn(II) metal nodes that are seldom observed in the domain of metal-organic frameworks. One Zn(II) metal node is of trigonal bipyramidal (TBP) geometry, connected to three ligands, one μ_2 -hydroxo group, and one water molecule (Figures 4.1c, Appendix Figure 4.2), while the other Zn(II) metal node is tetrahedral (Td), coordinated to three ligands and one μ_2 -hydroxo group (Figures 4.1d, Appendix Figure 4.2). Crystallographic studies indicate the presence of two different types of adjacent centers in iMOF-12C. Firstly, two tetrahedral metal nodes are bridged via the μ_2 -hydroxo group (Appendix Figure 4.3) and the other one bearing a tetrahedral and a trigonal bipyramidal metal nodes are bridged via the μ_2 -hydroxo group (Appendix Figure 4.4). The framework backbone of iMOF-12C was found to be cationic in nature with Zn providing +2 charge and μ_2 -OH carrying -1 charge, while the coordinated water and ligand provide no charges to the metal center, leaving a net positive charge on the framework. This positive charge was counterbalanced by uncoordinated 1,5-naphthalenedisulfonic acid, which provides two negative charges per molecule. The average Zn-L distance was determined as 2.004 Å. iMOF-12C was found to possess a 2D porous architecture (Appendix Figure 4.5-4.7). The 2D layers of iMOF-12C are stacked together in an ABAB fashion (Figures 4.1e, Appendix Figure 4.8) to form a 1D porous channel (Figures 4.1b, Appendix Figure 4.9). The counter ion, 1,5-NDSA, interestingly, was fully located inside the 1D channels (Appendix Figure 4.10). One of the 1,5-NDSA ions is located along with the pore featuring its exposed approachable π -surface (Appendix Figure 4.10), while the other 1,5-NDSA anion is vertically aligned with the pore with its accessible $-\text{SO}_3\text{H}$ group (Appendix Figure 4.11) to the incoming guest. The uniqueness of the crystal structure was further validated with the novel topology of the iMOF-12C framework, calculated using TOPOS, with the symbol $(1,2\text{M}3\text{-}1)(3^4,4^3\text{-c})$.⁵⁹ After the successful synthesis and establishment of the structure of the iMOF-12C framework from the SC-XRD data, the basic characterization of iMOF-12C was thoroughly performed with PXRD, TGA, FT-IR, and FESEM. The bulk-phase purity of iMOF-12C was validated by

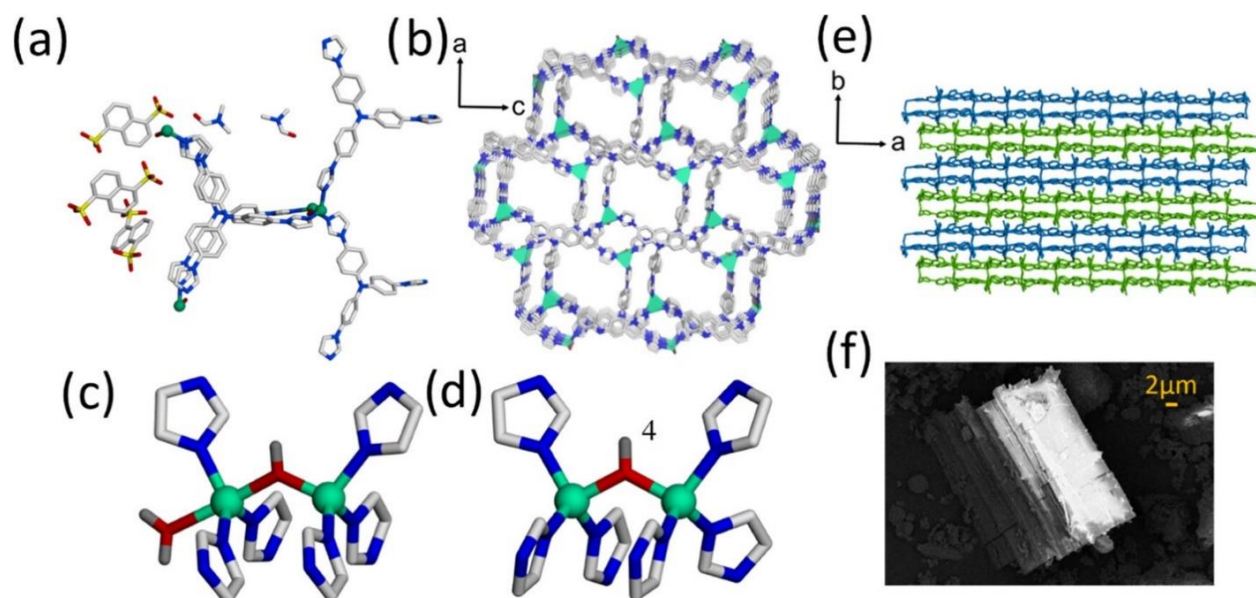


Figure 4.1. (a) Asymmetric unit; (b) 2D porous framework (sulfonic acid is omitted for clarity); (c, d) two different types of coordination environments (color code: C - light gray, H - deep gray, N - blue, O - red, S - yellow, Zn - green) of iMOF-12C; (e) 2D-layer structure of iMOF-12C; and (f) FESEM images of iMOF-12C.

PXRD and elemental analysis. The PXRD pattern of the compound suggested an identical nature (with a slight shift in 2θ value) with the simulated pattern, which is common in a 2D framework²⁰ and confirms that the overall framework integrity is maintained in its bulk phase (Appendix Figure 4.12) and this phase is maintained in different chemical conditions. The desolvated phase of iMOF-12C also displayed an intact PXRD pattern, which validated the retention of crystallinity, phase purity, and the rigid nature of iMOF-12C (Appendix Figure 4.13). The FT-IR spectra of iMOF-12C affirmed the abundance of all of the relevant peaks corresponding to the organic linker along with peaks at 1506 and 1606 cm^{-1} associated to the free 1,5-NDSA inside the pore (Appendix Figure 4.14). TGA matched well with the initial loss corresponding to the free guest solvent molecules, i.e., DMF, and coordinated as well as free water molecules within the framework (Appendix Figure 4.15). FESEM images probed for the surface morphology of iMOF-12C displayed block-shaped crystals (Figures 4.1f, Appendix Figure 4.16) and EDX spectra validated the elemental composition (Appendix Figure 4.17). Additionally, iMOF-12C illustrated an exemplary aqueous-phase stability on account of its protected metal nodes as the coordinating sites of the Zn metal center that are connected by the three ligands and one or two oxygen atoms owing to its coordination environment (Appendix Figure 4.3). Furthermore, the compound exhibited outstanding chemical robustness even in a broad spectrum of pH solutions ($\text{pH} = 4\text{--}10$) as the PXRD patterns matched well with the pristine phase of

iMOF-12C, confirming the preservation of framework integrity under various pH conditions (Appendix Figure 4.18). Further, in order to evaluate the porosity of iMOF-12C, nitrogen gas sorption analysis at 77 K was conducted. The MOF demonstrated a very low N₂ gas uptake at 77 K (Appendix Figure 4.19). This phenomenon can be explained by the presence of bulky counter anions in the pores of the cationic framework of iMOF-12C. Such phenomena are frequently observed in the case of ionic MOFs.^{20,21,55} Moreover, CO₂ gas sorption analysis at 195 K was further performed to validate the porosity of iMOF-12C, which showed a significant amount of gas uptake (Appendix Figure 4.20).

4.3.2. Photoluminescence Studies

A strategic combination of d¹⁰ metal ions (Zn²⁺) with the π -conjugated neutral N-donor luminescent ligand system serves effectively toward fabricating luminescent cationic MOFs. Considering the luminescent and cationic framework of iMOF-12C, we hypothesized that the approaching organic arsenic molecules could diffuse inside the cationic framework of iMOF-12C to some extent and selectively interact with the framework. To confirm its luminous nature, both solid-state and aqueous-phase fluorescence spectra of iMOF-12C were recorded. Upon excitation at 363 nm in solid phase (Appendix Figure 4.21), iMOF-12C showed an intense broad peak with emission maxima at 413 nm, which overlapped with the emission maxima of the ligand itself, attributed to the ligand-centered luminescence caused by ligand-to-ligand charge transfer (LLCT) (Appendix Figure 4.22). Also, a new peak arises at 435 nm, which may be due to the ligand-to-metal charge transfer (LMCT).⁴³

The excellent hydrolytic stability and steady photoluminescence properties of iMOF-12C make it promising as an aqueous medium chemosensor to explore its potential application in detection and monitoring of organic arsenics in water. In this work, the photoluminescence property of iMOF-12C was analyzed in detail in the presence of two main frequently used organic arsenic compounds in the poultry feed stock, roxarsone (ROX) and nitarosone (NIT) (Scheme 4.1, Appendix Figure 4.23). Considering the luminescence property of iMOF-12C, initially we added organic arsenic (ROX and NIT) to the dispersed phase of iMOF-12C in water under UV light and observed an immediate turn-off behavior of iMOF-12C in the presence of ROX and NIT (Appendix Figure 4.24). With this observation, we went ahead to investigate the ability of iMOF-12C in sensing trace amounts of organic arsenic in water. With incremental addition of 300 ppm aqueous solution of organic arsenic into the dispersed phase of 1 mg of iMOF-12C in 2 mL of water, fluorescence titrations were performed. iMOF-12C indeed showed excellent sensing performance toward these two organic arsenic compounds via rapid fluorescence quenching. As predicted, with increasing addition of ROX and NIT, a high gradual fluorescence quenching was observed in iMOF-12C (Figure 4.2a, d). The fluorescence quenching was observed to be rapid in the case of NIT compared to ROX owing its more electron-deficient nature. It was observed that iMOF-12C displayed efficient fluorescence quenching

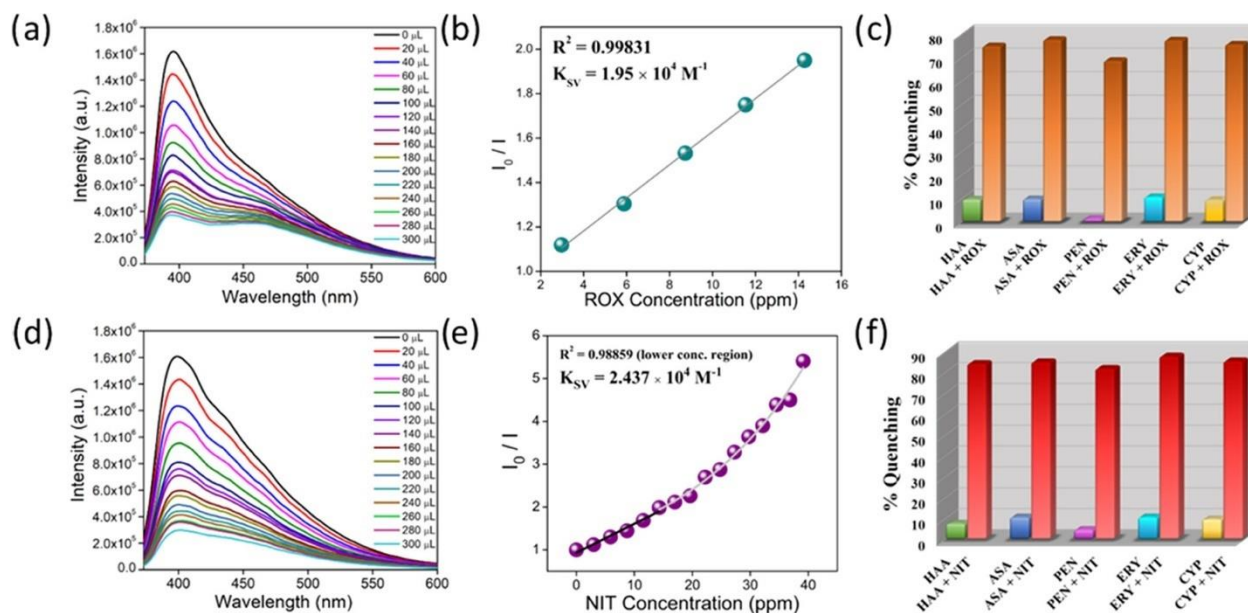


Figure 4.2. Fluorescence quenching intensity of iMOF-12C after incremental addition of 300 ppm of (a) ROX and (d) NIT. Stern-Volmer plot for (b) ROX and (e) NIT. Fluorescence quenching of iMOF-12C in the presence of different analytes for (c) ROX and (f) NIT

of 78 and 82% for both ROX (Appendix Figure 4.25) and NIT (Appendix Figure 4.26), respectively. Additionally, the fluorescence quenching efficiency was quantified by analyzing the acquired experimental data via the Stern-Volmer (SV) equation $I_0/I = 1 + K_{SV}[Q]$, where I_0 and I represent the fluorescence intensity of the dispersed iMOF-12C before and after addition of organic arsenic, respectively, $[Q]$ represents the concentration of the analyte, and K_{SV} is the Stern-Volmer constant.⁶⁰ iMOF-12C has K_{SV} values of $1.95 \times 10^4 \text{ M}^{-1}$ and $2.437 \times 10^4 \text{ M}^{-1}$ toward ROX and NIT, respectively. The SV plot presented a linear curve in the low-concentration as well as higher-concentration range for ROX (Figure 4.2b), but in the case of NIT, a linear plot was observed in the lower-concentration range but subsequent deviation from linearity followed by an upward bend prevailed at higher concentration (Figure 4.2e). Such a nonlinear trend in SV plots may be attributed to the involvement of an energy transfer process or self-absorption.^{61,62} Furthermore, a competent sensory probe should be capable of detecting such analytes even at trace concentrations for real-time applications. The limit of detection (LOD) of a sensory material can disclose the probe's efficacy in detecting specified analytes at low concentrations. Based on the values of standard deviations (σ) for five blank fluorescence experiments and the value of the slope (m) of the linear plot of the first five intensity values of iMOF-12C after addition of analyte, the limit of detection (LOD) ($3\sigma/m$) toward ROX (Appendix Figure 4.27) and NIT (Appendix Figure 4.28) was calculated to be 3.95 and 1.35 ppb, respectively (Appendix Table 4.1-4.2), which is a lower than <10 ppb safety limit as determined by

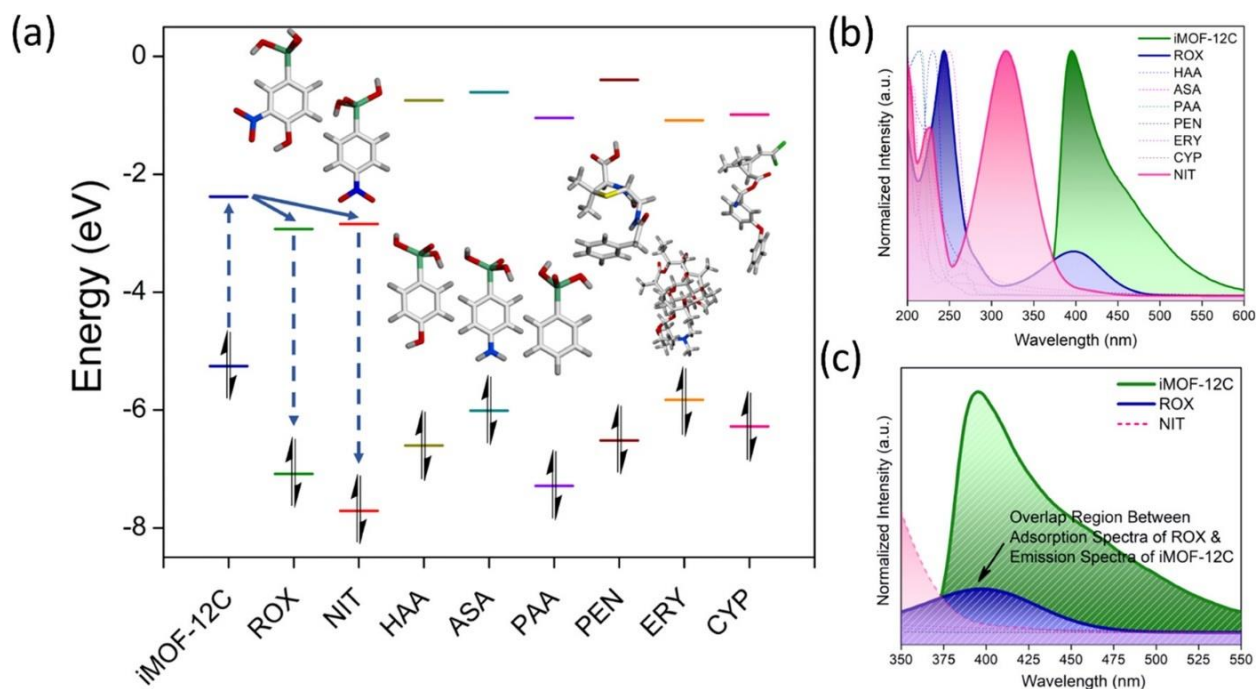


Figure 4.3. (a) HOMO-LUMO energies of all analytes. (b, c) Overlap between absorption spectra of analytes and the emission spectra of iMOF-12C

the World Health Organization (WHO).⁷ Also, it is worth mentioning that the LOD value for NIT detection was found to be the lowest in the domain of porous materials (Appendix Table 4.3). For correlation, we further briefly studied the detection competence of the iMOF-12C toward more organic arsenics, including 4-hydroxyphenylarsonic acid (HAA), 4-aminophenylarsonic acid (ASA), and phenylarsonic acid (PAA) (Appendix Figure 4.23). In the presence of HAA and ASA, iMOF-12C shows a very low quenching of fluorescence intensity (Appendix Figure 4.29, 4.30) and also, the SV plots were found to be linear in the whole concentration region. The two main groups present in ROX and NIT are $-\text{NO}_2$ and $-\text{AsO}(\text{OH})_2$. To understand the exact effect of the $-\text{AsO}(\text{OH})_2$ group toward quenching, we also performed a controlled experiment with phenylarsonic acid (PAA) bearing only $-\text{AsO}(\text{OH})_2$ functionality, and observed moderate quenching in the fluorescence intensity (Appendix Figure 4.31). This finding suggests that a synergistic combination of both the $-\text{NO}_2$ group and the $-\text{AsO}(\text{OH})_2$ group plays a pivotal role in the fluorescence quenching process. Furthermore, in order to find out the effect of exposure time of the organic arsenic analytes on the fluorescence quenching efficiency pertaining to real-time application of iMOF-12C, we performed time-dependent sensing studies. For this, in a typical experiment, the fluorescence emission intensity of iMOF-12C was recorded at particular time intervals from 30 s to 10 min, after adding 100, 200, and 300 μL of 300 ppm ROX and NIT, respectively. The maximum quenching of the PL intensity was observed within 30 s of exposure time for both ROX (Appendix Figure 4.32) and NIT (Appendix Figure 4.33), which remained almost unaltered for a whole exposure period of 10 min. It should be kept in mind

that, in poultry litter and effluent from livestock farms, several other organic additive molecules co-exist, and the selectivity of a chemosensor is another important aspect that governs its real-time applicability. Considering this, we explored the potency of iMOF-12C for selective detection of organic arsenics and investigated the impact of other organic molecules. The fluorogenic response of iMOF-12C was recorded in the presence of other organic molecules including penicillin (PEN), erythromycin (ERY), and cypermethrin (CYP) (Appendix Figure 4.23) at the same concentration as that of organic arsenic. Interestingly, no striking change in the photoluminescence response was seen in case of PEN, ERY, and CYP (Appendix Figure 4.34-4.36). Also, we plotted the quenching percentage and Stern-Volmer value of all analytes for comparable studies and found the highest value in both cases for ROX and NIT as well (Appendix Figure 4.37-4.38). Encouraged by these findings, we proceeded further to check the potency of iMOF-12C toward selective sensing of ROX and NIT in the presence of these other organic molecules. For this experiment, 1 mg of iMOF-12C was dispersed in 2 mL of water and its fluorescence spectra were recorded before and after adding the solution of organic interfering molecules. Then, after 1 min of equilibrium time, the solution of ROX or NIT was added to it and fluorescence response was recorded. It was observed that the respective interfering molecule did not have any significant impact on the fluorescence spectra, but the addition of ROX or NIT yielded substantial quenching in the fluorescence emission intensity (Figure 4.2c, f). These findings, in turn, confirm the high selectivity and sensitivity of iMOF-12C toward both ROX and NIT even in the presence of concurrent interfering organic molecules.

4.3.3. Detection Mechanism

To disseminate insights into the high selectivity and sensitivity of iMOF-12C toward ROX and NIT, we delved into the mechanistic aspect of the fluorescence quenching process. In the domain of MOF-based sensing, the detection mechanism mainly depends on deformation of the structure of MOF's framework after analyte treatment, or is due to electrostatic interactions such as photoinduced electron transfer (PET), fluorescence resonance energy transfer (FRET), and internal filtration effect (IFE). Therefore, in order to evaluate the underlying sensing mechanism, we carried out various characterizations of iMOF-12C after the sensing study. It was found from the PXRD, FT-IR, and TGA that the crystallinity as well as integrity of the framework of iMOF-12C was well maintained, while the identical thermal behavior was also intact (Appendix Figure 4.39-4.46). The FESEM images confirmed the maintained morphology of iMOF-12C without any changes after the sensing study (Appendix Figure 4.42, 4.45). From the EDX spectra, we found "As" as a new element while the other elemental composition was found to be well retained after the sensing studies (Appendix Figure 4.43, 4.46). With these results, we ruled out the first factor for the detection mechanism, i.e., structural breakdown. Then, we focused on the other possibilities of sensing mechanisms. MOFs are generally documented as giant molecules constituting an infinite framework. The valence and

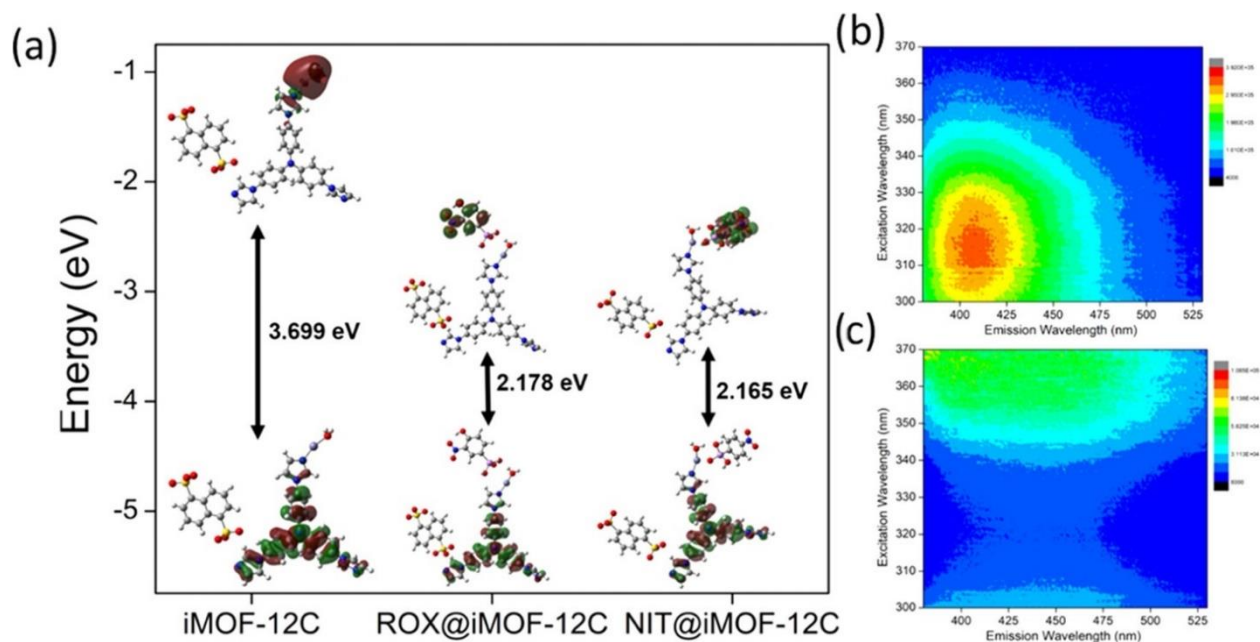


Figure 4.4. (a) HOMO-LUMO energies of iMOF-12C, ROX@iMOF-12C, and NIT@iMOF-12C, (b) and (c) PLE spectrum of pristine iMOF-12C in aqueous medium and after addition of 300 ppm and 300 μ L of ROX.

conduction bands of MOFs can be considered in a comparable model to molecular orbitals (MOs). When the lowest unoccupied molecular orbital (LUMO) of an analyte possesses lesser energy than the LUMO of MOF, it functions as driving force in the transfer of excited electron in MOF to the LUMO of electron-deficient analytes, causing the quenching in fluorescence intensity.⁶³ In order to probe the underlying mechanism, we calculated the orbital energies of LUMOs and the highest occupied molecular orbitals (HOMOs) of the analytes and iMOF-12C, respectively, to establish if photoinduced electron transfer (PET) was the prevailing process. The HOMO and LUMO energies were calculated by employing density function theory (DFT) calculations using the B3LYP-6-31g* basis set with Gaussian 9 software package.⁶⁴ It was found that the LUMO energies of HAA, ASA, PAA, PEN, ERY, and CYP are much higher than the LUMO energy of the iMOF-12C, indicating that the injection of the electron from the excited MOF to the above-mentioned analyte molecules are thermodynamically forbidden. The LUMO energy levels of ROX and NIT were found to be lower than the LUMO of iMOF-12C, as expected. Thus, it can be inferred that the PET process is involved in the recognition of ROX and NIT by iMOF-12C (Figure 4.3a). In addition, fluorescence resonance energy transfer (FRET) may also have a significant contribution to the fluorescence quenching.^{61,62} If the emission spectrum of a donor overlaps with the absorption spectra of the acceptor, FRET becomes feasible. Interestingly, the emission spectra of iMOF-12C have the greatest overlap with the absorption spectrum of ROX. The other analyte's absorption spectra, including NIT, have an almost insignificant overlap with the emission spectrum of iMOF-12C (Figure 4.3b, c). In order to evaluate the

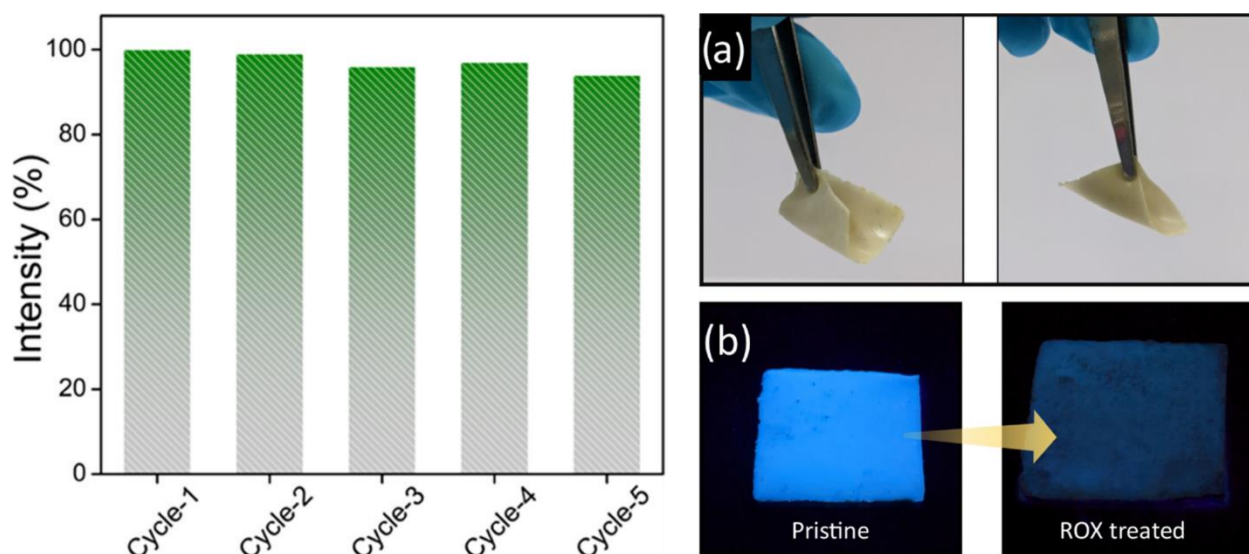


Figure 4.5. Recyclability of iMOF-12C toward ROX detection, (a) Photograph of flexible and robust MMM of iMOF-12C and (b) images of pristine and ROX-treated iMOF-12C-based MMMs under UV light.

internal filtration effect in the quenching process, we plotted the excitation spectra of iMOF-12C and the absorption spectra of ROX and NIT. We found a significant overlap of the excitation spectra of iMOF-12C and the absorption spectra of both the analytes (Appendix Figure 4.47), suggesting that IFE is one of the mechanisms for the quenching process.^{65,66} As the LUMO energy of ROX is less than that of iMOF-12C, we can conclude that the FRET along with PET and IFE are the mechanisms for the detection of ROX. On the other hand, for the detection of NIT, it is found that PET and IFE are the main processes. Also, we found the most probable interaction site in iMOF-12C with the ROX and NIT from the ESP diagram (Appendix Figure 4.48) and the HOMO-LUMO energy of the complex of iMOF-12C with ROX and NIT was found to be lower than that of only iMOF-12C (Figure 4.4a). This result confirmed that the complex gets stabilized by the energy transfer. Also, we performed a photoluminescence excitation (PLE) experiment to confirm the change in energy between the pristine iMOF-12C and the one after the addition of ROX. By exciting the aqueous suspension of iMOF-12C in the range of 300–370 nm, we recorded the emission spectra between 380 and 530 nm. It was found that for pristine iMOF-12C, the maximum excitation was at 313 nm, which changes to 368 and 365 nm for ROX- and NIT-treated iMOF-12C, respectively, while the maximum emission remains the same (Figures 4.4b, c, Appendix Figure 4.49). This bathochromic shift well matched with the theoretical results. To further confirm the results, a time-resolved fluorescence experiment was carried out in order to investigate the collision encounter mechanism between the excited state of iMOF-12C and the organic arsenic (ROX). The luminescence lifetime decay profiles indicated no significant change in the average lifetime between the pristine iMOF-12C and the ROX-treated iMOF-12C (Appendix Figure 4.50), which exhibited the presence of a static quenching mechanism behind such a

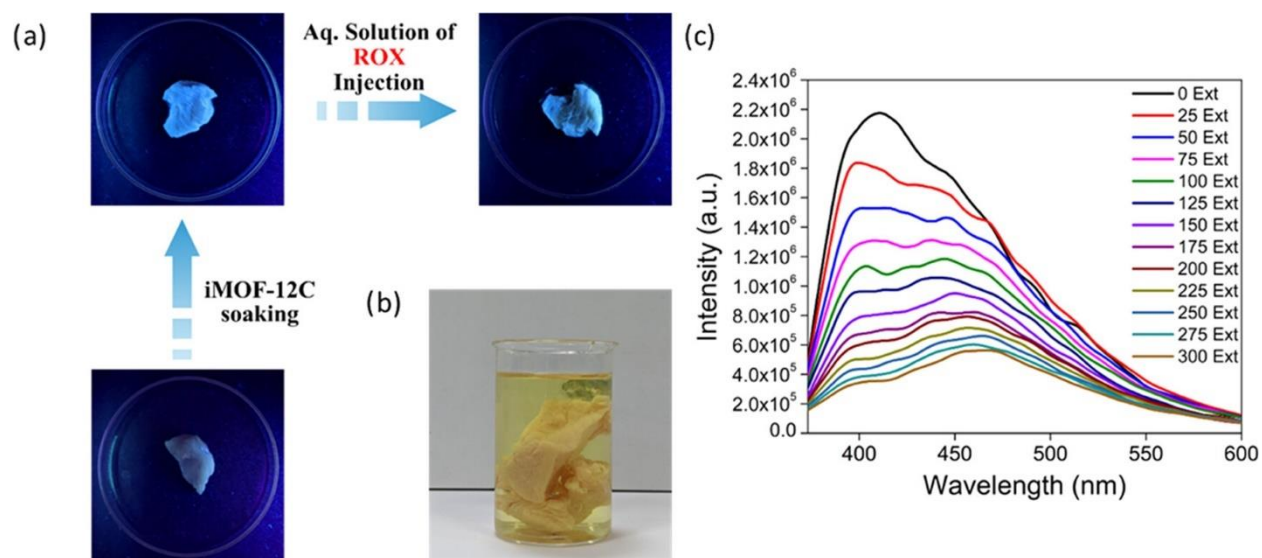


Figure 4.6. (a) Fluorescence response of raw chicken under UV light after soaking in iMOF-12C followed by addition of aqueous solution of ROX, (b) raw chicken in ROX solution, (c) quenching of iMOF-12C fluorescence intensity after incremental addition of ROX extraction from chicken.

response. This result further indicated the formation of a nonfluorescent ground-state complex between iMOF-12C and organic arsenic.

4.3.4. Recyclability and Practical Application

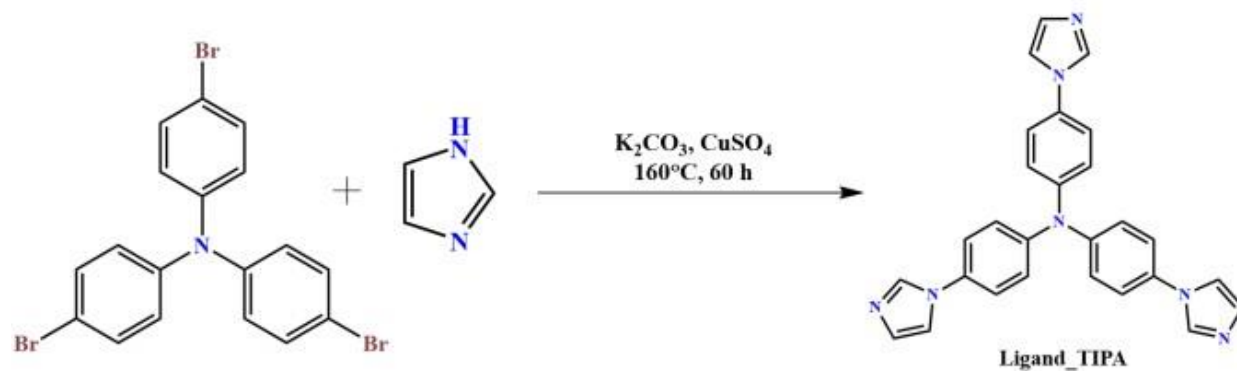
In the real-world application, recycling and using the same material for long-term application is an important parameter. Thus, we also performed the regeneration of iMOF-12C being used in ROX and NIT sensing as described in the Experimental Section. It was found that iMOF-12C showed almost intact quenching efficiency even up to five cycles of sensing, validating the high recyclability and stability of iMOF-12C toward sustainable organic arsenic sensing (Figures 4.5, Appendix Figure 4.51). Inspired by the above-discussed results, we further attempted to investigate the mixed matrix membranes (MMMs)-based organic arsenic detection by iMOF-12C as a proof of concept. According to the reported literature, PVDF was used to fabricate MOF-based films for this qualitative presentation of quick and easy detection. The self-standing iMOF-12C@PVDF membrane displayed robust nature and flexibility as well as strong luminescence when exposed to UV radiation (Figure 4.5a) and characterized by FT-IR and PXRD (Appendix Figure 4.52, 4.53). Thereafter, these MMMs were treated with ROX aqueous solution to examine the variations in the luminescent behavior of the films. When ROX solution was added, it was observed that the MOF-based film's strong emission was significantly reduced (Figure 4.5b). This observation indicated the potential use of iMOF-12C toward the practical implementation for device-based

sensing studies. All of these results motivated us further to explore the use of iMOF-12C for more practical sensing application. For this, we attempted to perform the ROX detection study in a real sample. Few pieces of raw chicken were collected from the local market and were soaked in the dispersed aqueous solution of iMOF-12C. The incorporation and homogeneous distribution of the fine MOF particles throughout the chicken pieces make them highly fluorescent under UV light (Figure 4.6a). Thereafter, when a portion of the MOF-loaded chicken was treated with ROX solution, there was significant quenching of the high luminescence intensity in a rapid manner (Figure 4.6a). Furthermore, in another experiment, we dipped raw chicken pieces into the ROX-spiked aqueous solution (Figure 4.6b) and after 2 h, we collected the extract by squeezing the dipped chicken. Then, we performed a titration experiment with this solution. With incremental addition of the extraction, it was found that the fluorescence intensity of iMOF-12C got quenched. About 75% of the fluorescent intensity of the MOF was observed to be gradually decreased upon 25 μL incremental addition of the extraction with a K_{SV} value of $4.2 \times 10^4 \text{ M}^{-1}$ (Figure 4.6c). Also, considering the fact of the presence of organic arsenic in ground water, herein, we applied our developed MOF-based sensor toward the detection of organic arsenic in ground water. In a typical sensing titration protocol, 1 mg of MOF was dispersed in ground water, and the PL intensity was monitored before and after addition of ROX solution. As a result, it was observed that almost $\sim 75\%$ of the PL intensity of the MOF got quenched upon addition of ROX in ground water (Appendix Figure 4.54).

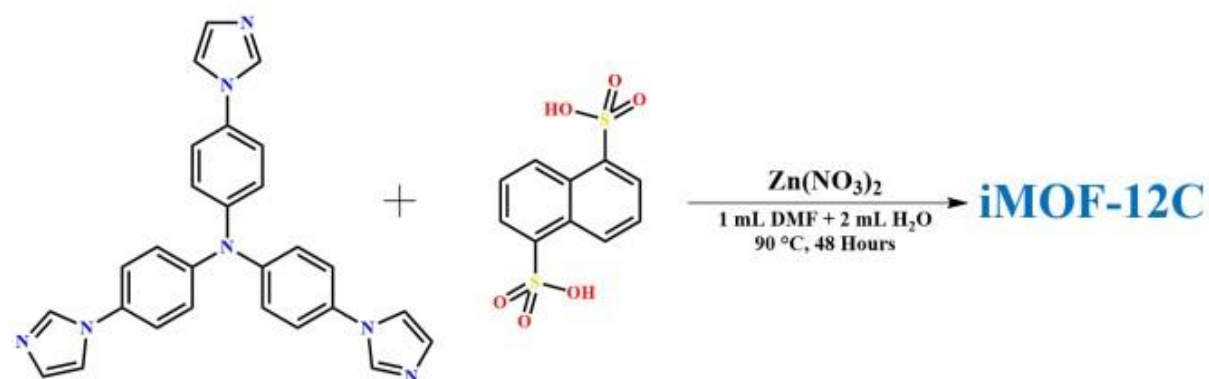
4.4 Conclusion

Briefly, we have designed and synthesized a new hydrolytically stable fluorescent cationic metal-organic framework, iMOF-12C, which shows selective and sensitive “turn-off” fluorogenic response toward toxic organic arsenic molecules ROX and NIT. Further, iMOF-12C displayed excellent selectivity toward ROX and NIT even in the presence of the competing drugs present in the poultry litter. The limit of detection (LOD) values toward NIT and ROX were determined to be 1.35 ppb and 3.95 ppb, respectively, well below the WHO safety limit. It is worth mentioning that these values stand tall among the reported literature values for porous materials, advocating the potency of iMOF-12C in real-world applications. The primary mechanism governing the fluorescence quenching of iMOF-12C toward ROX was identified as FRET as well as PET, while for NIT the dominant mechanism was PET. The change in electronic properties of iMOF-12C in the presence of ROX and NIT was unveiled by the theoretical studies to unfold the fluorescence quenching phenomenon. Additionally, an iMOF-12C-based MMM has been prepared for the real-time detection of ROX and NIT. We believe this piece of work will open an untapped paradigm of design and advancement of hydrolytically stable luminescent cationic MOFs in order to address the challenges of environmental issues toward selective and sensitive detection of toxic organic arsenic molecules.

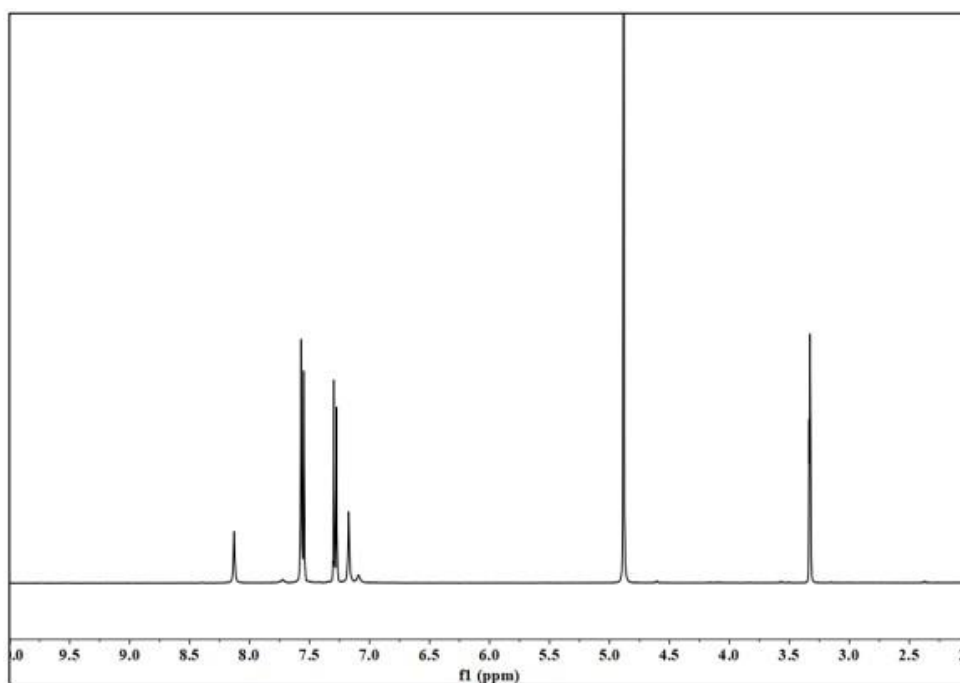
4.5 Appendix section



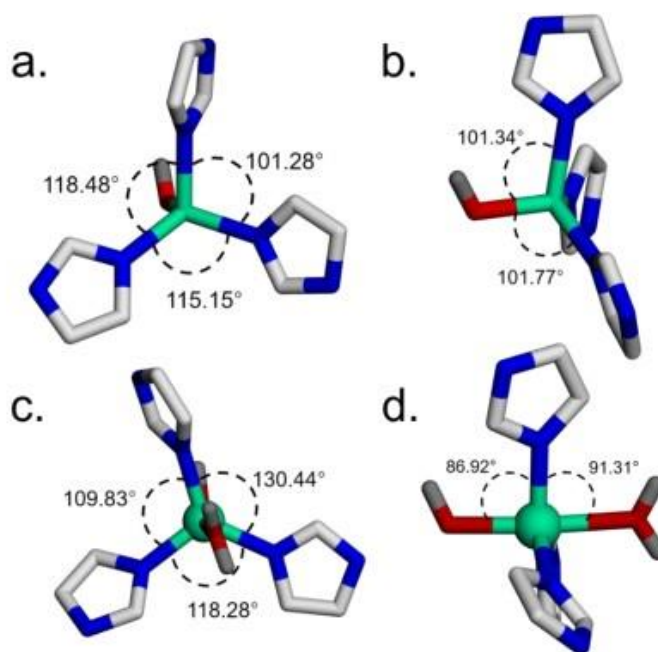
Appendix Scheme 5.1: Synthetic protocol of Ligand-TIPA



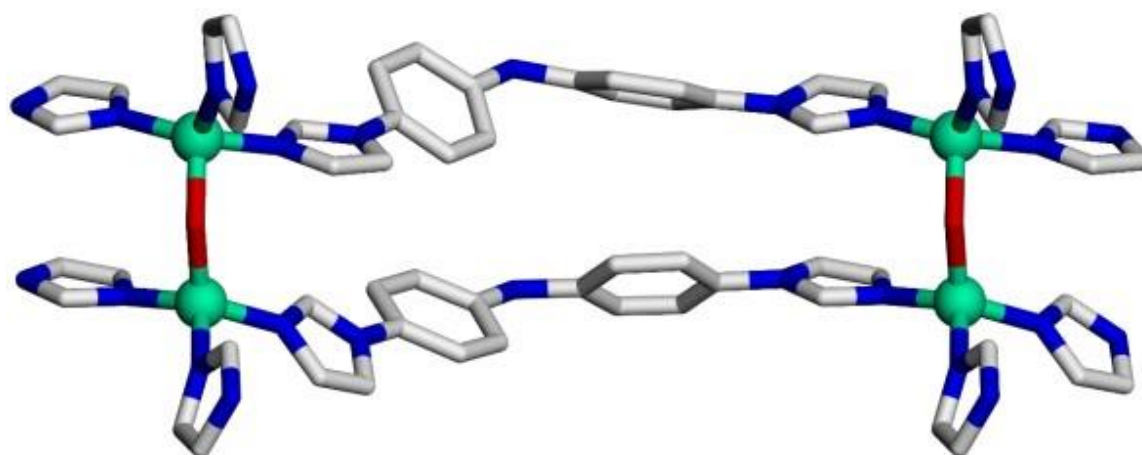
Appendix Scheme 5.2: Synthetic protocol of iMOF-12C.



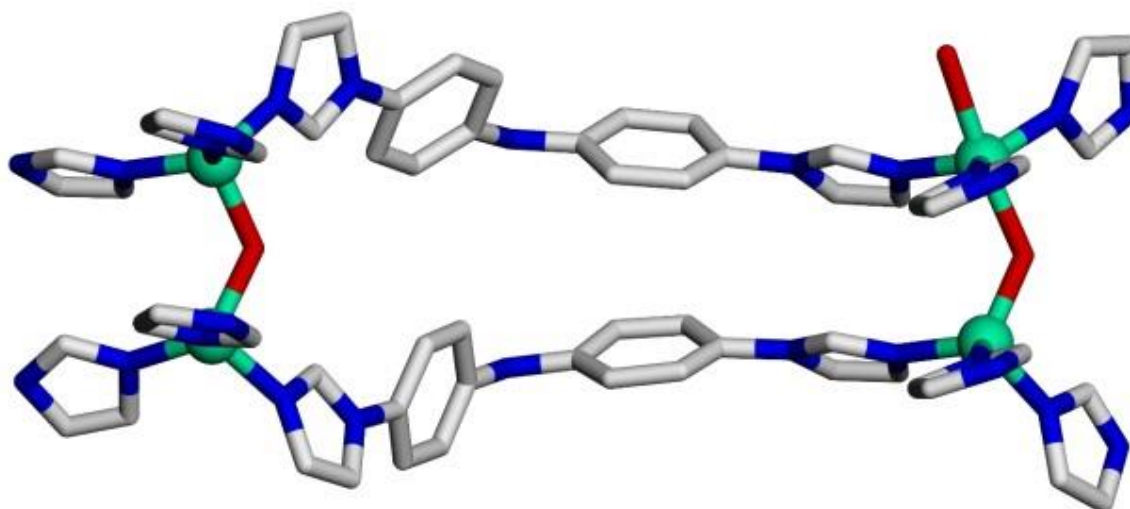
Appendix Figure 4.1: ^1H NMR of Ligand-TIPA



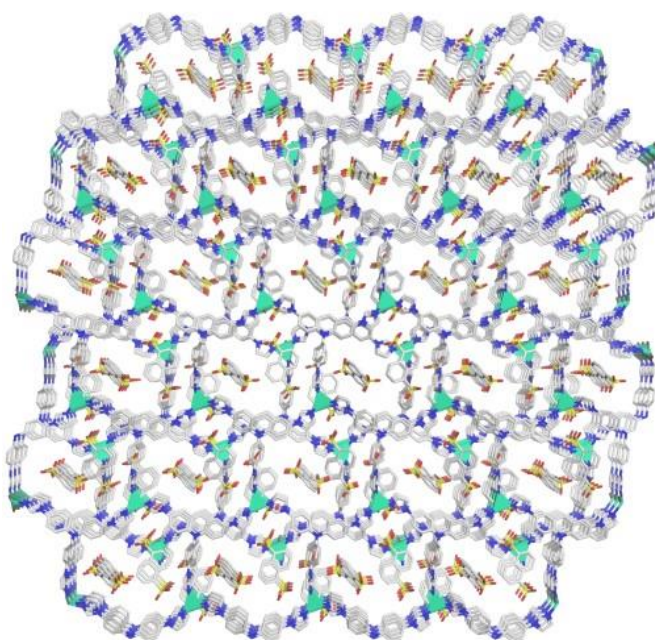
Appendix Figure 4.2: Different angle of coordination centre (a,b) tetrahedral centre, (c,d) trigonal bipyramidal centre (color: Gray - H, Light Gray - C, Blue - N, Red - O, Green - Zn)



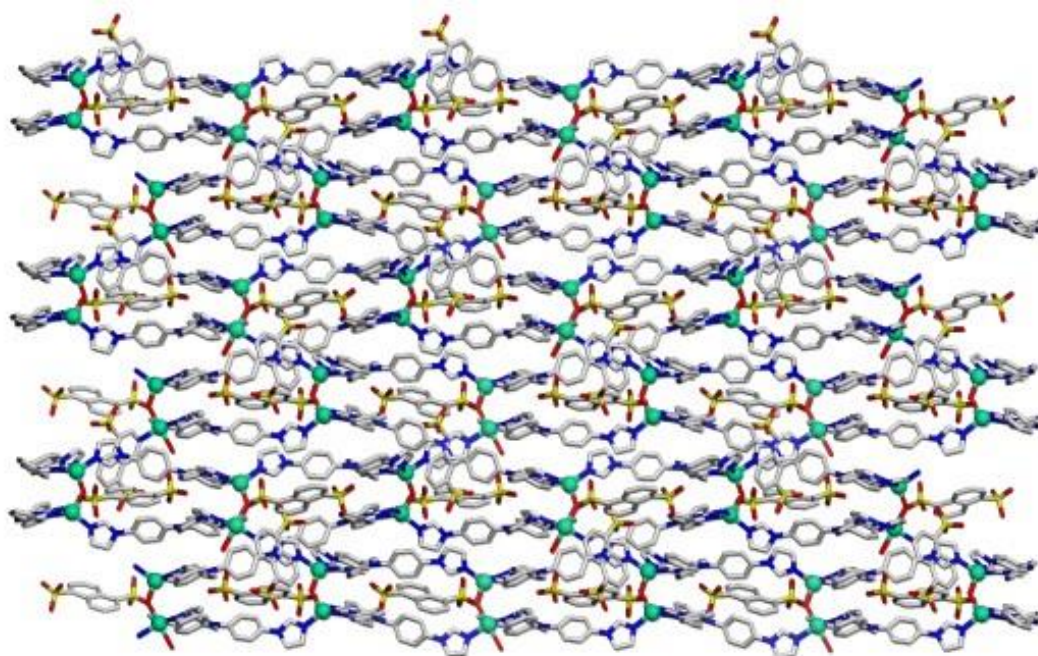
Appendix Figure 4.3: Two adjacent tetrahedral Zn (II) node in iMOF-12C (color: Light Gray - C, Blue - N, Red-O, Green- Zn)



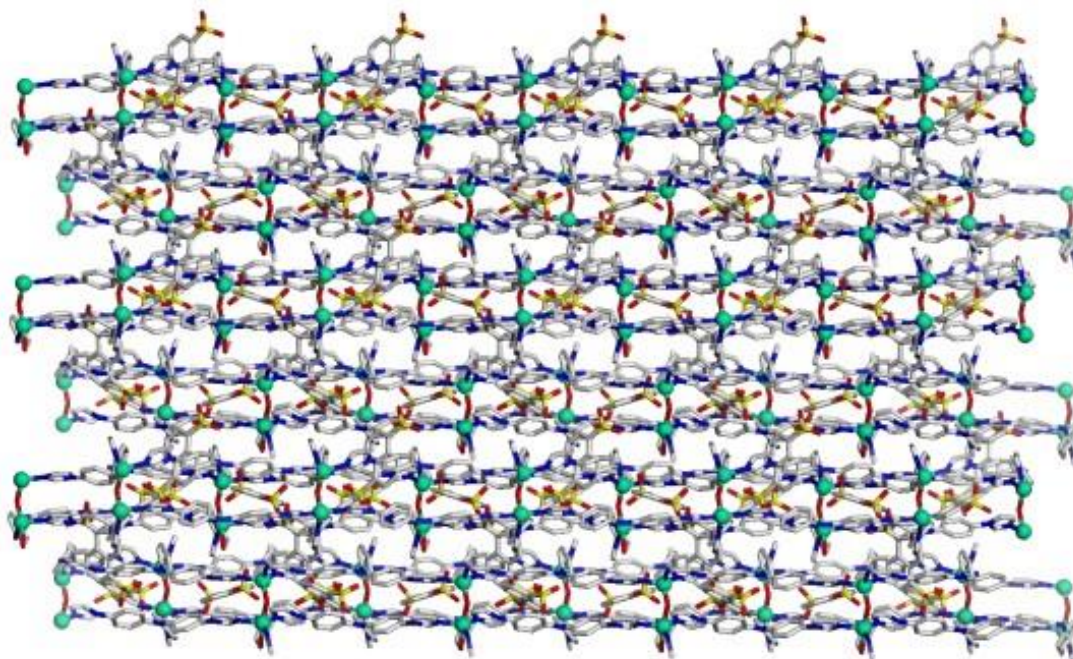
Appendix Figure 4.4: Two adjacent tetrahedral and trigonal bipyramidal Zn (II) node in iMOF-12C (color: Light Gray - C, Blue - N, Red-O, Green- Zn)



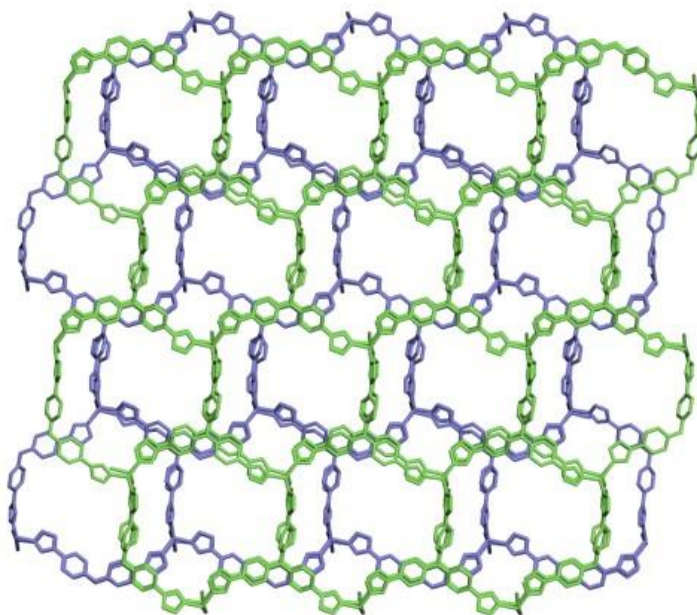
Appendix Figure 4.5: Overall packing of iMOF-12C along crystallographic “b” axis (color: Light Gray- C, Blue- N, Red- O, Yellow- S, Green polyhedron - Zn)



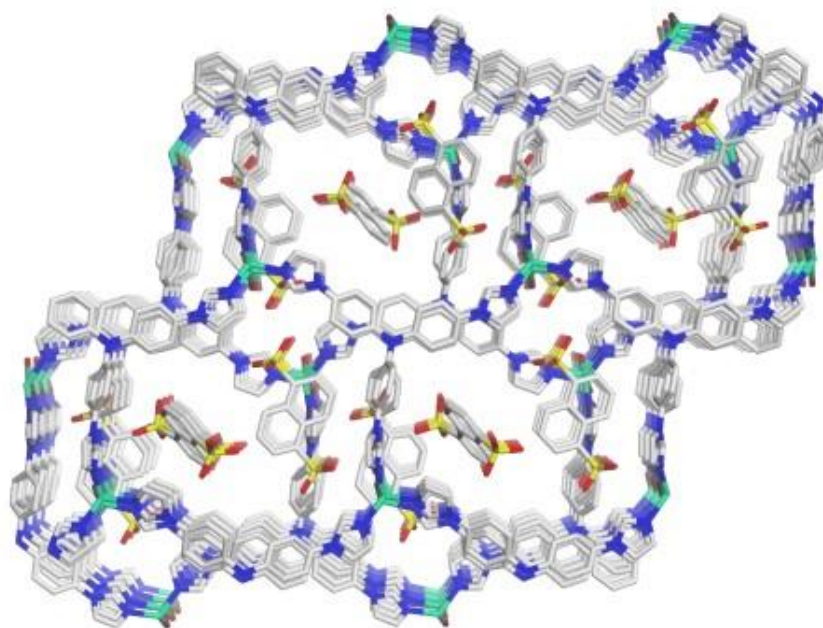
Appendix Figure 4.6: Overall packing of iMOF-12C along crystallographic “a” axis (color: Light Gray- C, Blue- N, Red- O, Yellow- S, Green- Zn)



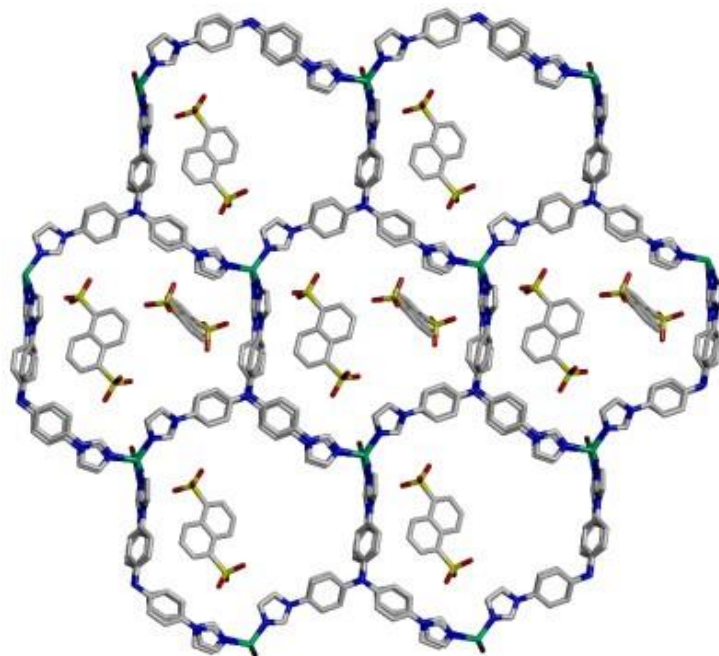
Appendix Figure 4.7: Overall packing of iMOF-12C along crystallographic “c” axis (color: Light Gray- C, Blue- N, Red- O, Yellow- S, Green- Zn)



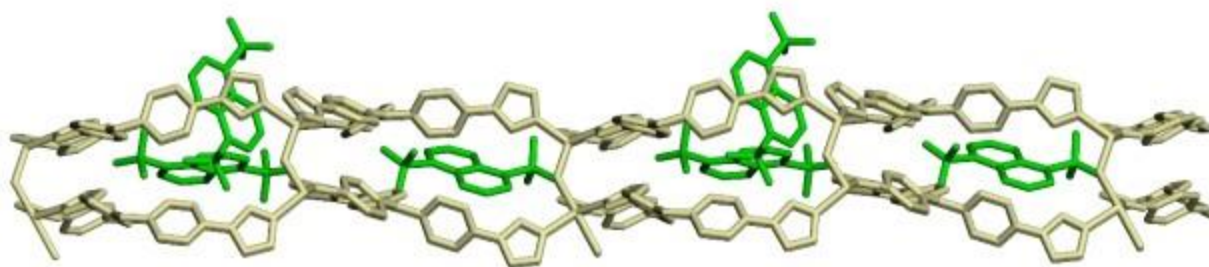
Appendix Figure 4.8: View of one of 2D-sheet along crystallographic “a” axis (anions are omitted for clarity)



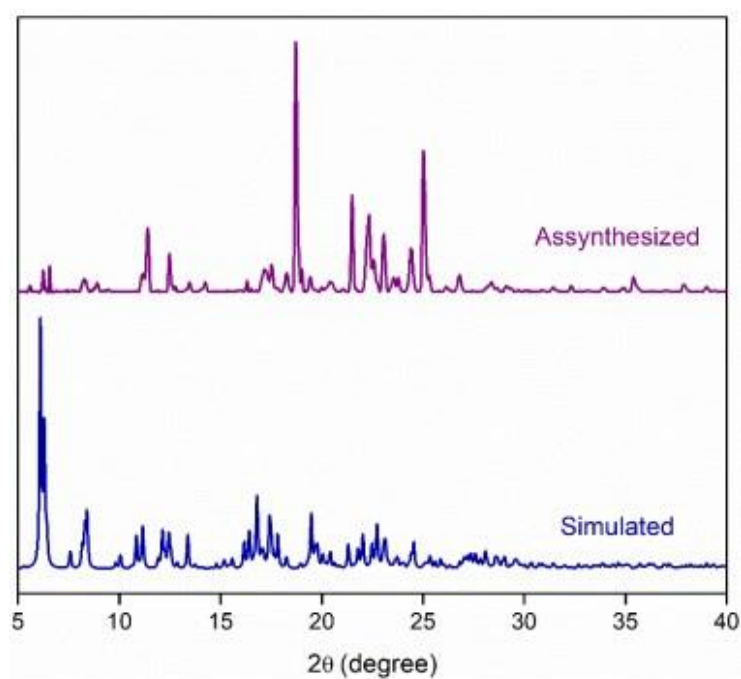
Appendix Figure 4.9: Position of 1,5-NDSA inside the pore of iMOF-12C (color: Light Gray- C, Blue- N, Red- O, Yellow- S, Green- Zn)



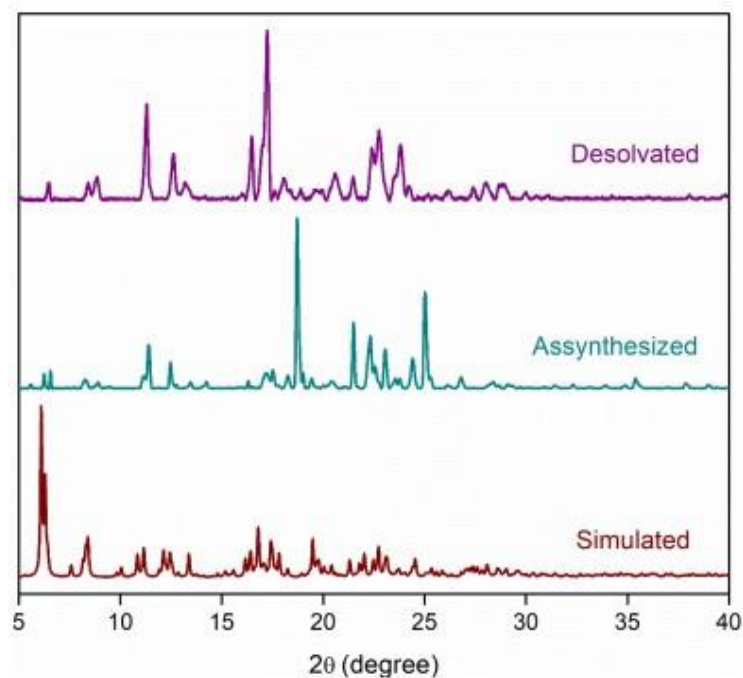
Appendix Figure 4.10: Position of 1,5-NDSA in 2D-sheet along crystallographic “b” axis (color: Light Gray- C, Blue- N, Red- O, Yellow- S, Green- Zn)



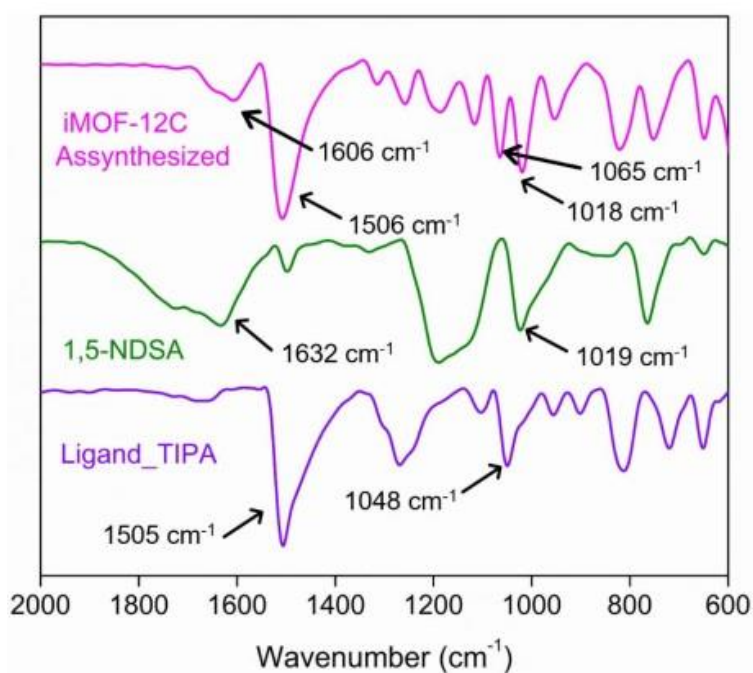
Appendix Figure 4.11: Position of 1,5-NDSA (color: green) in 2D-sheet along crystallographic “a” axis (Pale yellow: framework, Green: anions)



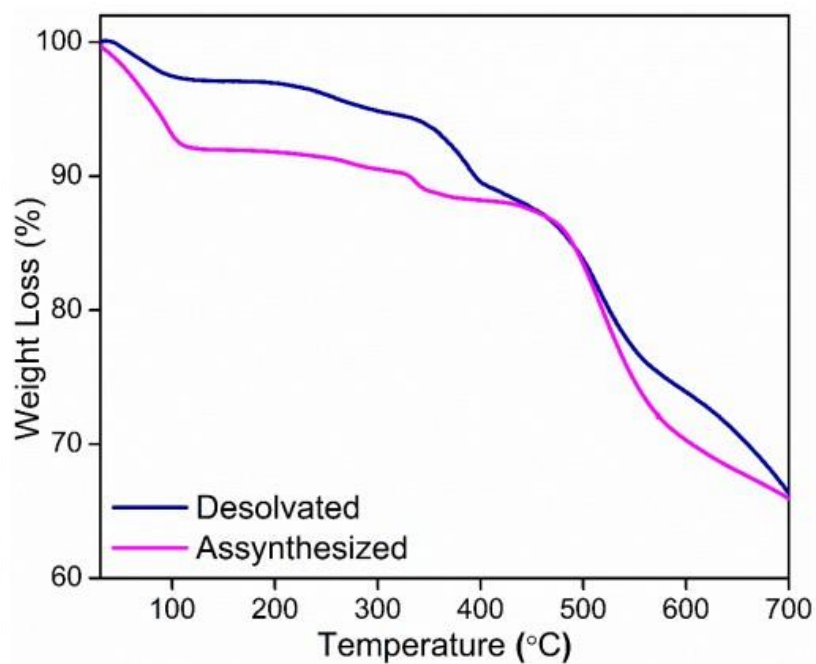
Appendix Figure 4.12: Powder X-ray diffraction patterns of simulated (blue) and assynthesized phase (violet)



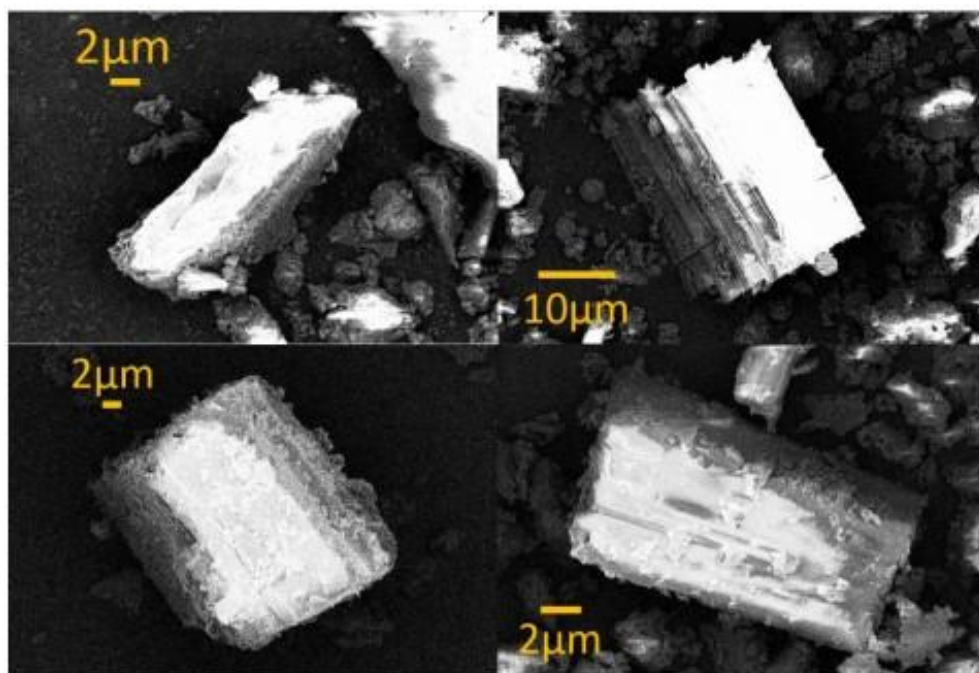
Appendix Figure 4.13: Powder X-ray diffraction patterns of simulated (wine), assynthesized phase (sea-green) and desolvated phase (violet) of iMOF-12C



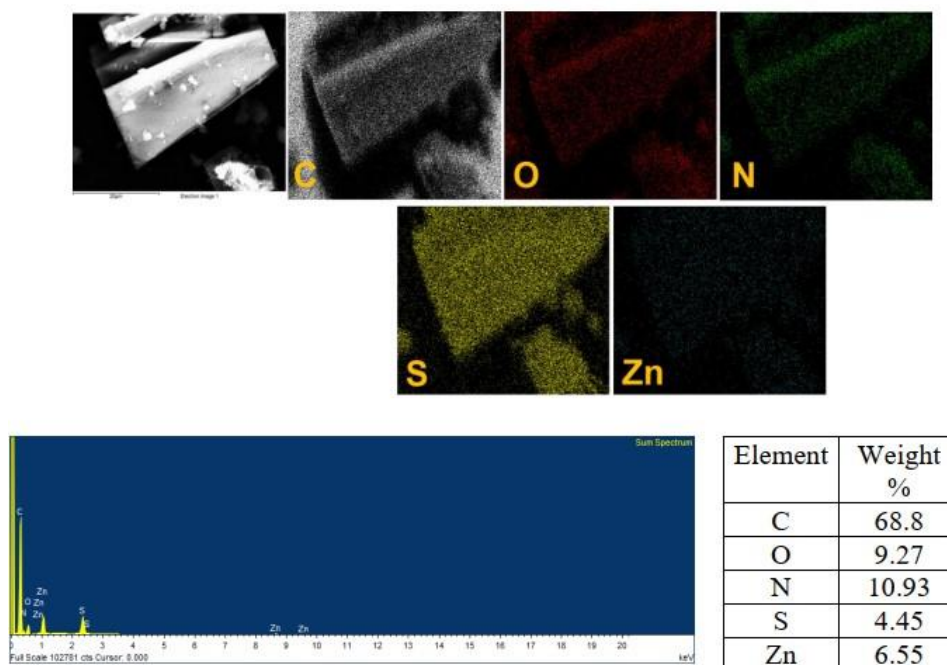
Appendix Figure 4.14: ATR of Ligand (violet), 1,5-Naphthalenedisulfonic acid (green) and iMOF-12C (pink)



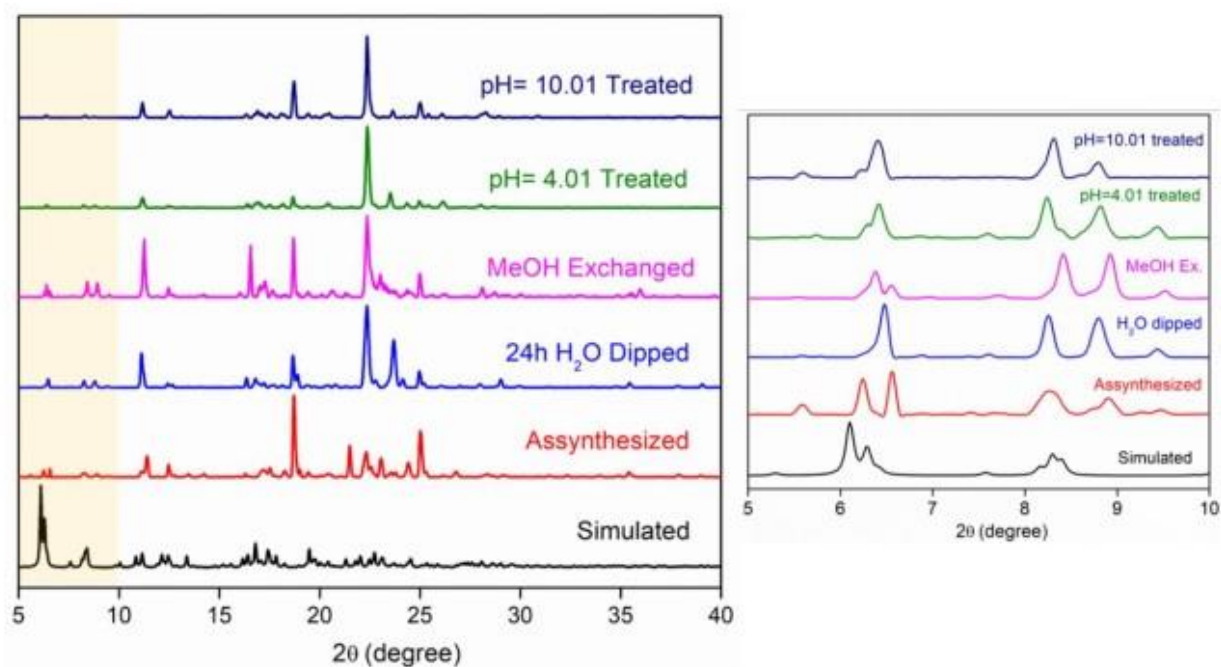
Appendix Figure 4.15: TGA profile of iMOF-12C of assynthesized phase (blue) and desolvated phase (violet)



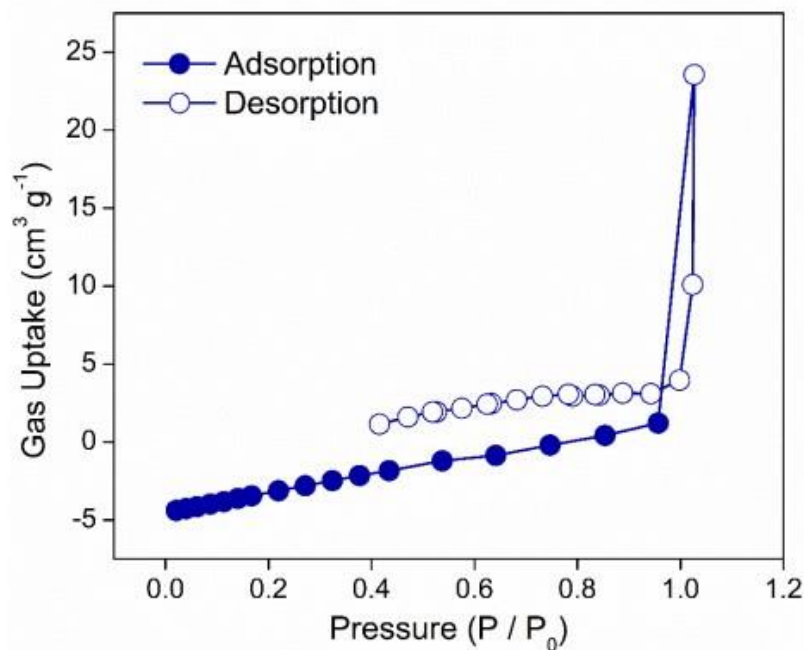
Appendix Figure 4.16: FESEM images of assynthesized iMOF-12C



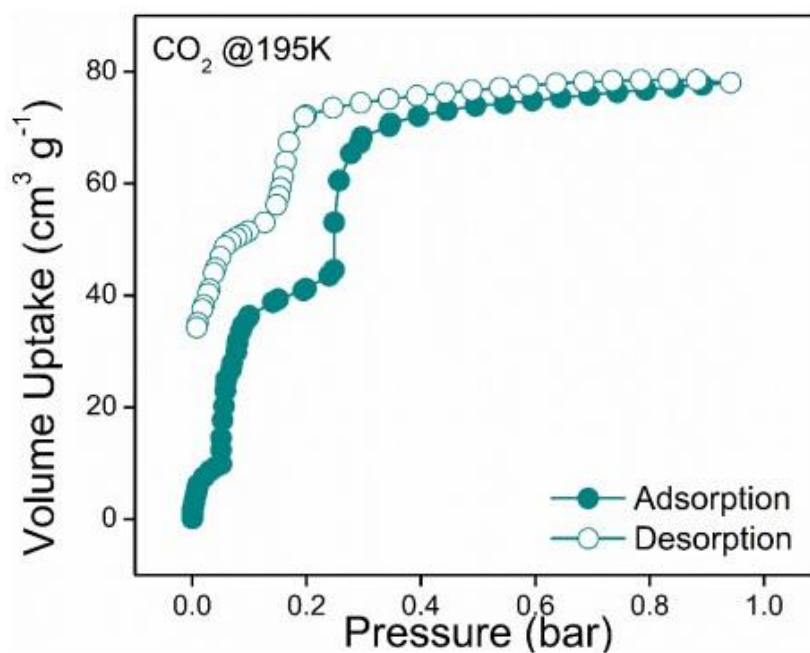
Appendix Figure 4.17: EDX analysis and Elemental mapping of assynthesized iMOF- 12C



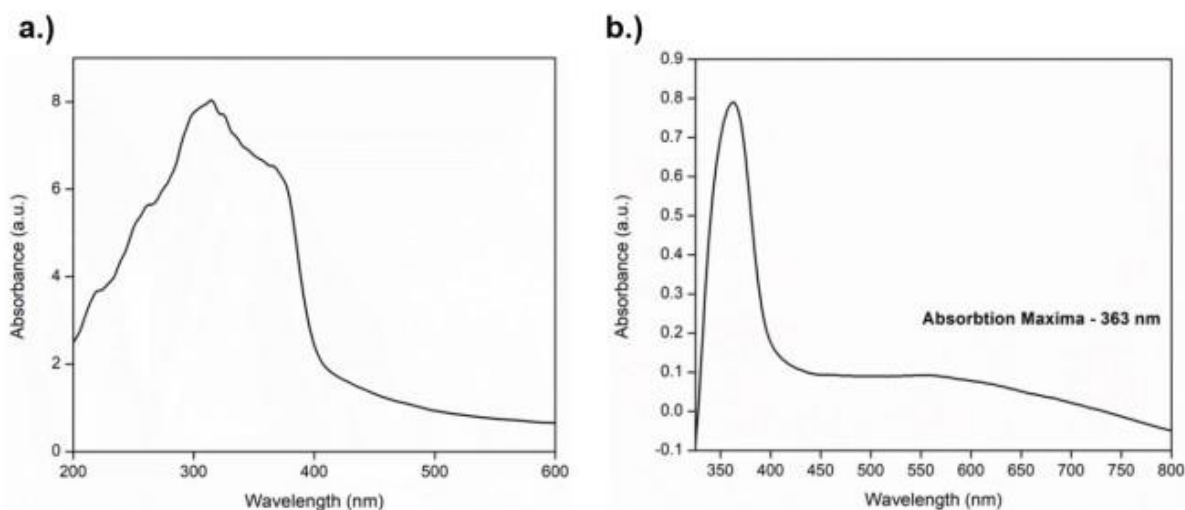
Appendix Figure 4.18: Powder X-ray diffraction patterns of iMOF-12C substantiating hydrolytically stability (Inset: Low angle region)



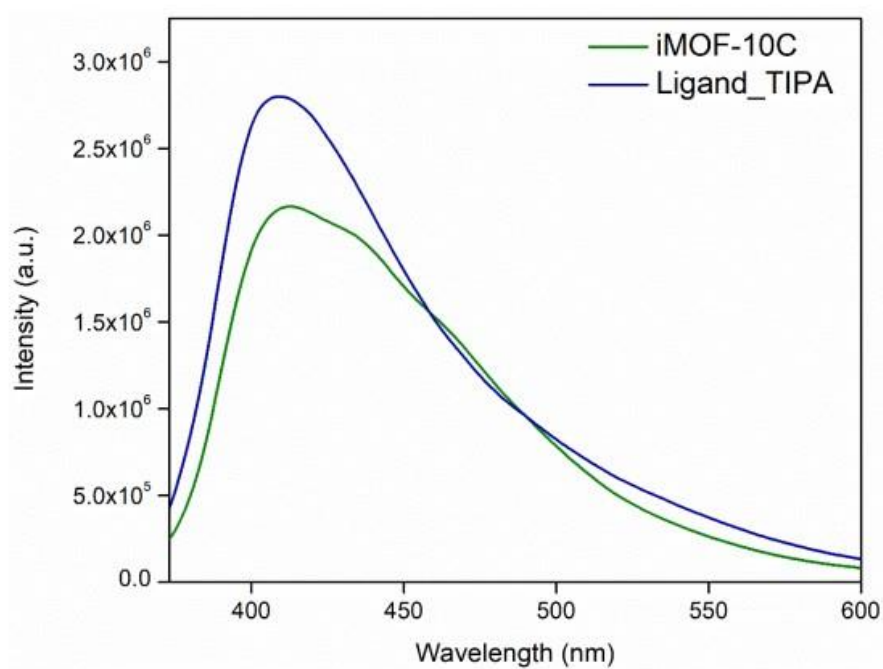
Appendix Figure 4.19: N₂ Adsorption curve of iMOF-12C at 77K



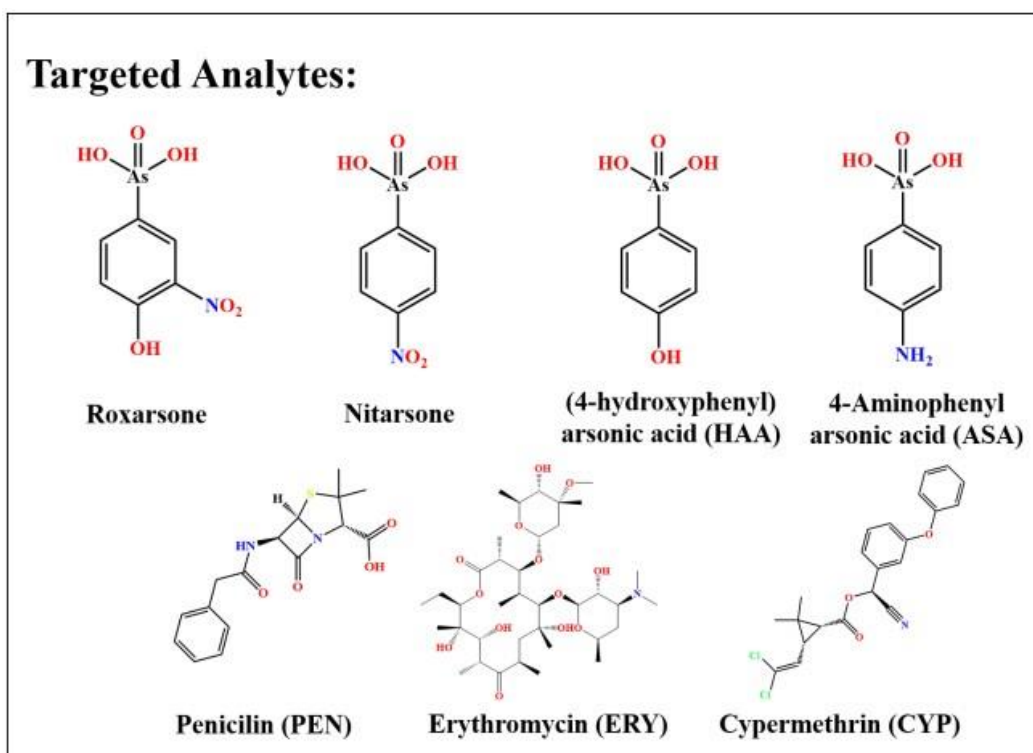
Appendix Figure 4.20: CO₂ Adsorption curve of iMOF-12C at 195K



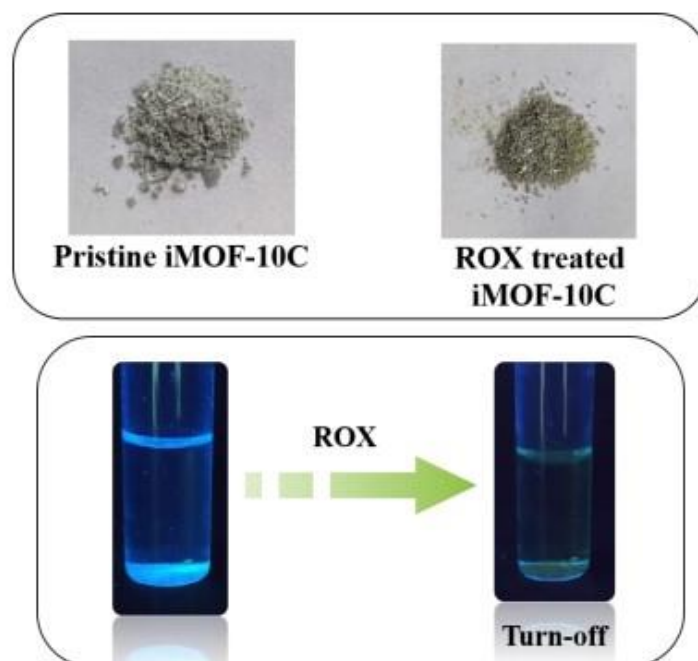
Appendix Figure 4.21: Solid state UV-Vis spectra of a) Ligand (TIPA) and b) Assynthesized iMOF-12C



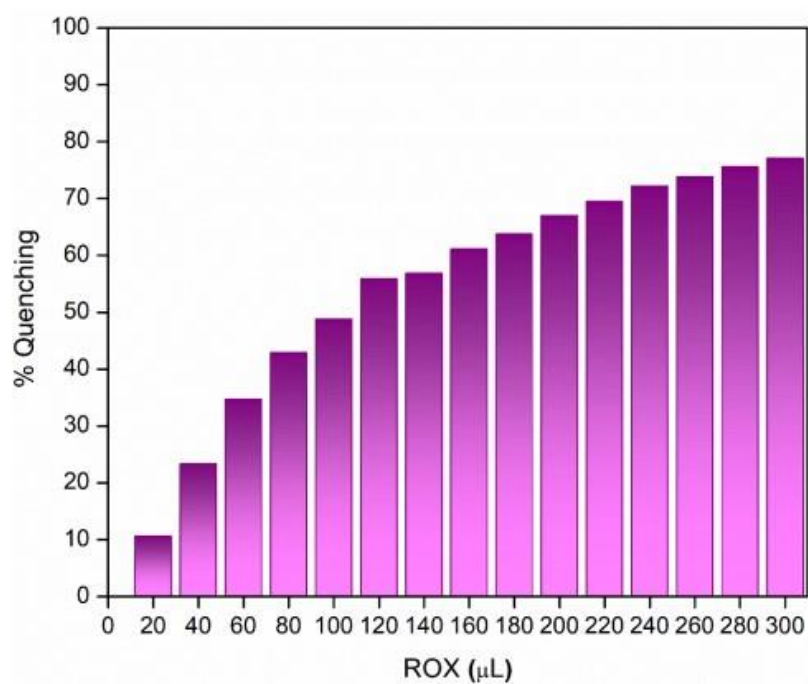
Appendix Figure 4.22: Solid state Fluorescence spectra of Ligand (blue) and Assynthesized iMOF-12C (green)



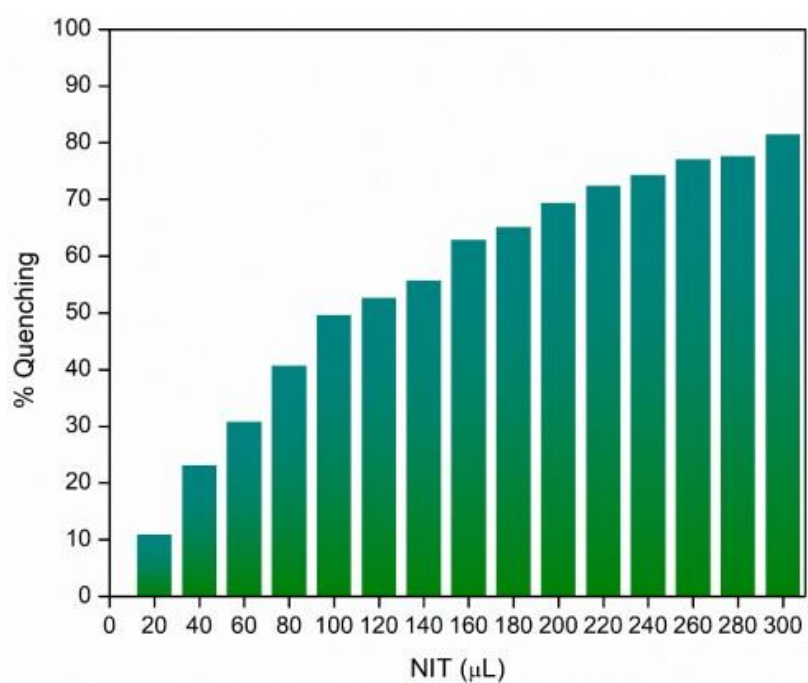
Appendix Figure 4.23: Molecular structure of the Analytes



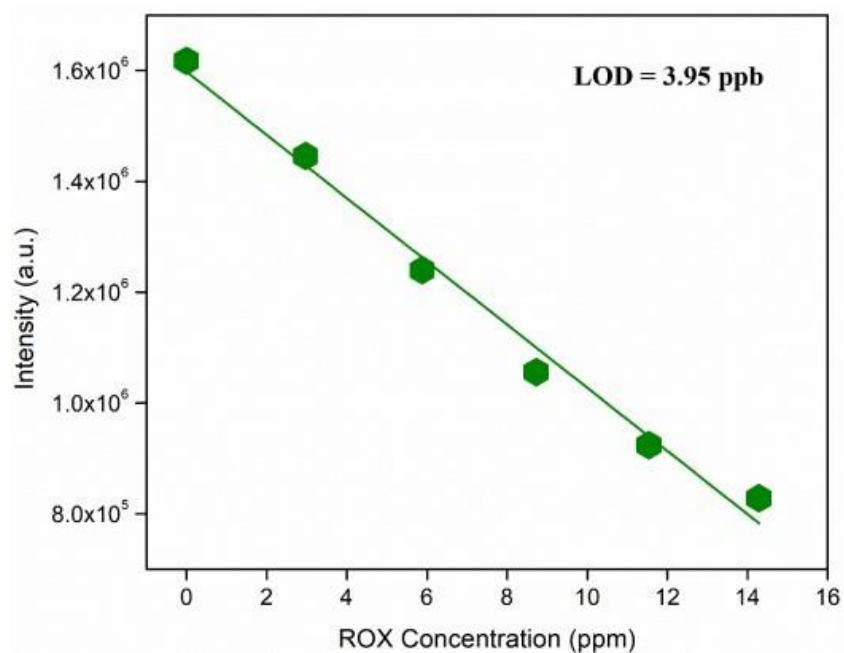
Appendix Figure 4.24: Picture of assynthesized and after ROX treated iMOF-12C (top). Assynthesized and ROX added iMOF-12C in aqueous medium under UV light (bottom)



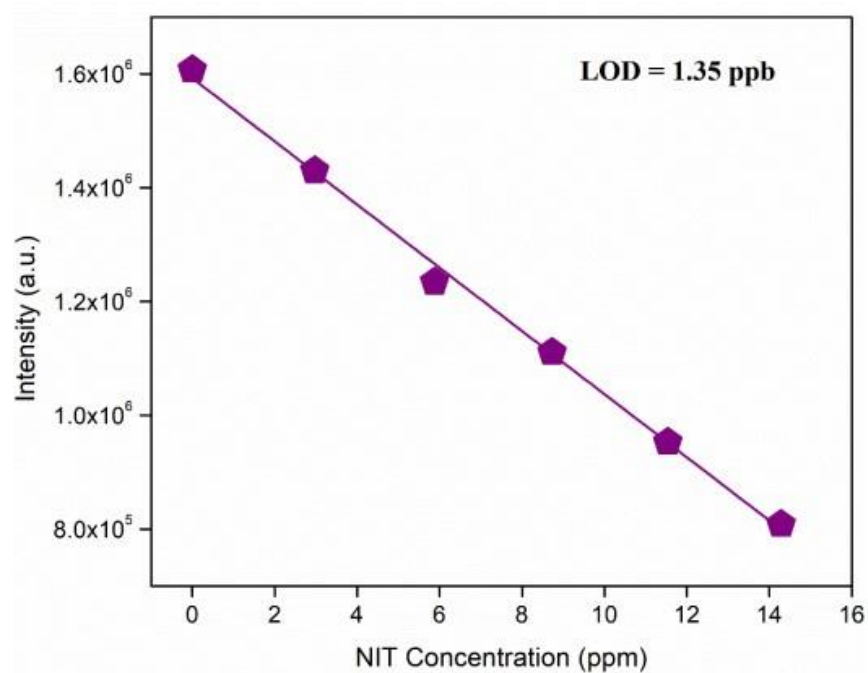
Appendix Figure 4.25: Increase in Quenching Percentage after incremental addition of 300 ppm ROX in iMOF-12C



Appendix Figure 4.26: Increase in Quenching Percentage after incremental addition of 300 ppm NIT in iMOF-12C



Appendix Figure 4.27: Limit of detection (LOD) for ROX of iMOF-12C



Appendix Figure 4.28: Limit of detection (LOD) for NIT of iMOF-12C

Blank Reading	Fluorescence Intensity
Reading 1	1617599.55
Reading 2	1617800.134
Reading 3	1617648.07
Reading 4	1617696.60
Reading 5	1617712.78
Standard Deviation (σ)	75.201

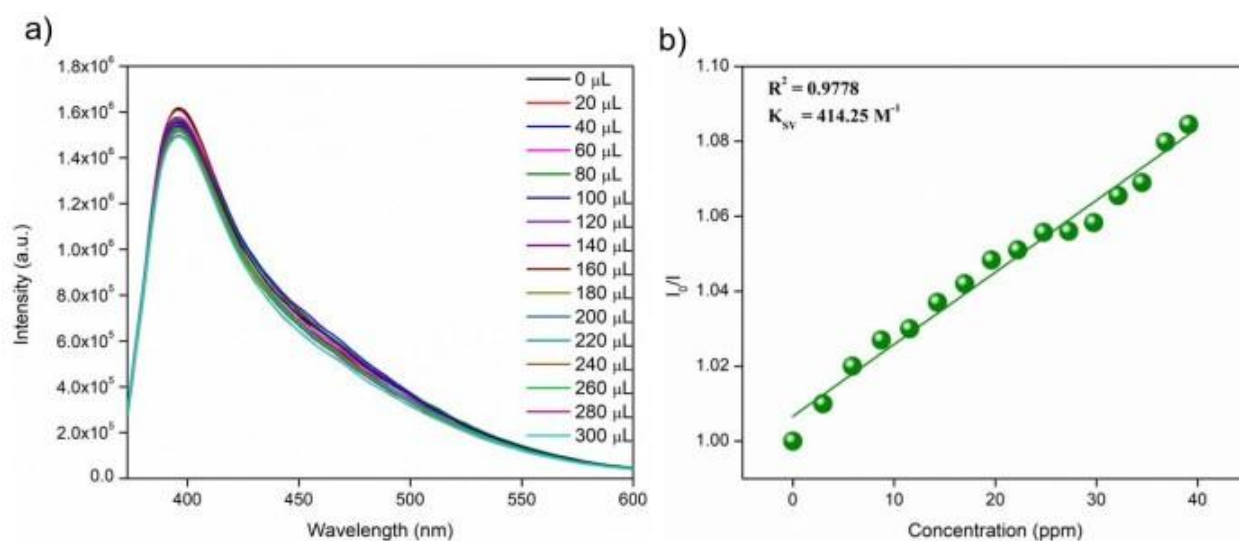
Appendix Table 4.1: Standard deviation calculation

Slope from graph (m)	57047.452 ppm ⁻¹
Detection Limit ($3\sigma/m$)	ROX = 3.95 ppb
	NIT = 1.35 ppb

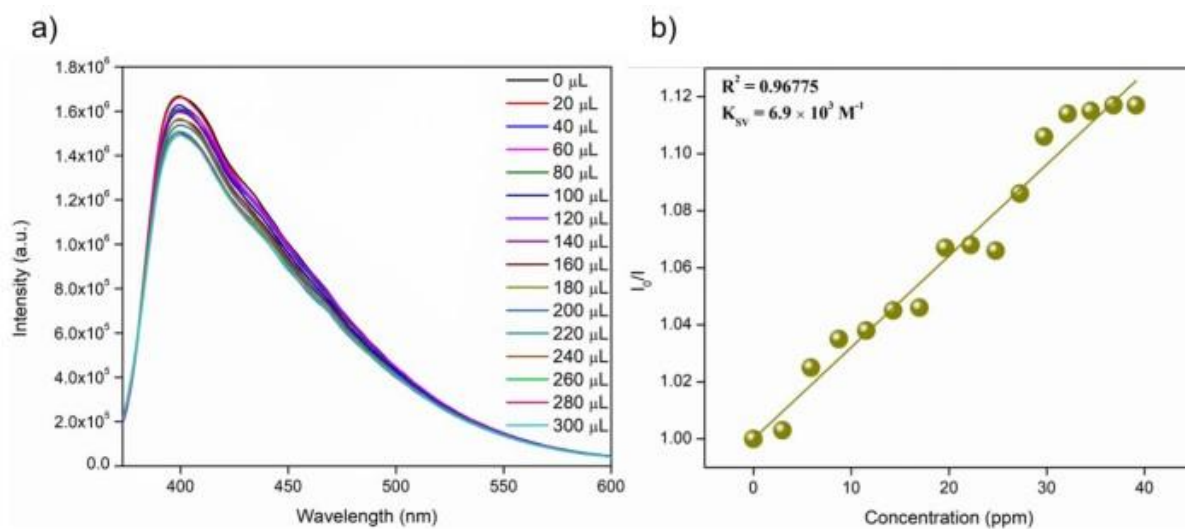
Appendix Table 4.2: Limit of detection (LOD) calculation

Material	LOD for ROX	LOD for NIT	Reference
BUT-18	15.7 ppb	32.2 ppb	7
BUT-19	13.5 ppb	13.3 ppb	7
AO-COF-ben	1.7097 ppb	NA	8
AO-COF-tri	3.235 ppb	NA	8
HOF-22	NA	NA	9
iMOF-12C	3.95 ppb	1.35 ppb	This work

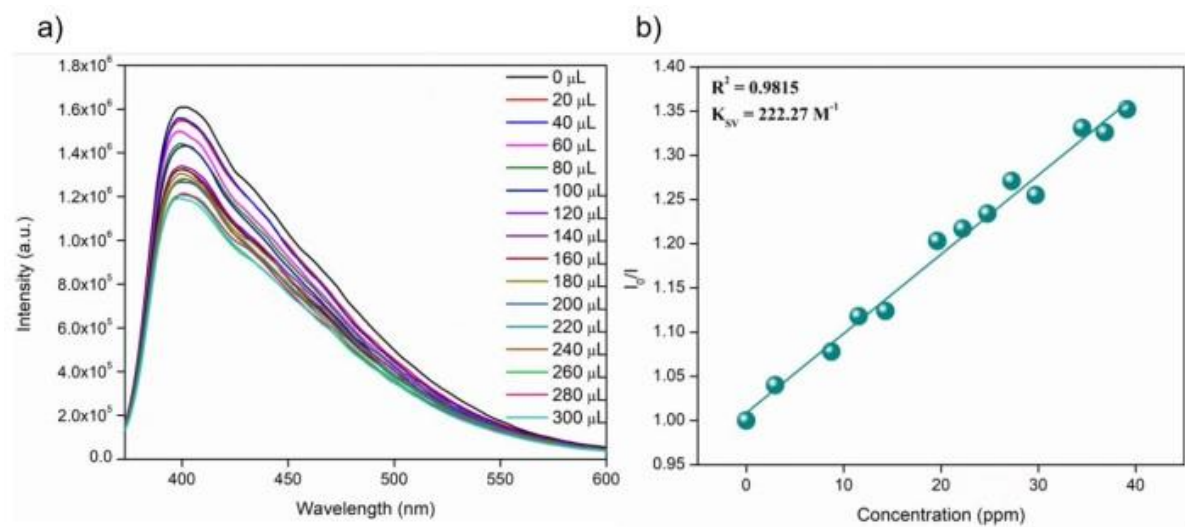
Appendix Table 4.3: Limit of detection (LOD) table of reported porous compound



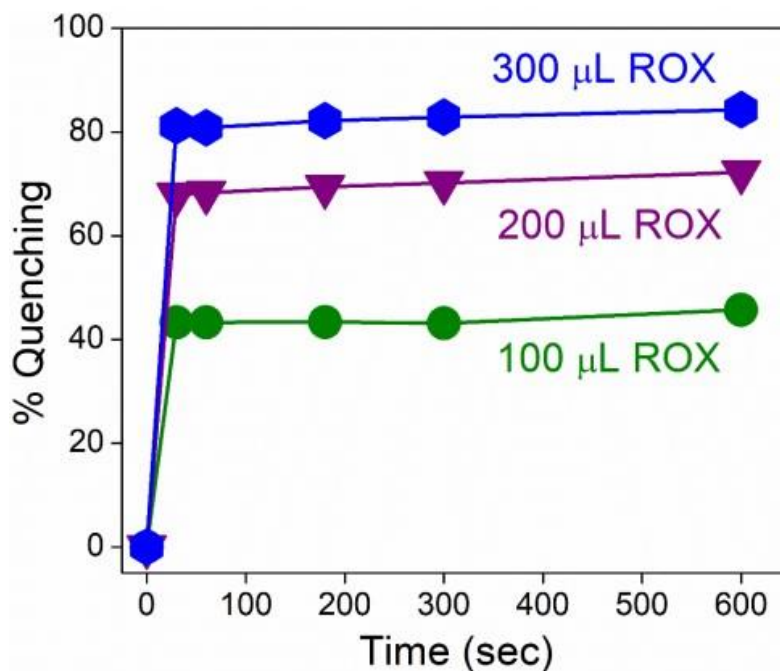
Appendix Figure 4.29: PL Studies of iMOF-12C with incremental addition of HAA a) Titration b) K_{sv} plot



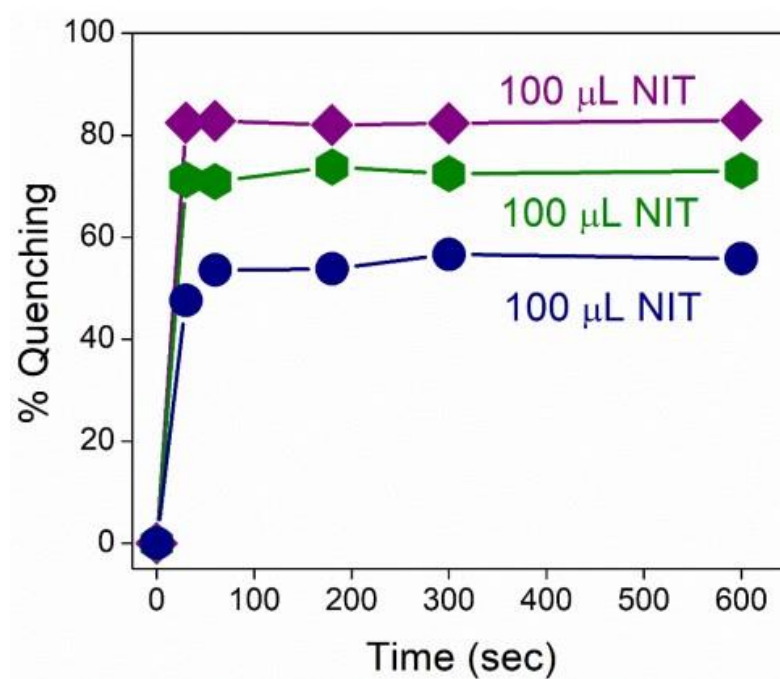
Appendix Figure 4.30: PL Studies of iMOF-12C with incremental addition of ASA a) Titration b) K_{SV} plot



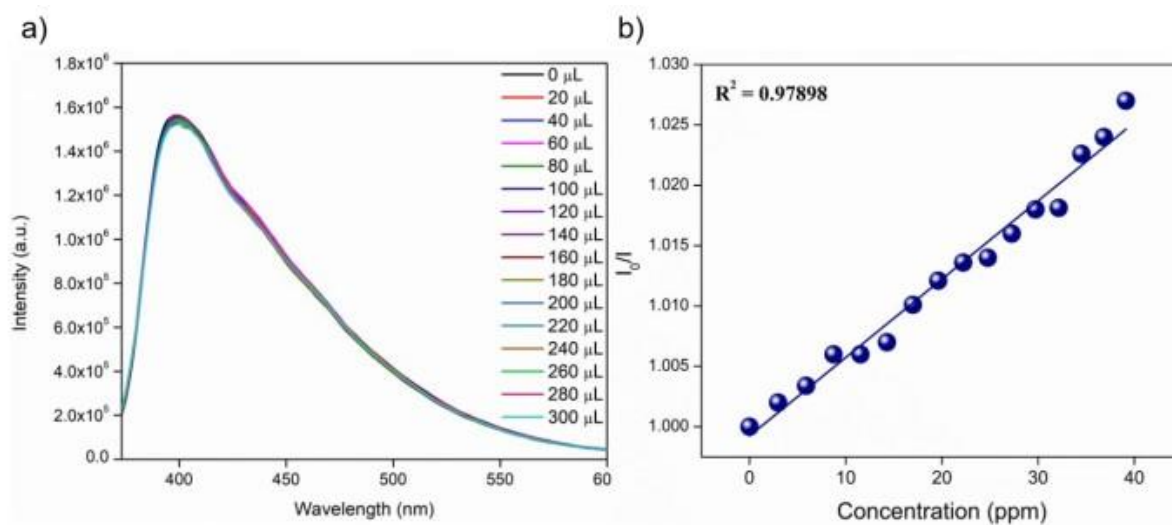
Appendix Figure 4.31: PL Studies of iMOF-12C with incremental addition of ASA a) Titration b) K_{SV} plot



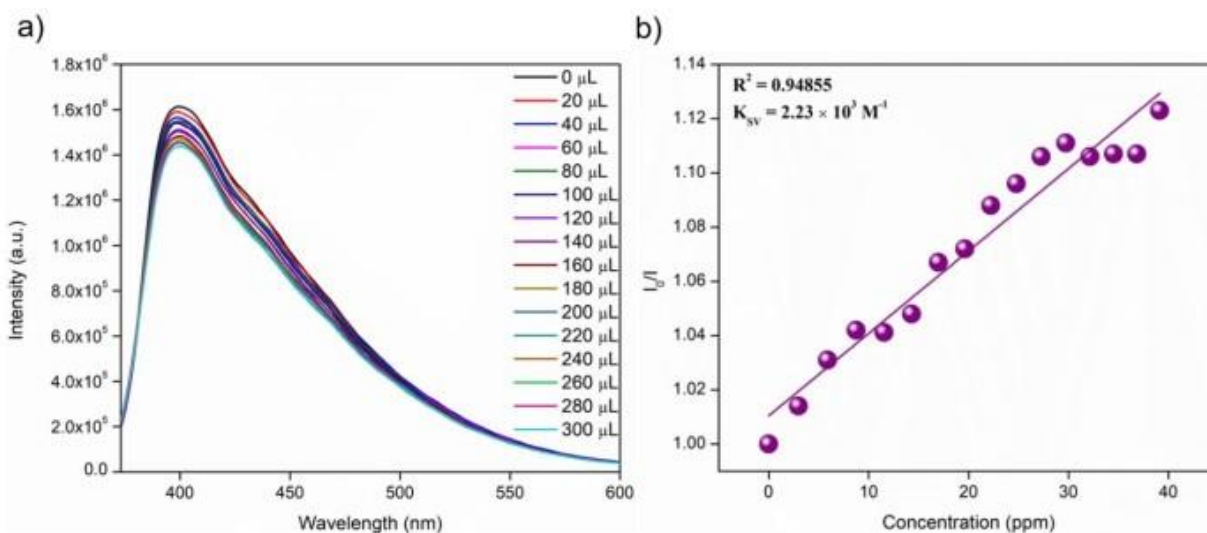
Appendix Figure 4.32: Fluorescence kinetics studies of iMOF-12C in presence of ROX



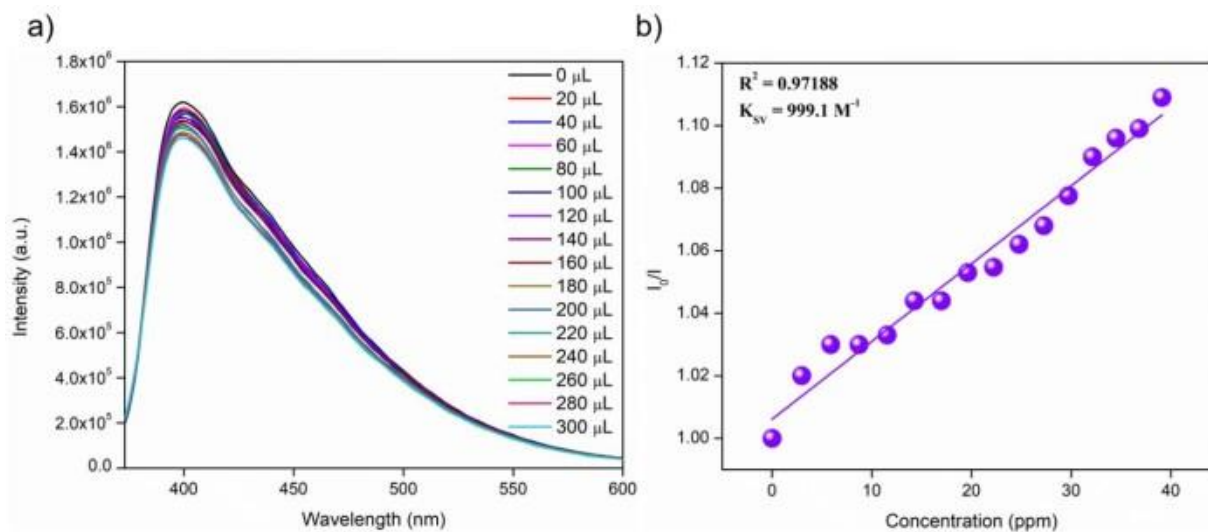
Appendix Figure 4.33: Fluorescence kinetics studies of iMOF-12C in presence of NIT



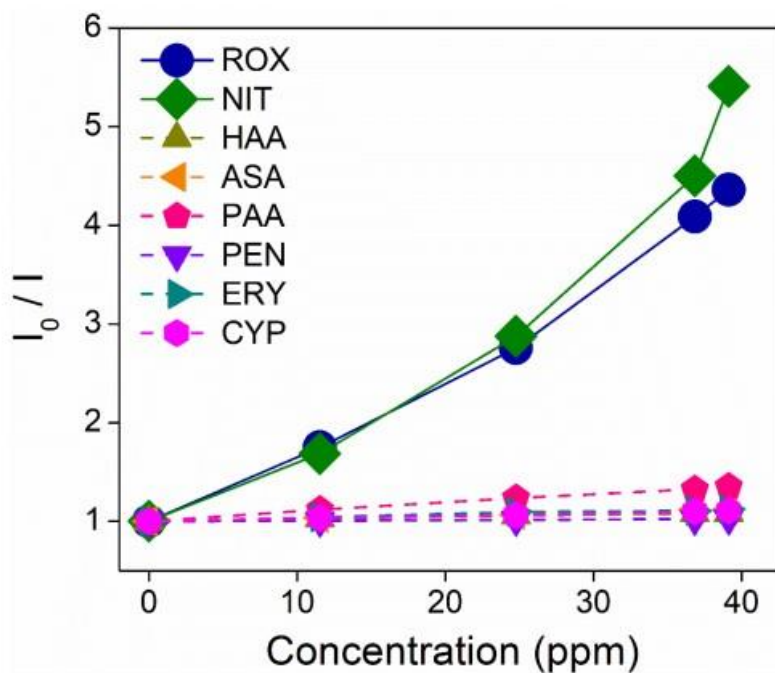
Appendix Figure 4.34: PL Studies of iMOF-12C with incremental addition of PEN a) Titration b) K_{sv} plot



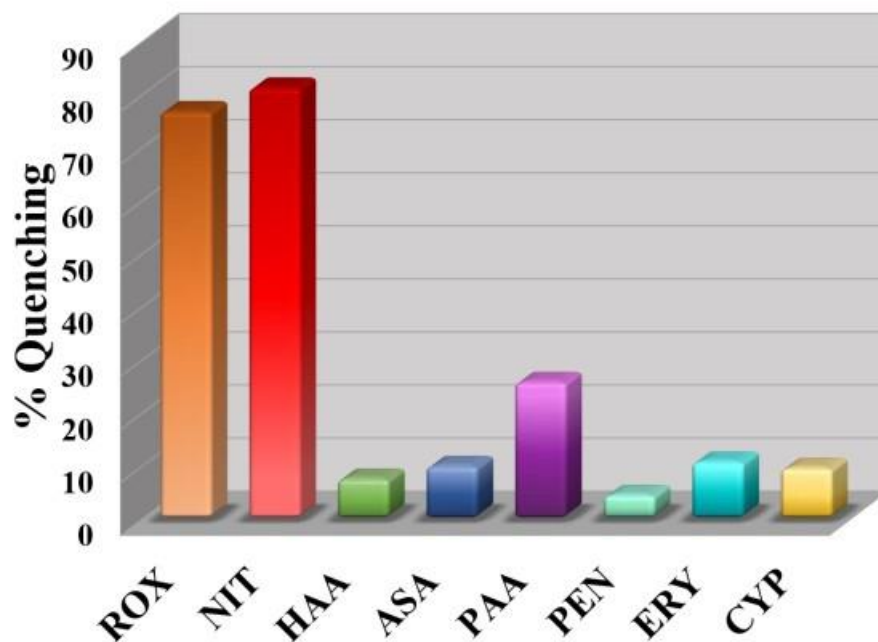
Appendix Figure 4.35: PL Studies of iMOF-12C with incremental addition of ERY a) Titration b) K_{sv} plot



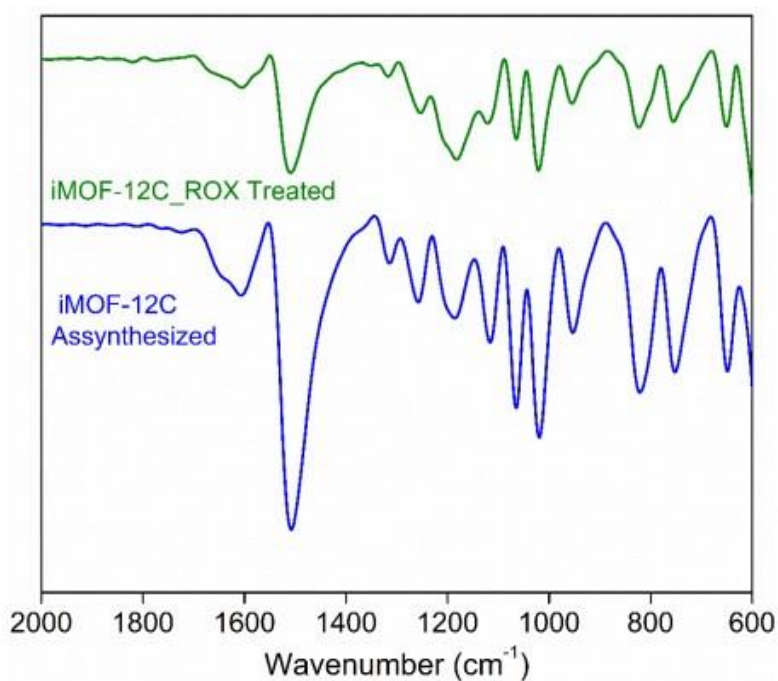
Appendix Figure 4.36: PL Studies of iMOF-12C with incremental addition of CYP a) Titration b) K_{sv} plot.



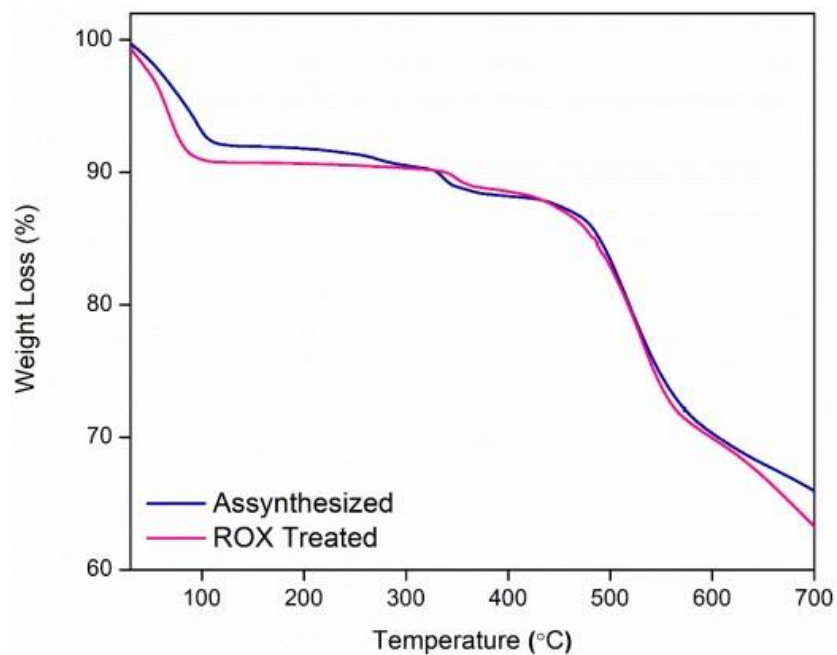
Appendix Figure 4.37: SV-plot comparison of iMOF-12C in presence of analytes



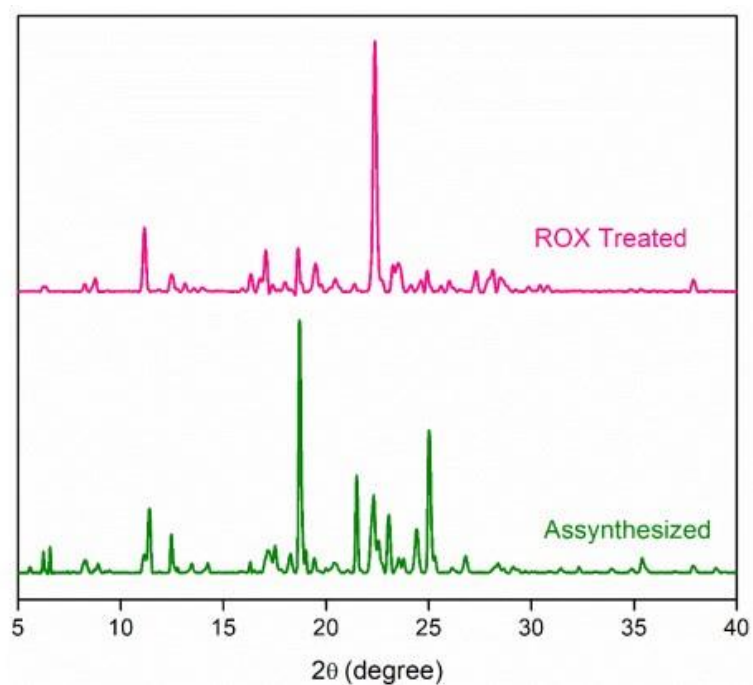
Appendix Figure 4.38: Quenching percentage of iMOF-12C in presence of different analytes



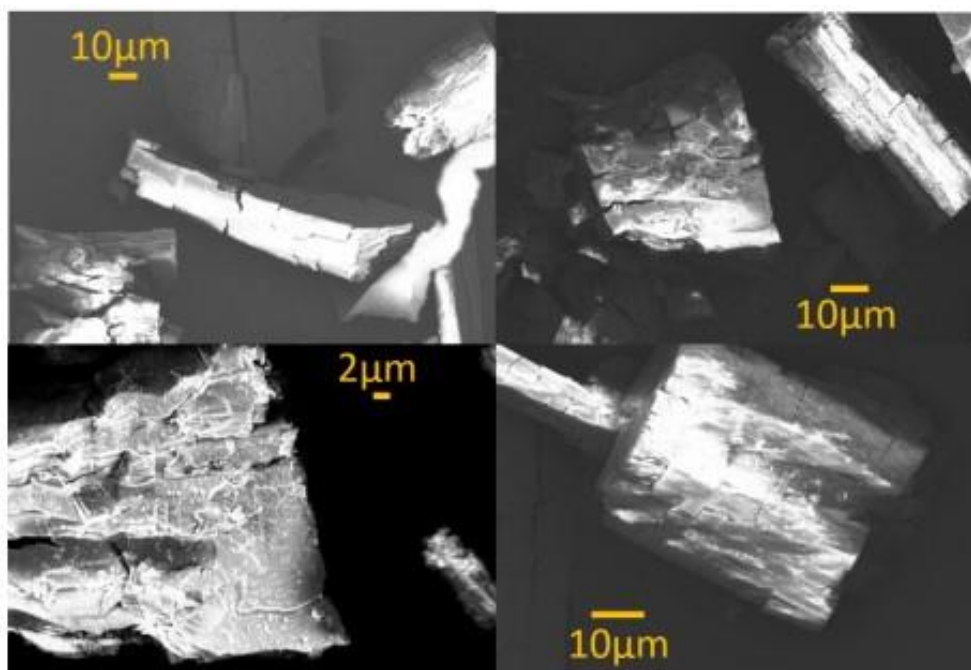
Appendix Figure 4.39: FT-IR spectra of iMOF-12C after ROX treatment



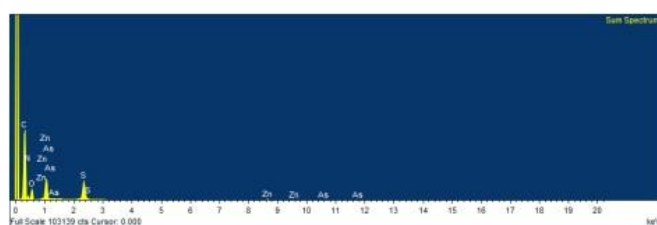
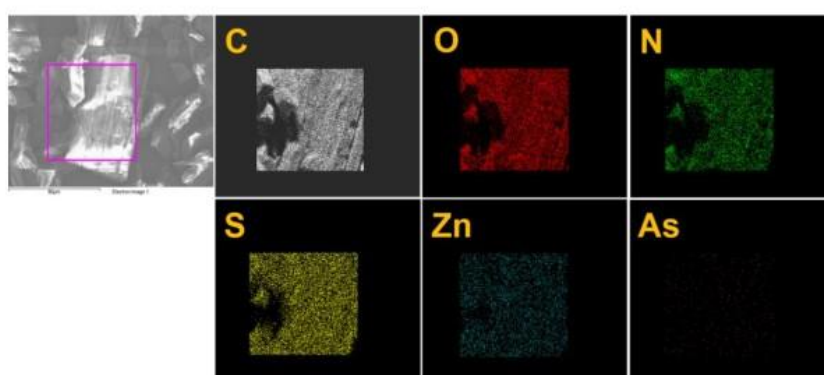
Appendix Figure 4.40: TGA spectra of iMOF-12C after ROX treatment



Appendix Figure 4.41: PXRD of iMOF-12C after ROX treatment

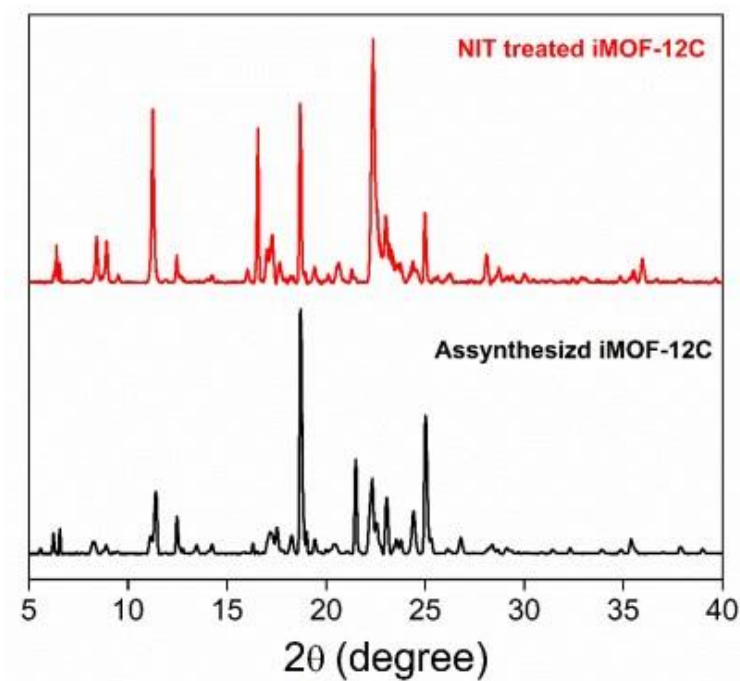


Appendix Figure 4.42: FESEM images of iMOF-12C after ROX treatment

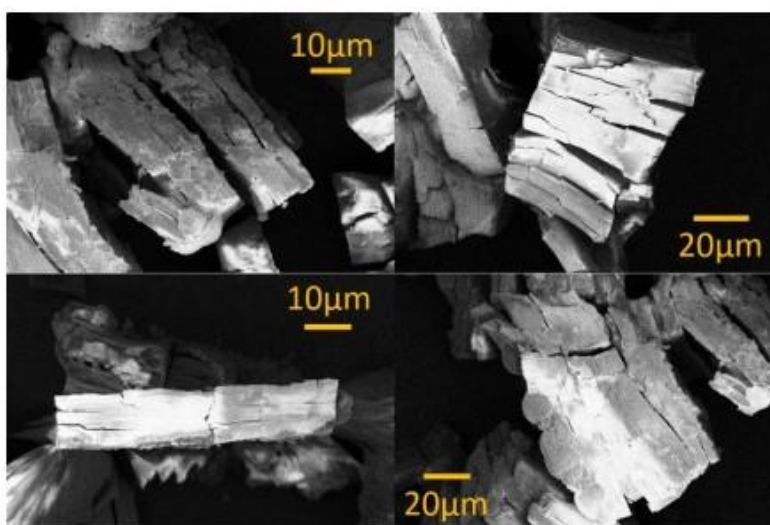


Element	Weight %
C	58.01
O	13.44
N	13.70
S	5.58
Zn	9.09
As	0.18

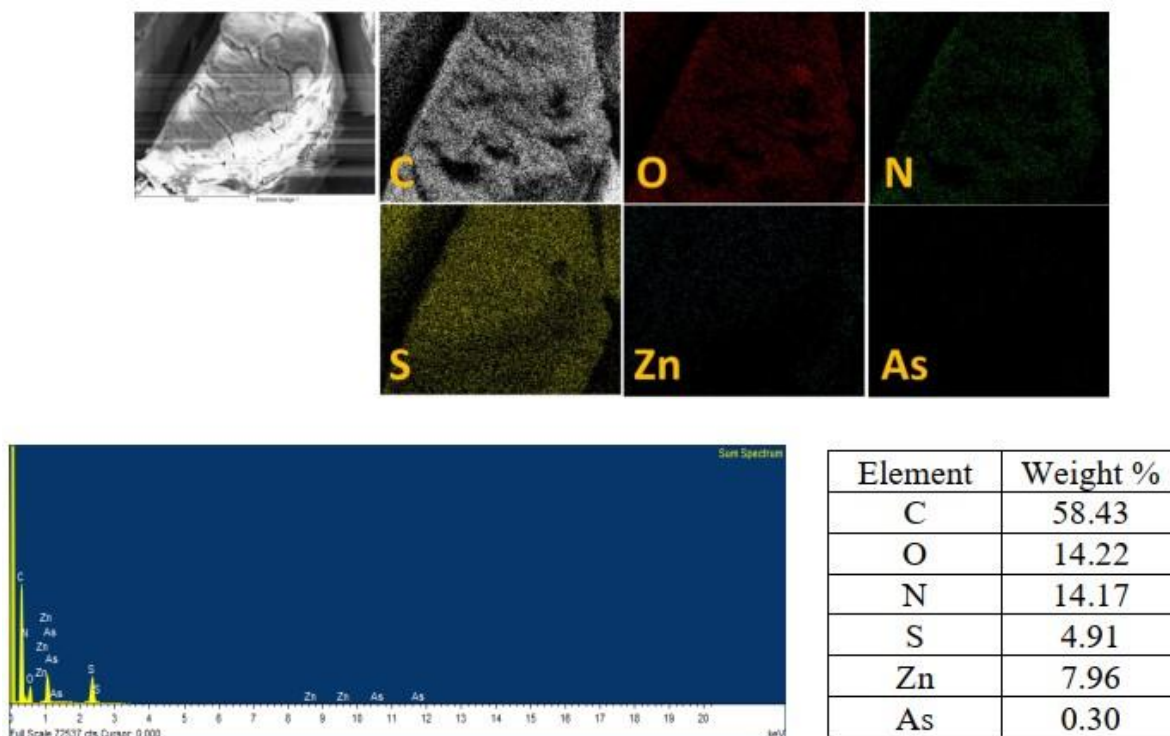
Appendix Figure 4.43: EDS and Mapping of iMOF-12C after ROX treatment



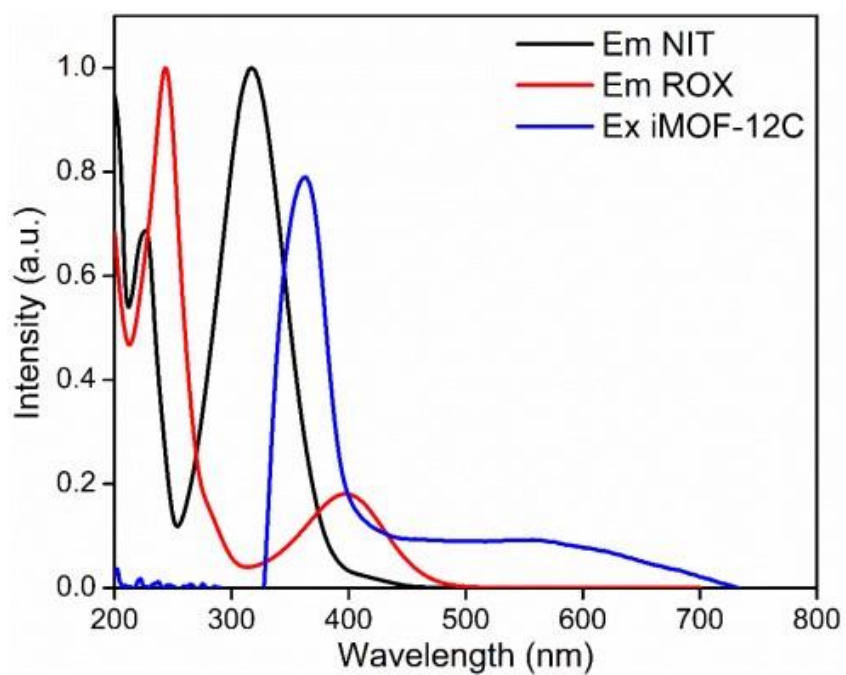
Appendix Figure 4.44: PXRD of iMOF-12C after NIT treatment



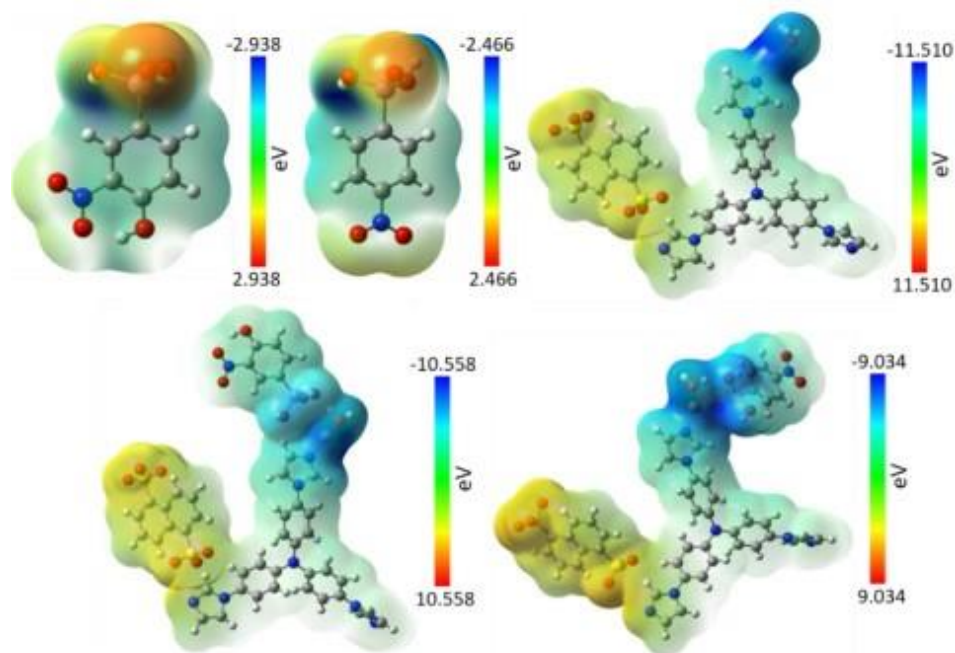
Appendix Figure 4.45: FESEM images of iMOF-12C after NIT treatment



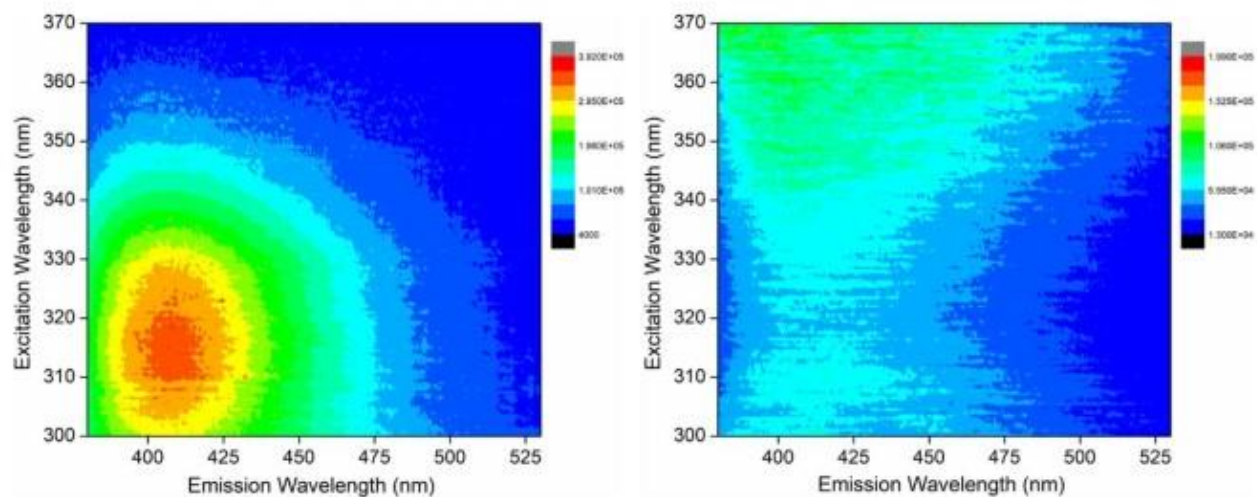
Appendix Figure 4.46: EDS and Mapping of iMOF-12C after NIT treatment



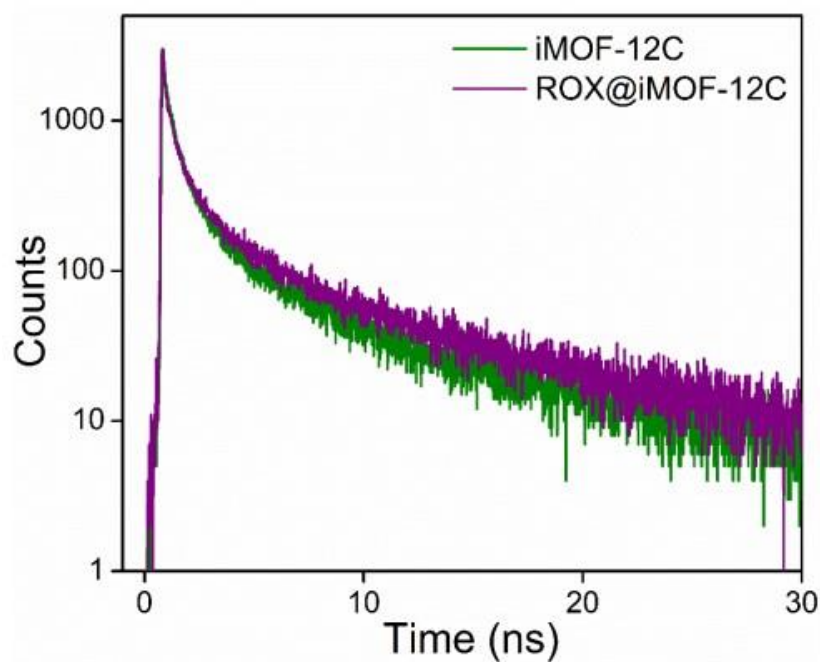
Appendix Figure 4.47: Excitation wavelength of iMOF-12C and absorption spectra of ROX and NIT



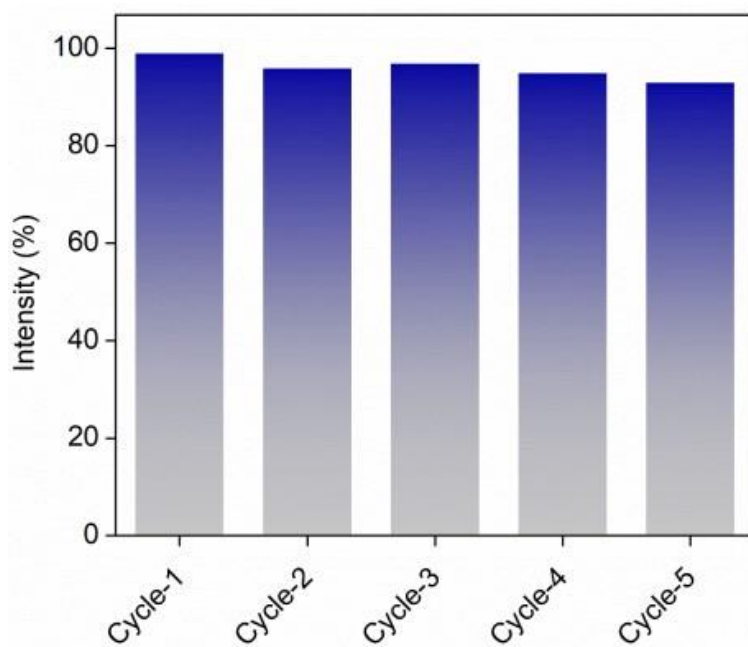
Appendix Figure 4.48: ESP of ROX, NIT, iMOF-12C, ROX@iMOF-12C and NIT@iMOF-12C



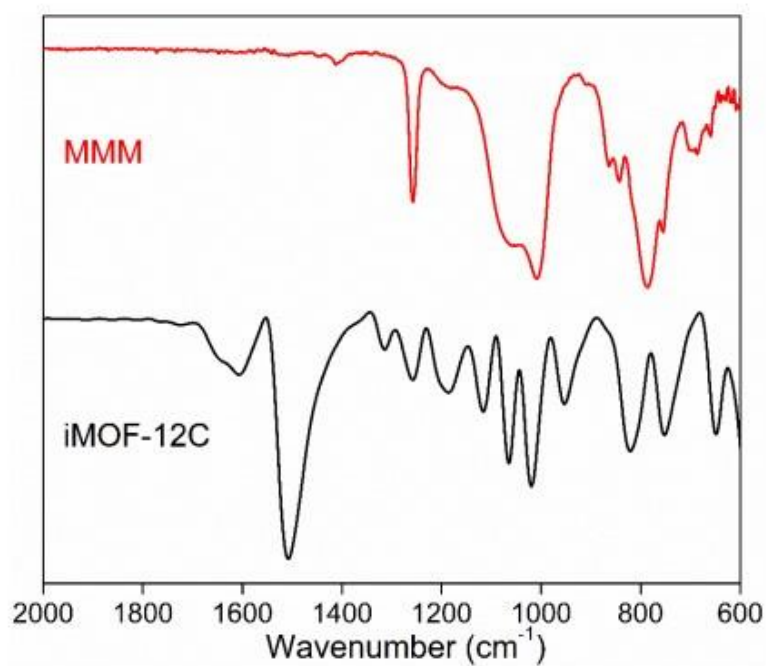
Appendix Figure 4.49: PLE spectrum of Pristine iMOF-12C in aqueous medium (left) and after addition (right) of 300 ppm 300 μ L NIT respectively



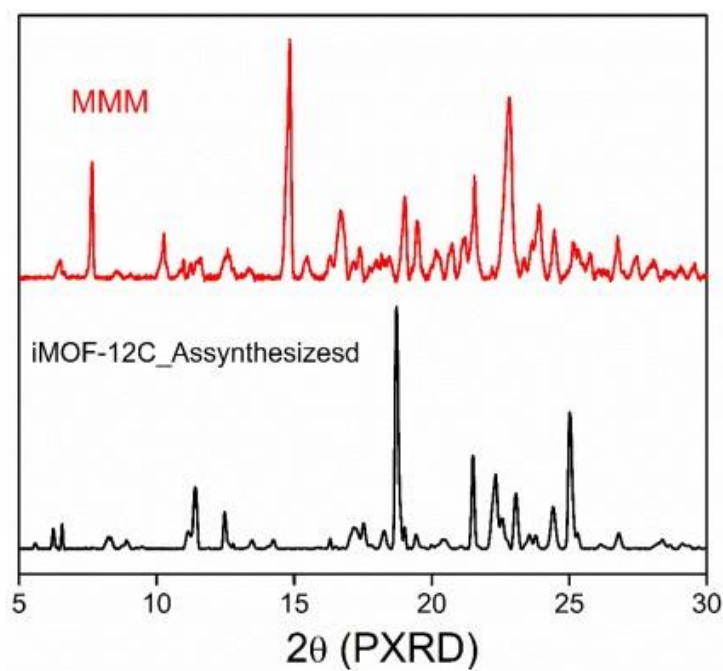
Appendix Figure 4.50: The luminescence lifetime decay profile of iMOF-12C before and after treatment of ROX aq. Solution



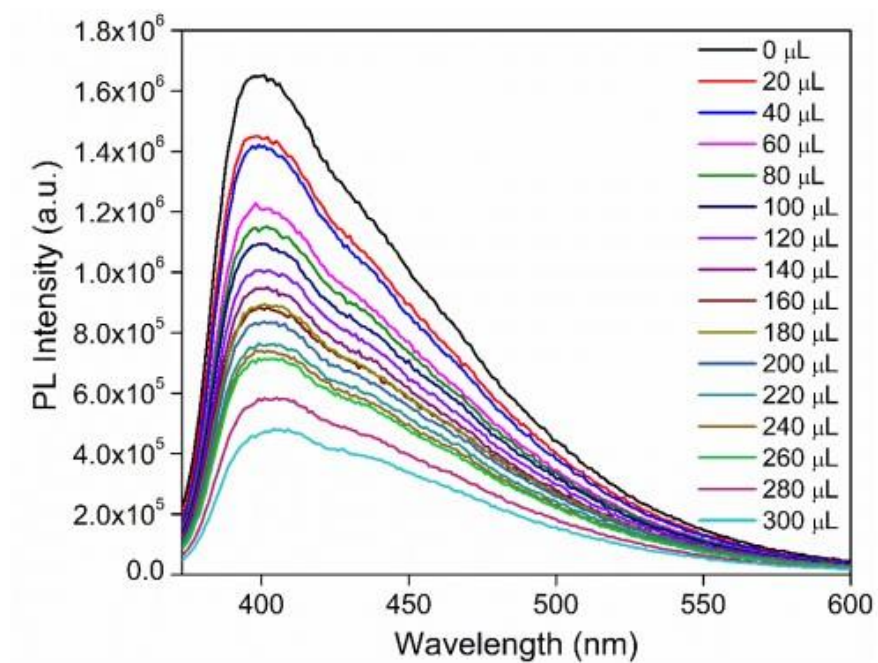
Appendix Figure 4.51: Recyclability of iMOF-12C towards NIT detection



Appendix Figure 4.52: FT-IR spectra of iMOF-12C and MMM fabricated by iMOF-12C



Appendix Figure 4.53: PXRD of iMOF-12C and MMM fabricated by iMOF-12C



Appendix Figure 4.54: PL Studies of iMOF-12C with incremental addition of ROX in Ground Water

Table S4. Crystal data and structure refinement for iMOF-12C.

Identification code	iMOF-12C	
Empirical formula	C ₁₄₄ H ₁₂₀ N ₃₀ O ₃₃ S ₆ Zn ₄	
Formula weight	3252.53	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 16.6819(16) Å	a = 90°
	b = 16.3118(17) Å	b = 91.873(3)°
	c = 27.527(3) Å	g = 90°
Volume	7486.3(13) Å ³	
Z	2	
Density (calculated)	1.443 Mg/m ³	
Absorption coefficient	0.802 mm ⁻¹	
F(000)	3348	
Crystal size	0.14 x 0.12 x 0.11 mm ³	
Theta range for data collection	1.937 to 28.385°.	
Index ranges	-22 ≤ h ≤ 18, -21 ≤ k ≤ 21, -36 ≤ l ≤ 36	
Reflections collected	171874	
Independent reflections	37063 [R(int) = 0.0644]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7457 and 0.6827	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	37063 / 1 / 1959	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0735, wR2 = 0.2013	
R indices (all data)	R1 = 0.1015, wR2 = 0.2209	
Absolute structure parameter	0.364(14)	
Largest diff. peak and hole	2.492 and -0.854 e.Å ⁻³	

4.6. Reference

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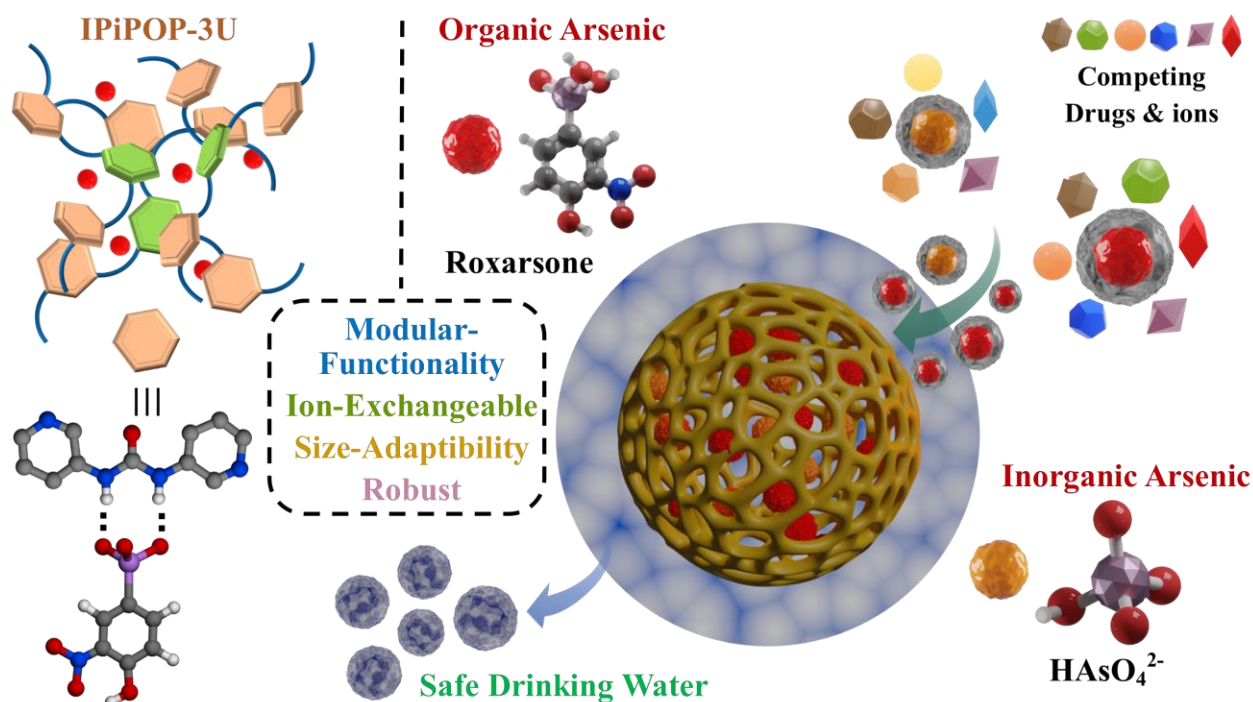
Chapter 5

A Chemically Robust Urea Tethered Adaptable Ionic Porous "Nanotrap": Ultrafast Organic and Inorganic Arsenic Water Decontamination

5.1 Introduction

The continued escalation of water pollution has come forth as an imminent threat to the global population and has spurt worldwide research.^{1, 2} Organic arsenic acids (OAAs), especially Roxarsone (ROX) have found their widespread usefulness in poultry industry as a potent feed additive to stimulate weight gain, control intestinal parasites, prevent dysentery as well as antibacterial agents.³ On the other hand, Arsenic (As), being a verified “class A” carcinogen to all forms of life, pose a direct threat to the global environment in the event of contamination.² Exposure to arsenic in the long-term bring about the genesis of arsenic poisoning leading to neurological disorders, cancer, cardiovascular disease, skin lesions, and even death to infants.⁴ Anticipatedly, researchers have put forward substantial efforts toward the detection and removal of arsenic from the environment. Having said that, majority of these works were zeroed in on inorganic arsenic while its organic congener has garnered less consideration.^{5, 6, 7}

The extensive usage of these organoarsenics invariably results in concomitant harm to the ecological environment. Additionally, when these water-soluble OAAs are introduced to the ambient environment, they can readily undergo abiotic and biotic process-driven biogeochemical transformation, subsequently converted into highly mobile and toxic inorganic arsenite (As [III]) and arsenate (As [V]), giving rise to augmented inorganic arsenic compounds in the habitat, polluting soil & groundwater and endangering human life (Appendix Figure 5.1-5.3).^{8, 9} Roxarsone (4-Hydroxy-3-nitrophenyl arsonic acid, known as ROX) is a typical representative aromatic organoarsenicals, which is hugely produced and extensively utilized as poultry feed additives.^{10, 11} There has been a significant increase in the quantity of ROX used in the feed additives over the past years. Howbeit, the overwhelming amount of ingested ROX in animals is scarcely adsorbed in tissues and excreted with manure reaching arsenic concentrations up to 1000 µg/kg, which is far beyond 0.5 ppm safety limit set by the World Health Organization (WHO)¹² and 10 ppb set by U.S. Environmental Protection Agency (EPA)¹³ Hence, it becomes pivotal to sequester and segregate soluble ROX before being converted to more harmful and highly toxic inorganic arsenic. For the past few years, research on organoarsenic compound segregation has mainly directed toward two kinds of techniques that include degradation (via advanced oxidation processes (AOPs) and adsorption.^{14, 15} Notwithstanding the fact that degradation technique usually avails high removal activity, the subsequently degradation products are often inorganic arsenic which may cause secondary pollution and should be carefully regulated and completely eliminated pertaining to environmental safety. To mitigate the abovementioned point at issue, selective and efficient trapping of organoarsenicals from water comes forth as a potent solution. To date, diverse materials featuring adsorption as the *modus operandi*, such as porous-carbon materials,¹⁶ multi-walled carbon nanotubes (MWCNTs),¹⁷ metal–organic frameworks (MOFs),¹⁸ chitosan-based copolymers¹⁹ etc. have been investigated towards removing ROX from water. However, often these



Scheme 5.1. Schematic diagram of selective ROX and HAsO_4^{2-} capture by IPiPOP-3U.

materials suffer from pitfalls such as sluggish sorption kinetics, inferior selectivity coupled with complex synthesis and suboptimal chemical stability. Moreover, most of the organoarsenic sequestration studies are focused on adsorption capacity at high concentrations (10-500 mg L⁻¹), overlooking that it actually exists at very low concentration (under 5 mg L⁻¹) in the environment. It is well established that the attractive forces at play between adsorbents and adsorbates, i.e., affinity plays a critical role in trapping pollutants at low concentrations.²⁰ Therefore, developing task-specific porous sorbents that offer the leverage of superior performance, straightforward synthesis and cost-effectiveness for efficient ROX removal is of priori necessity.

Under this backdrop, porous organic polymers (POPs), amorphous porous solids featuring purely organic skeleton have surfaced as intriguing materials attracting substantial research focus.²¹ High physiochemical stability in combination with the leverage of function-led material designability have made them potent sorbent materials toward water purification.^{22, 23} In addition, task-specific ionic POP can be easily synthesized by introducing (a.) meticulous choice of functional monomers for targeted analytes, (b.) flexible connecting units for size adaptability, (c.) ionicity for efficient ion exchange process.²⁴ Based on the above considerations, we envisioned that immobilizing functional “nano-traps” throughout a porous polymer matrix can bring about the culmination of a potent adsorbent targeted for ROX clean up. Herein, we report straightforward construction of a cationic porous organic polymer (IPiPOP-3U) bearing urea functionality displaying exceptional ROX segregation efficiency in terms of both kinetics and uptake

capacity. ROX capture efficiency was further verified with dynamic flow-through detoxification as well as trace amount capture studies. Additionally, IPiPOP-3U illustrated unaltered efficiency when tested for the inorganic counterpart, i.e., arsenate (As [V]) while simultaneous removal of ROX and HAsO_4^{2-} was also achieved (Scheme 5.1). The adsorption process was disseminated through a combination of theoretical density functional theory (DFT) studies, Molecular dynamics (MD) simulation and extended X-ray absorption fine structure (EXAFS) study.

5.2 Experimental

5.2.1. Materials

Materials used in this work as followings: 3-aminopyridine, 1,1'-carboxyldiimidazole (CDI), (4-Hydroxy-3-nitrophenyl)arsonic acid (Roxarsone, ROX), (4-Aminophenyl)arsonic acid (Arsinilic Acid, ASA), 4-hydroxyphenylarsonic acid (HAA), (4-Nitrophenyl)arsonic acid (Nitarsonic, NIT), Penicillin G Potassium Salt (PEN), Erythromycin (ERY), Sodium arsenate (Na_2HAsO_4), Sodium Nitrate (NaNO_3), Sodium Sulphate (Na_2SO_4), Sodium Chloride (NaCl), Sodium Phosphate (Na_3PO_4), Sodium Perchlorate (NaClO_4), Tetrahydrofuran (THF), N-Methyl-2-pyrrolidone (NMP). All the reagents, starting materials and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals, Alfa asar, Spectrochem, Rankem Chemicals depending on their availability and used without further purification. All Arsenic containing compounds and salt are toxic in nature and proper protective gear (masks, gloves) is always to be used.

5.2.2. Synthesis.

5.2.2.1. Synthesis of Monomer (1,3-di(pyridin-3-yl)urea) (L1): 3-aminopyridine (0.75 g, 7.95 mM) and 1,1'-carbonyldiimidazole (CDI) (0.72 g, 4.45 mM) was taken in a 100 mL R. B. and 40 mL of dry THF was added to it. Then the reaction mixture was refluxed for 48 hours. After the completion of the reaction, the reaction mixture was cooled down to room temperature and added to the ice-cold water. The white precipitate was filtered and dried to get the Ligand L2. $^1\text{H-NMR}$ (400 MHz, CD_3OD , 25°C , TMS), δ (in ppm): 8.63 (s, 2H, ArH), 8.2 (d, 2H, $J = 8$ Hz, ArH), 8.05 (m, 2H, ArH), 7.39 (s, H, Ali-H). (Appendix Scheme 5.1)

5.2.2.2. Synthesis of IPiPOP-3U: 1,3-di(pyridin-3-yl)urea (L1) (3 mM, 650 mg, 3 eqv.) and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (L2) (2 mM, 1.176 g, 2 eqv.) and was taken in a 100 mL round bottom flask with 40 mL NMP as solvent. The reaction mixture was stirred for 72 hours at 80°C in N_2 atmosphere. After completion of the reaction the pale-yellow color precipitate was filtered through vacuum filtration and wash thoroughly with different solvent like DMF, DMSO, THF, EtOH, MeOH to remove the unreacted monomer and different oligomers. After that the solid was dried in the hot air oven to get the powder. For

further purification the solid powder was Soxhlet using THF-MeOH solvent mixture. The desolvated phase was obtained by heating the polymer at 100 °C in the vacuum. (Appendix Scheme 5.2)

5.2.3. Measurement

5.2.3.1. X-ray Absorption Spectroscopy (XAS): X-ray Absorption Spectroscopy (XAS) measurements have been carried out at As K-edge in transmission mode at the Scanning EXAFS Beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 200 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [R1, R2]. The beamline uses a double crystal monochromator (DCM) which works in the photon energy range of 4-25 KeV with a resolution of 10^4 at 10 KeV. A 1.5 m horizontal pre-mirror with meridional cylindrical curvature is used prior to the DCM for collimation of the beam and higher harmonic rejection. The second crystal of the DCM is a sagittal cylinder with radius of curvature in the range of 1.28-12.91 meters which provides horizontal focusing to the beam while another Rh/Pt coated bendable post mirror facing down is used for vertical focusing of the beam at the sample position.

For the transmission mode measurement, three ionization chambers (300 mm length each) have been used for data collection, one ionization chamber for measuring incident flux (I_0), second one for measuring transmitted flux (I_t) and the third ionization chamber for measuring XAS spectrum of a reference metal foil for energy calibration. Appropriate gas pressure and gas mixtures have been chosen to achieve 10-20% absorption in first ionization chamber and 70-90% absorption in second ionization chamber to improve the signal to noise ratio. The absorption coefficient μ is obtained using the relation:

$$I_t = I_0 e^{-\mu x} \quad (1)$$

where, x is the thickness of the absorber.

The EXAFS spectra have been extracted using the standard procedure [R3-R5]. In order to take care of the EXAFS oscillations in the absorption spectra, the energy dependent absorption coefficient $\mu(E)$ has been converted to absorption function $\chi(E)$ defined as follows:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)} \quad (2)$$

Where, E_0 absorption edge energy, $\mu_0(E_0)$ is the bare atom background and $\Delta\mu_0(E_0)$ is the step in the $\mu(E)$ value at the absorption edge. After converting the energy scale to the photoelectron wave number scale (k) as defined by,

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (3)$$

the energy dependent absorption coefficient $\chi(E)$ has been converted to the wave number dependent absorption coefficient $\chi(k)$, where m is the electron mass. Finally, $\chi(k)$ is weighted by k^2 to amplify the oscillation at high k and the functions $\chi(k)k^2$ are Fourier transformed in r space to generate the $\chi(r)$ versus r plots (or FT-EXAFS spectra) in terms of the real distances from the centre of the absorbing atom. The k range used for Fourier transform is 3.0-12.0 Å⁻¹ for the samples.

5.2.4. Arsenic Capture Studies

5.2.4.1. General consideration: The aqueous solution of different organic arsenic and inorganic arsenic was prepared by dissolving a certain amount of organic arsenic sodium salts inorganic arsenic into deionized water and the different concentrations were obtained by diluting the stock solution with the proper amount of distilled water unless otherwise indicated. The pH values of the solutions were adjusted by HCl or NaOH aqueous solution. The concentrations of organic arsenic (> 10 ppm) during all the experiments were detected by UV-Vis spectroscopy and the all concentration of inorganic arsenic and organic arsenic (< 1 ppm) were detected by ICP-AES and ICP-MS (for ultra-low concentrations, < 1 ppm) analysis. All the adsorption experiments were performed at ambient conditions. All the data has been collected three times through UV-Vis and ICP analysis to plot the final adsorption results.

5.2.4.2. Adsorption kinetics studies: The standard procedure that we adopted for the adsorption kinetics experiments was as follows. The capture study of various organic arsenic (ROX, ASA, NIT) and inorganic arsenic (HAsO₄²⁻) was performed in 15 mL glass vial equipped with magnetic stir bars with a constant stirring rate of 350 r.p.m. Firstly; 5 mg of material was taken in 5 mL of stock solution of different concentration of different organic arsenic and inorganic arsenic individually. After continuous stirring for different time at room temperature the solution was collected by a syringe with having 0.22 µm nylon membrane filter. The concentration of this filtrate was measured through UV-Vis Spectroscopy (for ROX, ASA, NIT) ICP-AES (for HAsO₄²⁻) and the kinetic adsorption study were measured at different time intervals. From the time-dependent study, we calculated the removal % and decreasing concentration of the respective organic arsenic and inorganic arsenic with time using the following equations:

$D_t = \{(C_0 - C_t) \times 100\} / C_0 = \{(A_0 - A_t) \times 100\} / A_0$, Where, D_t = removal efficiency (%), C_0 = initial concentration, A_0 = initial absorbance, C_t = final concentration, A_t = final absorbance at specific time.

5.2.4.3. Roxarsone (ROX) and As(V) adsorption isotherm experiment: 5 mg of material was immersed in 5 mL aqueous solution of Roxarsone (ROX) and As(V) having different concentrations. After ~12 hours the filtrate was collected through syringe filter (0.22 μm) and measured the concentration through UV-Vis Spectroscopy and ICP-AES respectively, and further fitted with following equations,

Langmuir model- $Q_e = Q_m \cdot C_e / (K_d + C_e)$; Where, C_e (mM / ppm) and Q_e (mg g⁻¹) are the Roxarsone and HAsO₄²⁻ concentration at equilibrium and amount of Roxarsone and HAsO₄²⁻ adsorbed at equilibrium respectively. Q_m (mg g⁻¹) is the maximum amount of Roxarsone and HAsO₄²⁻ per mass of adsorbent to form a complete monolayer. K_d (mg L⁻¹) is a constant to the affinity of the binding sites.

Freundlich model- $Q_e = K_f \cdot C_e^{1/n}$; Where, K_f and $1/n$ are the Freundlich model constant, indicating capacity and intensity of adsorption respectively.

5.2.4.4. Pseudo-second-order model: The pseudo-second-order equation can be expressed as follows: $t/q_t = 1/K_2 q_e^2 + t/q_e$ Where, q_t and q_e represent the adsorbed amount (mg g⁻¹) at time and at equilibrium t (min), respectively, K_2 represent the Pseudo-second-order rate constant of adsorption (g mg⁻¹ min⁻¹). The experimental data was fitted using Pseudo-second-order kinetic model.

5.2.4.5. ROX and As(V) capture capacity: The amount of ROX and HAsO₄²⁻ adsorbed per gram of material was determined by exposing 5 mg of material to 5 mL of ~500/1000 mM / ppm concentrated solution of respective ROX and HAsO₄²⁻ salt for ~12 hours under stirring conditions at room temperature. After 24 hours, the composite material was filtered off and the filtrate was characterized through UV-vis / ICP-AES by diluting the solution. The adsorption capacity per gm was calculated using following equation:

$$Q_t = (C_0 - C_t) \times V / m;$$

Where, Q_t , C_0 , C_t , V and m are the capacity of adsorbent, initial concentration of the ROX and HAsO₄²⁻ solution, final concentration of ROX and HAsO₄²⁻ at a specific time, volumes of the solution and mass of the material used for the adsorption study respectively.

5.2.4.6. ROX and As(V) capture study in presence of other competing ions: For testing the influence of competing ions, large excess (~100-fold) of competing salts such as, HAA, ASA, PEN, ERY for ROX and NaCl, NaNO₃, NaClO₄, Na₂SO₄, Na₃PO₄ were added to the different aforementioned ROX and HAsO₄²⁻ aqueous solution and carried out the capture studies by following the aforementioned method. The capture studies were monitored through UV-vis spectroscopy (for ROX) and ICP-AES (for HAsO₄²⁻).

5.2.4.7. pH-dependent ROX and As(V) extraction study: The effect of pH on ROX and As(V) removal performance was recorded in a wide range of pH and compared with the data at pH-7 to check the relative

performance. The variation of pH values was realized by the addition of either acid (HCl) or base (NaOH). We adopted the similar adsorption experiment for this study.

5.2.4.8. Trace amount capture study: Trace amount (1 ppm) of ROX and As(V) capture study was performed following the similar kinetic adsorption experiment described above. The kinetic adsorption study was measured at different particular time interval, taking ~1000 ppb stock solution of ROX and As(V) in water. The ICP-MS experiments were carried out for analyze the removal efficiency of the materials.

5.2.4.9. Recyclability test: The first cycle of ROX and As(V) uptake in the recyclable experiment was performed according to the aforementioned adsorption protocol. After the first run of adsorption, the ROX and As(V) containing material was regenerated by treatment with a saturated tBuNH_4Br aqueous solution. The resulting solid was dried and washed three times with pure deionized water. After being finally dried under vacuum, the resultant material was used for the next cycle adsorption experiments.

5.2.4.10. Dynamic column exchange-based flow-through ROX and As(V) capture study: To check the continuous ROX and As(V) removal efficiency by the IPiPOP-3U, a column (S10) exchange-based flow-through experiment was conducted by packing the IPiPOP inside a column as bed for (50 mg for ROX & 80 mg for HAsO_4^{2-} respectively) capture. After that, to mimic the simulated industrial waste water system different volume of stock ~50 ppm of ROX aqueous solution along with ~50 ppm concentration of other interfering drugs (such as HAA, ASA, PEN, ERY) were mixed. Thereafter, this mixture was passed through the column bed with a constant flow rate of 0.5 mL/min, which was controlled by a regulator, and the drops per minute was recorded with the help of a stopwatch. A bed-volume of ~5 mL of column eluted solution was collected in a different respective container. The concentration of ROX and As(V) in these solutions were then analyzed through UV-Vis spectra and ICP-MS analysis respectively.

5.3 Results and Discussion

5.3.1. Synthesis and Structural Characterization

The urea functionalized cationic porous organic polymer (iPOP) was synthesized through a simple substitution reaction between 1,3-di(pyridine-3-yl)urea (L1, Appendix Scheme 5.1, Appendix Figure 5.4) and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (L2) and at 80 °C in N-Methyl-2-pyrrolidone (NMP) solvent system. After, completion of the reaction, pale-yellow colored precipitate was extensively washed with various organic solvents (Appendix Scheme 5.2, Figure 5.1a). The primary indication of the formation of the polymeric network was that the precipitate was found to be insoluble in all the common organic solvents. Further validation of the polymeric network formation and structural composition were extensively characterized by the following techniques, solid-state ^{13}C cross polarization magic-angle-

spinning Nuclear Magnetic Resonance (^{13}C -CP-MAS NMR), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), low-temperature nitrogen (N_2) and carbon dioxide (CO_2) gas sorption measurements, zeta potential etc. ^{13}C CP-MAS NMR spectroscopy confirmed the reaction between two monomers and the successful formation of the urea-functionalized cationic polymer network. The presence of several main broad peaks in the ^{13}C CP-MAS NMR authenticated the formation of the network along with its chemical composition. Peaks around ~ 64 and ~ 73 ppm were attributed to the formation of the sp^3 methylene linkages with both the nitrogen atoms of the urea ligand. The signals coming from the pyridinium moiety of ligand L1 and the aromatic carbon of the benzene ring of ligand L2 were observed in the range of ~ 105 ppm to ~ 139 ppm. Peak at ~ 152 ppm corresponds to the sp^2 carbon adjacent to pyridinium nitrogen. A carbon signal at ~ 169 ppm indicates the successful integration of triazine moiety into the polymeric network. Additionally, carbonyl carbon from the urea group showed a peak around ~ 192 ppm to 199 ppm, confirming the presence of the main urea group in the network of IPiPOP-3U (Figure 5.1b). FTIR spectroscopy unveiled peaks at approximately 1520 cm^{-1} , indicates the C=N stretching frequency from the triazine moiety. The peak around 1417 cm^{-1} indicates the methylene linkage ($-\text{CH}_2$) in the polymeric network while peak at 1366 cm^{-1} comes from triazine core. The Urea functionalization is confirmed from the peak at 1714 cm^{-1} for $-\text{C}=\text{O}$ stretching and the peaks from 2931 - 3075 cm^{-1} due to $-\text{NH}$ group from urea group (Figure 5.1c, Appendix Figure 5.5). The thermal stability and robustness of IPiPOP-3U was evaluated from the thermogravimetric analysis (TGA). From the TGA profile, we observed an initial loss of $\sim 20\%$ around 80 - 85°C , which can be attributed to the loss of entrapped solvents inside the pristine polymeric network of IPiPOP-3U. However, no significant as well as gradual weight loss was seen for the desolvated phase (Figure 1d) of IPiPOP-3U, suggesting good thermal stability and robustness of the polymeric network. Further, the surface morphology of the IPiPOP-3U was investigated by FESEM and TEM analysis. FESEM images revealed an irregularly shaped amorphous dense morphology of IPiPOP-3U (Figure 1e, Appendix Figure 5.6). The elemental analysis and corresponding spectroscopy (EDS) of IPiPOP-3U showed a homogeneous distribution of all the expected elements, i.e., C, N, O, and Br across the polymer matrix (Appendix Figure 5.7). The transmission electron microscope (TEM) images confirmed the layered structure of the IPiPOP-3U polymeric network (Figure 1f, Appendix Figure 5.8). Elemental analysis showed the $\% \text{C}=56.62$, $\% \text{N}=16.68$ and $\% \text{H}=3.95$ ($\text{C/N}=3.39$ and $\text{C/H}=14.3$) which matched with the EDS data. Further, the elements and surface composition, and chemical states were confirmed from the XPS analysis. The four main peaks at $\sim 67.7\text{ eV}$, 286 eV , 400 eV , and 532 eV were found in the XPS survey, which is characteristic and corresponds to the Bromine (Br), Carbon (C), Nitrogen (N), and Oxygen (O) respectively, present in IPiPOP-3U (Appendix Figure 5.9). Deconvoluted high-resolution peaks revealed the chemical state of the elements. The Carbon (C) 1s peaks

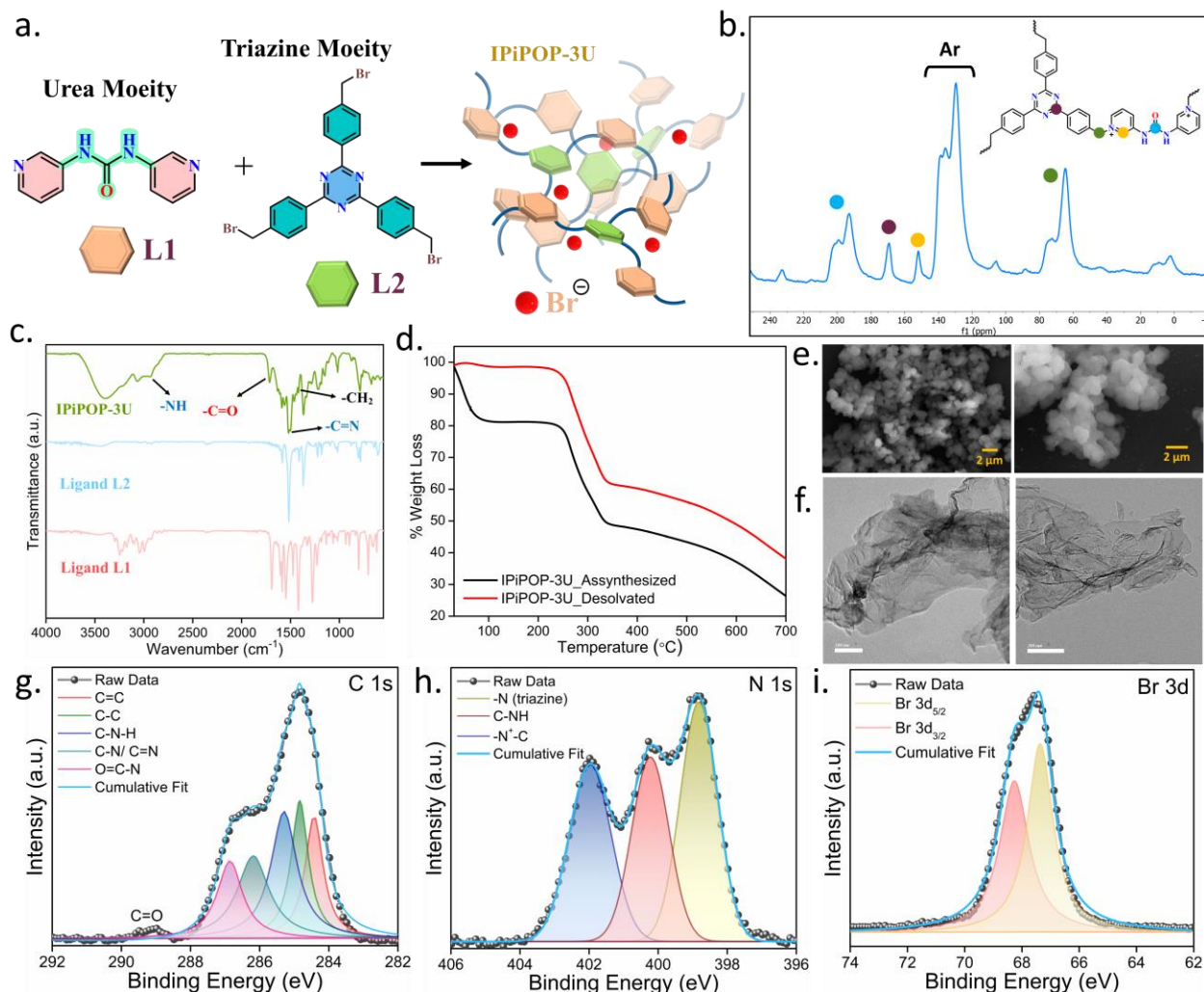


Figure 5.1: (a) Synthetic scheme of IPiPOP-3U (color code: light grey- Carbon, blue- Nitrogen, red- Oxygen, brown- Bromine), (b) ^{13}C CP-MAS NMR, (c) FT-IR spectra, (d) TGA profile, (e) FESEM images, (f) TEM images, and deconvoluted XPS spectra (g) C 1s, (h) N 1s, (i) Br 3d.

consist of six peaks ranging from 284.4 eV, 284.8 eV, 285.28 eV, 286.17 eV, 286.9 eV, and 289.1 eV that can be assigned to $\text{Csp}^2=\text{Csp}^2$ and $\text{Csp}^3=\text{Csp}^3$ of the aromatic rings and the methylene linkage, C-NH from the urea moiety, -C-N/C=N from triazine moiety, O=C-N from the urea functionalization respectively (Figure 1g). Nitrogen (N) 1s peak was fitted into three different peaks ranging from 398.8 eV, 400.2 eV, and 401.9 eV, which corresponds to $\text{Csp}^2\text{-Nsp}^2\text{-Csp}^2$ of triazine ring, -C-NH from urea moiety and -N $^+$ -C of pyridinium nitrogen respectively (Figure 1h). The Oxygen (O) 1s peak was fitted into two peaks at 531.8 eV and 533.4 eV and attributed to -C=O and -C-O from urea functionalization, respectively (Appendix Figure 5.10). The Bromine (Br) 3d peak was fitted into two peaks at 67.37 eV and 68.25 eV assigned for $3d_{5/2}$ and $3d_{3/2}$, respectively (Figure 1i). Further, N_2 adsorption-desorption isotherm at 77K of IPiPOP-3U does not show any significant uptake of nitrogen gas, suggesting that the presence of counter

bromide (Br^-) anions in the cationic network of the material blocking the internal pores (Appendix Figure 5.11) and NLDFT pore size distribution suggested hierarchical pore distribution consists with micro and meso pore (Appendix Figure 5.12). Additionally, CO_2 adsorption at 195K suggests the porous nature of the IPIPOP-3U (Appendix Figure 5.13). Additionally, Zeta potential showed +31.1 mV of the surface charge, indicating the cationic nature of the IPIPOP-3U polymeric network (Appendix Figure 5.14). Additionally, we can conclude the formation of the conjugated polymeric network from solid-state (SS) UV-Vis spectra from the DRS experiment. The SS UV-Vis spectra of IPIPOP-3U illustrated two main peaks present at 250 nm and 312 nm. The first peak comes from the triazine moiety of the L1 ligand, while the second peak of 312 nm corroborated the formation of the conjugated network in IPIPOP-3U (Appendix Figure 5.15). All these characterizations strongly suggest the successful formation of the cationic polymeric network of IPIPOP-3U.

We further tested the chemical stability of IPIPOP-3U after successful structural characterization. IPIPOP-3U was exposed to severe conditions, including acidic (1 N HCl) and basic (1 N NaOH) solutions, for 24 hours to assess its polymers robust nature. FT-IR, TGA, and FESEM were further utilized to characterize the post-treated sample. The characteristic FT-IR peaks remained unaltered for the post-treated samples when compared to pristine IPIPOP-3U (Appendix Figure 5.16). The TGA profile revealed similar behavior, confirming the thermal and chemical stability (Appendix Figure 5.17). Moreover, the FESEM images showed no definitive change in the surface morphology of acid-base treated IPIPOP-3U, confirming excellent chemical stability of the polymeric network of IPIPOP-3U (Appendix Figure 5.18, 5.19). Furthermore, when IPIPOP-3U was submerged in different-organic solvents, there was very little loss of weight %, supporting its extremely stable nature (Appendix Figure 5.20). All these results suggest the highly robust nature of the polymeric network of the IPIPOP-3U.

5.3.2. Capture Studies

Robust ionic porous organic polymers (iPOP) were extensively explored as potential detoxifying agents for eliminating organic and inorganic pollutants from wastewater.^{25, 26, 27} Interestingly, the role of functionalization in iPOPs has been not much investigated towards water remediation. Owing to the abundance of urea-based “nanotrap” functionality and the cationic skeleton of IPIPOP-3U, we were enthused to explore the adsorption potency of organic arsenic, especially (4-Hydroxy-3-nitrophenyl) arsonic acid (Roxarsone, ROX) and inorganic arsenic HAsO_4^{2-} . Urea functionalization can enable IPIPOP-3U to interact selectively with ROX and HAsO_4^{2-} via hydrogen bonding, and cationic nature of the polymeric network can amplify the ion exchange process with organic and inorganic arsenic analytes, enhancing the adsorption efficiency. IPIPOP-3UT demonstrated ultrafast removal efficiency (within 30 seconds) towards organic arsenic, i.e., ROX. From the kinetics experiment, it was found that IPIPOP-3UT

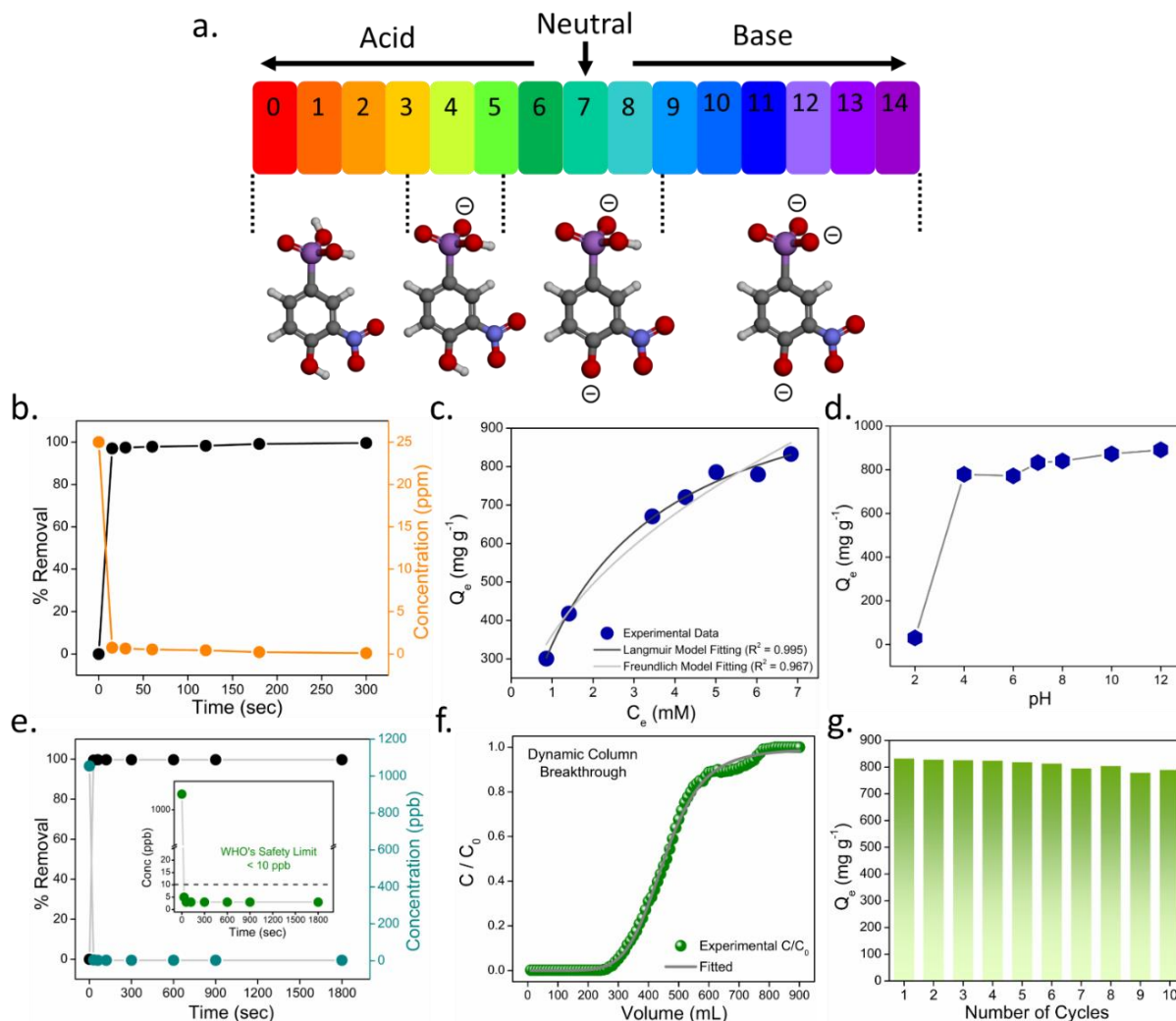


Figure 5.2: (a) pH dependent structural change in ROX, (b) % removal and the decrease in concentration of ROX over time (25 ppm), (c) adsorption isotherm fitting, (d) adsorption capacity of ROX in different pH, (e) kinetics study with ultra-low concentration, (f) result of dynamic column breakthrough removal, and (g) recyclability of ROX capture by IPiPOP-3U.

removed ~99% ROX within 30 seconds from its 25 ppm aqueous solution and achieved ~99.6 % removal in 5 minutes (Figure 5.2b, Appendix Figure 5.21). The equilibrium was achieved rapidly owing to the synergistic effect of its cationic framework and urea functionality, which accelerated the diffusion of ROX into the polymeric network of IPiPOP-3U. Additionally, from the concentration-dependent kinetics experiment, it was observed the removal efficiency was 95 % for 50 ppm (Appendix Figure 5.22) and 93 % for 125 ppm (Appendix Figure 5.23) ROX concentrations respectively, within 5 minutes by IPiPOP-3U (Appendix Figure 5.24). To further check the capture competence, the capacity of the ROX for varying concentrations has been calculated and further plotted against the contact time. The ROX adsorption was found to follow the pseudo-second-order kinetics with significant rate constant value (Appendix Figure

5.21-5.23). The saturation uptake capacity for ROX was found to be 833 mg g^{-1} , which stands tall among the previously reported adsorbent in the literature (Appendix Table 5.1). In order to explore the enhanced potential of this adsorbent, we were further performed ROX capture test with our previously reported materials (IPComp-3 (200), IPComp-6), where inorganic arsenate capture studies have been executed.^{28, 29} To our delight, IPiPOP-3U was found to exhibit significantly higher uptake efficiency with compare to these materials (Appendix Figure 5.26). The adsorption isotherm of ROX fitted well with the Langmuir Adsorption Isotherm model (Figure 5.2c, Appendix Figure 5.25). The pH-dependent ROX removal was also performed as ROX stays in its neutral form under extremely acidic conditions, and with increasing the pH, the -OH group in ROX gets deprotonated (Figure 5.2a), ROX^- ($\text{pK}_a = 3.49$), ROX_2^- ($\text{pK}_a = 5.74$) and ROX_3^- ($\text{pK}_a = 9.13$). The uptake capacity of ROX is negligible at $\text{pH} = 2$. However, it increases significantly with increasing pH value (Figure 5.2d), indicating the of anion exchange process, one of the dominant driving forces of adsorption process, due to the presence of exchangeable bromide anions inside the cationic network, which plays a crucial role in the adsorption of ROX. ROX is found mainly in real-world water bodies. To replicate this scenario, we performed kinetics and uptake capacity in ROX spiked river, lake, sea, tap and bottled water. We found $\sim 99\%$ removal efficiency in every system within 30 seconds (Appendix Figure 5.27-5.32). The uptake capacity was calculated to be 889.1 mg g^{-1} , 850.7 mg g^{-1} , 823.56 mg g^{-1} , 790.6 mg g^{-1} , and 843.92 mg g^{-1} in river, lake, sea, tap and bottle water respectively (Appendix Figure 5.33). Furthermore, Arsinilic Acid (ASA) and Nitarstone (NIT) (Appendix Figure 5.34) are organic arsenics drugs that are used widely and abundant in aquatic systems as pollutants.^{30, 31, 32} We performed a kinetics experiment with these two representative organic arsenics and found that IPiPOP-3UT could remove 78.4% of ASA and 44.5% NIT within 5 minutes Appendix Figure 5.35-5.37). ROX is mostly use as a drug and exposed to the environment with other different drugs. So, it is important to be able to capture ROX selectively in the presence of other competing drugs. To our delight, we found that IPiPOP-3U was able to remove ROX from water in the presence of different competing drugs such as ASA, NIT, HAA, PEN, and ERY, with great efficiency (Appendix Figure 5.38).

In most cases, in the real-world water bodies, the concentration of the pollutants remains very low (in ppb level), and it is immensely important for materials to afford trace concentration capture toward real water treatment.³³ As the performance of IPiPOP-3U was found to be excellent in the high concentration of ROX, we were interested to investigate its removal efficiency at very low concentration ($\sim 1 \text{ ppm}$) of ROX. To check this, we performed a capture study with 1 ppm aqueous stock solution of ROX and analyzed the performance by ICP-MS (Inductively coupled plasma-mass spectrometry). It was found that within 1 min the As concentration decreased beyond the permissible level ($< 10 \text{ ppb}$) as set by WHO and EPA in the drinking water (Figure 5.2e).

Encouraged from the ultrafast capture efficiency of IPiPOP-3U owing to its urea functionalization and cationic backbone, we were motivated to perform a dynamic flow-through capture experiment by packing IPiPOP-3U in a column in simulated ROX contaminated water system. In a typical experiment, a ~50 ppm ROX contaminated water, along with other interfering drugs (HAA, ASA, ERY, PEN), was flow through a 50 mg IPiPOP-3U packed column with a constant flow rate 0.5 mL min^{-1} , and the concentration of ROX was measured from UV-Vis spectra. Surprisingly, almost ~99% removal rate of ROX was observed after passing ~ 275 mL of ROX-contaminated water (Figure 5.2f). In addition, to the capture efficiency, the material's recyclability is of priori necessity and a prerequisite toward real-world application. The reusability of IPiPOP-3U towards remediation of ROX was tested using a 50 ppm ROX solution. It was observed that IPiPOP-3U showed excellent recyclability even after ten cycles showcasing almost unaltered removal efficiency of ROX (Figure 5.2g), which makes IPiPOP-3U an exceptional material towards organic arsenic remediation.

It is well known that, after exposure to the environment, ROX could convert into inorganic arsenic (As(V)) via different aerobic and anaerobic microbial pathways.^{34, 35} As(V) is one of the most lethal pollutants prevailing in soil and water that must be removed from the environment. Inspired by the efficient removal of ROX by IPiPOP-3U, we explored its potency toward trapping As(V) from water bodies. Interestingly, IPiPOP-3U achieved ~99.9% removal efficiency for 10 ppm aqueous solution of HAsO_4^{2-} within only 60 seconds (Figure 5.3a). The HAsO_4^{2-} removal efficiency when plotted against time, displayed the adsorption process to follow pseudo-second-order kinetics (Appendix Figure 5.39).

Additionally, the saturation uptake capacity for HAsO_4^{2-} was found to be 264 mg g^{-1} , which, to our knowledge is, one of the highest reported values in the domain of functional porous materials (Appendix Table 5.2). The adsorption isotherm for HAsO_4^{2-} was fitted well with Langmuir Adsorption Isotherm (Appendix Figure 5.40.-5.41). The pH-dependent removal efficiency was further tested by taking 10 ppm HAsO_4^{2-} in a wide range of pH aqueous solution from pH=2 to pH=14. As (V) removal efficiency remained almost unaltered (~99.9%) in the range of pH=2-8 while IPiPOP-3U showed a good removal efficiency (~90-95 %) in the range of pH= 10-14 (Figure 5.3b). To mimic the real-world scenario, we further performed HAsO_4^{2-} removal experiment of by IPiPOP-3U in different water systems such as river, lake, sea, tap, and bottled water. IPiPOP-3U could successfully remove ~99% of As(V) with ease from every system (Appendix Figure 5.42) validating its potency. We also tested the removal of HAsO_4^{2-} in the presence of competing anions (NO_3^- , SO_4^{2-} , Cl^- , ClO_4^- , PO_4^{3-}) in 1:1 and 1:10 ratios which are relevant to the real-world scenario. Delightfully, IPiPOP-3U removed HAsO_4^{2-} with almost unaltered efficiency despite the presence of excessive competing anions (Appendix Figure 5.43-5.44). Furthermore, we also tested the efficacy of IPiPOP-3U towards the removal of HAsO_4^{2-} at ultralow concentration (~ 1000 ppb). Interestingly, IPiPOP-3U illustrated ~99.9% removal of HAsO_4^{2-} within 30 seconds (Figure 5.3c), and the

concentration decreased below the safety level of

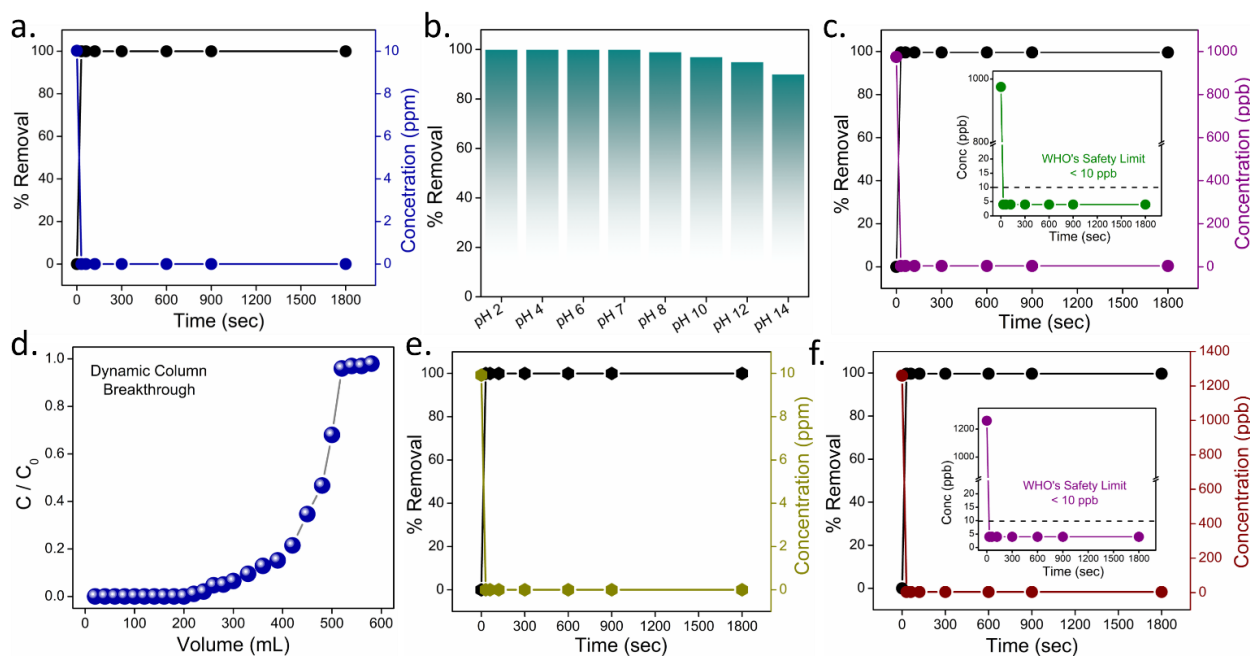


Figure 5.3: (a) % removal and the decrease in concentration of HASO_4^{2-} over time (10 ppm), (b) removal efficiency of HASO_4^{2-} in different pH, (c) kinetics study with ultra-low concentration (1 ppm), (d) result of dynamic column breakthrough removal experiment of HASO_4^{2-} by IPiPOP-3U, (e) % removal and the decrease in concentration over time (10 ppm) of ROX and HASO_4^{2-} mixture, and (f) kinetics study with ultra-low concentration (1 ppm) of ROX and HASO_4^{2-} mixture.

arsenic concentration (~ 10 ppb) in drinking water as set by the WHO and EPA. Towards implementing IPiPOP-3U in practical application, it was employed in column-based flow-through adsorption experiment which was performed with 50 ppm HASO_4^{2-} feed solution with 80 mg of IPiPOP-3U with a flow rate of 0.5 mL min^{-1} . Interestingly, we observed that IPiPOP-3U can efficiently remove about $\sim 99\%$ HASO_4^{2-} after passing nearly 200 mL of HASO_4^{2-} contaminated water (Figure 5.3d). We also performed the recyclability of IPiPOP-3U for HASO_4^{2-} remediation. Satisfyingly, we observed almost unvarying removal efficiency up to 10 cycles (Appendix Figure 5.45) making IPiPOP-3U an excellent material for real-time application.

As is mentioned previously, after exposure to the environment, organic arsenic aerobically and anaerobically can convert to inorganic arsenic, and both can be present simultaneously in the same water bodies. Considering this real-time scenario, we performed simultaneous removal of arsenic from 10 ppm aqueous solution of a mixture of ROX and HASO_4^{2-} and calculated the removal efficiency by ICP-AES measurement. A remarkable removal efficacy of $\sim 99\%$ by IPiPOP-3U was observed for As within 30 seconds (Figure 5.3e) and the sorption procedure followed the pseudo-second-order kinetics (Appendix

Figure 5.46). In the context of real-time application, we also performed the capture study at ultralow concentration of this binary mixture (~ 1000 ppb) and the remaining concentration was measured by ICP-MS. Surprisingly, we found that IPiPOP-3U could reduce the As concentration below the safety level (~ 10 ppb) set by WHO and EPA from aqueous mixture of ROX and HAsO_4^{2-} (Figure 5.3f).

5.3.3. Mechanistic Insight Towards Arsenic Capture

We were further motivated towards investigating the probable interactions between organic (ROX) and inorganic (HAsO_4^{2-}) arsenic with the structure of IPiPOP-3U owing to the excellent adsorption of both types of arsenics by IPiPOP-3U. The exploration of the mechanistic binding interactions of arsenics with IPiPOP-3U were assessed primarily by FT-IR, FESEM-EDS, elemental mapping, TEM and TGA as well as by Solid State UV-Vis spectra, Fluorescence, Isothermal Titration Calorimetry (ITC), X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS). Initially, from FT-IR spectra, we validated the successful loading of ROX and HAsO_4^{2-} into the framework of IPiPOP-3U. New peaks in ROX@IPiPOP-3U at $\sim 1610\text{ cm}^{-1}$ and 1246 cm^{-1} were assigned as the N-O stretching frequencies from the $-\text{NO}_2$ group from ROX, while peak at 892 cm^{-1} was attributed to the $-\text{C}-\text{As}$ bond and the peaks at 1074 cm^{-1} and 1096 cm^{-1} were assigned as the As-O bonds present in the ROX molecule (Appendix Figure 5.47). It should be mentioned that all these assigned peaks in ROX@IPiPOP-3U matched well with ROX, confirming the ROX adsorption in the IPiPOP-3U framework. Also, in the FT-IR spectrum of HAsO_4^{2-} @IPiPOP-3U, two new peaks were observed at 852 cm^{-1} and 874 cm^{-1} , which were assigned as the As-O bonds (Appendix Figure 5.48). This observation validates the HAsO_4^{2-} adsorption in the IPiPOP-3U framework. From the FESEM-EDS and the corresponding elemental mapping of both ROX@IPiPOP-3U (Appendix Figure 5.50) and HAsO_4^{2-} @IPiPOP-3U (Appendix Figure 5.52), we found the homogenous distribution of the Arsenic throughout the surface of the IPiPOP-3U. From this data, we substantiated the successful loading of arsenic inside the IPiPOP-3U framework for both inorganic & organic arsenic adsorption. It is worth mentioning that the surface morphologies after the capture of both organic and inorganic arsenic were found to be unchanged, as was observed from the respective FESEM images of ROX@IPiPOP-3U (Appendix Figure 5.49) and HAsO_4^{2-} @IPiPOP-3U (Appendix Figure 5.51). This data further confirmed the robustness of IPiPOP-3U towards arsenic capture from water. Additionally, TEM images also suggested the robustness and stability of IPiPOP-3U after arsenic sequestration as we found almost identical surface morphology as compared to pristine IPiPOP-3U (Appendix Figure 5.53-5.54). TGA profile of ROX@IPiPOP-3U showed the similar thermal behavior as pristine IPiPOP-3U but extra weight loss was noticed between $\sim 259\text{ }^\circ\text{C} - 290\text{ }^\circ\text{C}$, which was assigned to the weight loss corresponding

to the entrapped Roxarsone molecules inside the IPiPOP-3U network (Appendix Figure 5.55). The TGA

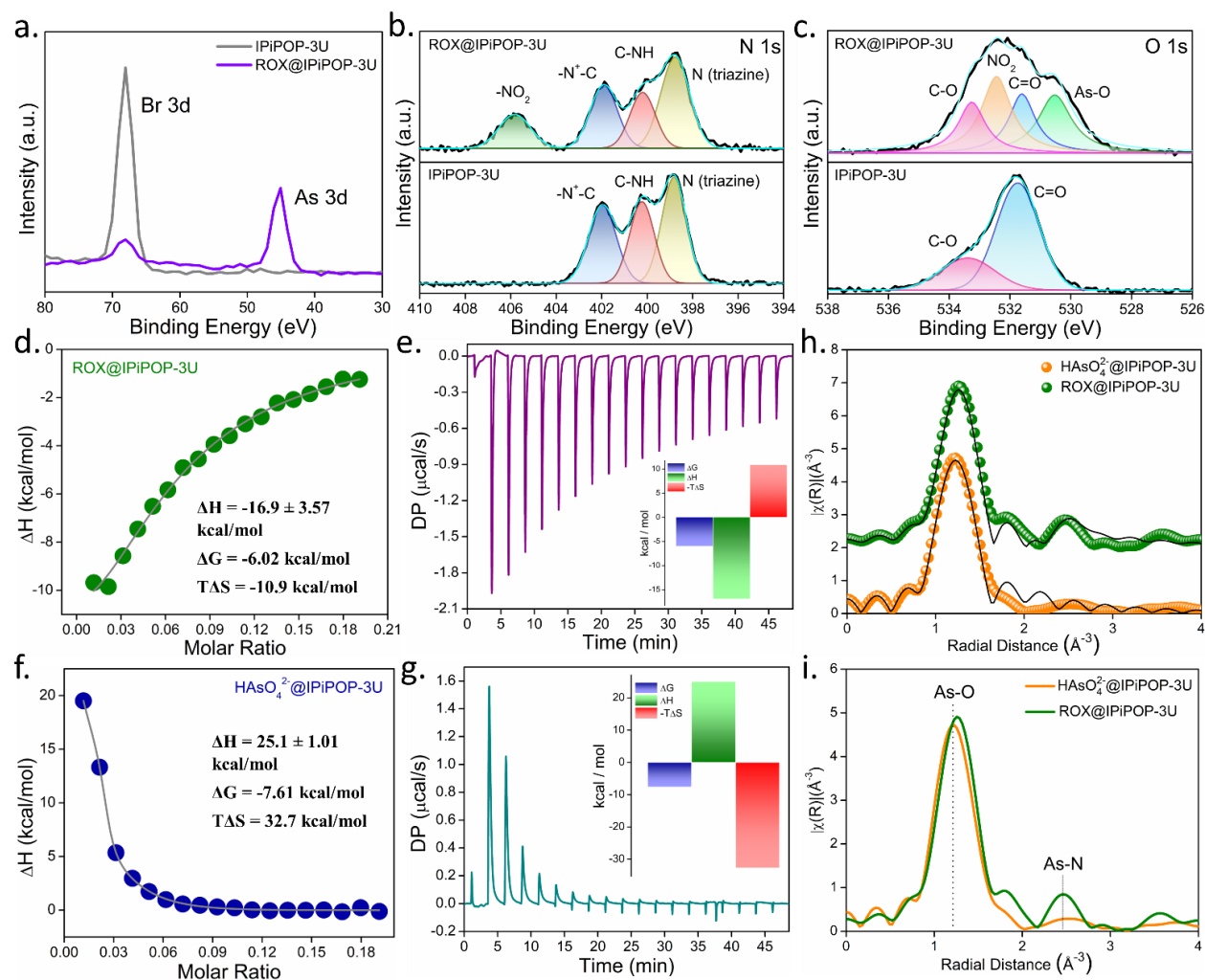


Figure 5.4: (a) XPS survey spectra of Br and As before (grey) and after (violet) ROX capture by IPiPOP-3U, deconvoluted compare XPS spectra of (b) N 1s and (c) O 1s, (d) integrated heat plots simultaneously for injections (e) ITC thermogram and thermodynamic parameter (inset) of ROX titrated against IPiPOP-3U, (f) integrated heat plots simultaneously for injections (g) ITC thermogram and thermodynamic parameter (inset) of HASO₄²⁻ titrated against IPiPOP-3U and (h- i) Fourier transformed EXAFS spectra measured at As K edge after capture.

profile of HASO₄²⁻@IPiPOP-3U showed the similar thermal trend as pristine IPiPOP-3U (Appendix Figure 5.56), confirming the thermal stability of the polymeric network after the Arsenic capture.

To further understand the interaction of IPiPOP-3U polymeric network with ROX and HASO₄²⁻, we recorded the solid-state UV-Vis spectra of ROX loaded IPiPOP-3U. Interestingly, we observed a shift of the peak position. The peak at 312.4 nm in pristine IPiPOP-3U was shifted at 329.8 (red shift), indicating

the interaction of ROX with the polymeric network. Also, a new peak at 410 nm was found to appear, which could be ascribed to the entrapped ROX molecules (Appendix Figure 5.57). From the photoluminescence emission spectra, we found decreased intensity of ROX captured IPIPOP-3U than that of pristine IPIPOP-3U (Appendix Figure 5.58). Encouraged by this result we performed fluorescence titration experiment by incremental addition of aqueous ROX solution to dispersed IPIPOP-3U in water. We observed that after incremental addition of 100 ppm of ROX aq. solution the fluorescence intensity of IPIPOP-3U gradually decreased (Appendix Figure 5.59), indicating the strong interaction of ROX molecules with the polymeric network of IPIPOP-3U. Also, from the PLE spectrum we observed a red shift in the emission maxima (Appendix Figure 5.60) suggesting strong interactions between the incoming ROX and IPIPOP-3U network. This results also suggests that the presence of favorable interactions enable ROX molecules to easily get entrapped inside IPIPOP-3U and stabilize it. Also, in the case of HAsO_4^{2-} , IPIPOP-3U showed red shift of the peaks in the solid-state UV-Vis spectra (Appendix Figure 5.61) indicating the feasible interaction between HAsO_4^{2-} and IPIPOP-3U.

Additionally, the XPS analysis was performed to understand the involvement of elements or different functional sites of IPIPOP-3U and their core energy levels towards the interaction with organic arsenic Roxarsone and inorganic counterpart HAsO_4^{2-} . From the XPS survey spectra of ROX@IPIPOP-3U, we found that the peak intensity at ~68 eV, assigned for Bromine, (Br) decreased while a new peak at ~45 eV appeared (Figure 5.4a, Appendix Figure 5.62), indicating the presence of As on the surface of the polymeric network of IPIPOP-3U which was fitted into two peaks at 44.6 eV and 45.4 eV for As $3d_{5/2}$ and $3d_{3/2}$ respectively (Appendix Figure 5.62). After the adsorption of ROX, the binding energy of N 1s electron ~398.8 eV, corresponding to -C-N=C, was found to shift from higher binding energy to a lower value, as well as the intensity of the peak at ~400.2, assigned for -C-NH bond from urea functionalization, got attenuated in a significant amount, confirming the interaction of ROX with urea group in the IPIPOP-3U network. We also observed a new peak at ~405.8 eV, which could be assigned to the -NO₂ group, present in the Roxarsone molecule (Figure 5.4b, Appendix Figure 5.65), further confirming the ROX adsorption. The O 1s binding energies at ~531.8 eV corresponding to -C=O bond was observed to shift from higher to lower binding energy and peak at ~533.4 eV, corresponding to -C-O bond was found to shift from relatively higher to lower binding energy along with the formation of two new peaks at ~530.5 eV, which was assigned for As-O bond and the peak at ~532.45 eV, corroborated to the -NO₂ group (Figure 5.4c, Appendix Figure 5.66). These observations further validate the successful capture of ROX by IPIPOP-3U. Similarly, from the XPS survey of HAsO_4^{2-} @IPIPOP-3U, we observed decrease in peak intensity corresponding to Bromine along with a new peak at ~45 eV (Appendix Figure 5.67-5.68), suggesting the presence of As on the surface of IPIPOP-3U which was fitted into two peaks at 44.5 eV and 45.2 eV for As $3d_{5/2}$ and $3d_{3/2}$ respectively (Appendix Figure 5.68). Further, N 1s binding energy at ~ 398.8 eV assigned for -C-N=C of

triazine ring was observed to shift to a relatively lower binding energy after adsorption of HAsO_4^{2-} . The peak intensity at ~ 400.2 eV, corresponding to the -C-NH bond from urea moiety, subsided, suggesting the interaction of HAsO_4^{2-} with IPiPOP-3U (Appendix Figure 5.71). Also, the binding energy of O 1s electrons ~ 531.76 eV and ~ 533.4 eV, corresponding to -C=O and -C-O bonds respectively, were found to shift to a lower binding energy along with a new peak formation at ~ 530.2 eV which was assigned to the As-O bond (Appendix Figure 5.72), suggesting the efficient adsorption of both types of arsenic by IPiPOP-3U.

Further, to explore the thermodynamically favorable interactions between IPiPOP-3U and the organic & inorganic arsenic, we performed isothermal titration calorimetry (ITC) experiment (Appendix Section 5.5.1). The ITC results for the ROX adsorption showed negative value of ΔH (-16.9 ± 3.57 kcal/mol), indicating the process to be exothermic in nature along with a negative ΔG value (-6.02 kcal/mol), which suggested that the strong adsorption of ROX by IPiPOP-3U is a thermodynamically favorable process (Figure 5.4d, 5.4e, Appendix Figure 5.73-5.74, Appendix Table 5.3). Whereas for HAsO_4^{2-} adsorption by IPiPOP-3U, we found a positive ΔH value (25.1 ± 1.01 kcal/mol), suggesting it was an endothermic process. Having said that, the ΔG value, in this case, was also found negative in value (-7.61 kcal/mol), indicating that the capture of HAsO_4^{2-} by IPiPOP-3U to be thermodynamically favorable adsorption process (Figure 5.4f, 5.4g, Appendix Figure 5.75-5.76, Appendix Table 5.4). To verify the chemical environment of analytes after adsorption into the IPiPOP-3U network, we performed the X-ray Adsorption Spectroscopy (XAS) experiment.^{36, 37, 38} The experimentally derived $\chi(r)$ versus r data are fitted with theoretical plots simulated using the structural information of the material. The $\chi(r)$ versus r plot has been fitted from 1.15-3.2 Å in ROX@IPiPOP-3U assuming one As-O shell and As-N shell and from 1.5-2.0 Å in AsV@IPiPOP-3U sample assuming one As-O shell. Figure 5.4h, 5.4i shows the experimental $\chi(r)$ versus r plots of the ROX@IPiPOP-3U and HAsO_4^{2-} @IPiPOP-3U at As K edge, along with the best fit theoretical simulations. The intensity of the As-N path is higher in the ROX@IPiPOP-3U, confirming the strong interaction of ROX with the polymeric network of IPiPOP-3U resulting the high adsorption of ROX, while the As-N path in the HAsO_4^{2-} @IPiPOP-3U is absence, indicating the less adsorption of inorganic arsenic into the IPiPOP-3U network (Appendix Table 5.5). Additionally, 1H titration studies of ligand L1 with ROX shows the strong interaction between -NH proton of the L1 with ROX molecules (Appendix Section 5.5.3, Appendix Figure 5.77-5.81) further proves that urea moiety plays the crucial role in adsorption process.

To gain more insight into the suitable binding sites of ROX and HAsO_4^{2-} within IPiPOP-3U, we further conducted a density functional theory (DFT) simulation study (Appendix Section 5.5.4). From the structure IPiPOP-3U, it is evident that urea and triazine moieties are the main interactive sites for ROX and HAsO_4^{2-} . To evaluate these interactions, simulation studies were performed using the DMol3-B3LYP function, considering the respective repeating unit of IPiPOP-3U as model molecules to represent the structure of

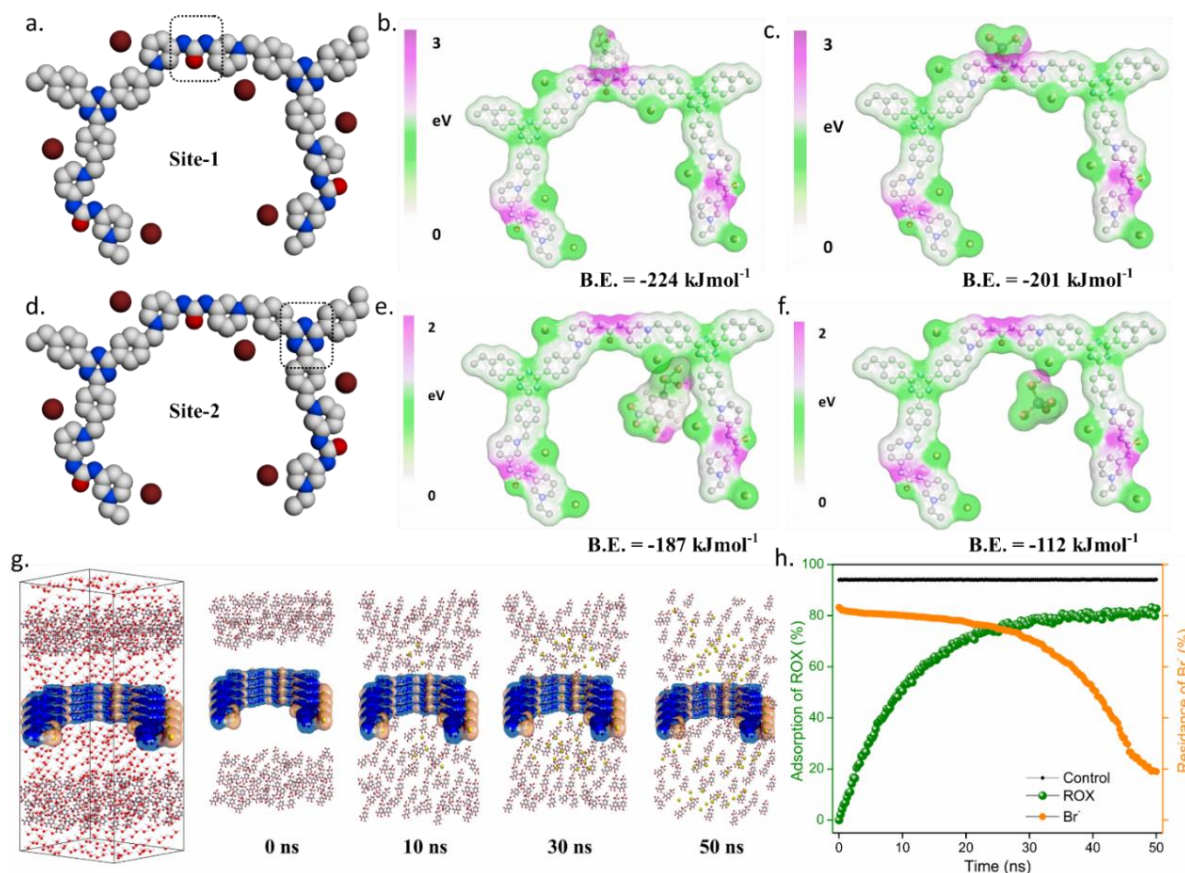


Figure 5.5: Density functional theory (DFT) calculations (a) interactive site-1 in the IPIPOP-3U, binding energy of (b) ROX and (c) HASO_4^{2-} with IPIPOP-3U at Site-1, (d) interactive site-2 in the IPIPOP-3U, binding energy of (e) ROX and (f) HASO_4^{2-} with IPIPOP-3U at Site-2, (g) A time series of snapshots to show the adsorbing dynamics of ROX molecules into the IPIPOP-3U structure at 0, 10, 30, 50 ns (h) Time evolution of the adsorption rate of ROX molecules (green) and residence rate of Br^- (orange) in IPIPOP-3U.

IPIPOP-3U, as shown in Figure 5.5a and Appendix Figure 5.82, 5.84. Site-1 in the Figure 5.5b, 5.5c indicating the interaction of ROX and HASO_4^{2-} with urea moiety of IPIPOP-3U revealed the binding energy of -224 kJmol^{-1} and -201 kJmol^{-1} respectively. On the other hand, Site-2 (Figure 5.5d) referring to the interaction of ROX and HASO_4^{2-} with triazine moiety of IPIPOP-3U revealed the binding energy of -187 kJmol^{-1} and -112 kJmol^{-1} , respectively (Figure 5.5e, 5.5f). Thus, from these calculations it is clear that the interaction of ROX and HASO_4^{2-} with the urea moiety in the IPIPOP-3U is more favorable and the driving force for the Arsenic adsorption.

Moreover, to gain further mechanistic insights into the experimental sorption pathway, we investigated the adsorption dynamics of ROX and HASO_4^{2-} into the polymeric network of IPIPOP-3U using all-atom molecular dynamics (MD) simulations.³⁹ In the case of ROX adsorption, it was observed from the

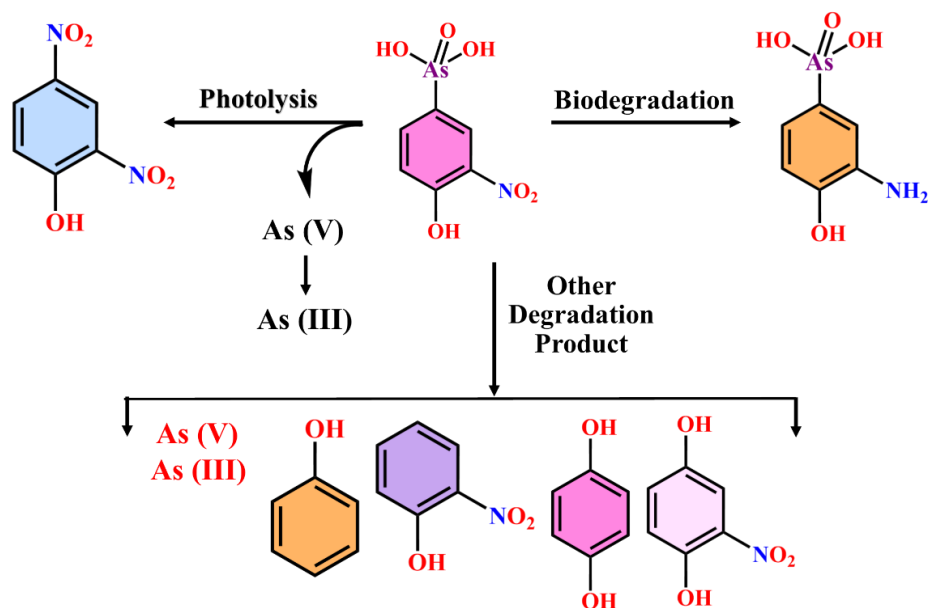
simulation study, the simulation shows that initially, a large number of ROX molecules started diffusing and were rapidly adsorbed into the pores of the IPiPOP-3U (Figure 5.5g). During this sorption process Br anions originally present in the pores of IPiPOP-3U were desorbed from the solid structure. As time progressed, the concentration of the adsorbed ROX molecules on the pore surface of IPiPOP-3U increased over time. Figure 5.5h illustrates this dynamic adsorption process; the rate of adsorption of ROX molecule in an aqueous system from the external environment into the polymeric network of IPiPOP-3U with the simulation time was calculated. Initially, in less than 10 ns, ~51% ROX molecules were adsorbed and increased to about ~78% within 30 ns and reached ~83% after 50 ns of the contact time, and dynamic equilibrium was reached with IPiPOP-3U. Meanwhile, the residence percentage of Br⁻ anion is nearly unchanged at ~19% after 50 ns (Figure 5.5h).

On the other hand, when the analyte was HAsO₄²⁻, diffusibility and the adsorption on the surface of IPiPOP-3U were a little slow as compared to ROX (Appendix Figure 5.85). It was also observed that the HAsO₄²⁻ concentration increased over time in the pores of the IPiPOP-3U. The simulation study showed (Appendix Figure 5.86), initially, in 10 ns, ~26% HAsO₄²⁻ were adsorbed, which increased over time to ~39% in 30 ns and ~41% in 50 ns of the contact time with the polymeric network of the IPiPOP-3U. Meanwhile the residence of Br⁻ anion was very slow at first, but with increasing time it was decreased to 2% after 50 ns.

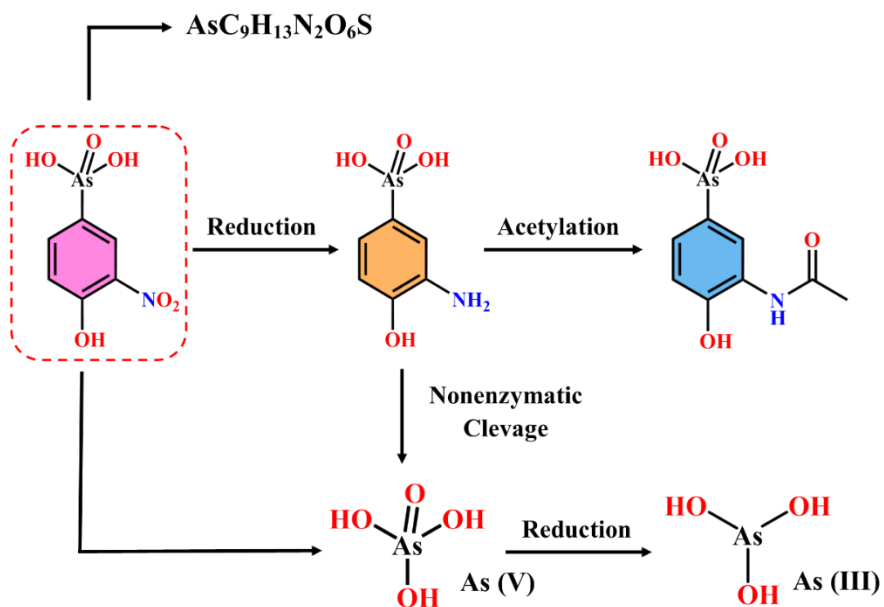
5.4 Conclusion

To summarize, a cationic urea tethered ionic porous organic polymer (IPiPOP-3U) was easily synthesized for the successful removal of Roxarsonate (ROX) from water. The strategic incorporation urea-based “nano-traps” coupled with cationic nature of the polymer network enables it with amplified interaction with the incoming ROX molecules as well as arsenate. IPiPOP-3U illustrated excellent competence toward efficient removal of both ROX and HAsO₄²⁻ with swift kinetics and high capacity. Moreover, IPiPOP-3U showed conceptual feasibility pertaining to trace amount capture, flow-through study as well as intact efficiency in real water samples and reusability. Satisfyingly, IPiPOP-3U could also achieve simultaneous removal of ROX and HAsO₄²⁻ without compromised efficacy. Moreover, mechanistic insight was investigated with a combination of various techniques such as DFT studies, EXAFS measurements and MD simulation studies while thermodynamic feasibility was also established. This work provides an outline for strategic design of a functional ionic POP adsorbent where mingling ionicity and functionality acts as a boon toward specific pollutant segregation. We believe the outcome of the current work may help toward design rationale of task-specific porous polymers featuring structural engineering aimed at targeted pollutants removal pertaining to water purification.

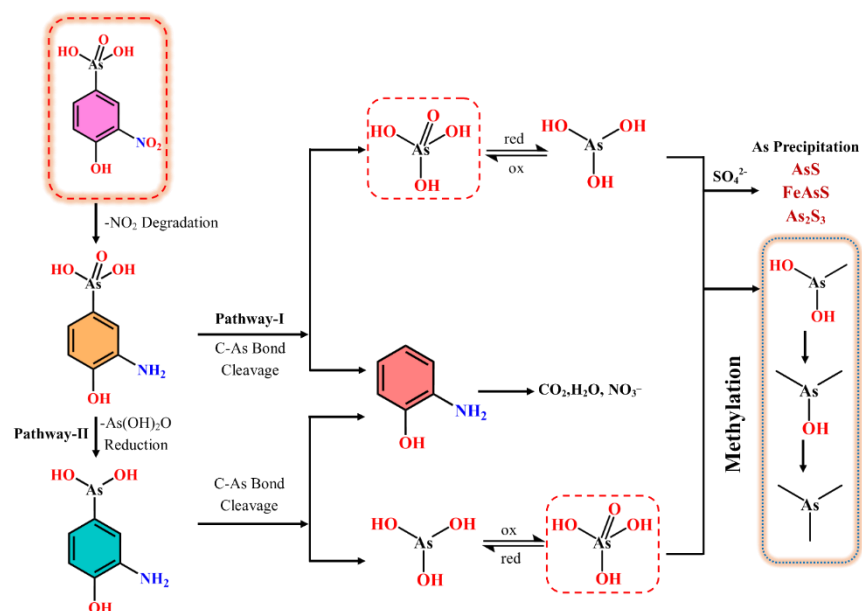
5.5 Appendix section



Appendix Figure 5.1: Potential degradation products of Roxarsone (R6)



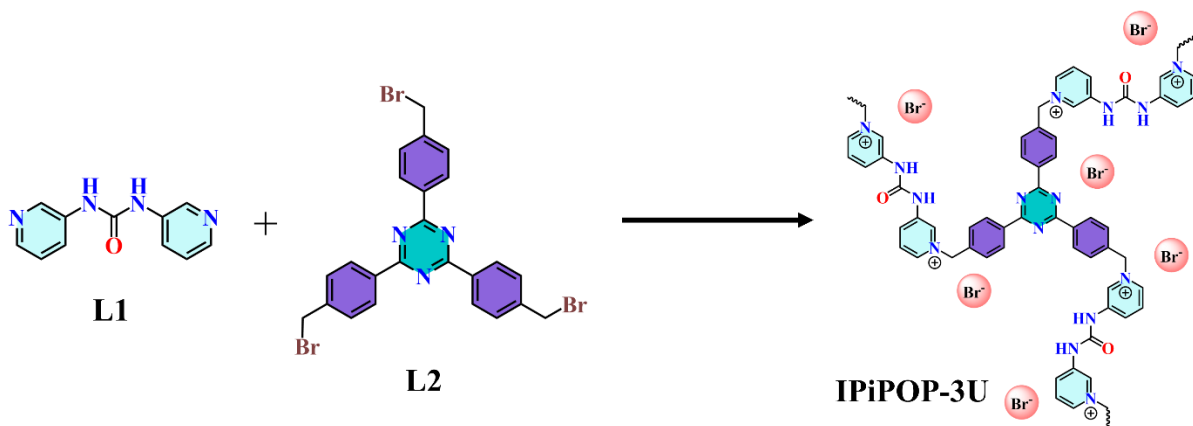
Appendix Figure 5.2: Aerobic Transformation of ROX into Inorganic Arsenic (R7)



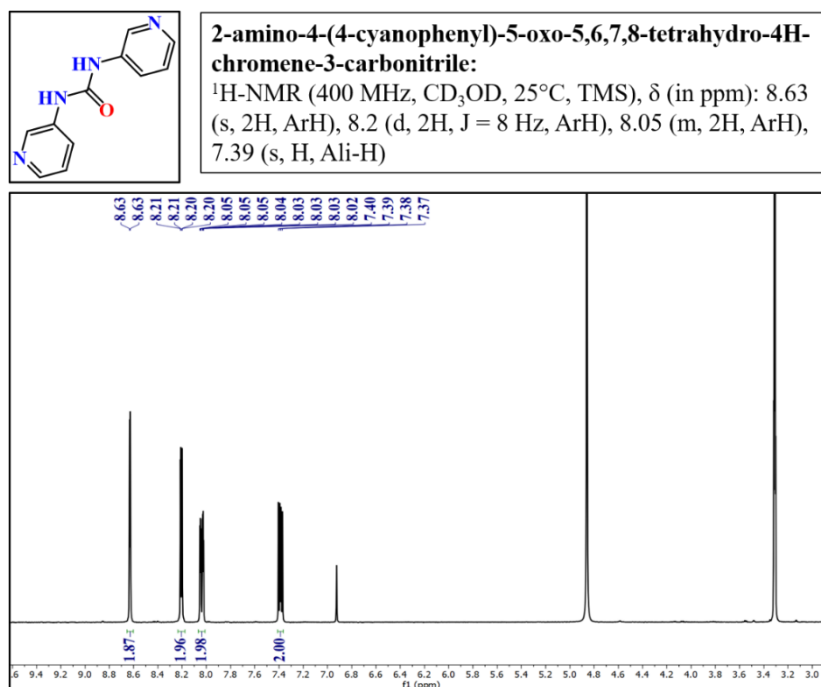
Appendix Figure 5.3: Microbial transformation pathway of ROX under anaerobic conditions (R8)



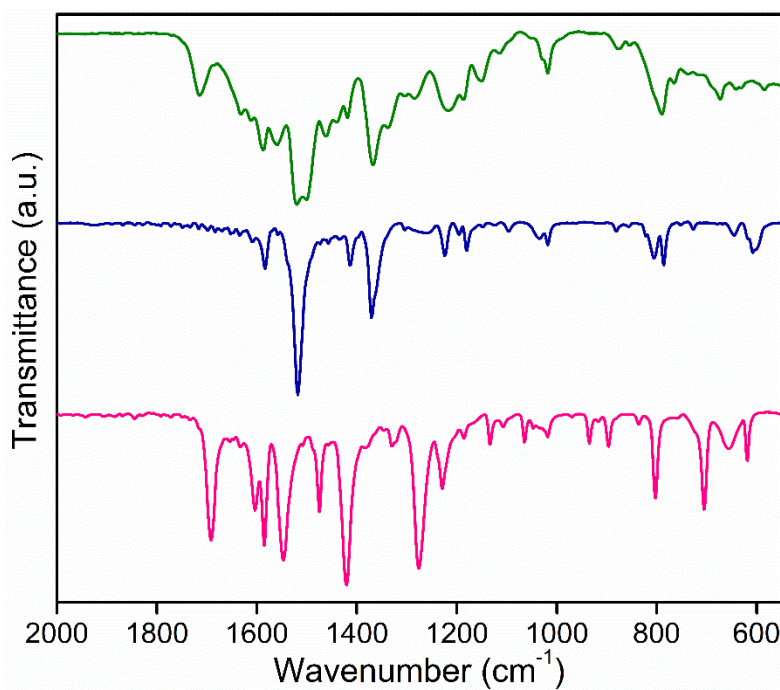
Appendix Scheme 5.1: Synthetic scheme of Ligand L1



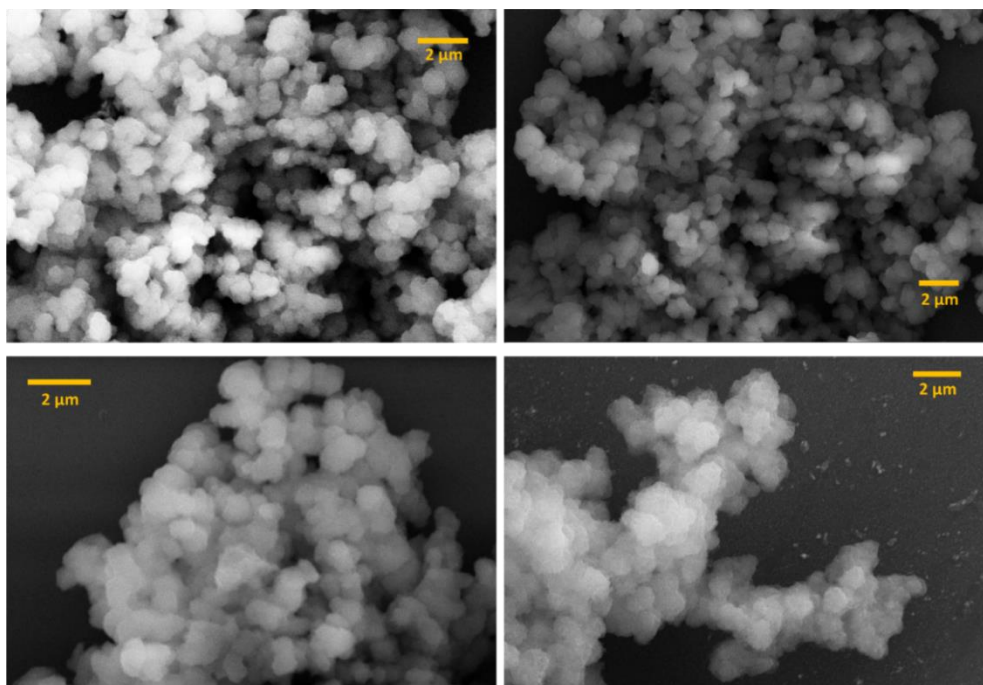
Appendix Scheme 5.2: Synthetic scheme of IPiPOP-3U.



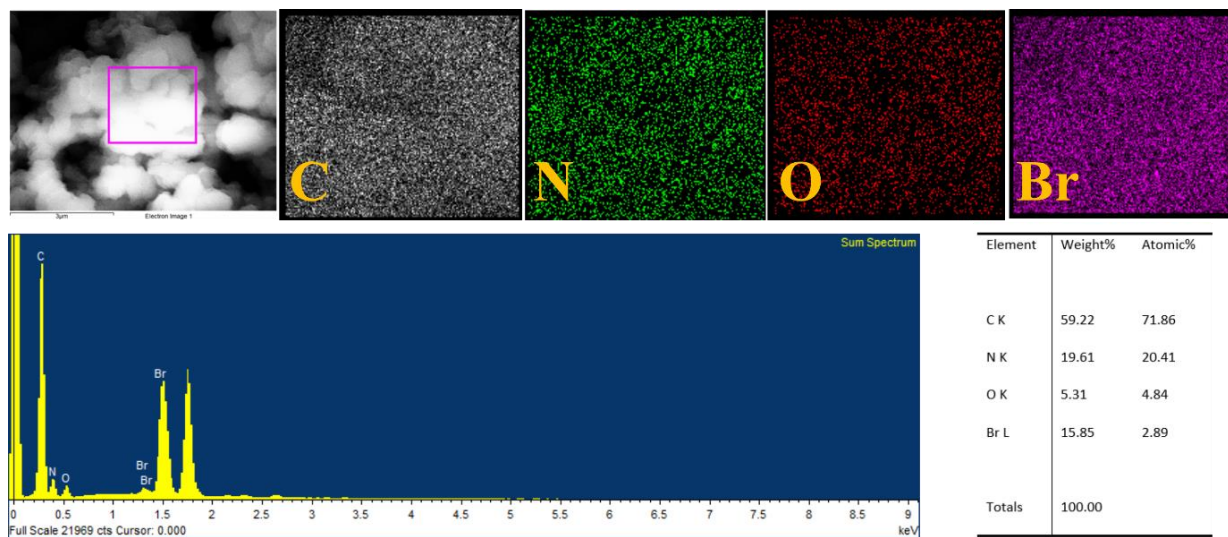
Appendix Figure 5.4: ¹H NMR of the ligand L1



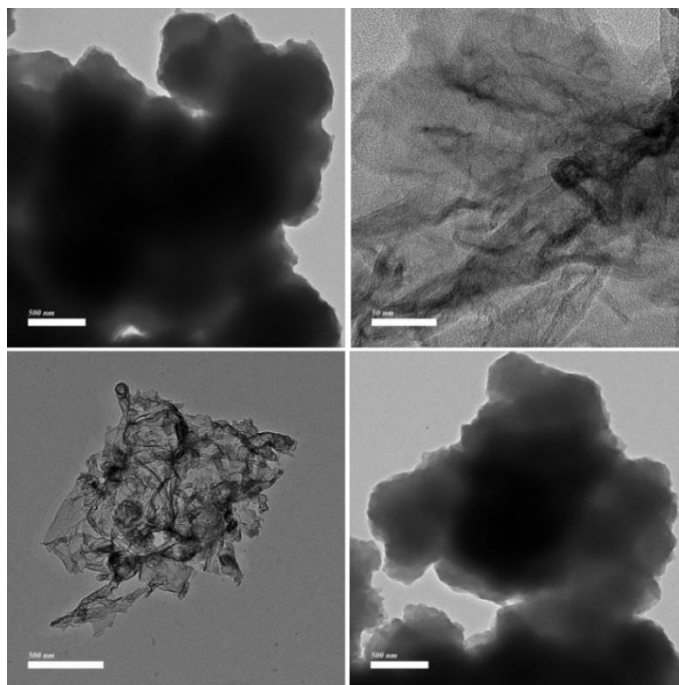
Appendix Figure 5.5: FT-IR spectra of IPiPOP-3U (urea ligand L1 (pink), tribromomethyl ligand L2 (blue), IPiPOP-3U (green))



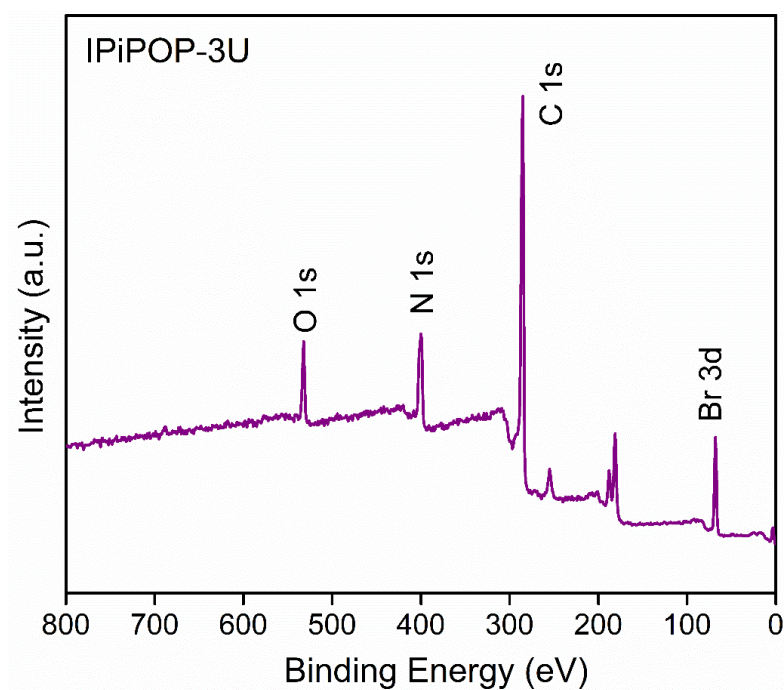
Appendix Figure 5.6: FESEM images of pristine IPiPOP-3U



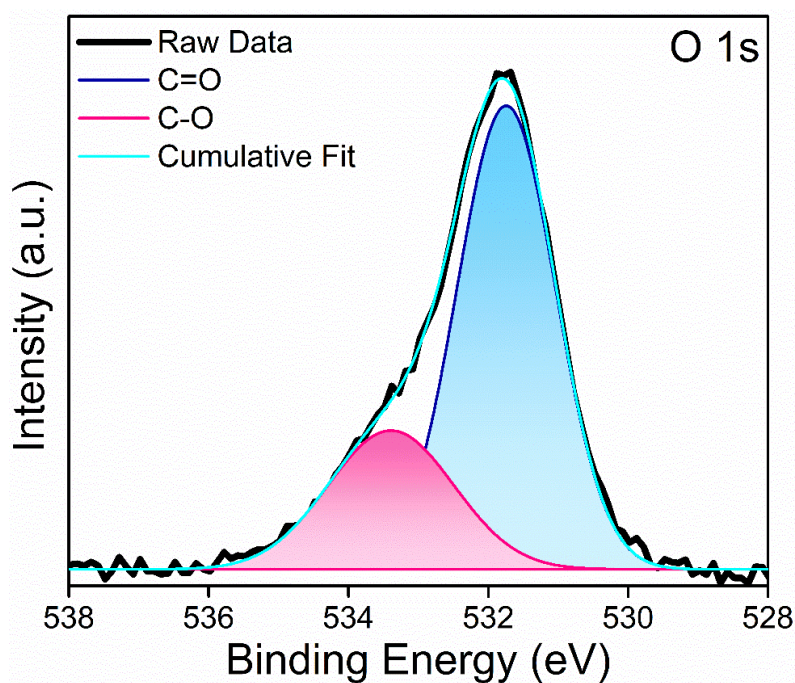
Appendix Figure 5.7: EDS and elemental mapping of pristine IPiPOP-3U



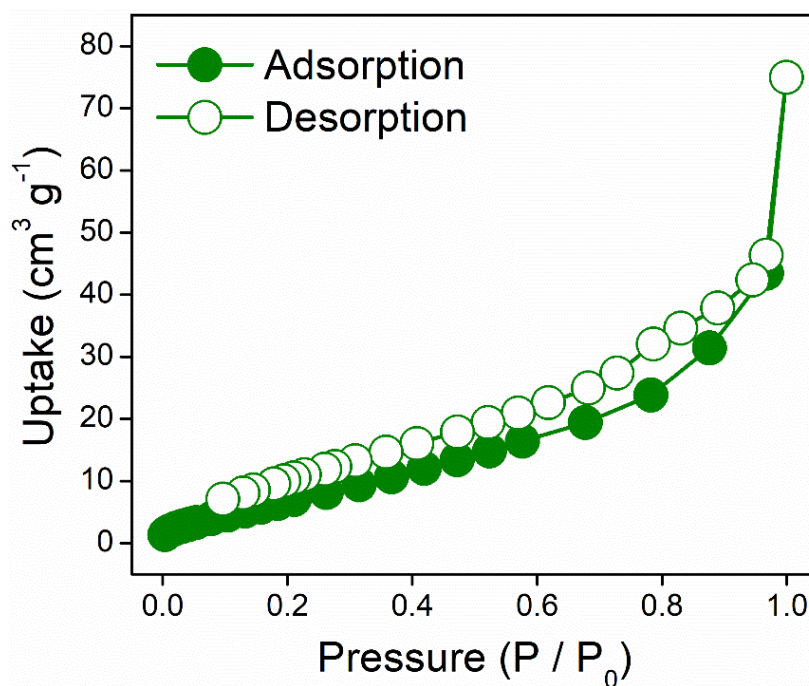
Appendix Figure 5.8: TEM images of pristine IPiPOP-3U



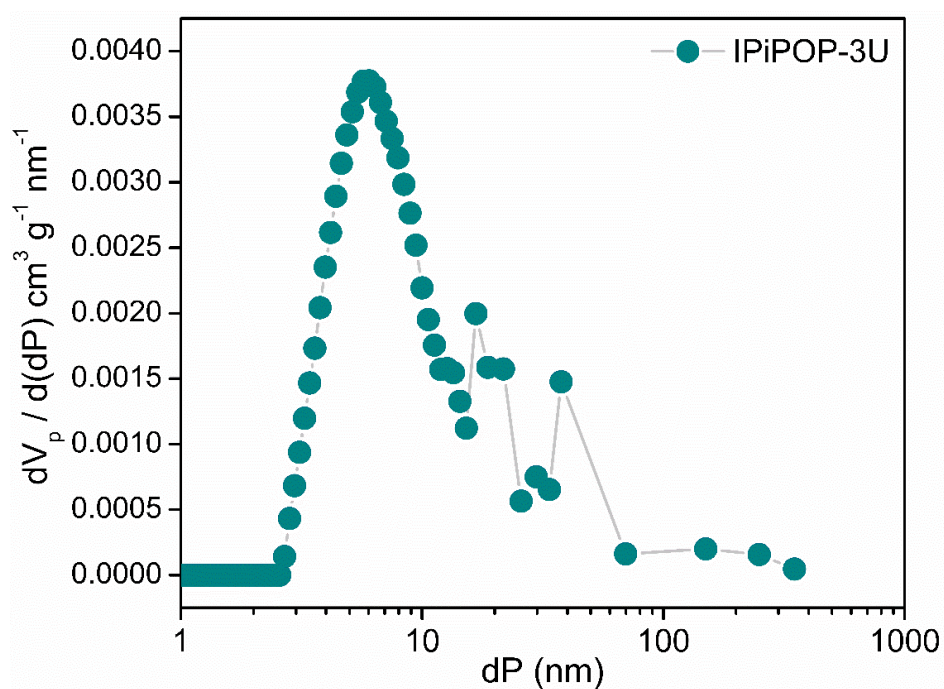
Appendix Figure 5.9: XPS survey of IPiPOP-3U



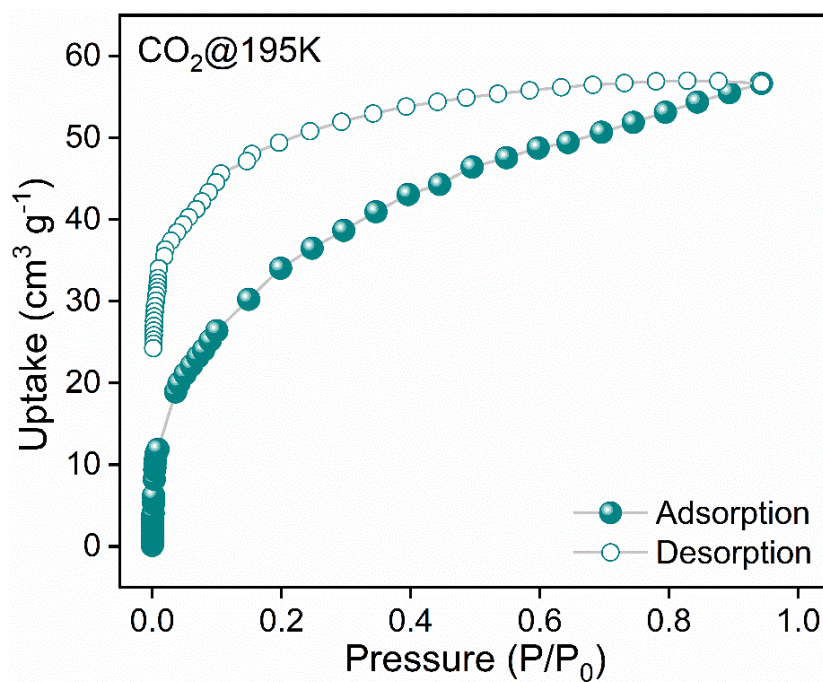
Appendix Figure 5.10: Deconvoluted XPS spectra of O1s of IPiPOP-3U



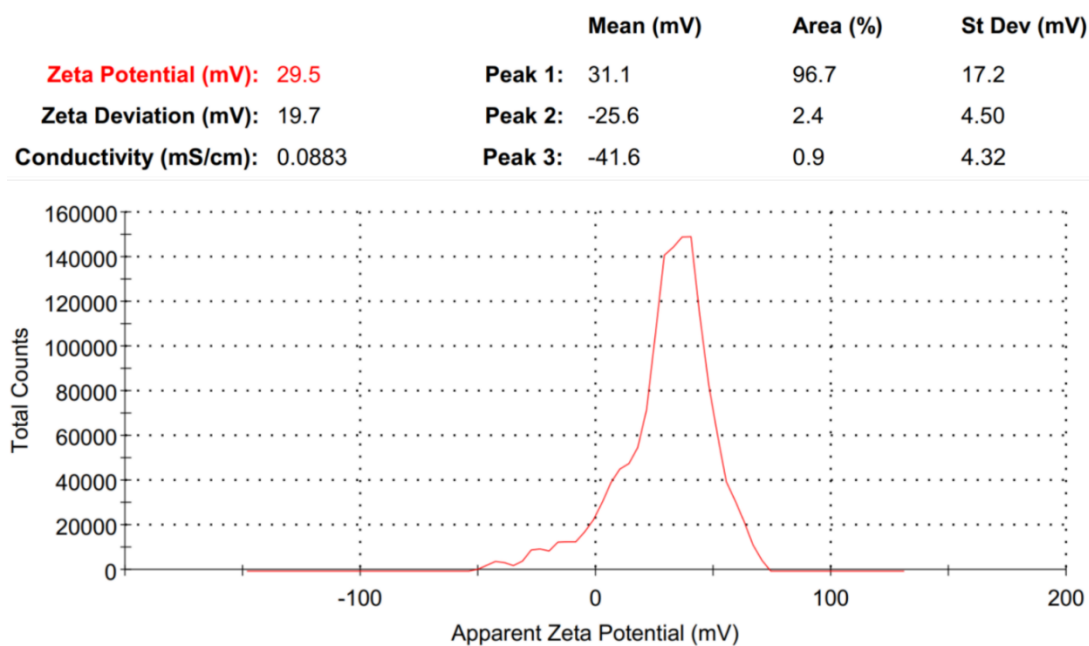
Appendix Figure 5.11: N₂ adsorption isotherm at 77K of IPiPOP-3U



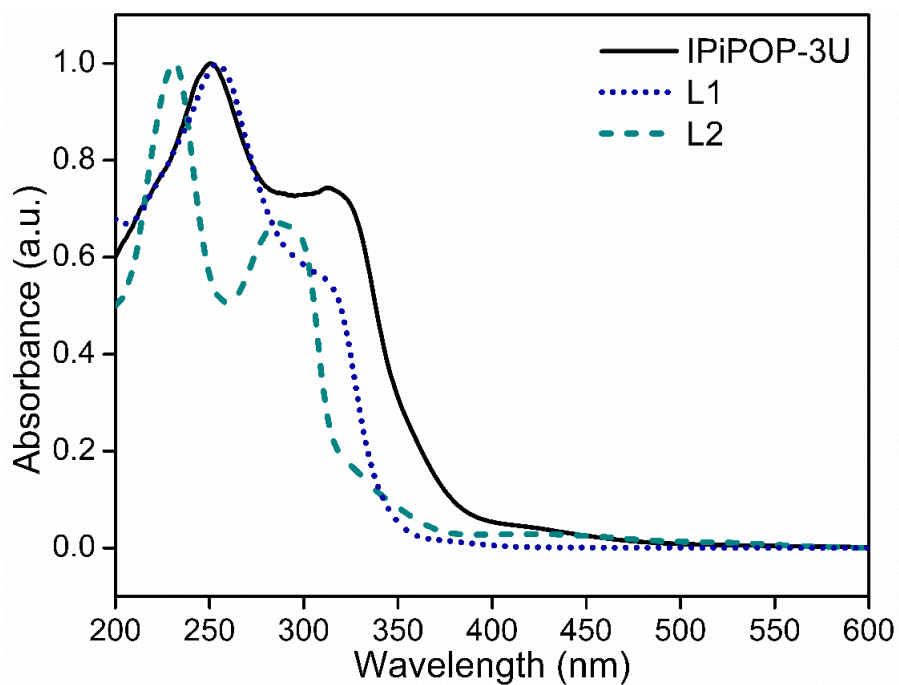
Appendix Figure 5.12: NLDFT pore size distribution of IPiPOP-3U



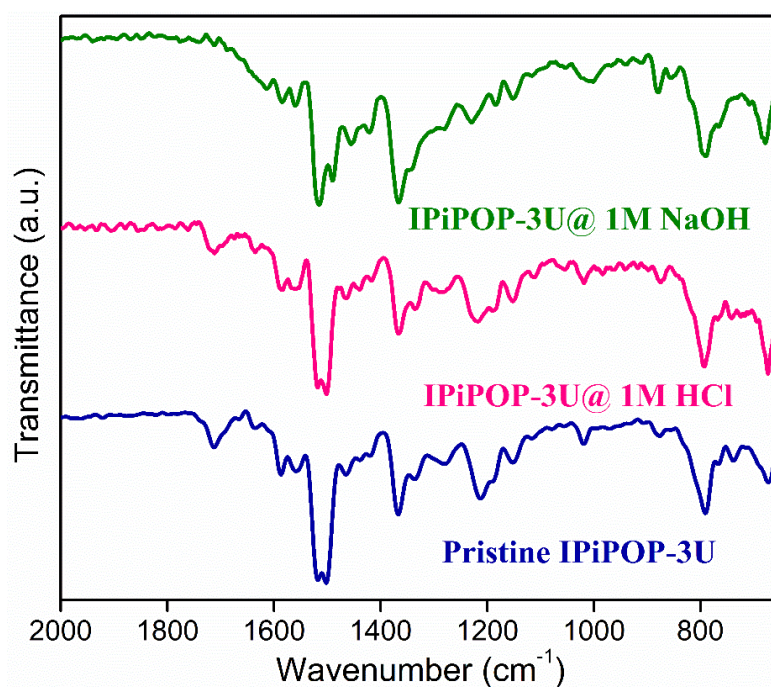
Appendix Figure 5.13: CO_2 adsorption isotherm at 195K of IPiPOP-3U



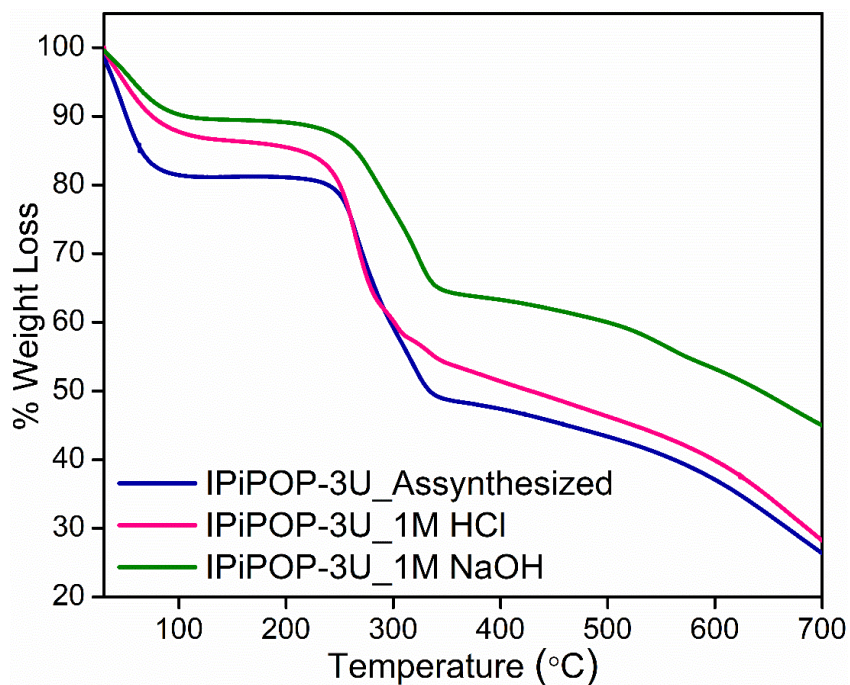
Appendix Figure 5.14: Zeta potential of IPiPOP-3U



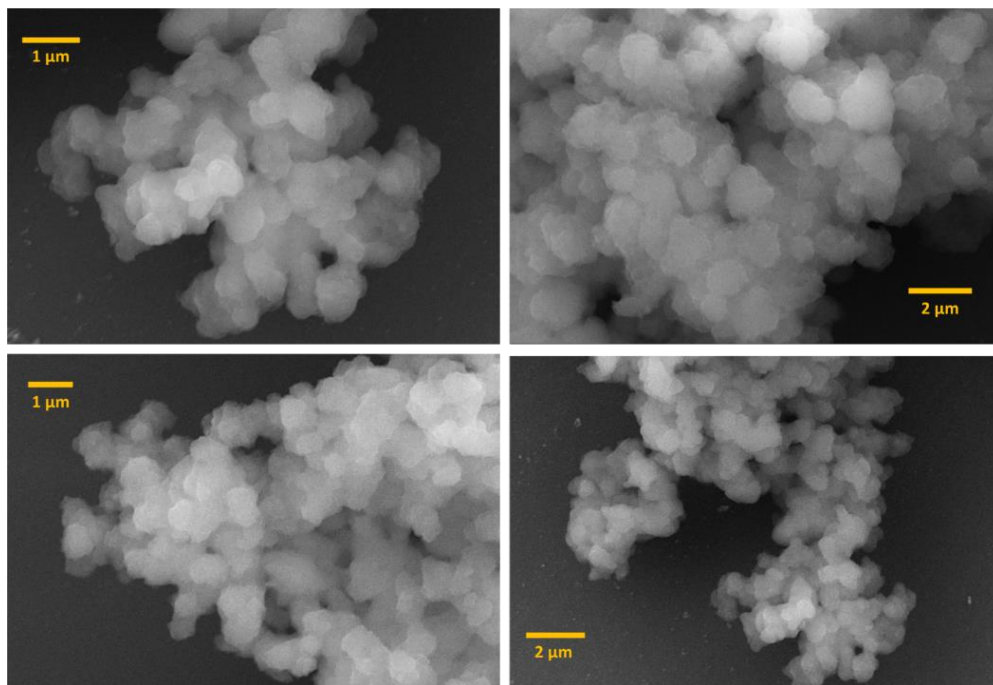
Appendix Figure 5.15: Solid State UV-Vis spectra of ligands and IPiPOP-3U



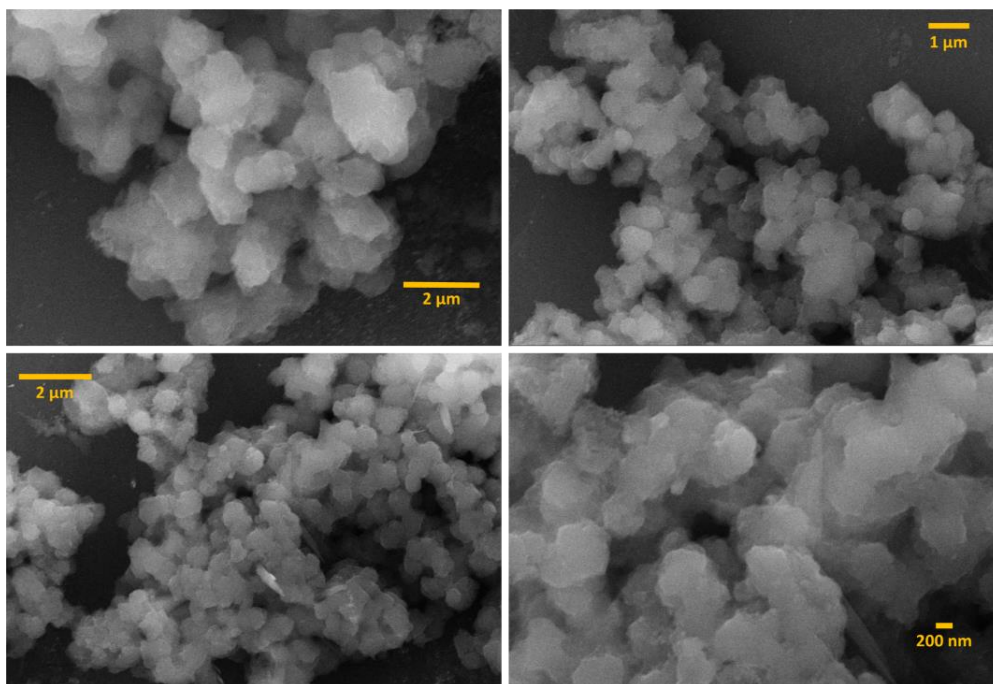
Appendix Figure 5.16: FT-IR spectra of chemical stability of IPiPOP-3U



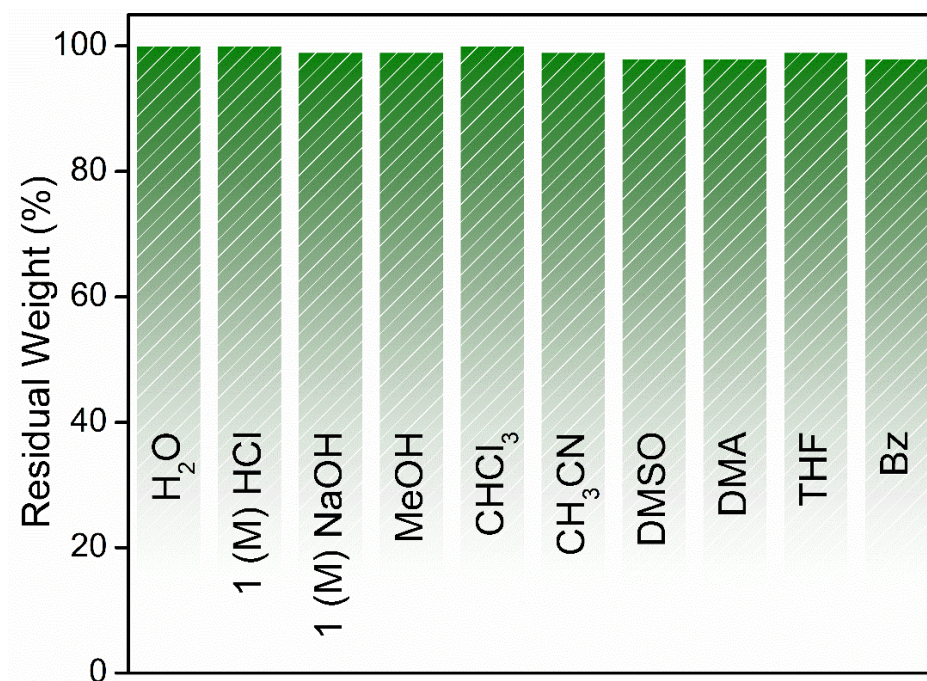
Appendix Figure 5.17: TGA spectra of chemical stability of IPiPOP-3U



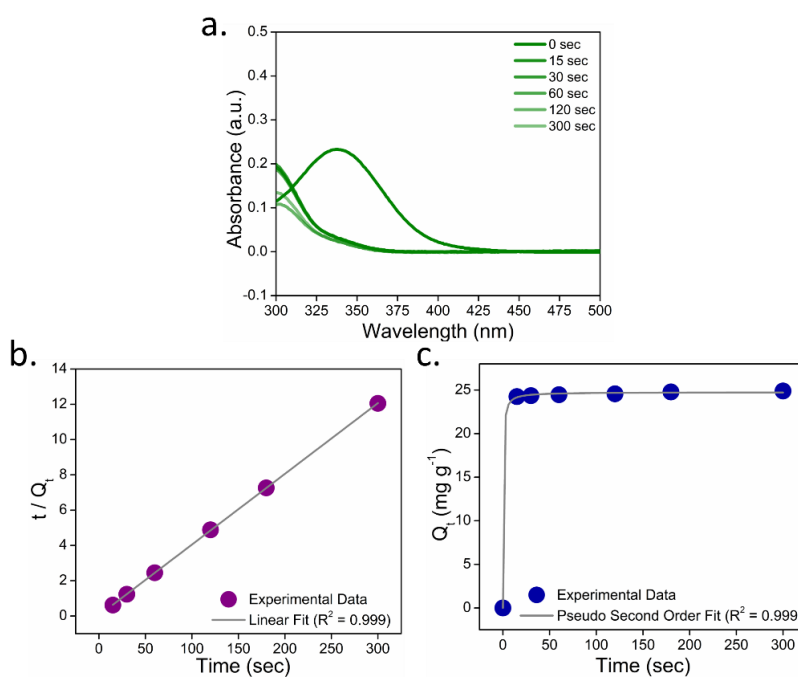
Appendix Figure 5.18: FESEM images of 1M HCl treated IPiPOP-3U



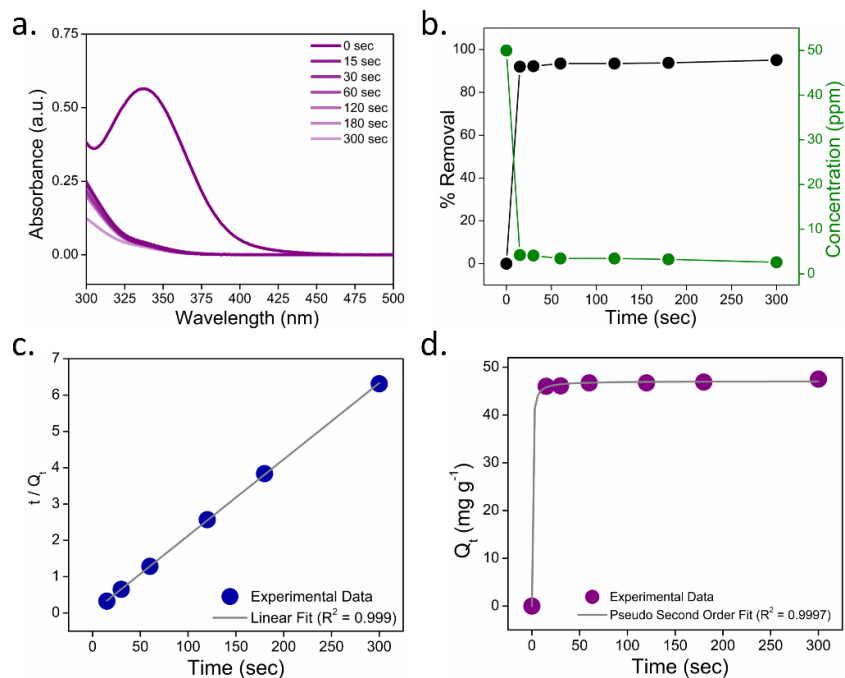
Appendix Figure 5.19: FESEM images of 1M NaOH treated IPiPOP-3U



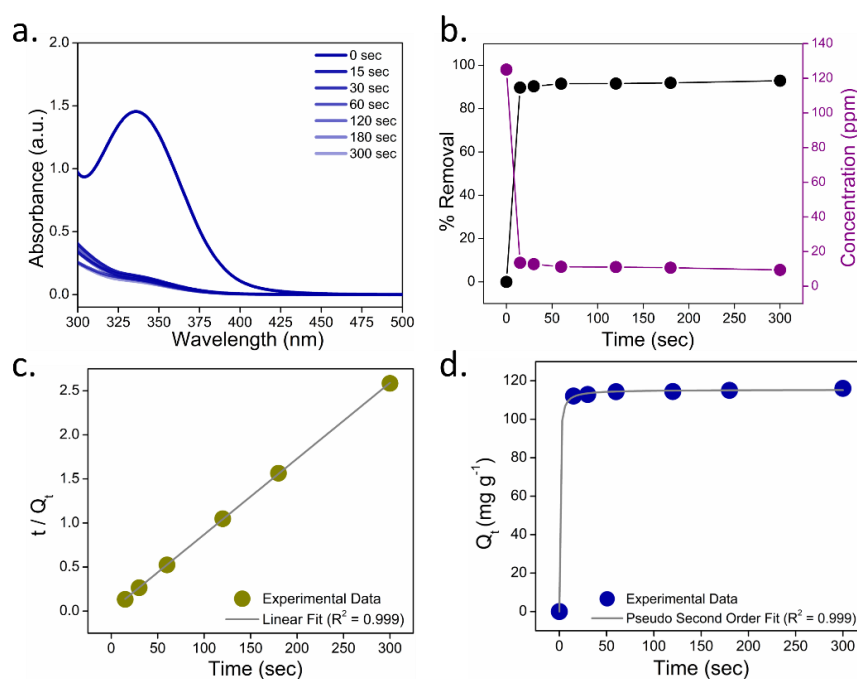
Appendix Figure 5.20: Residual weight of IPIPOP-3U treated by different solvent



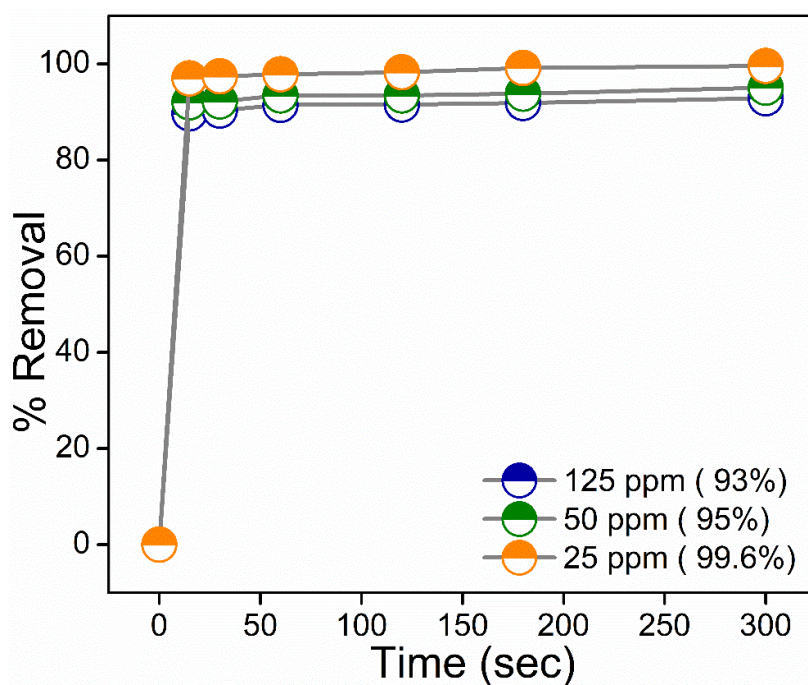
Appendix Figure 5.21: Kinetics of 25 ppm ROX capture, a. UV-Vis Spectra b. Pseudo-second-order model linear fitting, and c. sorption capacity with time



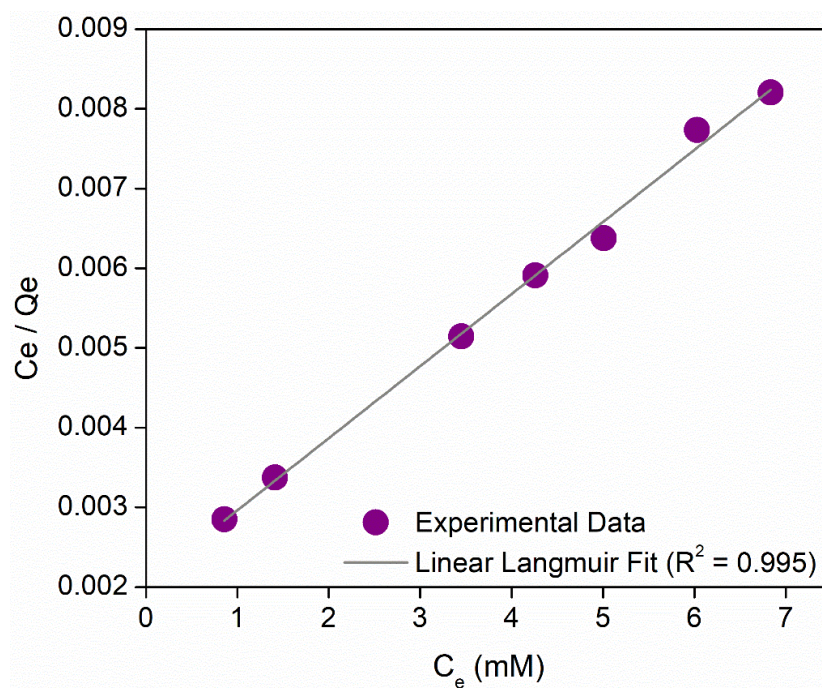
Appendix Figure 5.22: Kinetics of 50 ppm ROX capture, a. UV-Vis Spectra, b. removal percentage, c. Pseudo-second-order model linear fitting, and c. sorption capacity with time



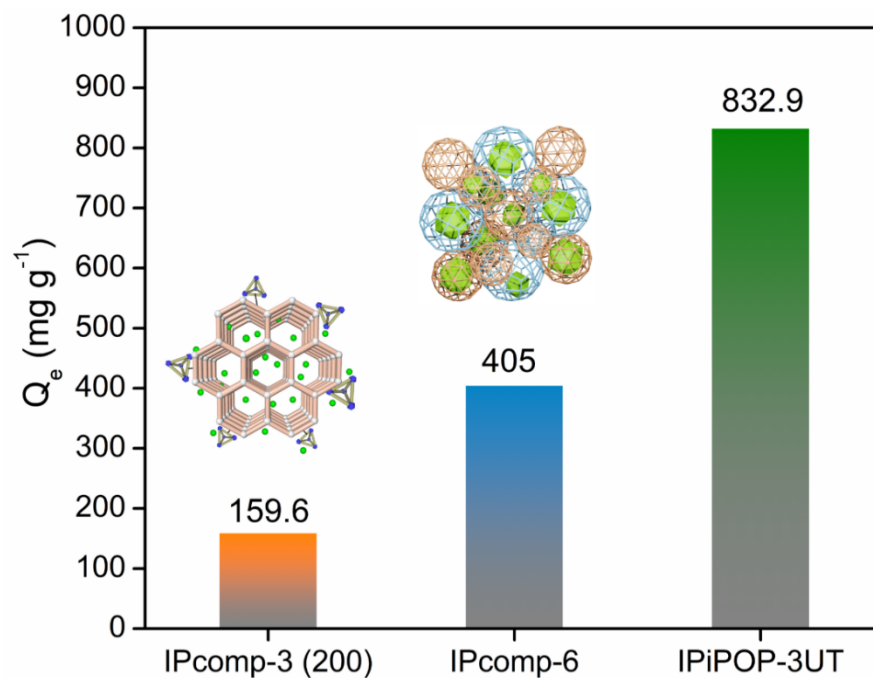
Appendix Figure 5.23: Kinetics of 125 ppm ROX capture, a. UV-Vis Spectra b. Pseudo-second-order model linear fitting, and c. sorption capacity with time



Appendix Figure 5.24: Removal efficiency of ROX in different concentration



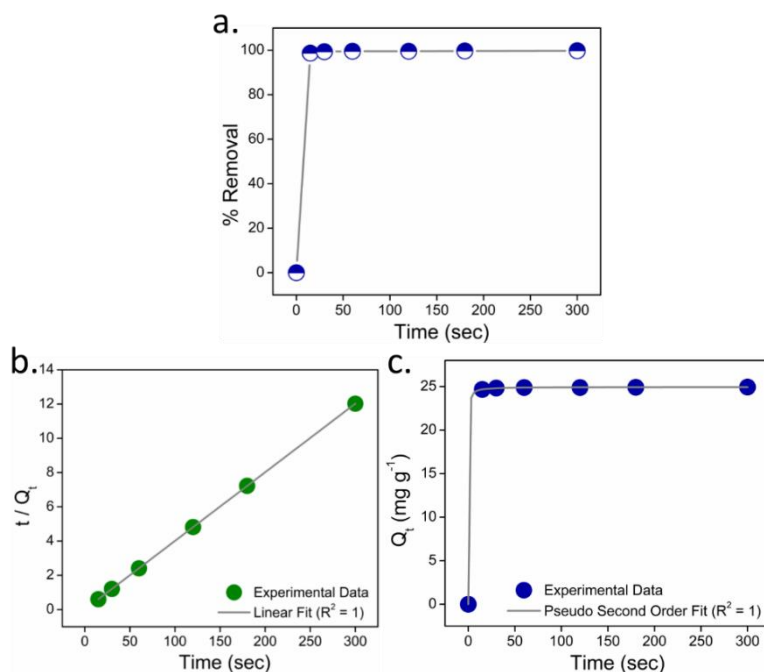
Appendix Figure 5.25: Langmuir fitting of ROX adsorption isotherm



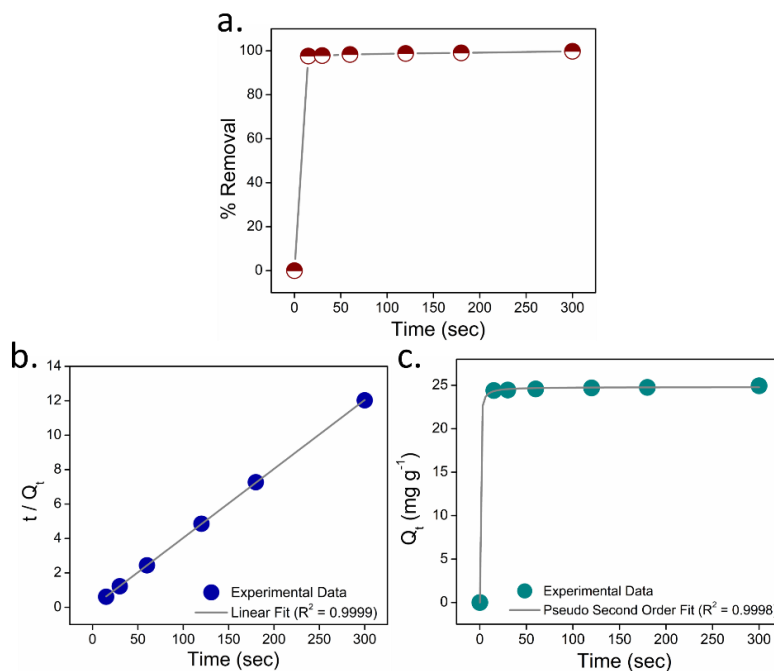
Appendix Figure 5.26: Comparative capture studies of ROX with the reported compound

Appendix Table 5.1: Comparison of this work with other related investigations of ROX capture by various adsorbents.

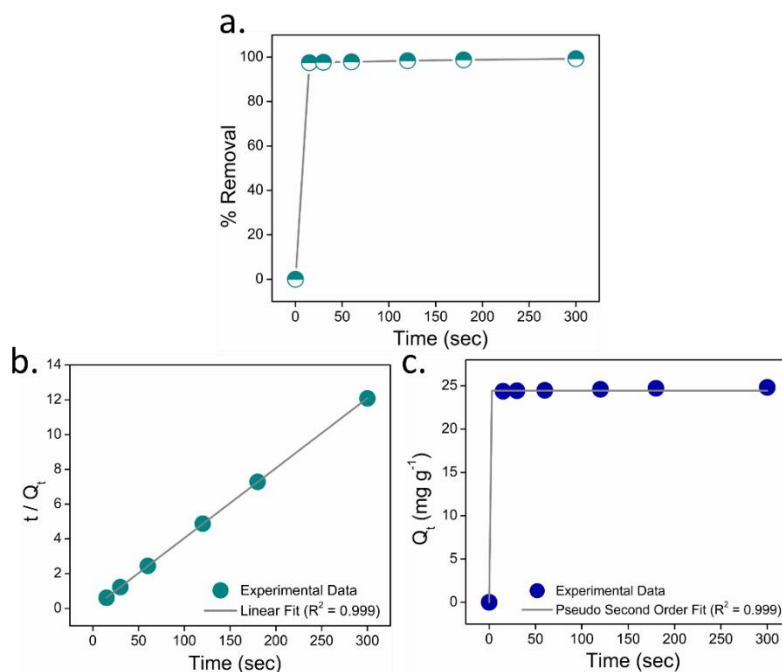
Material	Removal Time	Capacity (mg/g)	Competing Anions	Reference
IPiPOP-3U	30 sec	833	ASA, HAA, NIT, PEN, ERY	This Work
AO-COF-ben	20 min	732		R9
AO-COF-tri	25 min	787		
UiO-66-20	30 min	730	Cl ⁻ , OAc ⁻ , SO ₄ ²⁻	R10
Fe ₃ O ₄ @RGO	720 min	454		R11
Chitosan Based Copolymers		259		R12
Porous magnetic carbon composites		417		R13
MC-160		515.5		R14
MOF-808F	4 hours	709.2	Cl ⁻ , OAc ⁻ , SO ₄ ²⁻	R15
MOF-808		641		
NU-1000		298		
MIL-100Fe	12 hours	387		R16



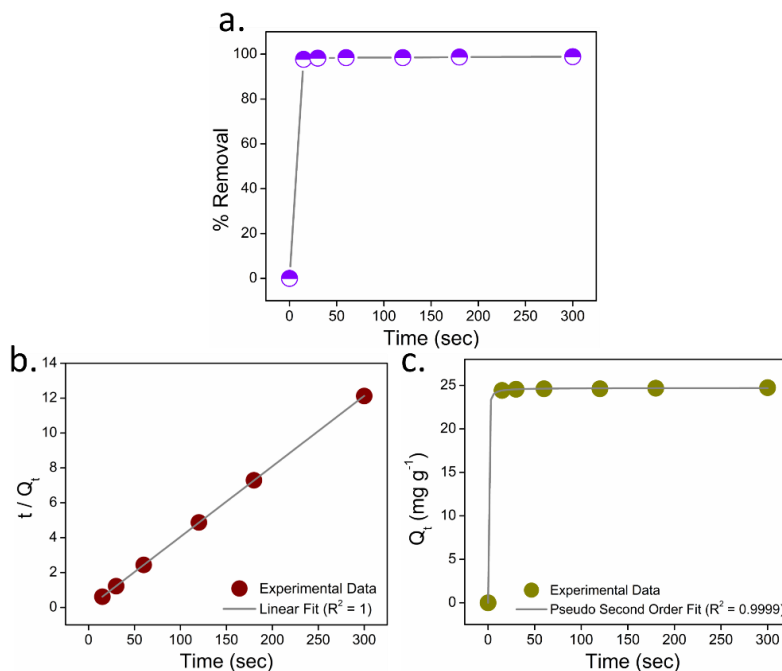
Appendix Figure 5.27: Kinetics of 25 ppm ROX capture in River Water, a. removal percentage, b. Pseudo-second-order model linear fitting, and c. sorption capacity with time



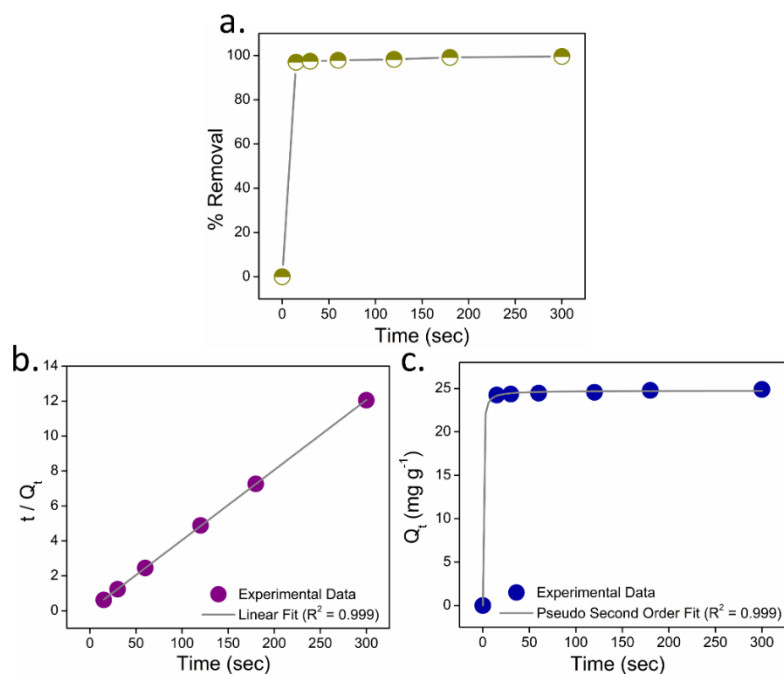
Appendix Figure 5.28: Kinetics of 25 ppm ROX capture in Lake Water, a. removal percentage, b. Pseudo-second-order model linear fitting, and c. sorption capacity with time



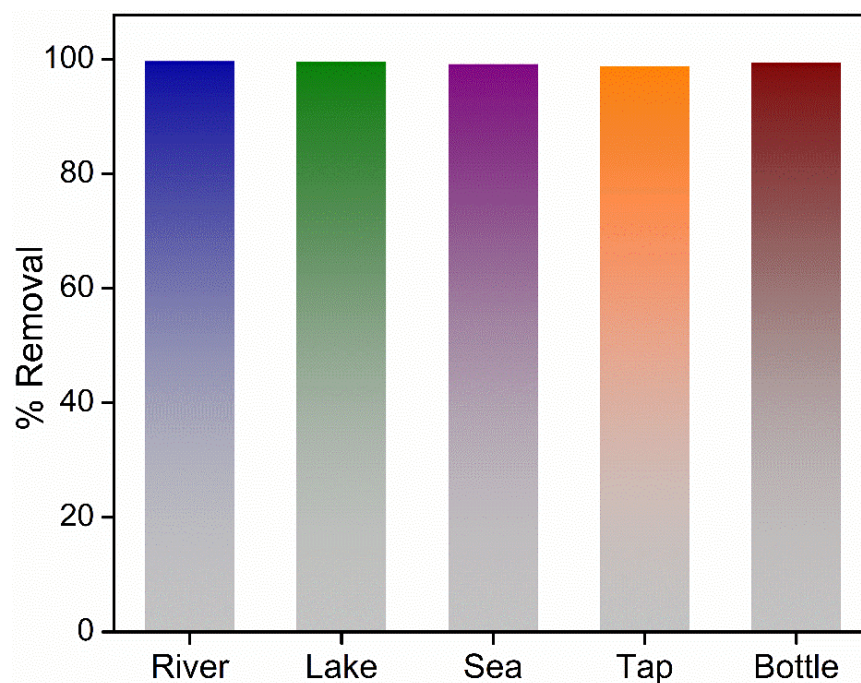
Appendix Figure 5.29: Kinetics of 25 ppm ROX capture in Sea Water, a. removal percentage, b. sorption Pseudo-second-order model linear fitting, and c. sorption capacity with time



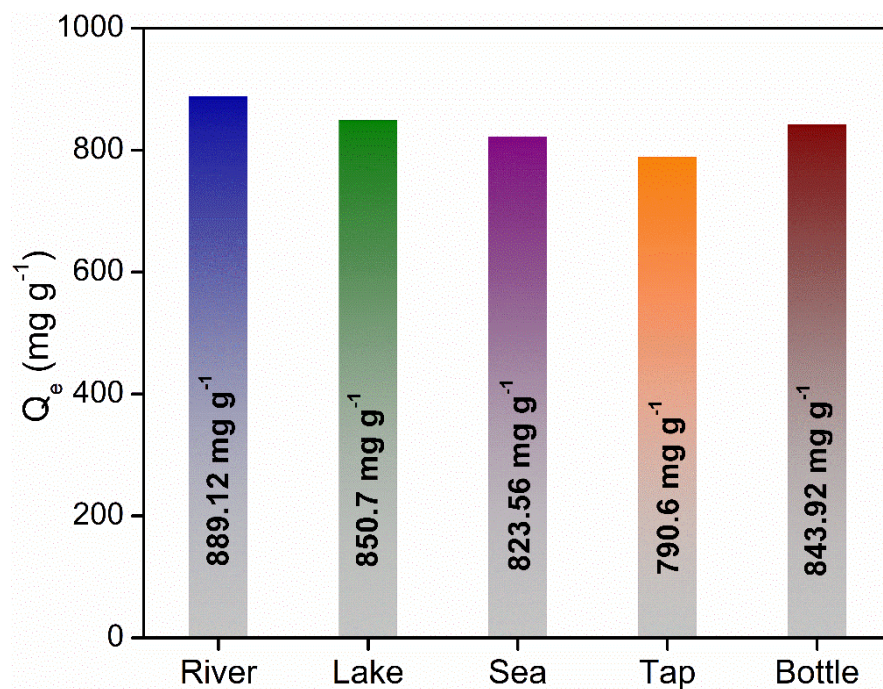
Appendix Figure 5.30: Kinetics of 25 ppm ROX capture in Tap Water, a. removal percentage, b. sorption Pseudo-second-order model linear fitting, and c. sorption capacity with time



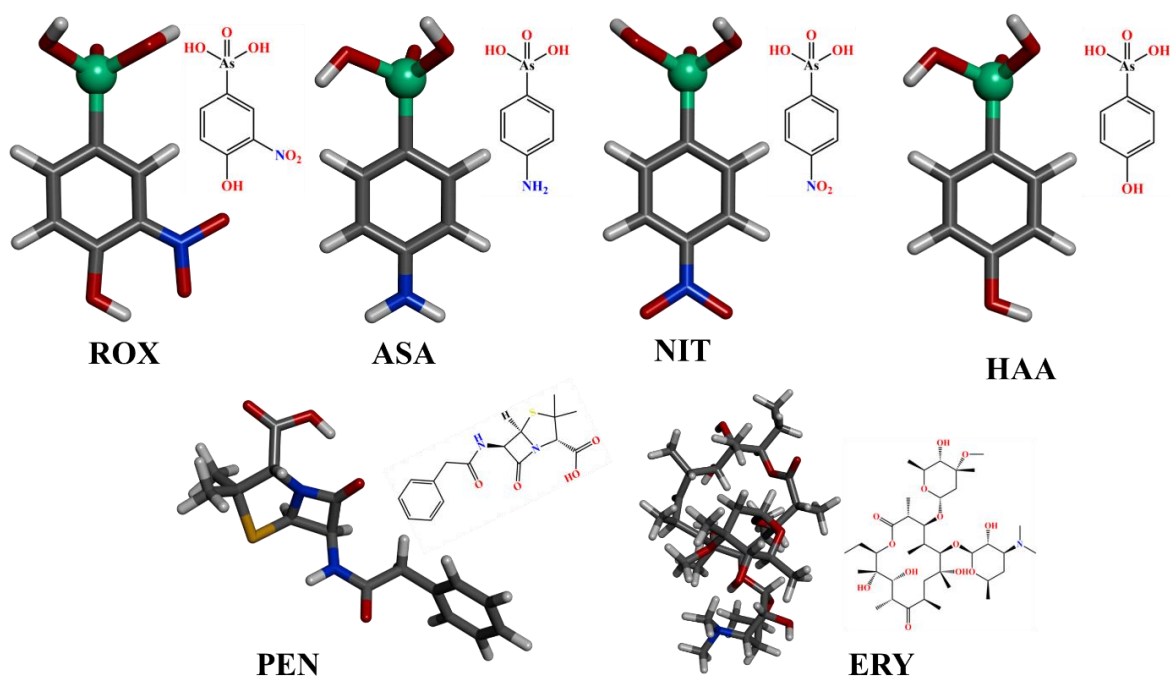
Appendix Figure 5.31: Kinetics of 25 ppm ROX capture in Bottle Water, a. removal percentage, b. Pseudo-second-order model linear fitting, and c. sorption capacity with time



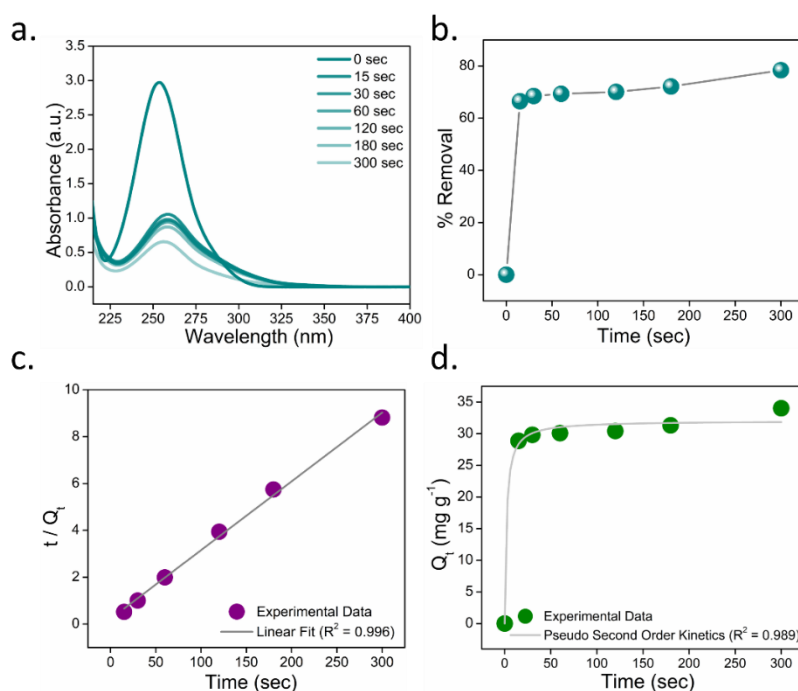
Appendix Figure 5.32: Removal Efficiency of ROX in different water bodies



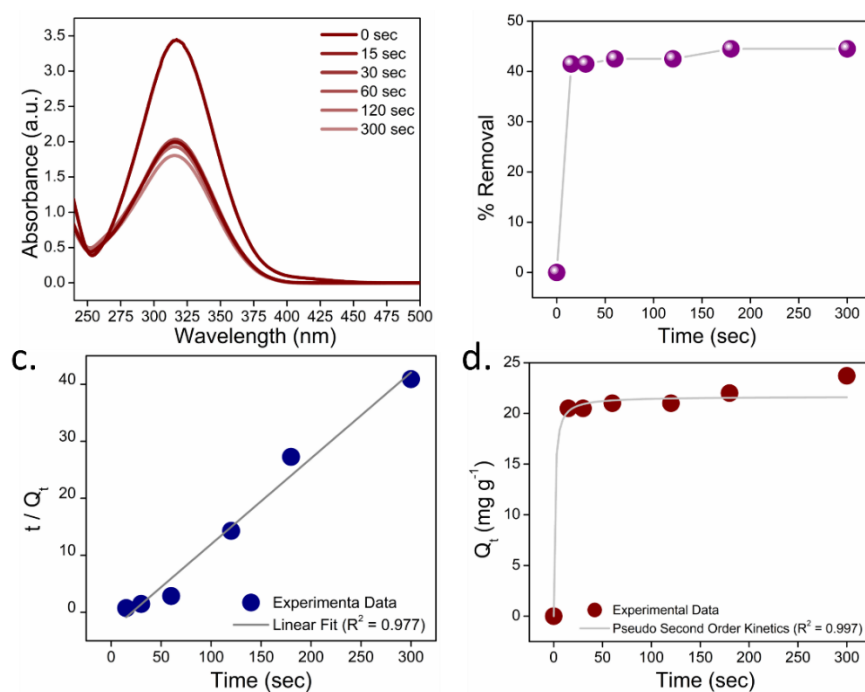
Appendix Figure 5.33: Capacity of ROX in different water bodies



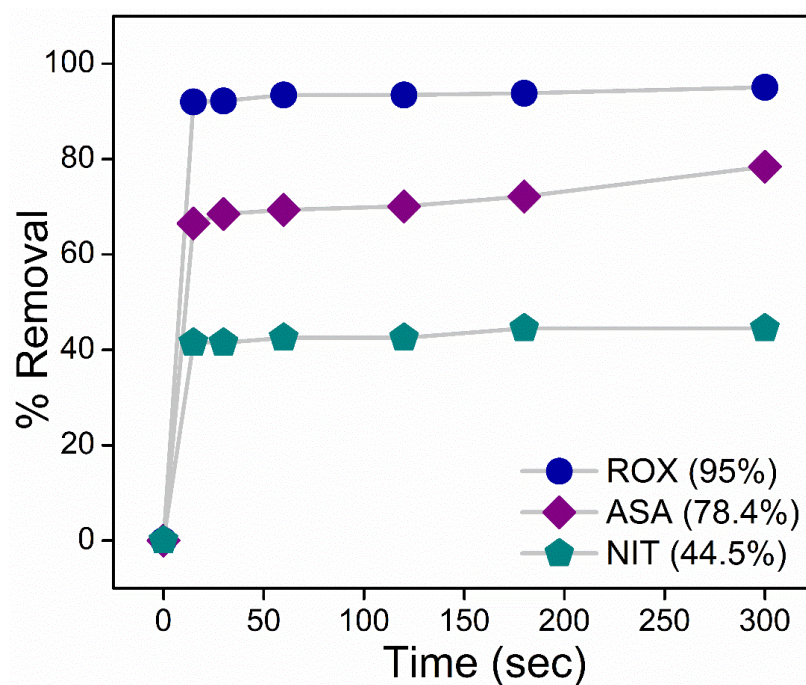
Appendix Figure 5.34: Different organic arsenics and competing drugs



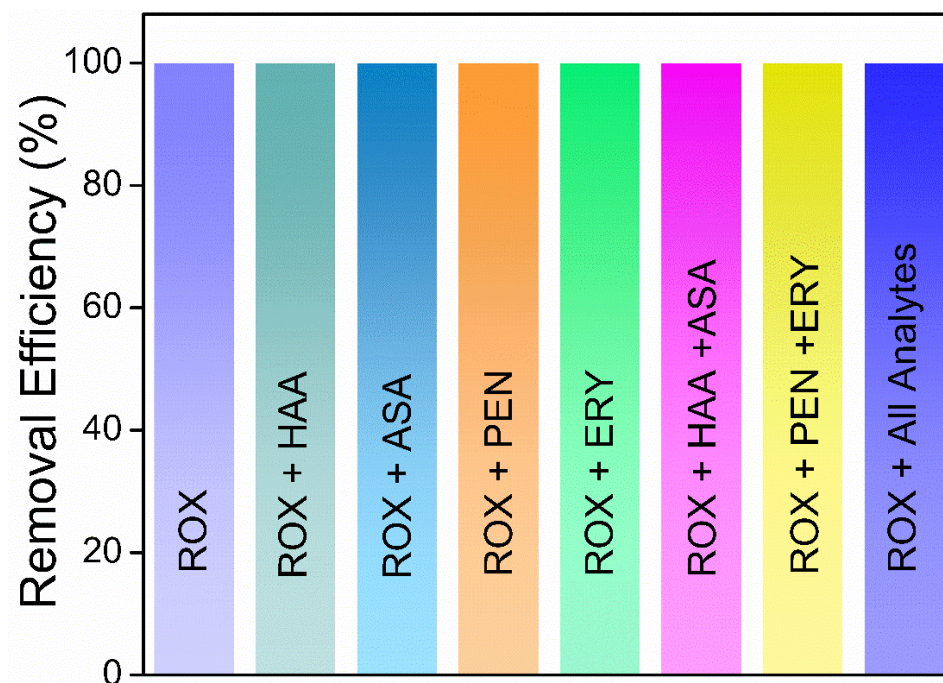
Appendix Figure 5.35: Kinetics of 50 ppm ASA capture, a. UV-Vis Spectra, b. removal percentage, c. Pseudo-second-order model linear fitting, and d. sorption capacity with time



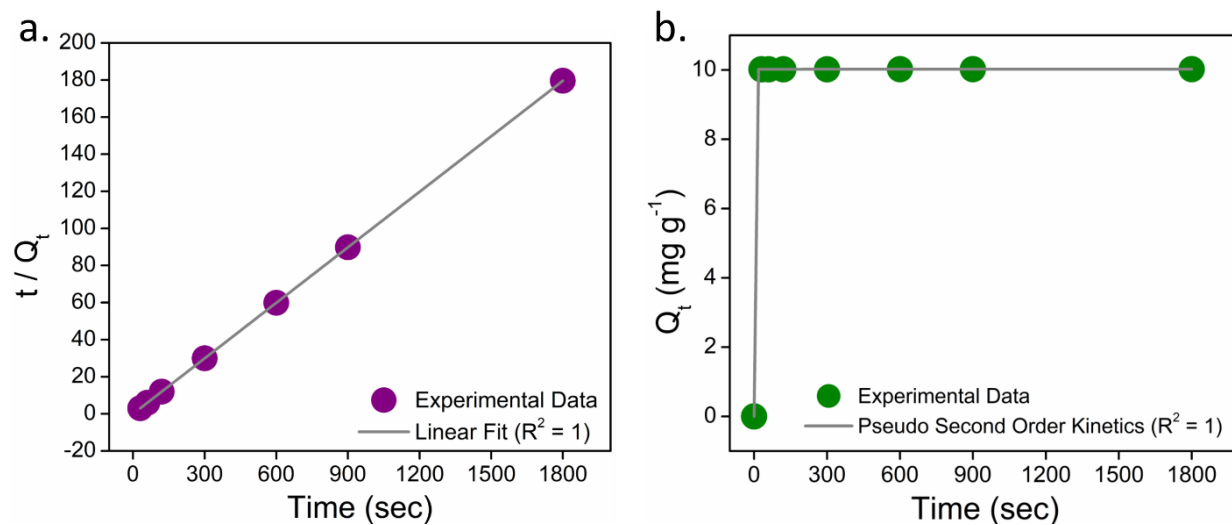
Appendix Figure 5.36: Kinetics of 50 ppm NIT capture, a. UV-Vis Spectra, b. removal percentage, c. Pseudo-second-order model linear fitting, and d. sorption capacity with time



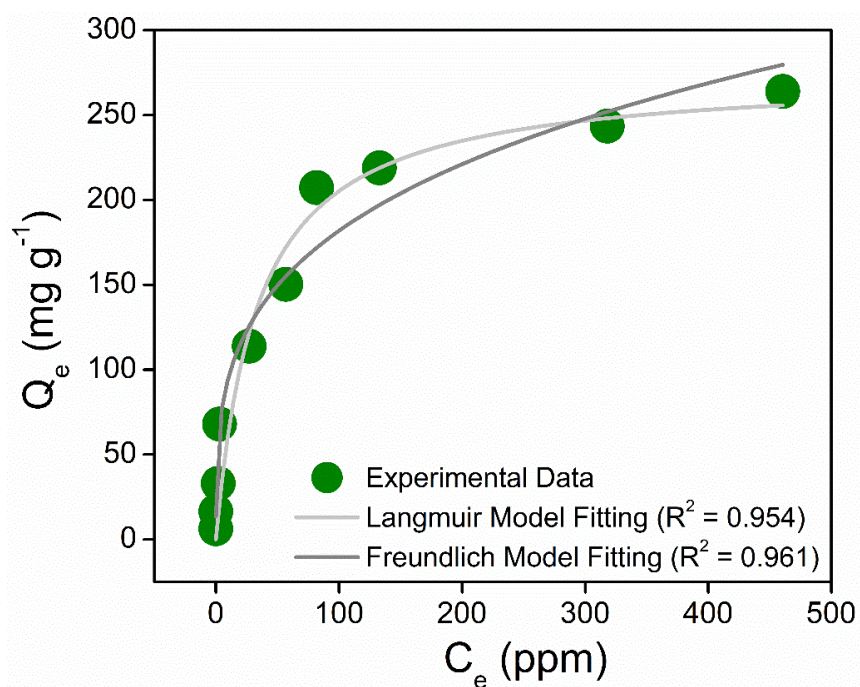
Appendix Figure 5.37: Removal efficiency of different organic arsenic (50 ppm) by IPiPOP-3U



Appendix Figure 5.38: Capture studies of ROX in presence of different competing compounds



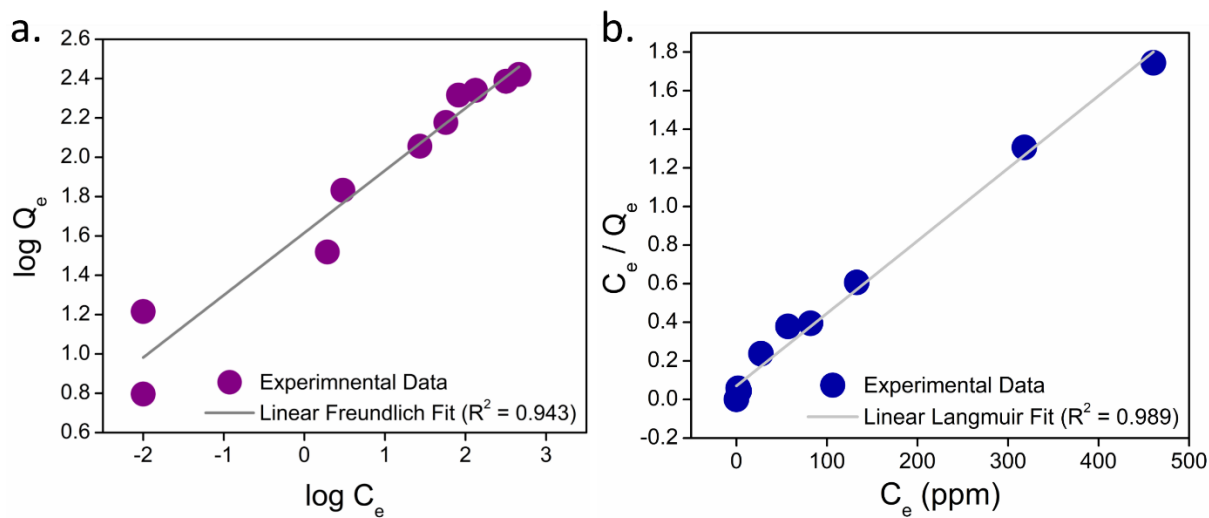
Appendix Figure 5.39: Kinetics of 10 ppm HAsO_4^{2-} , a. Pseudo-second-order model linear fitting, and b. sorption capacity with time



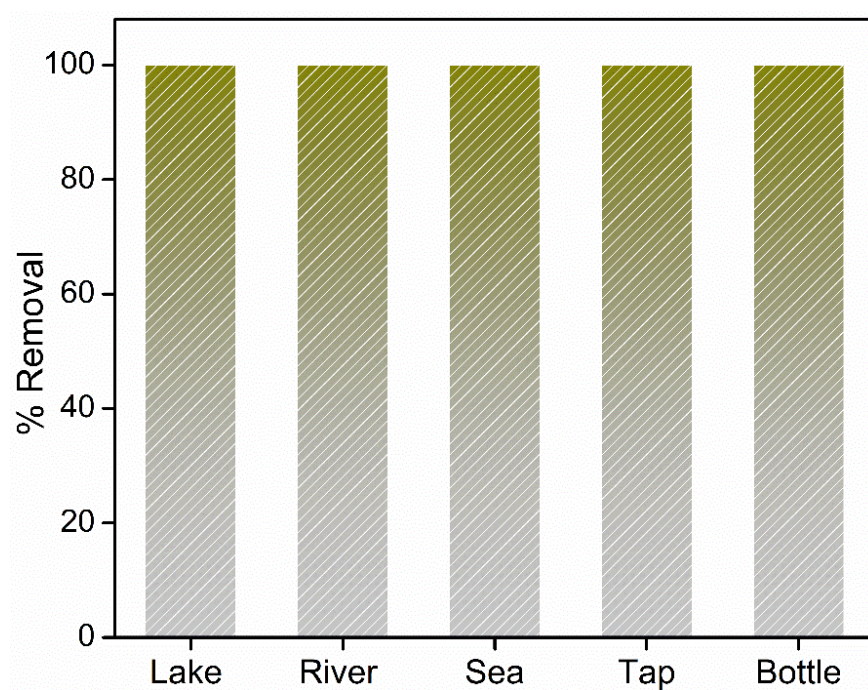
Appendix Figure 5.40: Kinetics of 10 ppm HAsO_4^{2-} , a. Pseudo-second-order model linear fitting, and b. sorption capacity with time

Appendix Table 5.2: Comparison of this work with other related investigations of As (V) capture by various adsorbents.

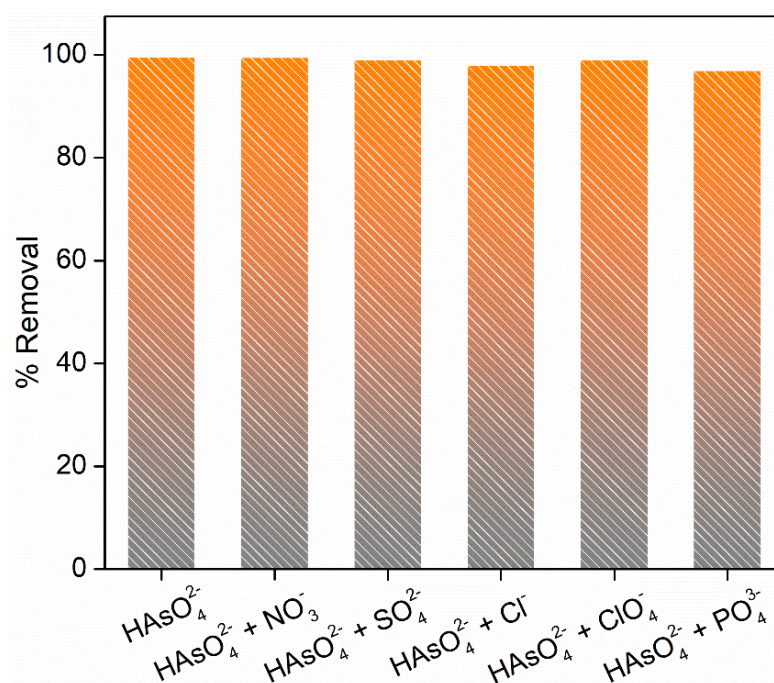
Material	Removal Time	Capacity(mg/g)	Competing Ions	Reference
IPiPOP-3U	1 min	264	NO_3^- , SO_4^{2-} , Cl^- , ClO_4^- , PO_4^{3-}	This Work
iMOF-3C	5 min	75.5	Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , HCO_3^-	R17
iMOF-1C	72 h	85	Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , HCO_3^-	R18
UiO-66	24 h	303 (pH=2)	Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , HCO_3^-	R19
Mg/Al -LDH	5 min	56	N.D.	R20
Fe-BTC	10 min	57.705	N.D.	R21
MIL-53(Al)	11 h	106.5	Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , HCO_3^- , F^- , PO_4^{3-}	R22
MIL-53(Fe)	N.D.	21.27		
IPcomp-6	5 min	157	Cl^- , Br^- , SO_4^{2-} , NO_3^- , ClO_4^-	R23
IPcomp-3(200)	< 2 min	N. D	Cl^- , Br^- , SO_4^{2-} , NO_3^- , ClO_4^-	R24
RT-Zn-MOF-74	120 min	99	N.D.	R25
HT-Zn-MOF-74	120 min	48.7	N.D.	
HIO-P-alginate		8.16		R26
HFOR	20 h	71.56	SO_4^{2-}	R27
NH2-MIL-88(Fe)	60 min	125	Various cations and anions	R28
Zn-MOF-74	150 min	325	Cl^- , NO_3^- , PO_4^{3-}	R29
AUBM-1	3 h	103.1	CO_3^{2-} , NO_3^-	R30
$\text{Fe}_3\text{O}_4@\text{UiO-66}$	100 min	73.2	N.D.	R31
MOF-808	4 h	24.83	N.D.	R32
ZIF-8	7 h	76.5	Cl^- , NO_3^- , SO_4^{2-} , F^- , PO_4^{3-}	R33



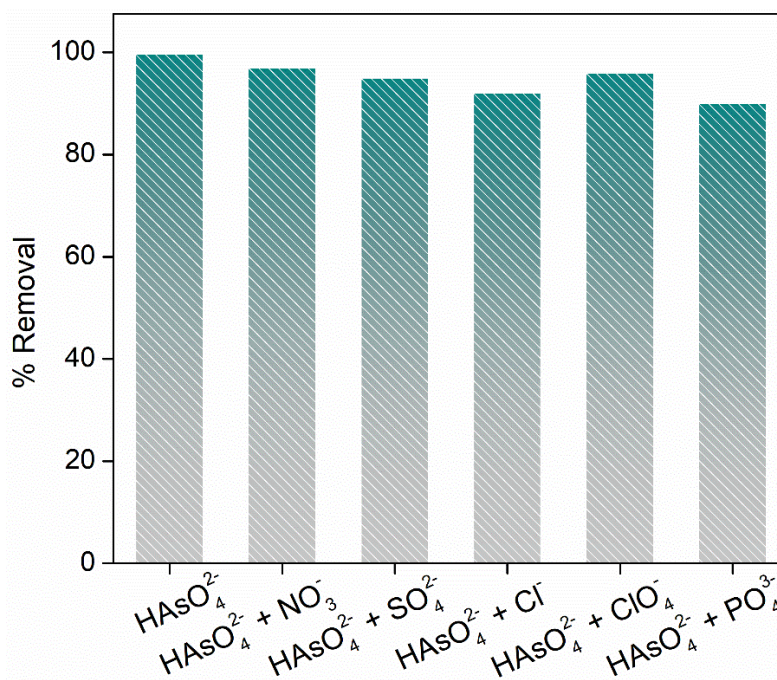
Appendix Figure 5.41: HAsO_4^{2-} adsorption isotherm fitting, a. Langmuir Fitting and b. Freundlich Fitting



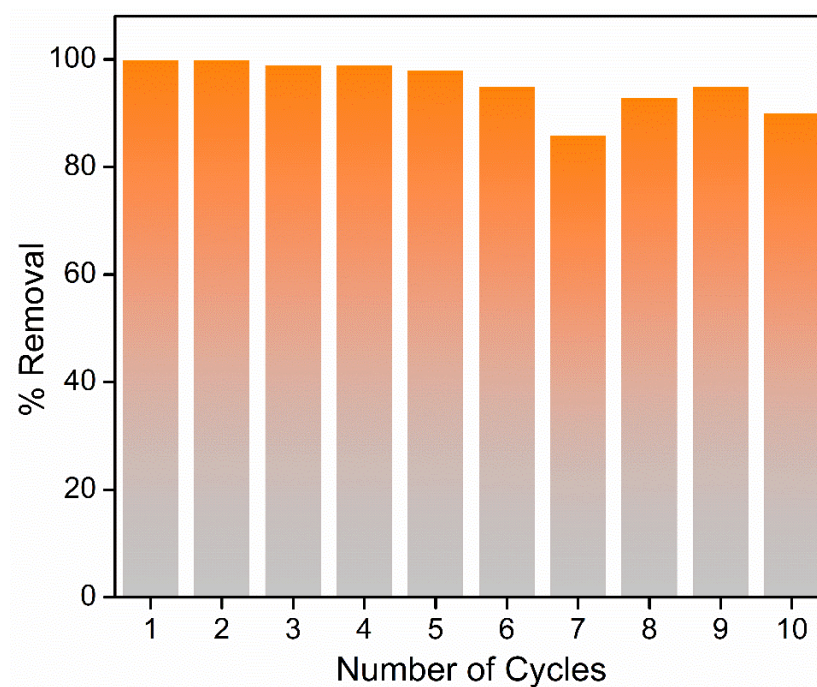
Appendix Figure 5.42: As(V) removal efficiency in different water bodies



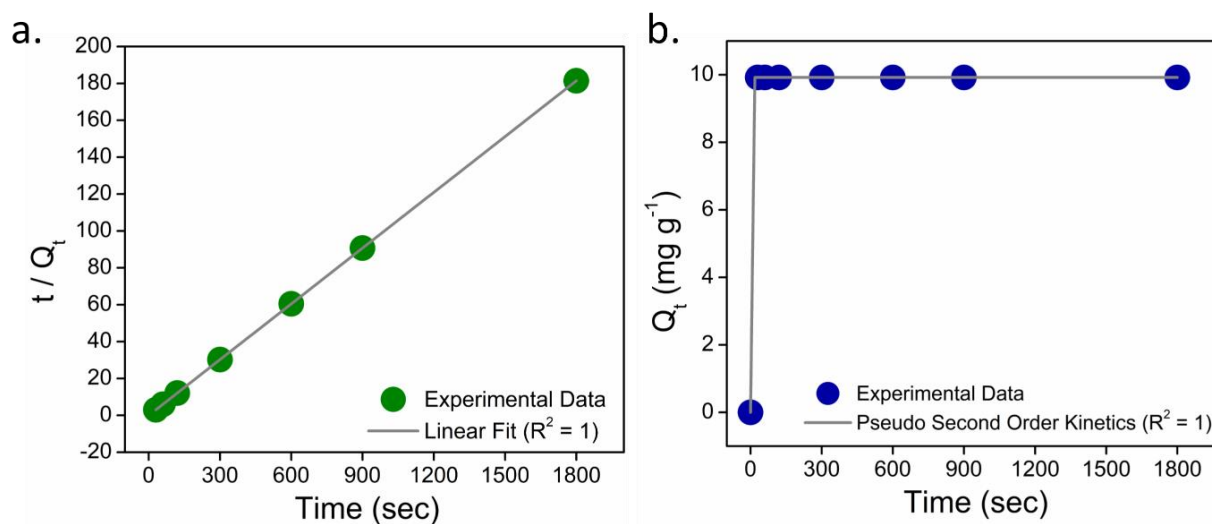
Appendix Figure 5.43: Removal efficiency of As(V) in presence of competing anions (1:1)



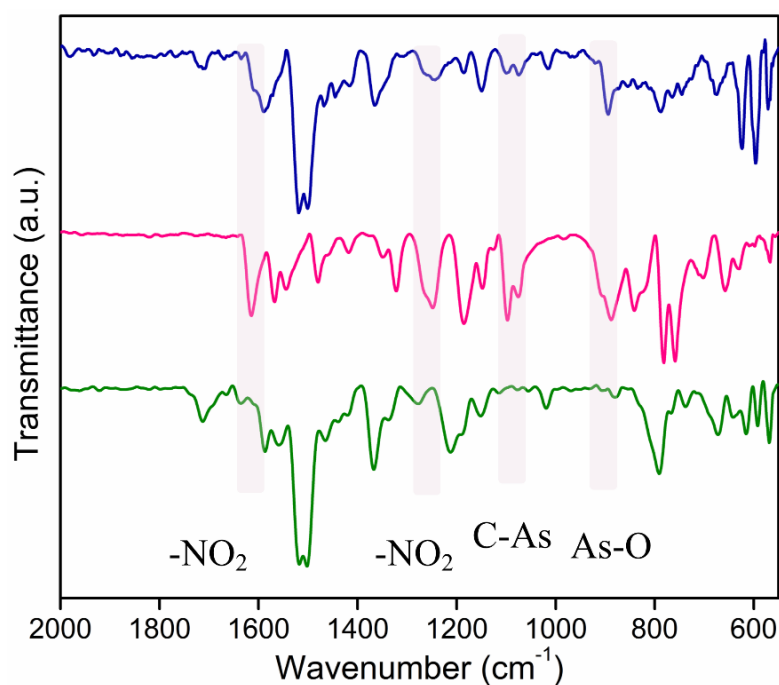
Appendix Figure 5.44: Removal efficiency of As(V) in presence of competing anions (1:10)



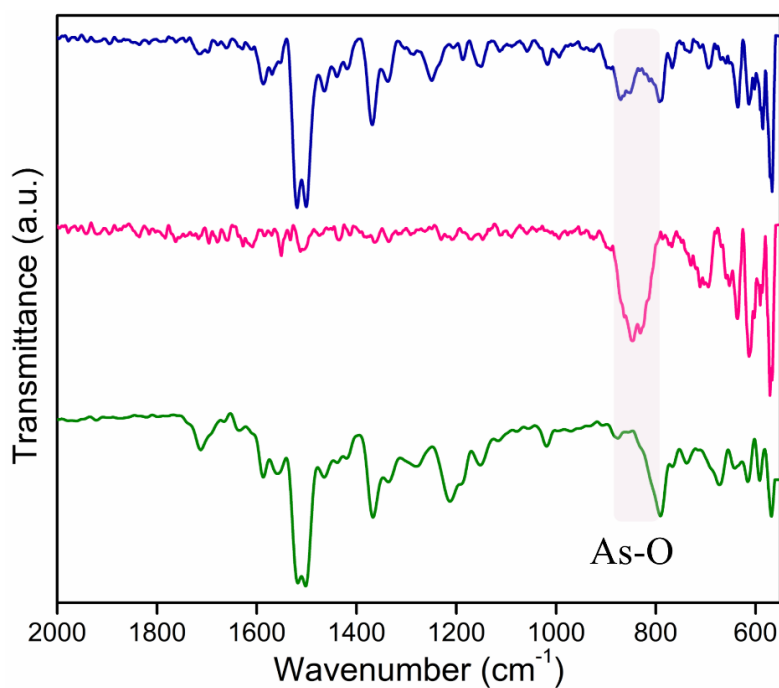
Appendix Figure 5.45: Recyclability of As(V) capture in IPiPOP-3U



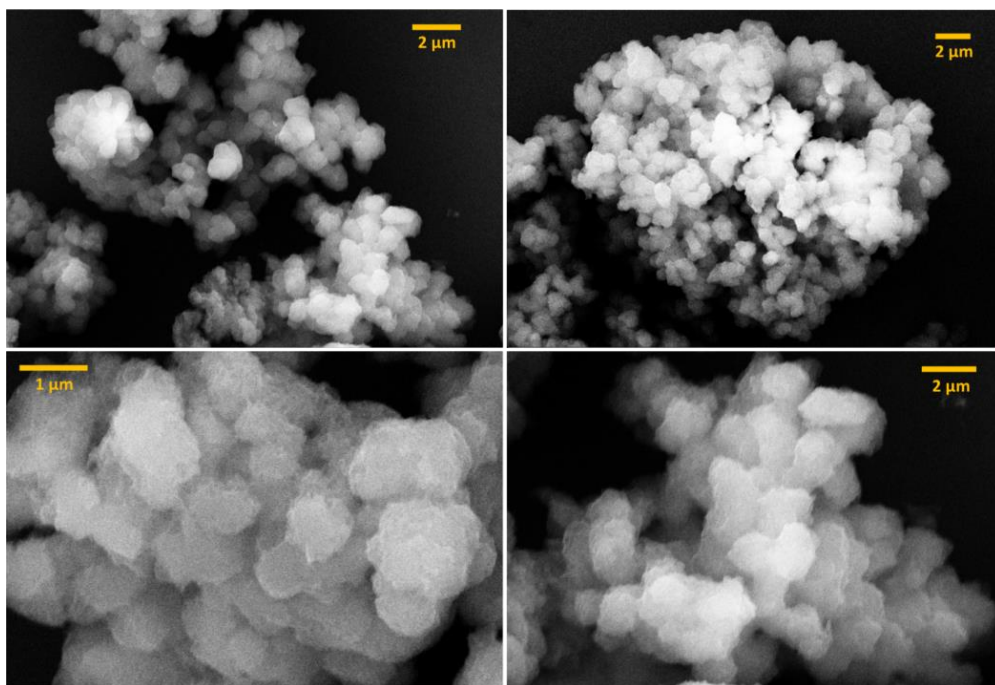
Appendix Figure 5.46: Kinetics of 10 ppm of mixture of ROX and HAsO_4^{2-} , a. Pseudo-second-order model linear fitting, and b. sorption capacity with time



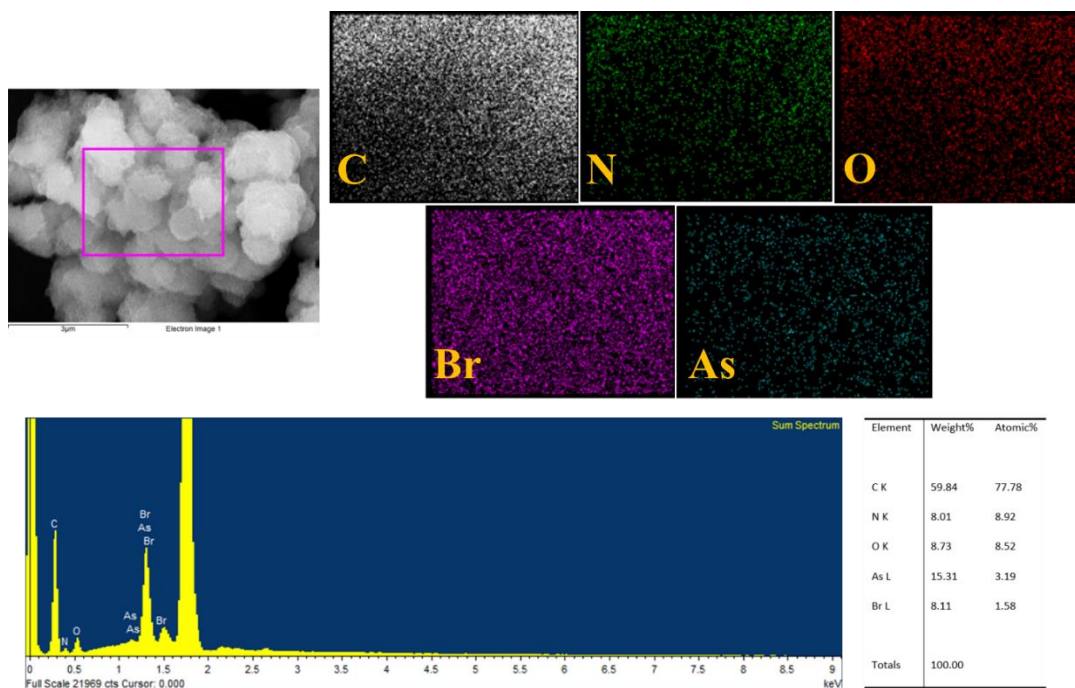
Appendix Figure 5.47: FT-IR spectra of IPIPOP-3U after ROX Capture (green-pristine IPIPOP-3U, pink- ROX, blue- ROX@IPIPOP-3U)



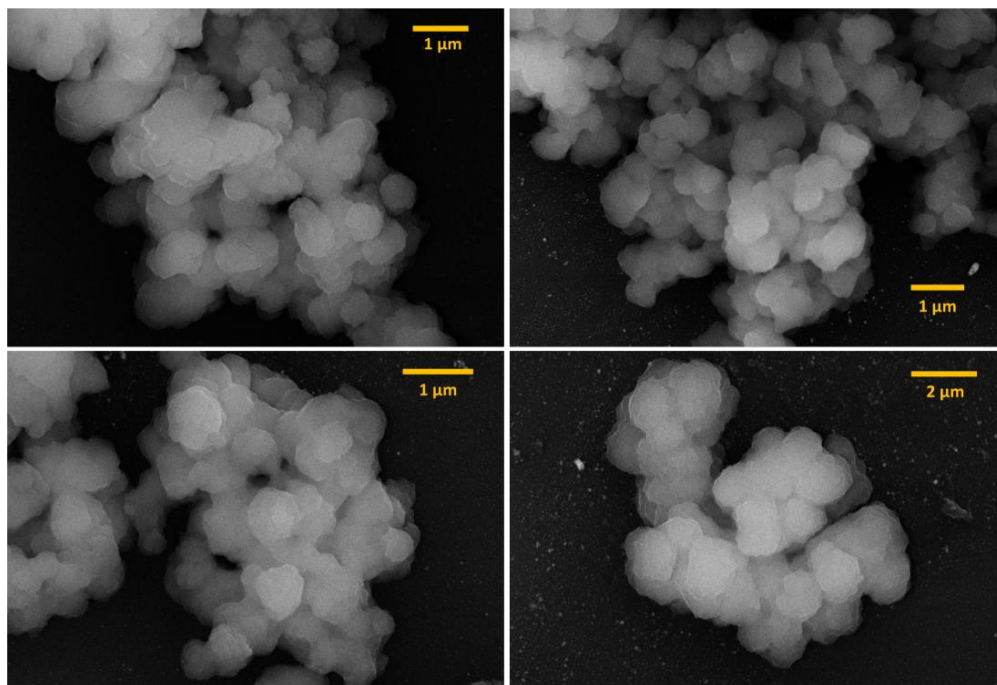
Appendix Figure 5.48: FT-IR spectra of IPIPOP-3U after HAsO_4^{2-} Capture (green-pristine IPIPOP-3U, pink- HAsO_4^{2-} , blue - HAsO_4^{2-} @IPIPOP-3U)



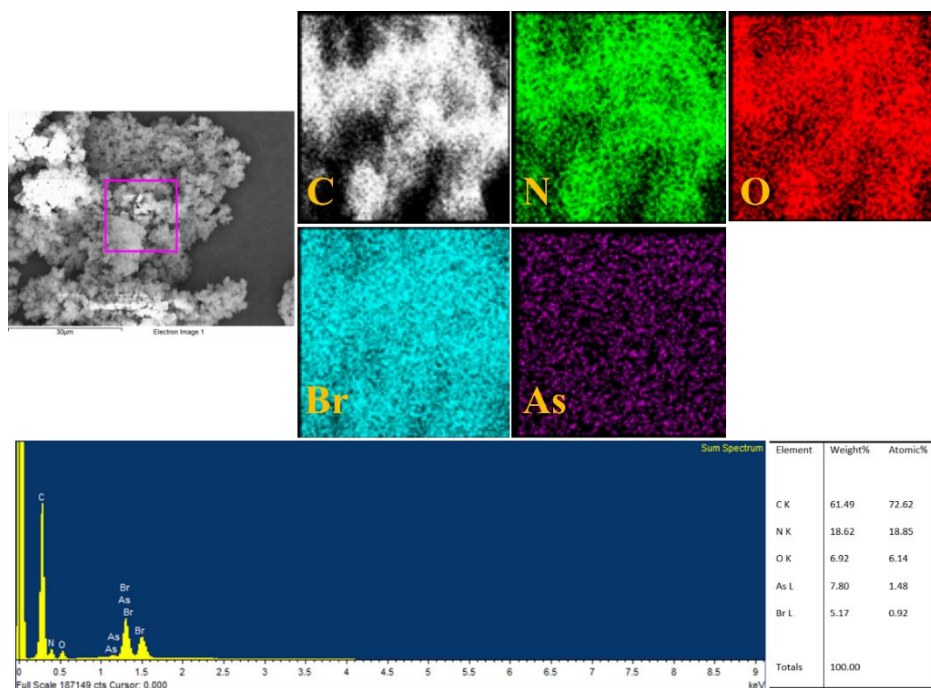
Appendix Figure 5.49: FESEM images of IPiPOP-3U after ROX capture



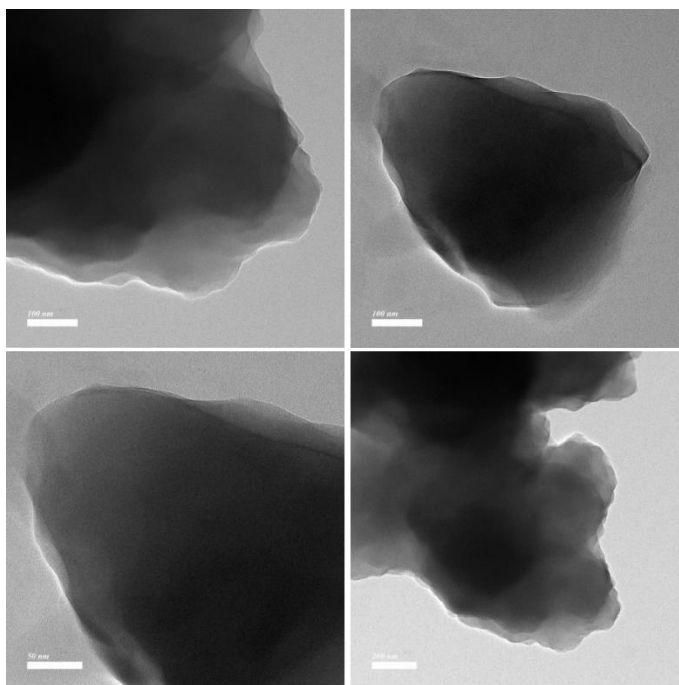
Appendix Figure 5.50: EDS and elemental mapping of IPiPOP-3U after ROX capture



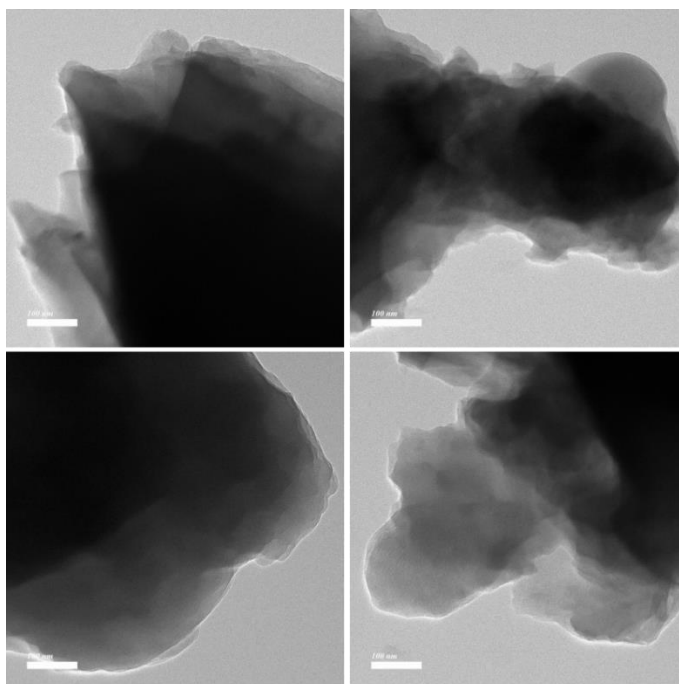
Appendix Figure 5.51: FESEM images of IPIPOP-3U after HAsO_4^{2-} capture



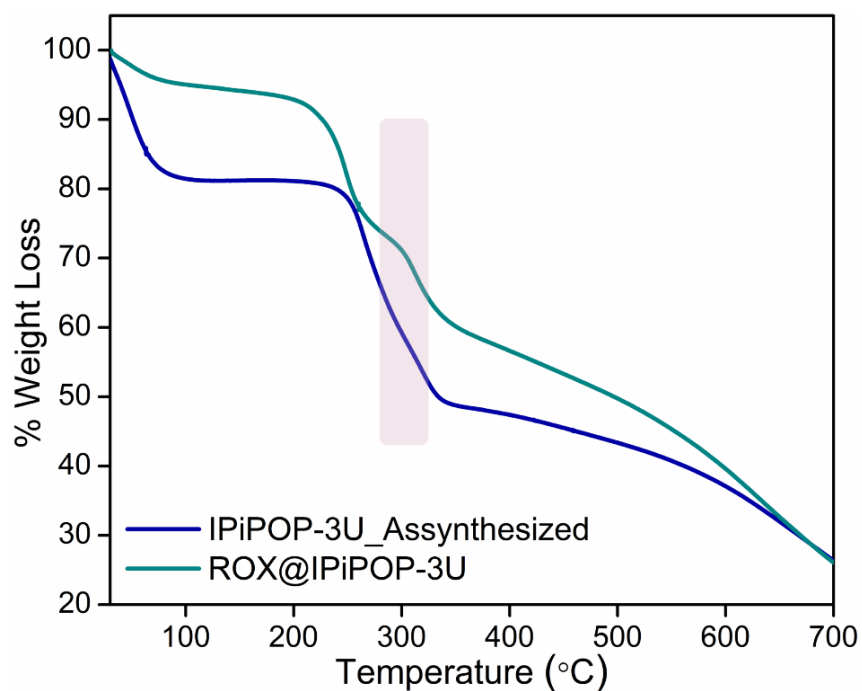
Appendix Figure 5.52: EDS and elemental mapping of IPIPOP-3U after HAsO_4^{2-} capture



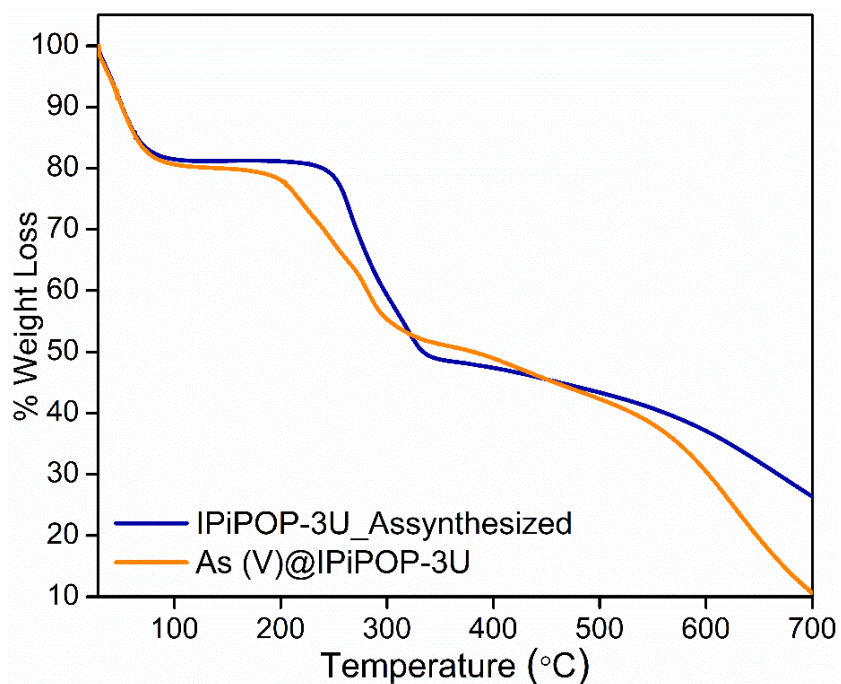
Appendix Figure 5.53: TEM images of IPiPOP-3U after ROX capture



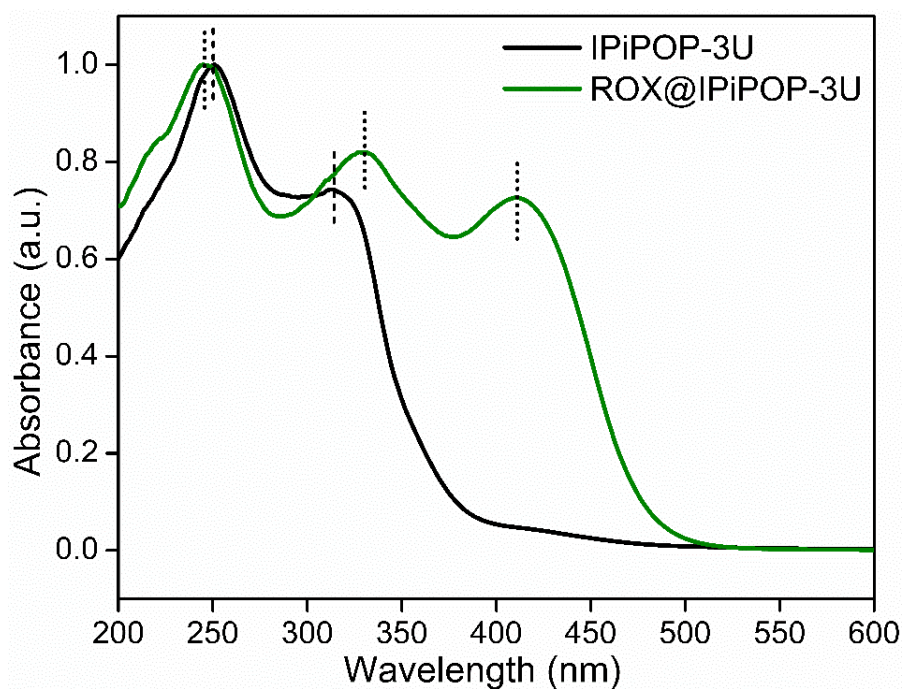
Appendix Figure 5.54: TEM images of IPiPOP-3U after HAsO_4^{2-} capture



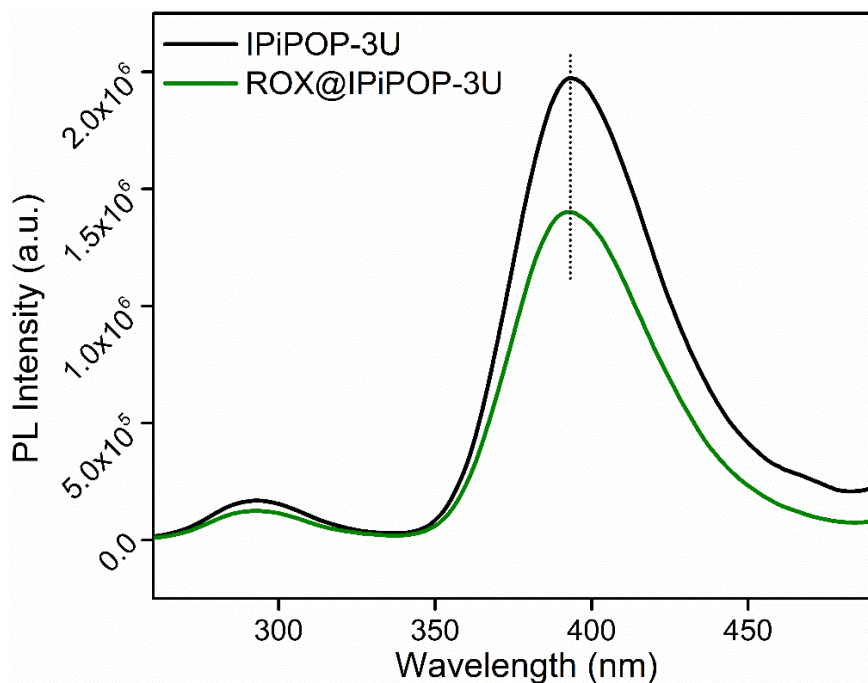
Appendix Figure 5.55: TGA of IPIPOP-3U after ROX capture



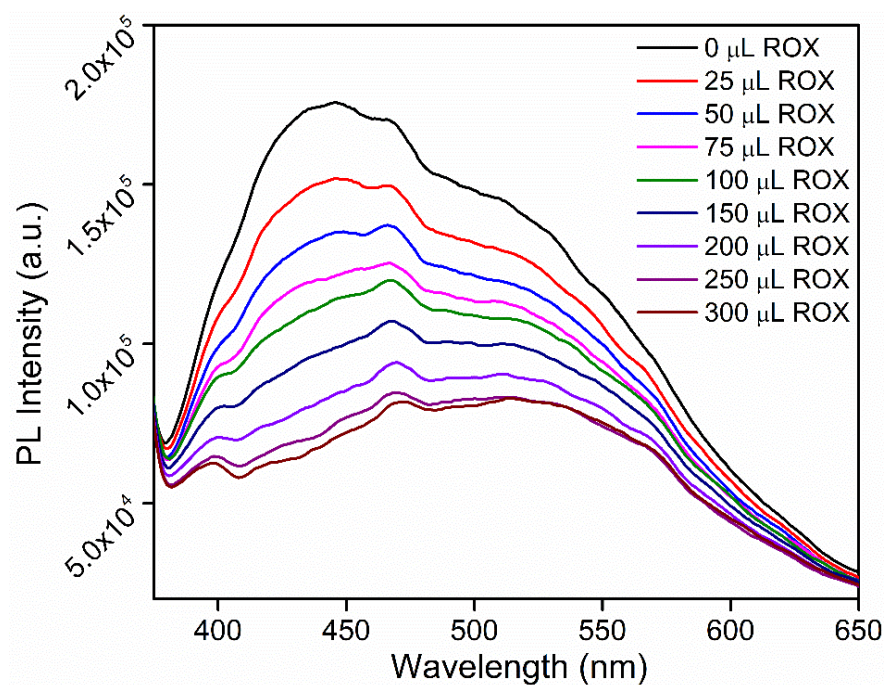
Appendix Figure 5.56: TGA of IPIPOP-3U after HAsO₄²⁻ capture



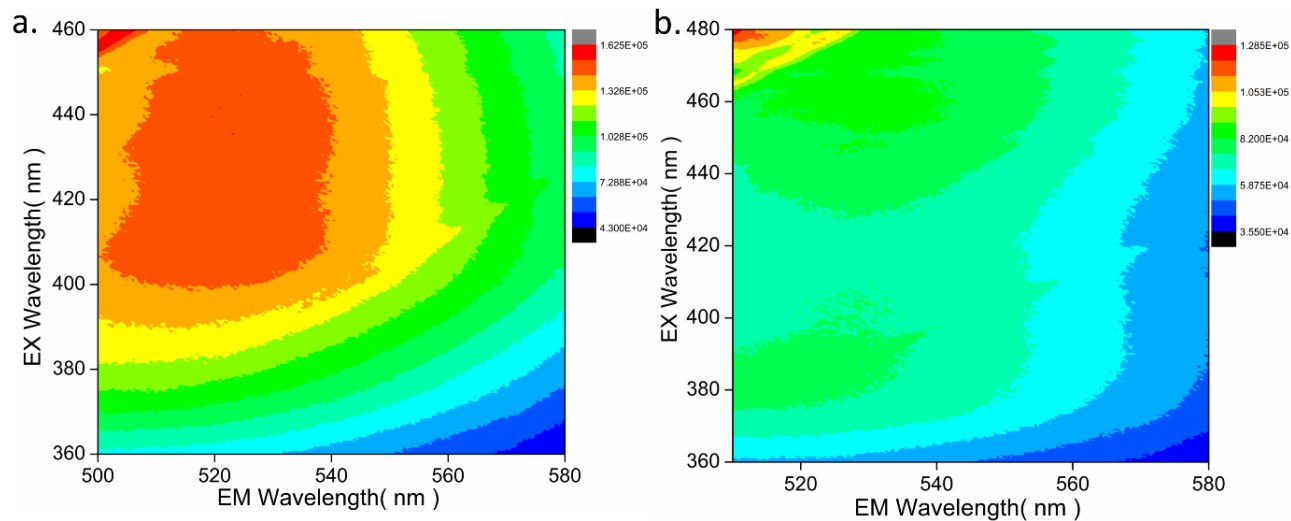
Appendix Figure 5.57: Solid state UV-Vis spectra of IPiPOP-3U after ROX capture



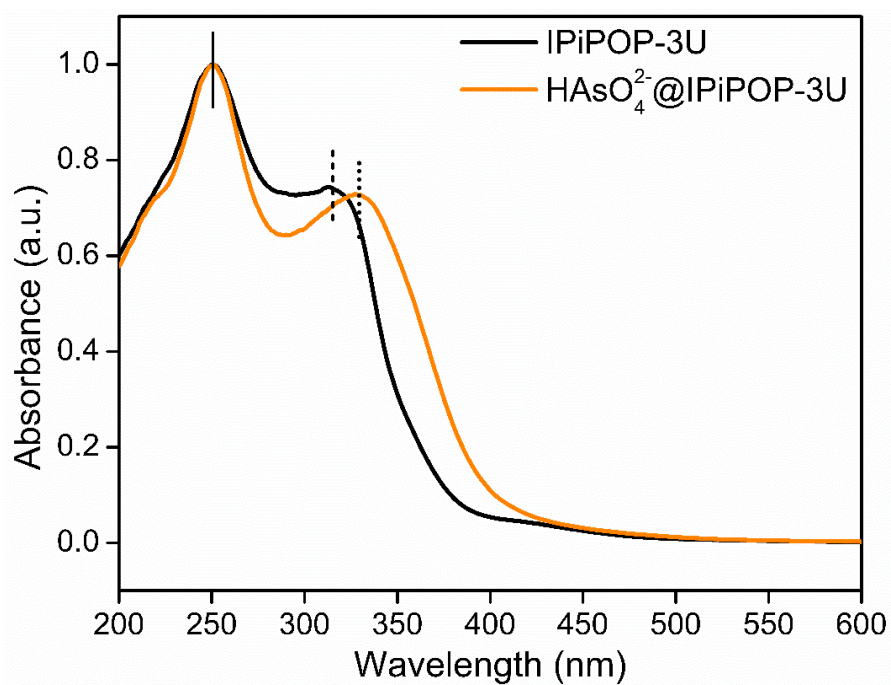
Appendix Figure 5.58: Solid state Fluorescence spectra of IPiPOP-3U after ROX capture



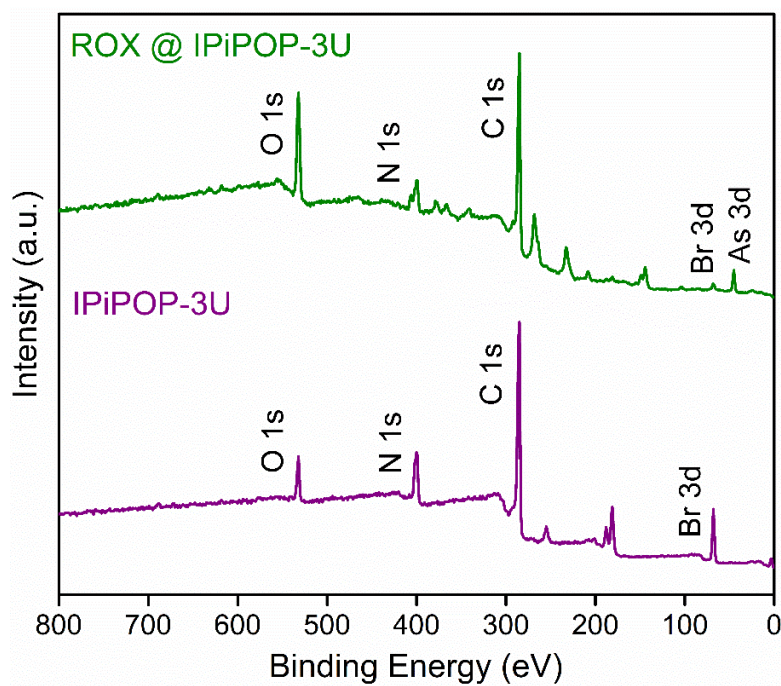
Appendix Figure 5.59: Fluorescence spectra of IPiPOP-3U after incremental addition of ROX aq. solution



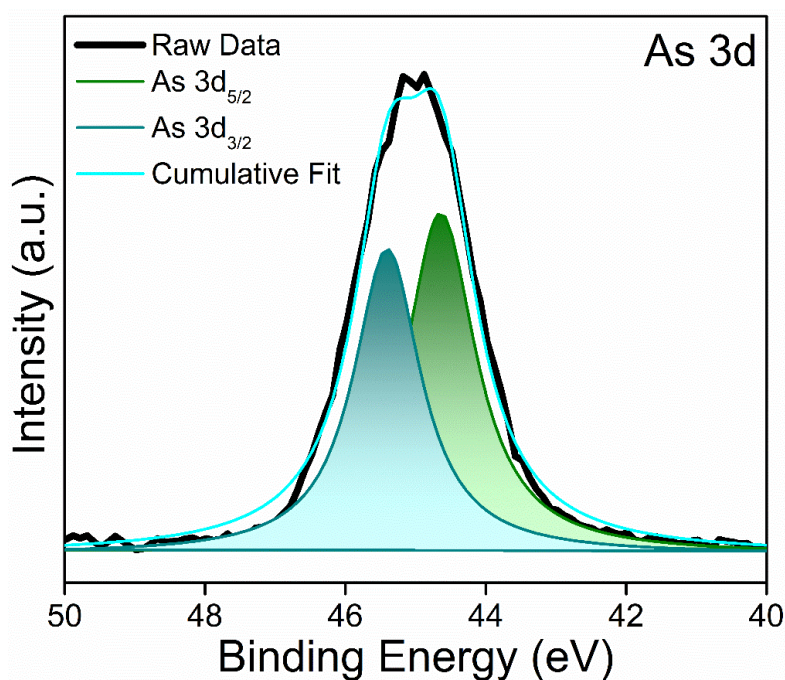
Appendix Figure 5.60: PLE spectra of a. dispersed IPiPOP-3U in H₂O and, b. after addition of ROX



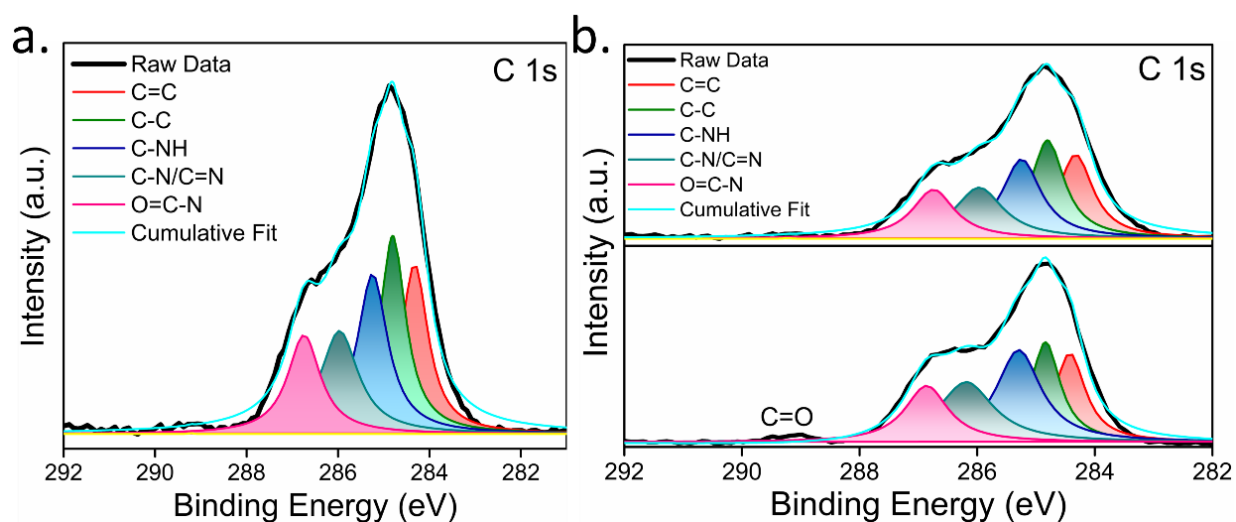
Appendix Figure 5.61: Solid state UV-Vis spectra of IPIPOP-3U after HAsO₄²⁻ capture



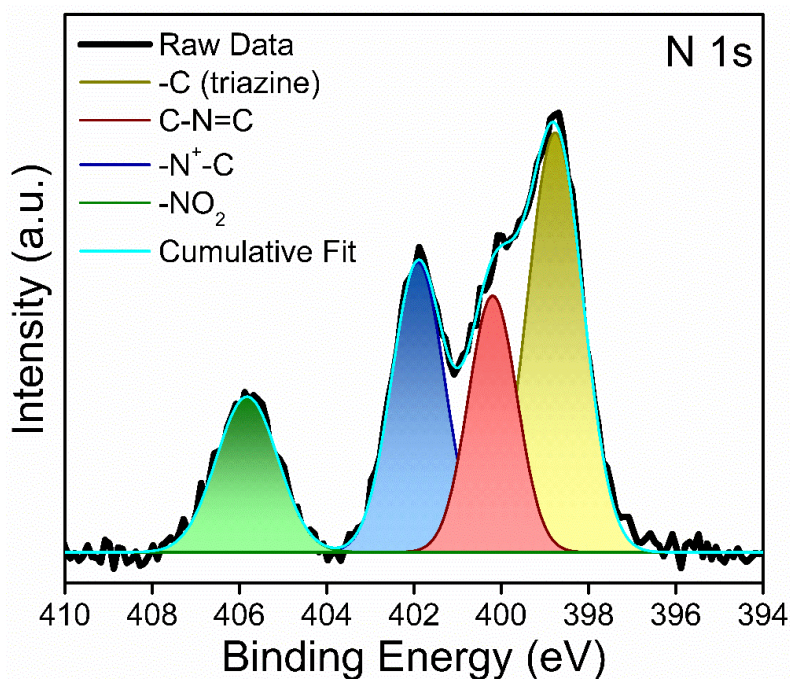
Appendix Figure 5.62: XPS survey of IPIPOP-3U after ROX capture



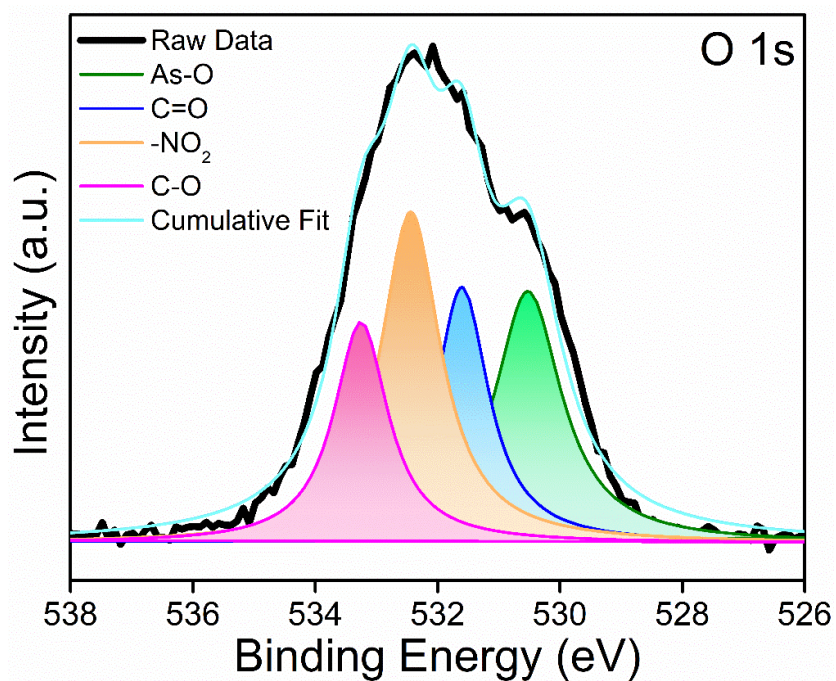
Appendix Figure 5.63: Deconvoluted XPS spectra of As3d of IPiPOP-3U after ROX capture



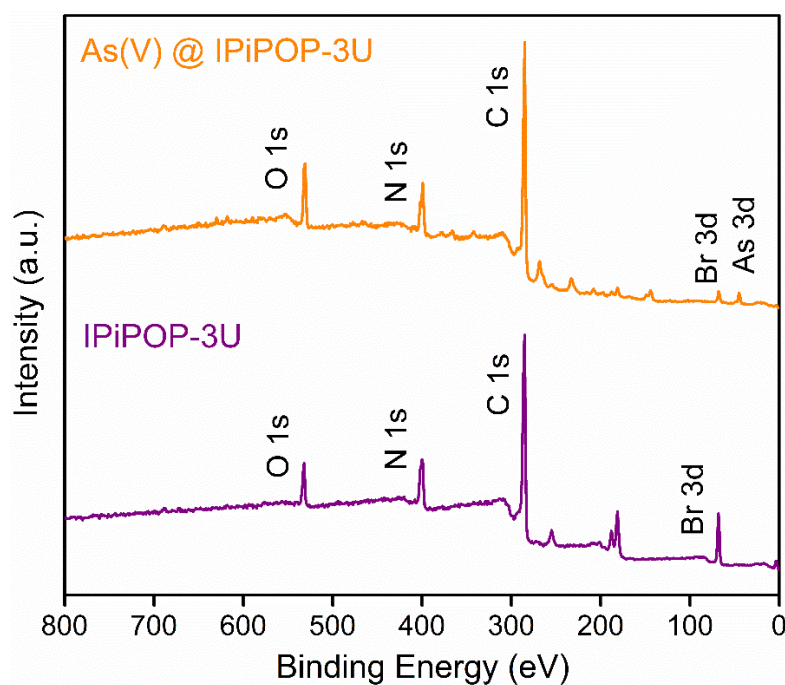
Appendix Figure 5.64: a. Deconvoluted XPS spectra of C1s of IPiPOP-3U after ROX capture, and b. comparison C1s XPS between pristine IPiPOP-3U (bottom) and ROX captured IPiPOP-3U (top)



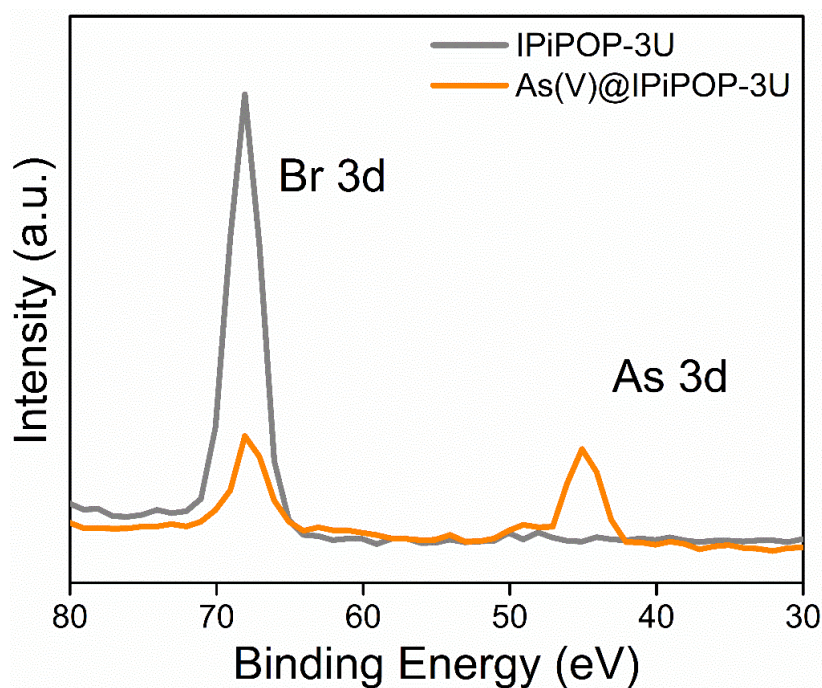
Appendix Figure 5.65: Deconvoluted XPS spectra of N1s of IPiPOP-3U after ROX capture



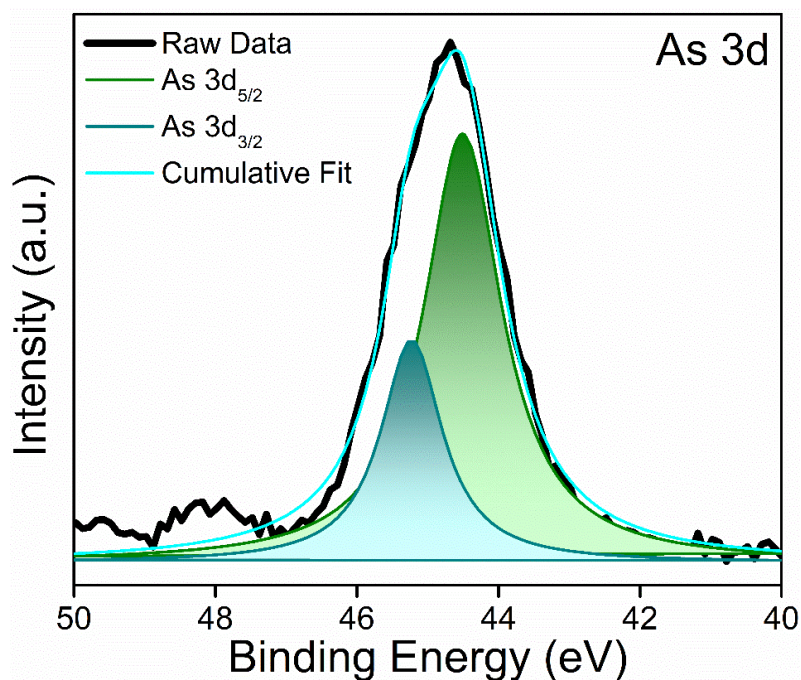
Appendix Figure 5.66: Deconvoluted XPS spectra of O1s of IPiPOP-3U after ROX capture



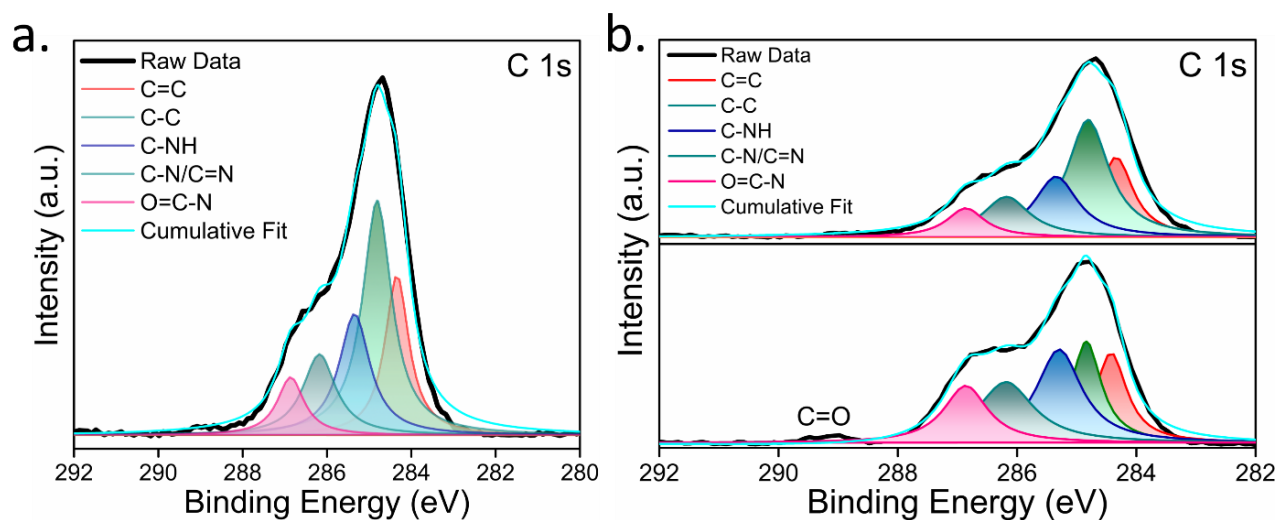
Appendix Figure 5.67: XPS survey of IPIPOP-3U after HAsO_4^{2-} capture



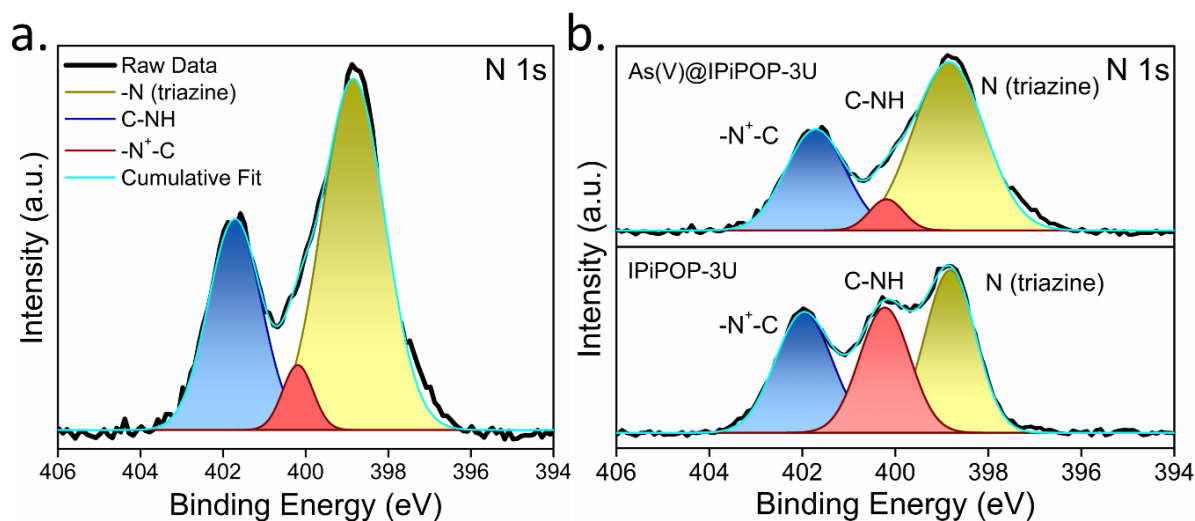
Appendix Figure 5.68: XPS survey of Br3d and As3d of IPIPOP-3U before (grey) and after (orange) HAsO_4^{2-} capture



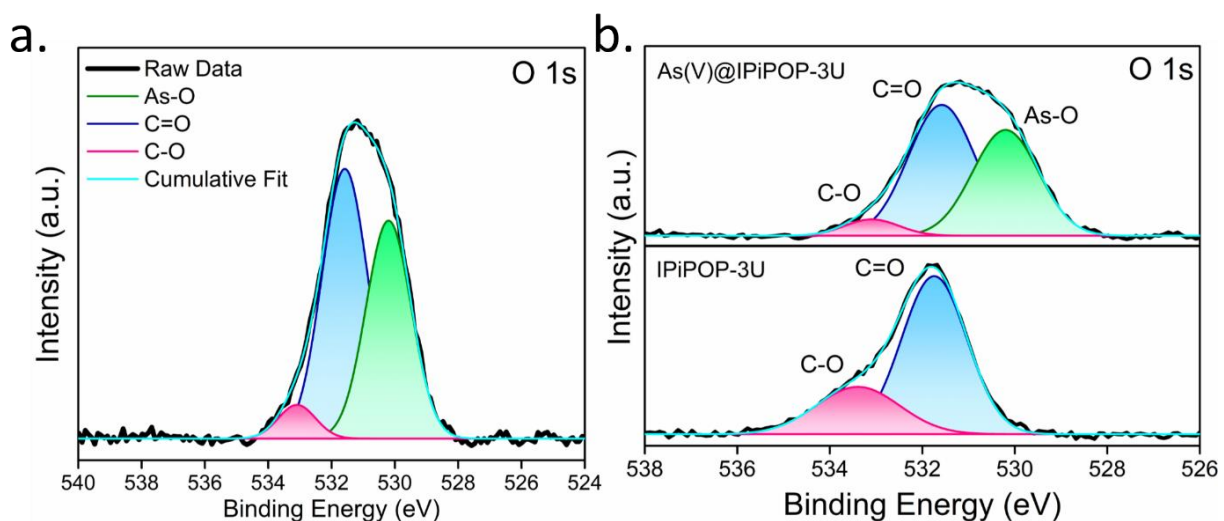
Appendix Figure 5.69: Deconvoluted XPS spectra of As3d of IPiPOP-3U after HAsO_4^{2-} capture



Appendix Figure 5.70: a. Deconvoluted XPS spectra of C1s of IPiPOP-3U after HAsO_4^{2-} capture, and b. comparison C1s XPS between pristine IPiPOP-3U (bottom) and HAsO_4^{2-} captured IPiPOP-3U (top)



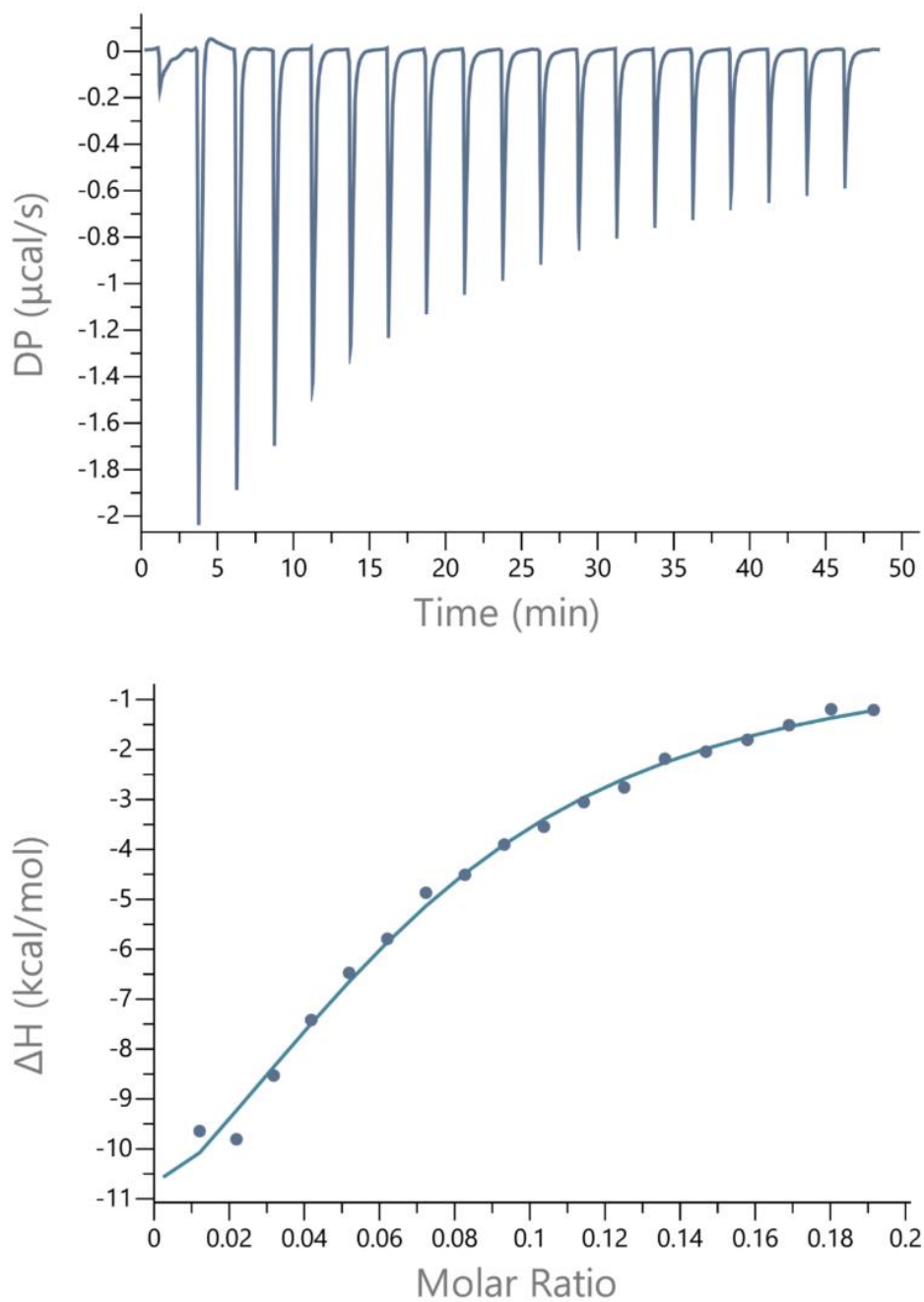
Appendix Figure 5.71: a. Deconvoluted XPS spectra of N1s of IPiPOP-3U after HAsO_4^{2-} capture, and b. comparison N1s XPS between pristine IPiPOP-3U (bottom) and HAsO_4^{2-} captured IPiPOP-3U (top)



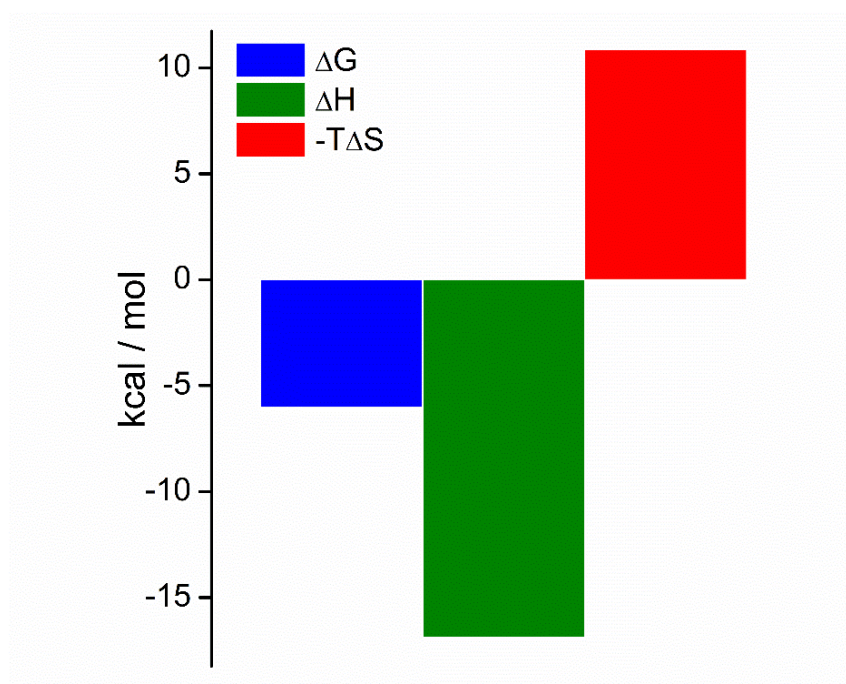
Appendix Figure 5.72: a. Deconvoluted XPS spectra of O1s of IPiPOP-3U after HAsO_4^{2-} capture, and b. comparison O1s XPS between pristine IPiPOP-3U (bottom) and HAsO_4^{2-} captured IPiPOP-3U (top)

Appendix Section 5.5.1. Isothermal titration calorimetry (ITC)

Isothermal titration calorimetry (ITC) experiment has been conducted for the thermodynamic validation of such favorable interactions between the organic arsenic Roxarsone (ROX) and the inorganic arsenic HAsO_4^{2-} and IPiPOP-3U in aqueous medium.[R37] ITC experiment quantitatively provides the change in enthalpy, entropy and Gibbs free energy associated with the adsorption followed by the ion-exchange process between adsorbent and adsorbate.[R38] In this typical experiment, first, the reference cell was filled with deionized water, and a homogeneous aqueous suspension of adsorbate (IPiPOP-3U) (stock as, 1 mg compound in 10 mL of H_2O ($\text{pH} = 7.38$)) (consider as 1 mmol in the experiment) was poured into the sample cell and the 10 mmol concentration of adsorbent (ROX / HAsO_4^{2-}) aqueous solution ($\text{pH} = 7.4$) was placed into the syringe, while the complete mixture was stirring at 750 rpm. In this study, we recorded the thermograms for ROX / HAsO_4^{2-} molecule adsorption by the IPiPOP-3U. The first injection of each titration was fixed at 0.4 μL . At least two titrations for each analyte-compound pair were collected. Data analysis was performed in y. MicroCal PEAQ-ITC analysis software. The heats of injection for blank titrations (analytes [ROX / HAsO_4^{2-}] into blank) were subtracted from the heats of injection into compound suspensions. The recorded thermogram for ROX capture (in the main text, Figure 5d), (Figure S52) demonstrated a high association constant with the exothermic binding event along with the following thermodynamic parameters (Table S3) and for HAsO_4^{2-} capture demonstrated a high association constant with the exothermic binding event along with the following thermodynamic parameters (Table S4). This result indicated the adsorption of ROX by IPiPOP-3U was thermodynamically favorable as the Gibbs free energy of the process was found to be negative with positive association constant (K_a) and negative entropy and the adsorption of HAsO_4^{2-} by IPiPOP-3U was thermodynamically favorable with negative Gibbs free energy and positive entropy.[R39] Thus, these ITC data clearly indicated the similarities between the thermodynamic parameters and the bulk-scale experimental data of strong interactions between both type of arsenics and IPiPOP-3U in water.



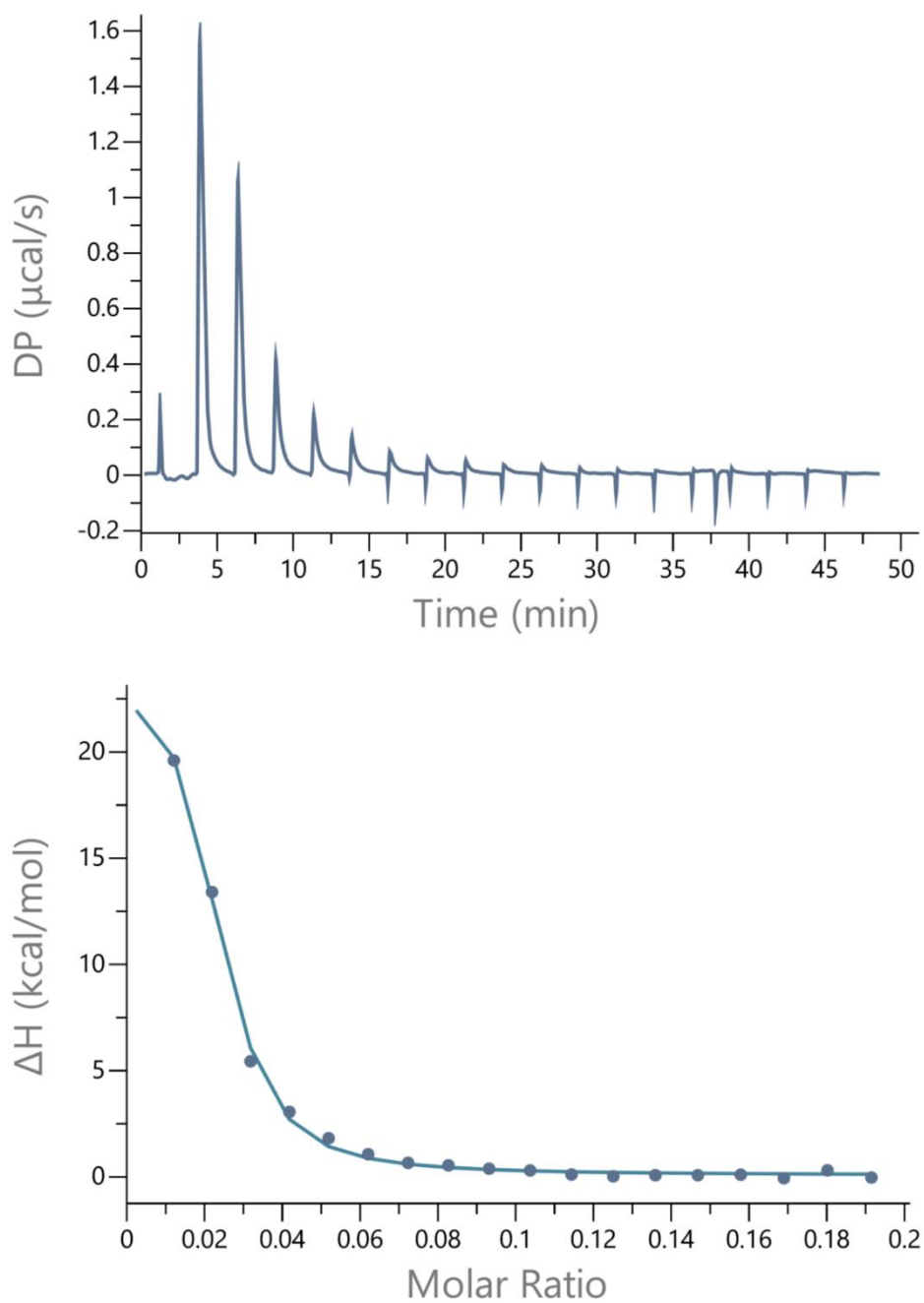
Appendix Figure 5.73: ITC data with incremental addition of ROX. Raw Thermograms (top) and normalised heat injection (bottom)



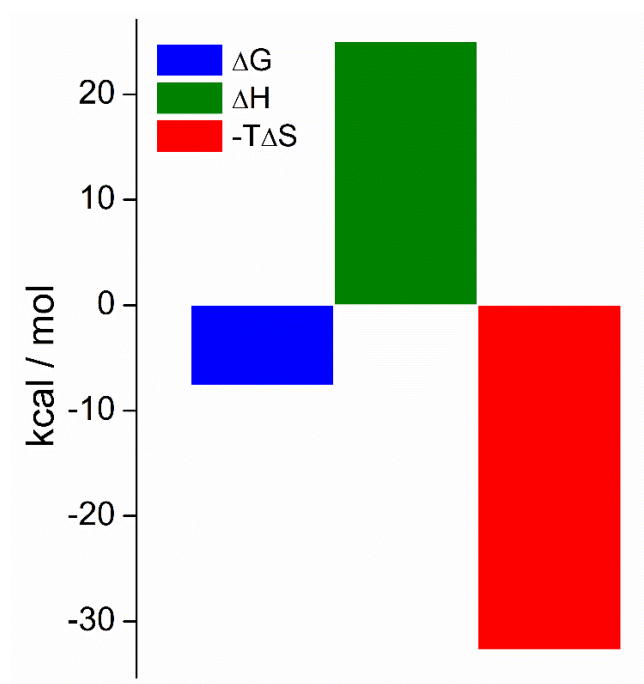
Appendix Figure 5.74: Thermodynamic parameters for interacting analytes ROX indicating changes in Gibbs free energy, enthalpy, entropy for the interactions with IPIPOP-3U

Appendix Table 5.3: The concentration and thermodynamic parameters derived from ITC experiment for injections of ROX titrated against IPIPOP-3U.

Molecule	ROX
Temperature (°C)	25
Bin	Binding
Syr [M]	0.01
Cell [M]	0.001
Model	One Set of Sites
N (sites)	$6.7e-2 \pm 4.3e-3$
KD (M)	$38.8e-6 \pm 14.8e-6$
ΔH (kcal/mol)	-16.9 ± 3.57
ΔG (kcal/mol)	-6.02
$-T\Delta S$ (kcal/mol)	10.9



Appendix Figure 5.75: ITC data with incremental addition of HAsO_4^{2-} . Thermograms (top) and normalised heat injection (bottom)



Appendix Figure 5.76: Thermodynamic parameters for interacting analytes HAsO_4^{2-} indicating changes in Gibbs free energy, enthalpy, entropy for the interactions with IPIPOP-3U

Appendix Table 5.4: The concentration and thermodynamic parameters derived from ITC experiment for injections of HAsO_4^{2-} titrated against IPIPOP-3U.

Molecule	HAsO_4^{2-}
Temperature ($^{\circ}\text{C}$)	25
Bin	Binding
Syr [M]	0.01
Cell [M]	0.001
Model	One Set of Sites
N (sites)	$2.0\text{e-}2 \pm 5.2\text{e-}4$
KD (M)	$2.65\text{e-}6 \pm 367\text{e-}9$
ΔH (kcal/mol)	25.1 ± 1.01
ΔG (kcal/mol)	-7.61
$-T\Delta S$ (kcal/mol)	-32.7

Appendix Section 5.5.2. X-ray Adsorption Spectroscopy (XAS)

The experimentally derived $\chi(r)$ versus r data are fitted with theoretical plots simulated using the structural information of the sample provided. The $\chi(r)$ versus r plot has been fitted from 1.15-3.2 Å in ROX@iPOP sample assuming one As-O shell and As-N shell and from 1.5-2.0 Å in AsV@iPOP sample assuming one As-O shell. In the fitting process the atom to atom bond distance (R) between the respective atomic pairs, co-ordination numbers (N), and the disorder factor (Debye –Waller factor) (σ^2), which gives the mean square fluctuation in the atomic bond lengths and the thermal disorder in the system, have been used as fitting parameters. Figure- 5h, 5i shows the experimental $\chi(r)$ versus r plots of the ROX@IPiPOP-3UT and As(V)@IPiPOP-3UT at As K edge along with the best fit theoretical simulations and the best fit parameters have been shown in Table 1. The goodness of fit has been determined by the value of the R_{factor} defined by:

$$R_{factor} = \sum \frac{[\text{Im}(\chi_{dat}(r_i) - \chi_{th}(r_i))]^2 + [\text{Re}(\chi_{dat}(r_i) - \chi_{th}(r_i))]^2}{[\text{Im}(\chi_{dat}(r_i))]^2 + [\text{Re}(\chi_{dat}(r_i))]^2} \quad (4)$$

where, χ_{dat} and χ_{th} refer to the experimental and theoretical $\chi(r)$ values respectively and Im and Re refer to the imaginary and real parts of the respective quantities.

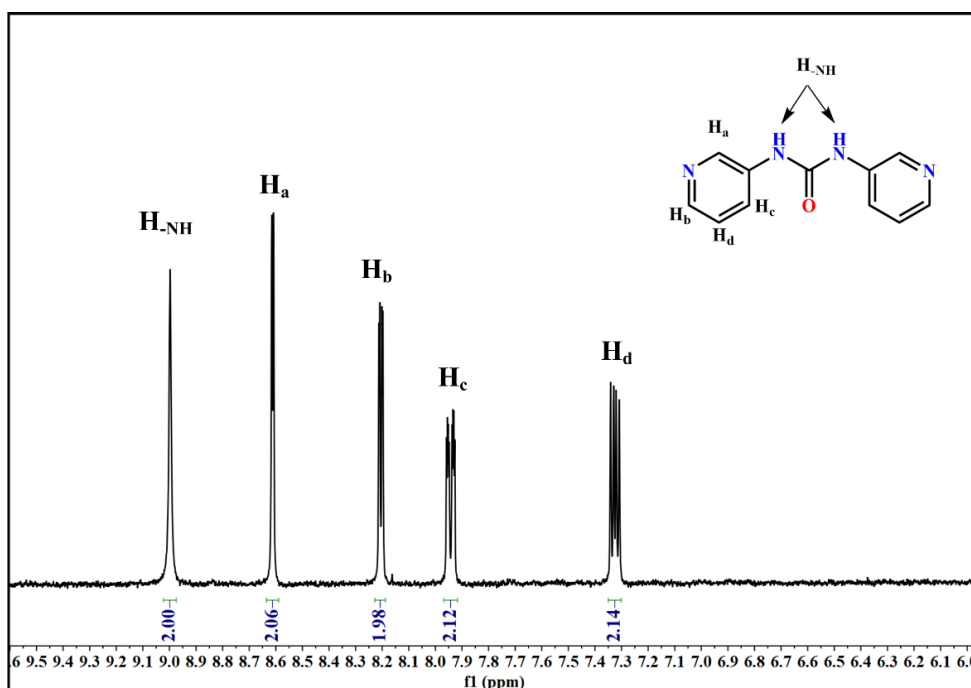
It should be mentioned here that a set of EXAFS data analysis program available within the Demeter software package [R40] have been used for reduction and fitting of the experimental EXAFS data. This includes data reduction and Fourier transform to derive the $\chi(r)$ versus r plots from the absorption spectra, generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of the experimental $\chi(r)$ versus r data with the theoretical ones using the FEFF 6.0 code.

Appendix Table 5.5: Fit parameters of EXAFS data.

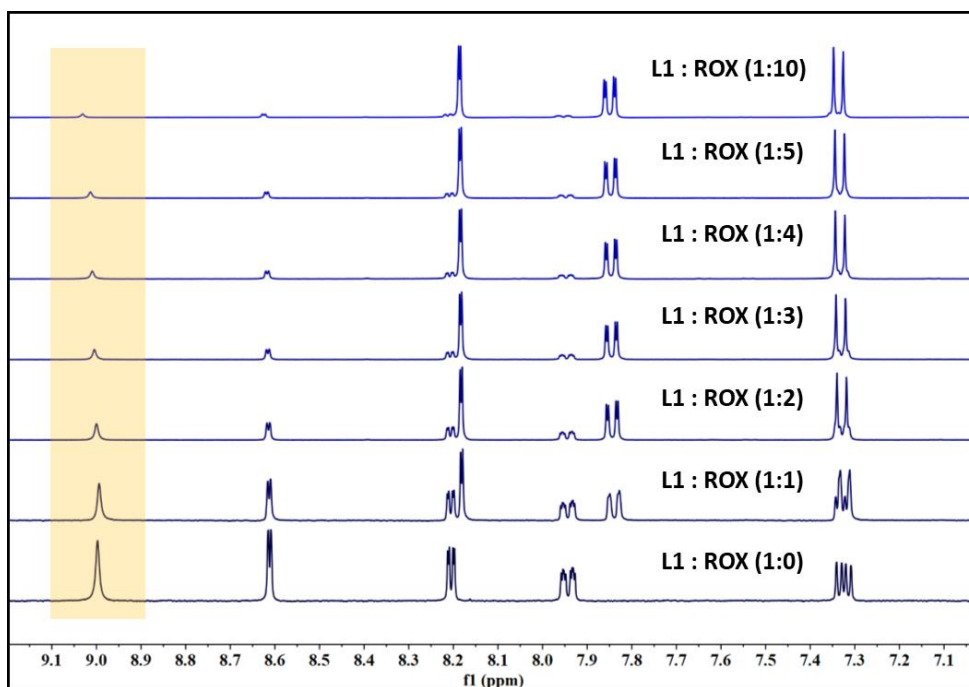
Compound					
HAsO₄²⁻ @IPiPOP-3U	As Edge				
		N	σ^2	R (Å)	R_{factor}
	As-O	7.2±0.7	0.0010 ±0.0009	1.67±0.01	0.0234025
Compound					
ROX@IPiPO P-3U	As Edge				
		N	σ^2	R (Å)	R_{factor}
	As-O	7.5±0.6	0.0010 ±0.0007	1.69±0.01	0.0352439
	As-N	6.3±1.6	0.0060 ±0.0062	2.93±0.04	

Appendix Section 5.5.3. Interaction between ROX and IPiPOP-3U by ¹H NMR:

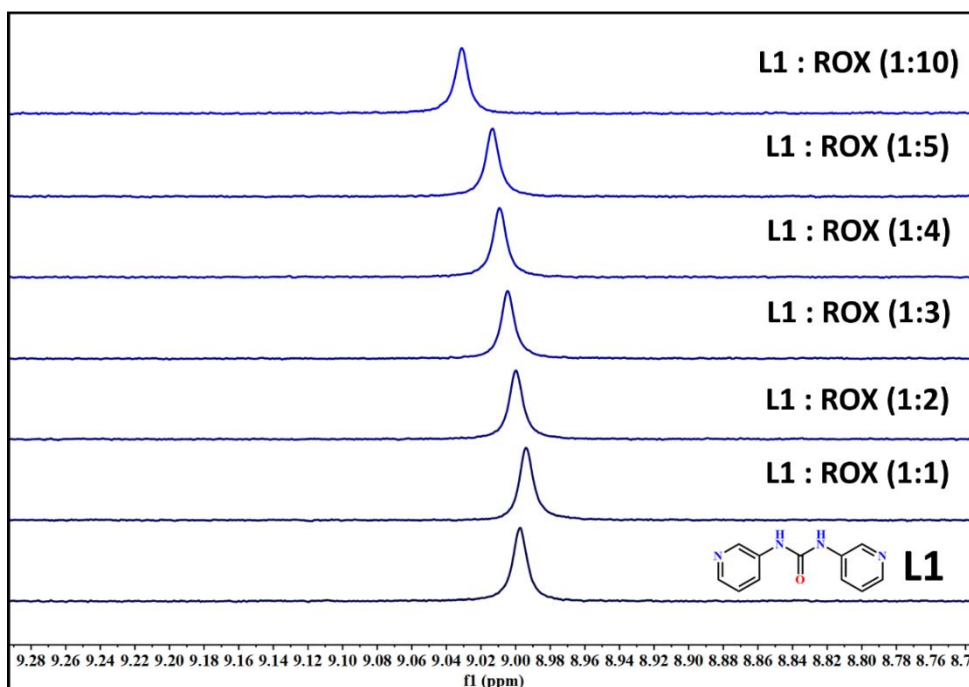
First, we took 2 mM solution of ligand L1 in DMSO- d_6 . Into that we added ROX solution in different concentration. From ^1H NMR it was found that with incremental addition of ROX solution into L1 solution (model complex-1) in DMSO- d_6 , there was a downfield shift in ^1H signal of -NH proton (from 8.9940 ppm to 9.0311 ppm) which clearly indicates the strong H-bond interaction between urea moiety and the ROX molecules in presence of competing solvent system. Also, we noticed shift in the position of H_a proton, adjacent to the urea moiety, also confirmed the interaction between ROX and L1. Also, we observed a clear up-field shift of the proton of the phenyl ring of the ROX molecule (Figure 80-81) in the adduct complex between ligand L2 and ROX (model complex-2). This result indicates the interaction between triazine moiety and the ROX molecule in the solution.



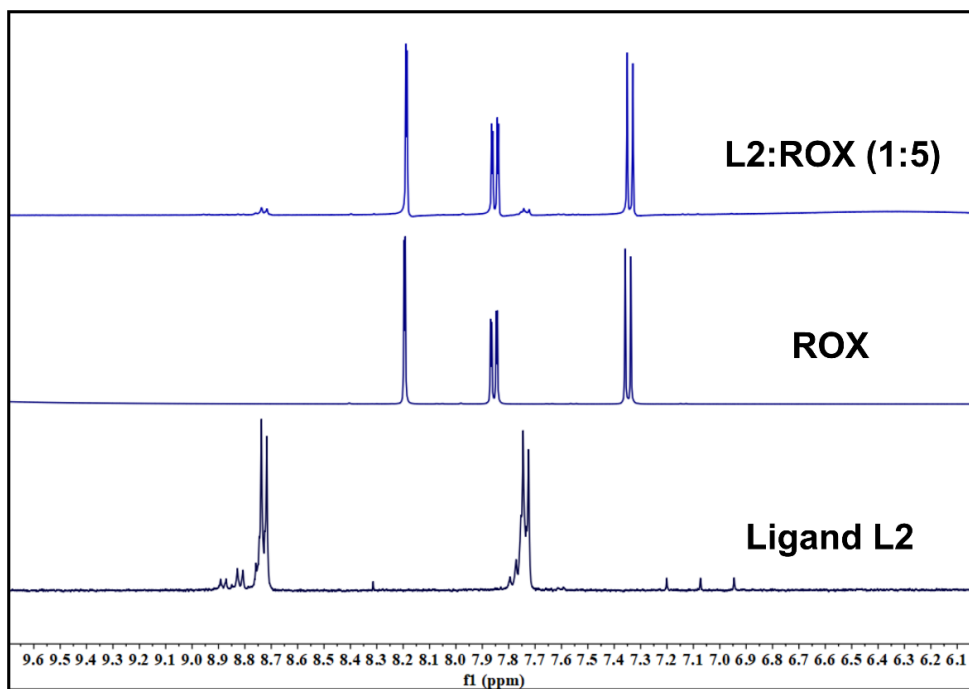
Appendix Figure 5.77: ^1H NMR of Ligand-L1 in DMSO- d_6



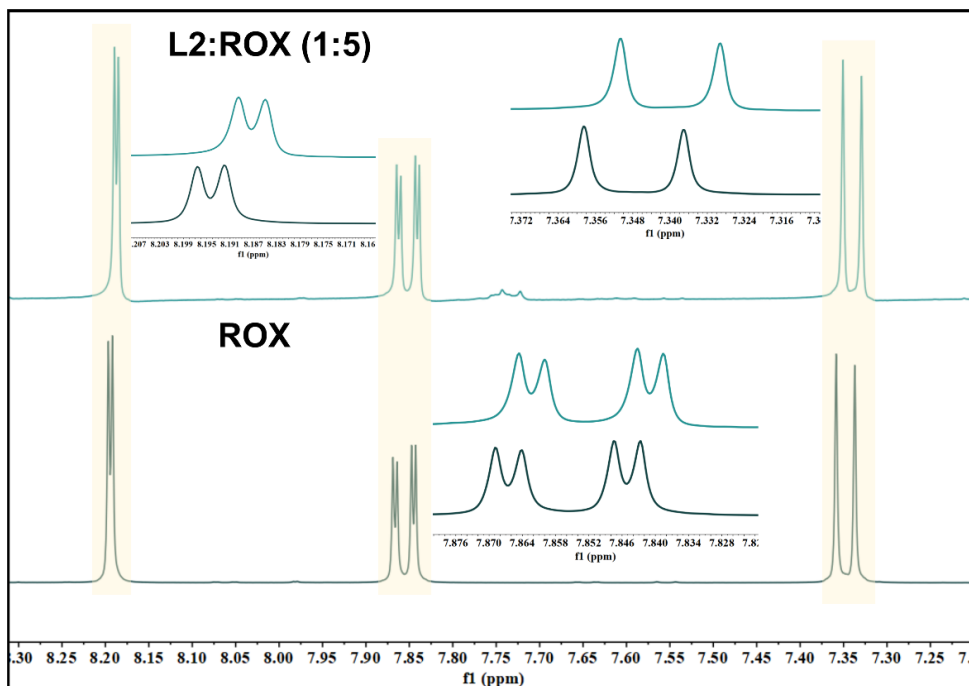
Appendix Figure 5.78: ^1H NMR titration of 2 mM Ligand-L1 with different concentration of ROX



Appendix Figure 5.79: ^1H NMR titration of 2 mM Ligand-L1 with different concentration of ROX and shift of -NH proton



Appendix Figure 5.80: ^1H NMR of 2 mM Ligand-L2, ROX and L2-ROX Mixture (1:5)



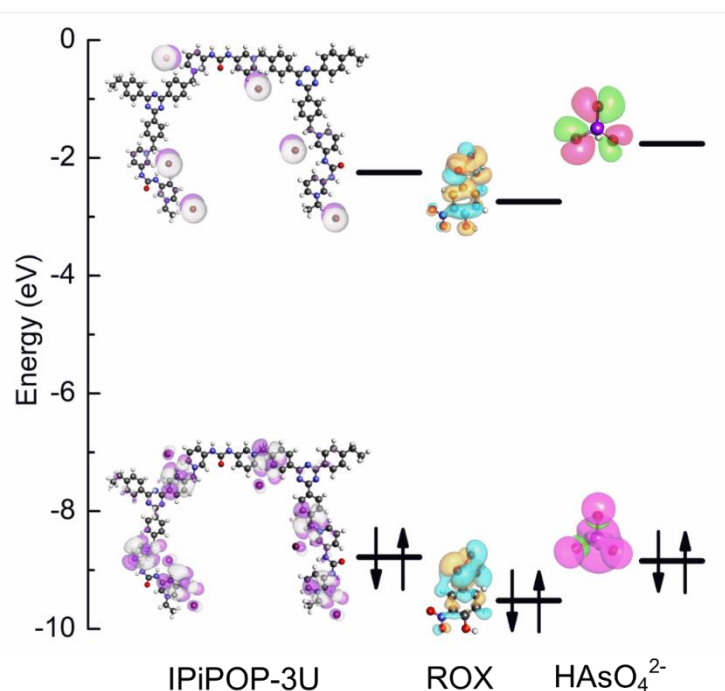
Appendix Figure 5.81: ^1H peak shift of ROX molecule after interacting with Ligand-L2

Appendix Section 5.5.4.: Theoretical Calculation

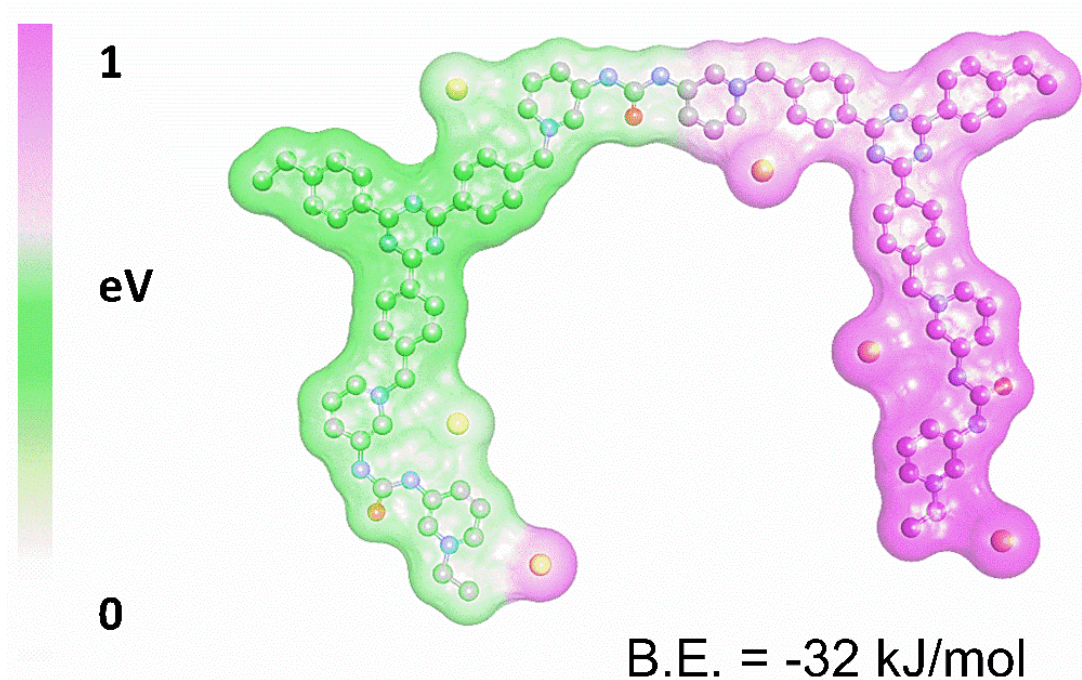
Determination of electrostatic surface potential (ESP), binding sites and binding energy of different interactions:

Density functional theory (DFT) computations were performed using the Discovery Studio 2016 [R41] to derive the ESP surface of model monomers of IPiPOP-3U. The geometry optimization of the monomer was carried out using hybrid B3LYP exchange correlation function and double numeric plus polarization (DNP) basis set with SCF density convergence of 1×10^{-6} . The electrostatic potential (ESP) on the van der Waals (VDW) surfaces (isodensity = 0.001 a.u.) of IPiPOP-3U monomer was derived based on its ground state electron density.

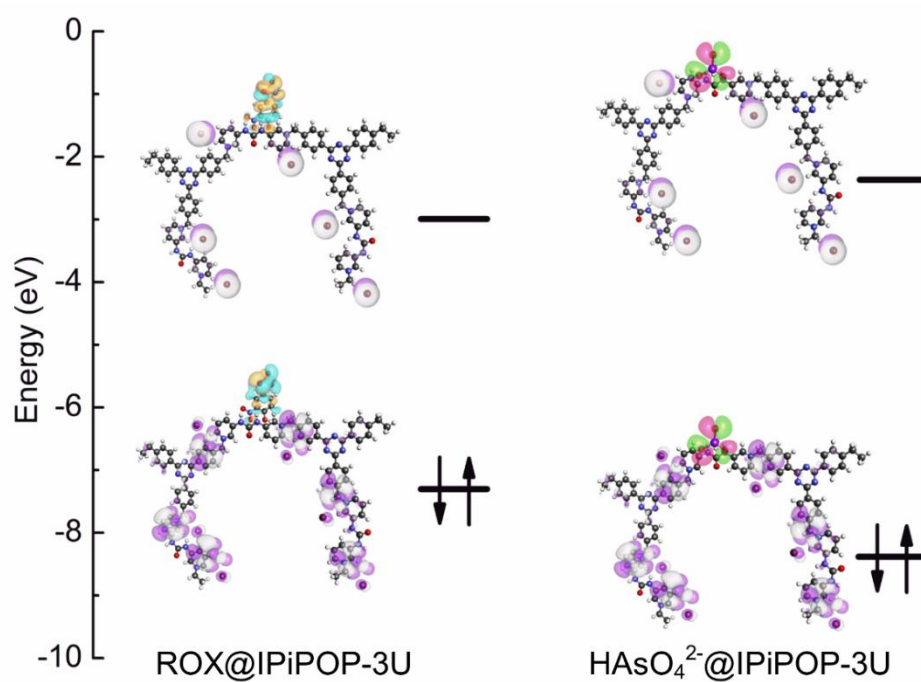
The MD simulation was performed using GROMACS 2022. Van der Waals interactions were considered with a cutoff scheme of 12 Å and periodic boundary conditions. The five production runs of 50 ns were performed during the interaction. 2.0 fs time step was used, and in every 5 ps interval data were recorded. For the simulation supercell of dimensions $3 \times 3 \times 3$ were created from subunit of IPiPOP-3U, ROX and HAsO_4^{2-} . Subsequently, the supercell composed of IPiPOP-3U interacted with the supercell consisted with ROX and HAsO_4^{2-} individually.



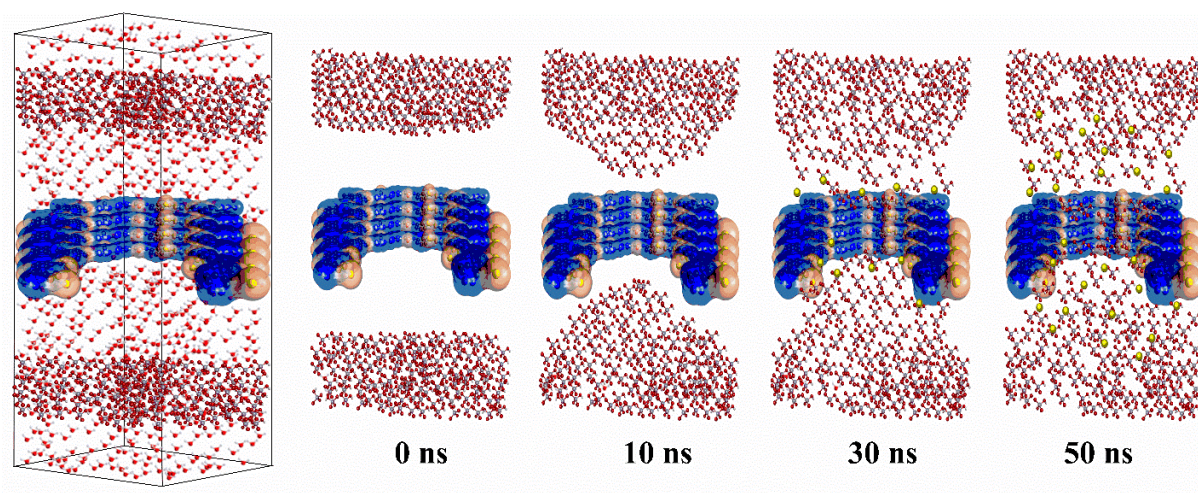
Appendix Figure 5.82: HOMO-LUMO of IPiPOP-3U, ROX and HAsO_4^{2-}



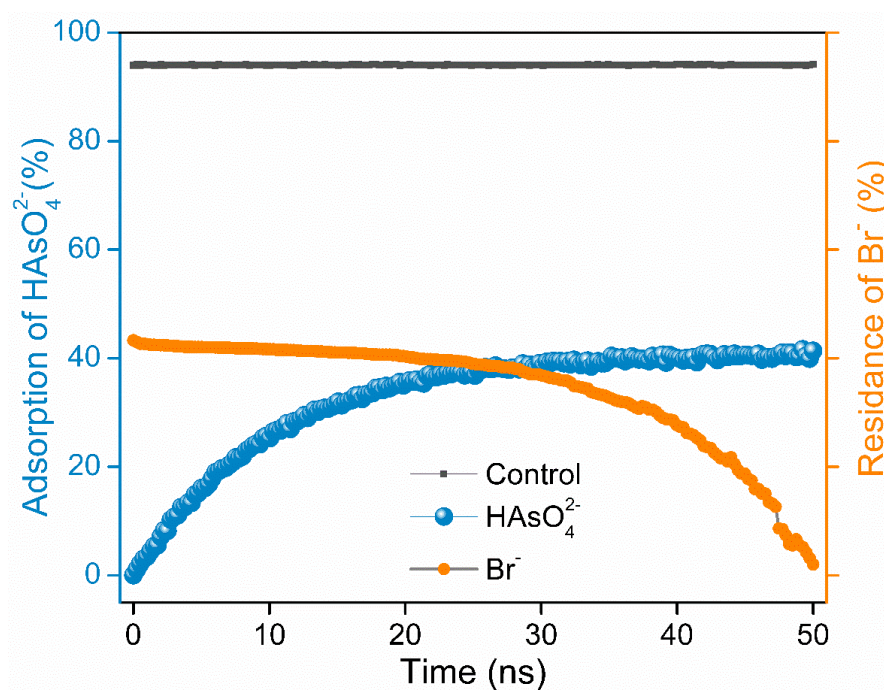
Appendix Figure 5.83: ESP of repeating unit of IPiPOP-3U



Appendix Figure 5.84: HOMO-LUMO of IPiPOP-3U after capture of ROX and HAsO₄²⁻



Appendix Figure 5.85: A time series of snapshots to show the adsorbing dynamics of HAsO_4^{2-} molecules into the IPiPOP-3U structure at 0, 10, 30, 50 ns



Appendix Figure 5.86: Time evolution of the adsorption rate of HAsO_4^{2-} molecules (blue) in IPiPOP-3U

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Chapter 6

Summary and Future Outlook

6.1 Summary and Future Outlook

Porous organic polymers (POPs) and ionic Metal Organic Framework (iMOF) have earned tremendous research attention as class of advanced functional porous materials (AFPMs) in the recent past owing to their potent applicability in myriad applications. The studies documented in the current thesis work include in-depth research into design & syntheses of function-led AFPMs. In the first part of the thesis, simple and strategic fabrication of task-specific POP-based heterogeneous catalysts were developed to drive important and industrially relevant organic transformations under mild and eco-friendly conditions with great efficiency and high photocatalytic production of H_2O_2 from seawater, air and sunlight. Additionally, pertaining to industrial aspect of bulk chemical synthesis, heterogeneous catalysis under continuous flow was also accomplished. Also, both the works are highlighted in their potency toward practical implementation in terms of scope, processability as well as scalability. The second part of the thesis work mainly focuses on rational design of iMOF based sensor and iPOP based nanotraps to detection and segregate toxic organic arsenic and inorganic arsenic from water. Ionic metal organic framework consists of Zn metal node, tripodal imidazole-based N-donor ligand and aromatic sulfonic acid, efficiently selectively detect organic arsenic, ROX and NIT, in ppb level from water in presence of several drugs present in the water. Also, urea functionalized size adaptable ionic porous organic polymer was employed for selectively capture organic and inorganic arsenic from water. Mentioned iPOP capture organic (ROX) and inorganic (HAsO_4^-) arsenic with ultrafast kinetics and high capacity. For the real time application, the capture study was performed in water from different water bodies and low concentration with dynamic flow column. The mechanistic aspects of this capture performance were further explored with EXAFS, DFT calculation and MD simulation studies.

The current thesis emphasizes the strategic design and synthesis of materials that integrate structural robustness, function-driven design, and enhanced performance. A critical challenge associated with the processability of powdered materials is addressed through the development of various composite forms, including beads and aerogels. The significance of targeted structural modifications is demonstrated by the fabrication of one metal-organic framework (MOF), three distinct functional polymers, and a porous organic polymer (POP) composite, each tailored for specific applications and exhibiting high efficacy. The central theme of the research is the creation of materials with task-specific functionalities, optimized for targeted applications. While the potential of advanced functional porous materials (AFPMs) is considerable, they remain underexplored, requiring further research to unlock their full potential. Additionally, ensuring performance retention under operational conditions, along with cost-effective scalability, is critical and demands further attention. The coming years hold substantial promise for researchers to advance the development of AFPMs, addressing significant industrial and environmental challenges.



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Urea-Tethered Porous Organic Polymer (POP) as an Efficient Heterogeneous Catalyst for Hydrogen Bond Donating Organocatalysis and Continuous Flow Reaction

Author: Gourab K. Dam, Sumanta Let, Vartika Jaiswal, et al

Publication: ACS Sustainable Chemistry & Engineering

Publisher: American Chemical Society

Date: Feb 1, 2024

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Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water

Author: Gourab K. Dam, Sahel Fajal, Subhajit Dutta, et al

Publication: ACS Applied Optical Materials

Publisher: American Chemical Society

Date: Jul 1, 2023

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Urea-Tethered Porous Organic Polymer (POP) as an Efficient Heterogeneous Catalyst for Hydrogen Bond Donating Organocatalysis and Continuous Flow Reaction

Gourab K. Dam,[§] Sumanta Let,[§] Vartika Jaiswal, and Sujit K. Ghosh*



Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 3000–3011



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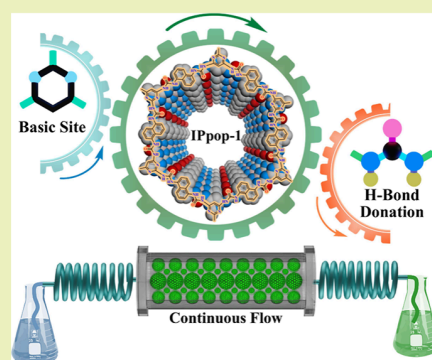
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ABSTRACT: Hydrogen bond donating (HBD) heterogeneous organocatalysis has come to light as a powerful surrogate to Lewis acid activation toward manufacturing biologically important C–C bonds. Notwithstanding the emergence of urea as a functionally diverse moiety to drive homogeneous HBD reactions, its catalytic competency is often muted by self-quenching behavior. Keeping this in perspective, spatial isolation of catalytically active urea functionality inside a porous framework can alleviate this pitfall, rendering a potential solution. The current work reports the fabrication of a porous urea network (IPpop-1) as a superior heterogeneous HBD catalyst toward Friedel–Crafts alkylation of β -nitrostyrene and indole (yield up to 99%) under mild conditions advocating green chemistry. Experimental evidence that supports the critical step of the catalytic reaction leading to a plausible mechanism was unveiled along with theoretical assistance. Additionally, the versatile bifunctional nature of the catalyst was established from its competence in catalyzing multi-component Knoevenagel–Michael condensation as well as cyanosilylation reactions efficiently. One-pot cascade catalysis was also achieved under milder reaction conditions with excellent product yields exploiting the dual active sites of IPpop-1. Pertaining to practicality, spherical composite beads were fabricated to perform continuous flow multicomponent Knoevenagel–Michael condensation without compromising the catalytic activity of IPpop-1. Furthermore, regeneration of the spent catalyst (up to 10 cycles) and scalability combined with wide substrate tolerance manifested conceptual feasibility of the polymer catalyst.

KEYWORDS: Friedel–Crafts alkylation, heterogeneous catalysis, composite, mechanistic insight, cascade reaction, flow chemistry



INTRODUCTION

Chemical reactions often necessitate additional energy input to surmount the barriers to activation energy. Apropos of that, introduction of a suitable catalyst enables accelerated chemical conversion under milder conditions through bypassing these energy barriers. Modern human life has become unimaginable beyond catalysis, a technology central to our fundamental requirements of livelihood.¹ Over the years, homogeneous catalysts have emerged showcasing their excellent activity and selectivity in numerous chemical reactions. Having said that, obvious pitfalls such as complex recyclability issue, costly nature, as well as tedious purification and isolation of desired products (particularly in pharmaceutical synthesis) have largely thwarted their advancement both in chemical industry and academia.² To combat these impediments, efforts have been put forward worldwide toward developing efficient heterogeneous catalysts that offer facile recyclability along with designable and easily accessible active sites.^{3–7} Along this line, diverse porous architectures such as zeolites,^{8,9} mesoporous silica,¹⁰ metal–organic frameworks,¹¹ covalent organic frameworks^{12,13} as well as porous organic polymers (POPs)^{14–18} have surfaced as a competent solid support

matrix in heterogeneous catalysis. Among them, POPs have shown tremendous potency in the field of heterogeneous catalysis providing leverage with their following unique features: (1) Akin to its homogeneous counterparts, POPs allow easy integration of diverse task-specific functional groups with their synthetic tunability.^{19,20} (2) Their insoluble and robust nature offer easy regeneration, while wettability of POPs can be engineered conveniently, enabling enhanced mass transfer to boost catalytic performance.²¹ (3) Harnessing confinement at the nanoscale with regard to space as well as electronic characteristics aid in yielding better activity in terms of yield and product selectivity.²² Additionally, framework stability, high permanent porosity, and function-led design

Received: September 23, 2023

Revised: February 1, 2024

Accepted: February 2, 2024

Published: February 15, 2024



Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water

Gourab K. Dam, Sahel Fajal, Subhajit Dutta, Sumanta Let, Aamod V. Desai, and Sujit K. Ghosh*

Cite This: *ACS Appl. Opt. Mater.* 2023, 1, 1217–1226

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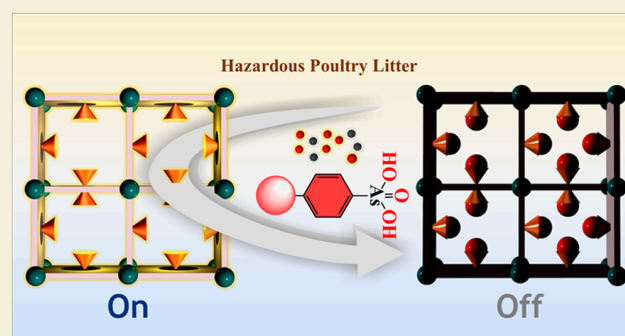
Supporting Information

ABSTRACT: Drugs containing organic arsenic moiety are extensively utilized as food additives in the poultry industry, and release of these organic arsenics through poultry litter to natural water bodies can prove fatal and noxious to the ecosystem. Pertaining to this, sensitive detection of organic arsenic drugs in a selective manner from livestock waste water remains pivotal but indeed very challenging. In this work, we explored a cationic MOF, viz., iMOF-12C, as a fluorescence sensor toward precise recognition of organic arsenic molecules such as roxarsone (ROX) and nitarosone (NIT). Here we explore the potential of ionic MOFs for the first time toward recognition of organic arsenic drugs. iMOF-12C displayed excellent potency as a suitable sensory material toward selective detection of both ROX and NIT in water medium. The quenching efficiency of iMOF-12C toward ROX and NIT recognition was found to be 78 and 82%, respectively. The limit of detection (LOD) of iMOF-12C for ROX and NIT was calculated as 3.95 and 1.35 ppb, respectively, well below WHO's safety limit. Further, for practical application, iMOF-12C-based mixed-matrix membranes (MMM) were casted, which showed excellent organic arsenic detection in water. The findings of this work highlight the potential of iMOF-12C toward real-time detection of organic arsenic molecules in water bodies.

KEYWORDS: cationic MOF, sulfonic acid, toxic organic arsenic, selective detection, PLE spectrum, limit of detection

INTRODUCTION

The poultry industry plays an indispensable role in the food industry, producing ~102 million metric tons of broiler meat per year globally as of 2021.¹ United States (US) produced an estimated 20.4 million metric tons of poultry meat, while India produced 4.2 million metric tons. The poultry industry uses several drugs including organic arsenic,² which inhibits diseases, accelerates growth, increases the feed efficacy, and enhances meat pigmentation in the poultry birds. Drugs such as 4-hydroxy-3-nitrophenylarsonic acid (roxarsone, ROX) and 4-nitrophenyl arsenic acid (nitarosone, NIT) are the two most extensively used arsenic-containing drugs in the poultry industry to accelerate growth³ and prevent blackhead disease (histomoniasis),² respectively, elevating the arsenic concentration in the broiler meat.⁴ Statistically, more than 90% of the organic arsenic fed to the poultry birds is excreted as unchanged drugs,^{5,6} resulting in serious contamination in the soil and water bodies. Survey shows that a geographical domain manufacturing 100 million poultry birds that consume 70% ROX would release ~4300 kg of arsenic per year to the environment, mostly in the agriculture field, as poultry manure is used as an effective fertilizer.² The discharge of such enormous amount of arsenic has escalated its concentration to 1000 µg/kg, which is much greater than the safety limit (10



ppb) determined by the World Health Organization (WHO).⁷ Additionally, in aerobic and anaerobic environmental conditions, these organic arsenics are converted to dimethylarsonic acid (DMA), monomethylarsonic acid (MMA), and inorganic arsenics ($\text{As}^{5+}/\text{As}^{3+}$),^{8,9} which are not only highly toxic but also more soluble and mobile than the organic arsenic in water.¹⁰ Elemental arsenic (As), also called the slow-death poison, features prominently among the lethal and carcinogenic elements,¹¹ and can reach the human body from ground water as well as from chicken intake as food. In the human body, arsenic mainly accumulates in keratin-rich tissues^{12,13} and disrupts the energy transduction reactions, retarding ATP production alongside causing endothelial damage.¹⁴ Keeping in mind the severe toxicity of organic arsenics, it is necessary to develop potential sensors toward recognition of these contaminants in water. Till date, the detection of organic arsenics, particularly ROX and NIT, has depended on

Received: March 31, 2023

Revised: May 29, 2023

Accepted: May 31, 2023

Published: June 15, 2023

