

Function-led Design & Syntheses of Advanced Porous Organic Polymers and their Composites: Heterogeneous Catalysis and Toxic Pollutants Separation

A Thesis

Submitted in Partial Fulfillment of the Requirements for the
Degree of

Doctor of Philosophy

by

Sumanta Let

Reg. ID: 20173499



**Indian Institute of Science Education and Research (IISER), Pune
2023**

Dedicated to

মা-বাবা ও মেজদা



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

Certificate

It is hereby certified that the work described in this thesis entitled "***Function-led Design & Syntheses of Advanced Porous Organic Polymers and their Composites: Heterogeneous Catalysis and Toxic Pollutants Separation***" submitted by *Mr. Sumanta Let* was carried out by the candidate, under my 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 institution.

Date: 15.03.2023

A handwritten signature in blue ink, likely belonging to Dr. Sujit K. Ghosh, positioned above his name and title.

Dr. Sujit K. Ghosh
Research Supervisor

Email: sghosh@iiserpune.ac.in
Contact No.: +91(20)25908076

Declaration

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Synopsis

The principal cornerstone of all the works described in this thesis include rational design, development and syntheses of advanced porous organic polymer composites aimed at heterogeneous catalysis and detoxification of water. Notwithstanding the fact that conventional porous materials are necessary in our day-to-day life, harnessing targeted applications on-demand with these materials is an almost impossible task. Porous solids representing an expansive domain are distinctly divided as metal-organic frameworks (MOFs), i.e., inorganic-organic hybrid porous materials assembled through inorganic metal ions-organic ligand co-ordination bond and porous organic materials (POMs) crafted from robust covalent bonding between organic synthons that perpetuate throughout the solid network. These materials offer leverage of function-led design, synthetic tuning, facile pore composition along with modulation of physical/chemical properties that allow probing host-guest chemistry on the principle of structure-property correlation. Likewise, porous organic polymers (POPs), a category of amorphous highly crosslinked polymers with abundant nanopores, have lately emerged as a suitable platform for wide spectrum of applications. POPs offering the leverage of control at molecular scale in order to generate custom made “nanospace” featuring both tunable porosity and required chemical functionality have shown potency in gas storage/separation, catalysis, energy storage, photoluminescence, drug delivery, detection and removal of pollutants/contaminants from water etc. Hitherto, rational design of task-specific advanced porous organic polymer composites toward wastewater remediation and eco-friendly heterogeneously catalysis still remains untapped. Further, porous organic polymers can be classified to neutral and ionic POPs based on their electrostatics. Additionally, post-synthesis structural engineering of these materials present convenience of introducing desired functionality in fabricating sophisticated supramolecular scaffolds. The crux of this thesis work revolves around systematic approach toward developing strategically synthesized function-led advanced POPs and their composite materials zeroing on heterogeneous catalysis and water contaminants sequestration. Thus designed functional porous solids were utilized to address two pertinent applications. Attempts were made to develop two potent porous polymer composite catalysts for organic transformations under milder conditions. Furthermore, to combat water pollution, ionic porous organic polymers (iPOPs) bearing specific functionality were also synthesized and investigated for segregation of toxic pollutants present in water.

Chapter-1. Introduction

To begin with, a concise discussion on porous materials is covered. This include naturally occurring porous materials along with advanced porous materials (APMs) such as inorganic–organic hybrids and porous

organic materials (POMs). In particular, inorganic-organic hybrid porous architectures, i.e., metal-organic frameworks (MOFs) and metal-organic polyhedral (MOPs) have been touched upon on the basis of synthetic approach and structural characteristics including potential applications. Additionally, porous organic materials (POMs), types thereof, such as covalent-organic frameworks (COFs), porous aromatic frameworks (PAFs), covalent triazine frameworks (CTFs), hydrogen-bonded organic frameworks (HOFs), porous organic polymers (POPs), , porous organic cages (POCs) along with their diverse applications have been discussed. Advanced porous organic polymers and their leverage in terms of targeted applications is also covered. Particularly, applications of POPs as superior materials toward heterogeneous catalysis as well as water purification is discussed. Finally, an overview regarding the advancement achieved in this thesis work in terms of designing function-led advanced porous organic polymers aimed at targeted applications is highlighted.

Part-I: Function-led Design and Syntheses of Porous Organic Polymers as Superior Heterogeneous Catalysts

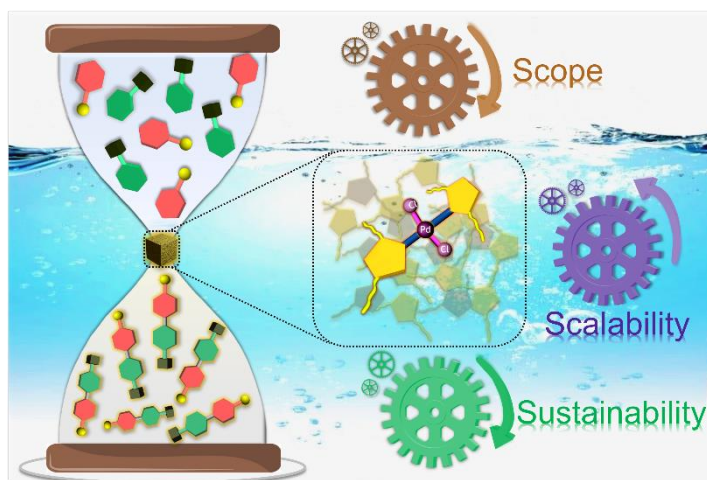
Heterogenization of homogeneous molecular catalysts by immobilizing them onto support matrix have come forth as a unique strategy to fabricate chemically homogeneous yet heterogeneous solid catalyst. . Heterogeneous catalysts offer leverage over its homogenous counterpart owing to easy separation post-catalytic reaction, reusability as well as convenience in flow chemistry. However, increased catalyst cost, reduced activity as well as a trade-off between active site accessibility for the substrate molecules present some bottlenecks of heterogeneous catalysis. Keeping these points under consideration, one should be judicious while choosing the support matrix for homogeneous molecular catalyst immobilization. Porous organic polymers (POPs) with inherent features like large specific surface area, ease of synthetic tuneability and chemical robustness serve as an ideal support matrix to immobilize active catalytic sites by simple methodology. In this section, a conscious effort is put forward toward developing potent heterogeneous catalysts by utilizing porous organic polymers (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 palladium (Pd) anchored N-heterocyclic carbene (NHC) on a porous polymer, its composite preparation and utilization in Suzuki-Miyaura coupling reaction under mild conditions. In Chapter-3, a metal free POP based heterogeneous catalyst with abundant antagonistic catalytic sites is developed to carry out one-pot cascade catalysis using water as a solvent.

Chapter-2. Palladium anchored N-Heterocyclic Carbene in a Porous Organic Polymer (POP): An Efficient Heterogeneous Composite Catalyst for Eco-Friendly Suzuki-Miyaura Coupling

The pursuit of organic transformation strategies aimed at sustainable and green chemistry has prompted a

definitive transition from unrecyclable homogeneous Pd complexes while heterogeneous Pd nanocatalysts have been further delved into. The Pd-catalysed cross-coupling reactions, despite recognized challenges of product separation & catalyst reusability mainly employs soluble metal complexes while attempts to anchor these homogeneous catalysts onto insoluble supports are thwarted by poor stability, leading to declining catalytic performance owing to the metal leaching or aggregation. In this chapter, we have strategically designed a Pd(II)-anchored N-heterocyclic carbene on a porous polymer support that catches the leverage of both worlds, being a heterogeneous solid catalyst, and also displaying robust stability in the reaction medium. Judicious choice of monomer building block in combination with precise chemical modifications yielded successful tethering of homogeneously dispersed spatially segregated Pd (II) units in 120-MI@Pd NHC & 120-EI@Pd NHC, respectively. Under optimized conditions, 120-EI@Pd NHC, the better performing catalyst displayed par excellence catalytic activity (yield >99%) in aqueous solution at room temperature. Wide functionality tolerance of 120-EI@Pd NHC was further validated with excellent yields observed over 42 electronically diverse substrates while sustainability was established over 10 catalytic cycles. Finally, practical applicability was also tested by crafting a 3D aerogel based nanocomposite.

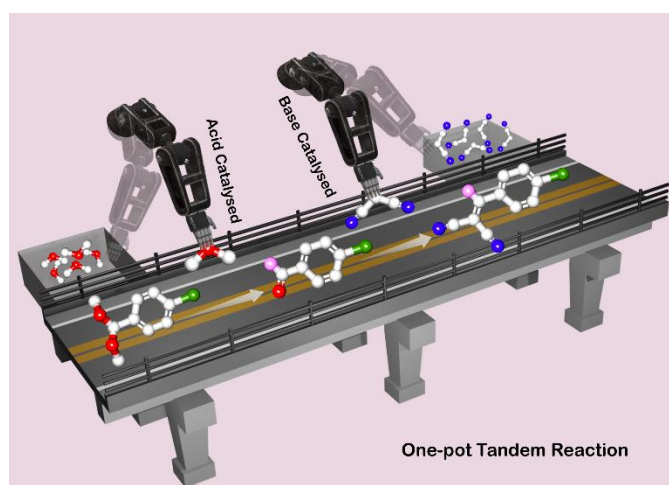
(*J. Org. Chem.* **2022**, 87, 24, 16655–16664)



Chapter- 3. A Bi-catalytic site-isolated Porous Polymer Featuring Incompatible Lewis pairs for Antagonistic one-pot Cascade Catalysis in water

Amid diverse catalytic reactions, cascade catalysis ($A \rightarrow B \rightarrow C$) are momentous and potent pathways to achieve one-pot multi-step organic transformations. This type of tandem catalysis offer the advantages of bypassing costly and time intensive purification and isolation of intermediate products. Having said that, the progress of tandem catalysis is inhibited by fundamental bottlenecks. Firstly, the rational design of a

catalyst with one-pot cascade *modus operandi* is arduous, specifically for those with sequential reactions requiring antagonistic catalytic sites (e.g., acidic sites in step 1 ($A \rightarrow B$) and basic sites in step 2 ($B \rightarrow C$) for deacetalization-Aldol condensation, deacetalization-Knoevenagel condensation etc.). Secondly, the anchoring of antagonistic active sites in nanomaterials often requires the mandate of synthesizing core-shell, yolk-shell type heterogeneous catalysts leading to restricted accessibility of the active catalytic sites. In this chapter, an efficient metal free ionic porous organic polymer (iPOP) bearing site-isolated bi-catalytic sites was crafted through simple post-synthesis structural modification. Thus prepared polymer catalyst displayed excellent potency toward one-pot cascade deacetylation- Knoevenagel condensation reaction under mild condition using water as a green solvent. The polymer catalyst also displayed excellent efficiency under continuous flow condition. Additionally, owing to the presence of isolated acidic as well as basic sites, the heterogeneous catalyst exhibited exceptional performance in cyanosilylation (acid catalysed) and Knoevenagel condensation (base catalysed) reactions. (*Manuscript under revision*)



Part-II: Fabrication of Task Specific Porous Polymer Nanotraps Toward Segregation of Toxic Pollutants in Water

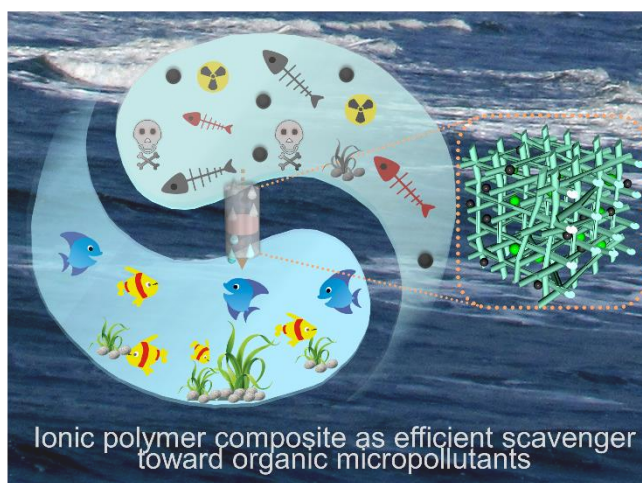
Water pollution has emerged as one of the biggest threat to humanity in the 21st century. Sequestration of toxic water contaminants in order to accomplish purified water has garnered consequential research attention globally. Having said that, the combat to ameliorate water pollution is far from finished given the fact that prominent water contaminations are still unaddressed and continue to endanger billions. To tackle this pressing problem that necessitates immediate mitigation, the potential of ionic porous organic polymer (iPOP) composites are explored. This segment is also separated into two chapters. Chapter-4 summarizes the development of a magnetic nanoparticle encapsulated cationic microporous polymer composite (120-

TMA@Fe) for effective trapping of toxic organics (dyes, aromatic models, plastic components, and pharmaceuticals) from water. In Chapter-5, bio-inspired antagonism was harnessed in a charged macroporous polymer network for enhanced segregation of heavy metal and heavy metal-based oxo-pollutants from water.

Chapter-4. Magnetic Nanoparticle-Embedded Ionic Microporous Polymer Composite as an Efficient Scavenger of Organic Micropollutants

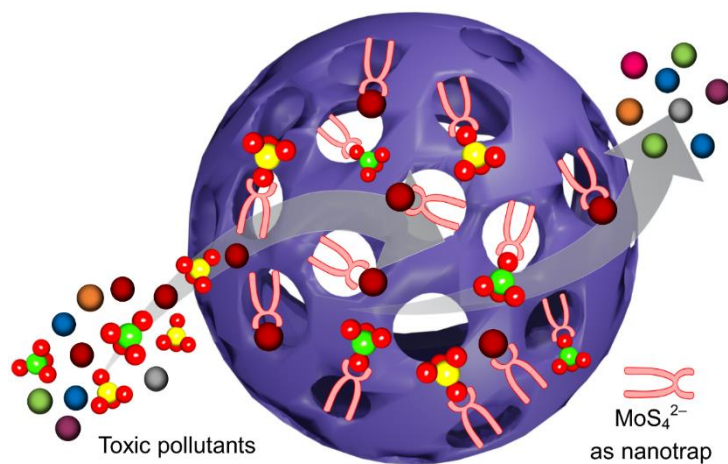
Organic micropollutants, on account of their diversity in nature as well as source of contamination, represent a more extensive family compared to inorganic pollutants. These aromatic molecules are often biologically non-degradable, have detrimental effects upon the aquatic environment, human health, and environment, even when abundant in trace amounts. To combat this issue, we have tapped into the potential of ionic composite polymer to capture a wide variety of organic micropollutants. Bearing free exchangeable anions along with its magnetic nature, 120-TMA@Fe was employed toward sequestering dye molecules, pharmaceuticals, plasticizers and aromatic compounds. The polymer showed swift kinetics toward all the pollutants with an equilibration time of ~5 minutes. Additionally, the composite displayed significant uptake capacity, comparable to the best-known values in the literature. The practical applicability of 120-TMA@Fe was explored with real-world water samples, wherein, a par excellence efficiency was observed for all the tested pollutants along with exceptional reusability performance to validate its sustainability.

Reference: S. Let, S. Dutta,[†] P. Samanta,[†] S. Sharma, S. K. Ghosh, *ACS Appl. Mater. Interfaces* **2021**, 13, 51474–51484.



Chapter 5. Harnessing Bio-inspired Antagonism in a Charged Macroporous Organic Polymer Toward Enhanced Pollutant Segregation from Water

In this chapter, a tailor made cationic macroporous superior sorbent material (mPOP@MoS₄²⁻) was designed to harness synergistic detoxification of water by exploiting Hg-Se antagonism observed in biota. Molecular level knowledge disseminated by biologists over the years was used as the cornerstone design strategy by judicious post synthesis modulation. Additionally, silica templated synthetic protocol was adapted to introduce inter-connected macropores throughout the polymer network. Thus synthesized macroporous polymer displayed exceptional performance in Hg²⁺ removal from water with swift kinetics and high uptake capacity. Furthermore, simultaneous removal of Hg²⁺/Se (VI) and Hg²⁺/Se (IV) was achieved with ultrafast kinetics. Practical relevance and conceptual feasibility was established by selective sequestration of the toxic pollutants in presence of concurrent interfering ions (10 fold & 100 fold excess) and real water samples. Also, significant enhancement of removal efficiency of both Se (IV) and Se (VI) both in terms of kinetics and uptake capacity was attained in presence of Hg²⁺. This study fosters one of the rare examples of trapping both cationic and anionic pollutants with a cationic sorbent material. (*Manuscript under preparation*)



Chapter 6. Summary and perspectives

In this section, an effort to summarize the insights gained through the library of task-specific porous organic 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 POPs, 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 porous organic polymers 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

Anal.	Analysis
Calc.	Calculated
DMF	N,N'-dimethylformamide
MeOH	Methanol
EtOH	Ethanol
DCM	Dichloromethane
FT-IR	Fourier transform infra-red spectroscopy
mg	Miligram
g	Gram
TEM	Transmission electron microscopy
SAED	Selected Area Electron Diffraction
STEM	scanning transmission electron microscope
RT	Room Temperature
min	Minutes
h	Hour
mL	Milliliter
mmol	Milli moles
mM	Millimolar
ppm	Parts per million
ppb	Parts per billion
MOF	Metal-Organic Framework
MOP	Metal-Organic Polyhedra
COF	Covalent-Organic Framework
MOG	Metal-Organic Gel
POP	Porous organic polymer
iPOP	Ionic porous organic polymer

PAF	Porous aromatic framework
COP	Covalent-Organic Polymer
CMP	Conjugated microporous polymer
UV–Vis	Ultraviolet–visible spectroscopy
HCP	Hyper-cross-linked polymer
PXRD	Powder X-Ray Diffraction
RT	Room Temperature
TGA	Thermo-gravimetric Analysis
UV	Ultraviolet
FE-SEM	Field Emission Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance
SSNMR	Solid State Nuclear Magnetic Resonance
EDX	Energy Dispersive X-ray Analysis
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
XPS	X-ray photoelectron spectroscopy
TPD	Temperature programmed desorption
TON	Turnover number
TOF	Turnover Frequency
NPs	Nanoparticles
NHC	N-heterocyclic carbene
SMC	Suzuki–Miyaura coupling
ITC	Isothermal Calorimetry

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Chapter 1

Introduction

1.1 Porous Materials

Porosity is an innate property immanent in nature. Traditionally, permanent & interconnected potential voids accessible to gas molecules or liquids is a prerequisite for porous materials. Naturally occurring porosity is generally observed in biological tissue, rocks, charcoal, soils etc. and have been employed in water purification, filtration, cooling since ancient Egyptian times.^[1] However, it's imperative to recognize that porous materials have existed around us for a lot longer than we might actually think. Documented literature from ancient Egypt such as reports from the Ebers papyrus, which dates back to around 1500 BC, describe medical procedures using porous charcoal for indigestion.^[2] Water purification using charcoal is also mentioned in ancient Hindu texts.^[3] During early exploration, the British navy also charred the interior of their wooden barrels to make the shelf life higher of potable water.^[4] In the latter half of the 20th century along with some early research works on charcoal adsorption, a separate category of porous materials, called zeolites (Greek word meaning “zeo” (to boil) and “lithos” (stone) were gaining reputation among scientists.^[5] Along the same line, past few decades have seen a remarkable upsurge in terms of evolution of porous materials (Figure 1.1). 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 (Figure 1.2).^[7-9] In the contemporary world, with ever increasing demand the utilization of porous solids are not only limited to sorption and catalysis, but they have also found huge applications in various sectors that include clean energy, environmental remediation as well as in 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 had a pervasive impact on our society and have long been essential to daily life. With such conventional porous solids, however, achieving target-specific applications are practically impossible because the structure-property relationship is still not clear. Consequently, it becomes pivotal to develop a new types of porous materials that allow molecular level fine-tuning of order and desired functionalities. Exquisite command on the porous materials overall framework comes forth with the opportunity to make tailor made materials aimed at demanding and appealing applications that are difficult to realize with otherwise conventional porous solids. Over the last 20 years or so, there has been a prudent revamp toward synthesizing novel materials via employing functional as well as engineered building blocks. These materials are generally termed as advanced porous materials (APMs).^[11-13]



Fig. 1.1 A brief illustration of the evolution of porous materials through the ages (Ref. 126).

Since their discovery, these APMs have brought about a renaissance in material engineering as well as chemistry. This is also punctuated by the ever-escalating number of participating researchers around the globe working on this newly developed research area that present chemists the possibility limitless chemical and structural features in this class of materials within their imaginative purview. The unique chemistry of organic as well as inorganic or the amalgamation of both can afford an exciting new class of porous materials that complement or even can be more attractive in comparison to conventional porous solids. ^[14-16]

1.2 Advanced Porous Materials (APMs)

Advanced porous materials (APMs) consist of a large spectrum of materials such as metal-organic frameworks (MOFs), metal-organic gel (MOG), metal-organic polyhedral (MOPs), porous organic materials (POMs) etc. Lately, the research attention into APMs have seen a remarkable upsurge worldwide pertaining to their exclusive features and advantages of molecular level control. APMs featuring high

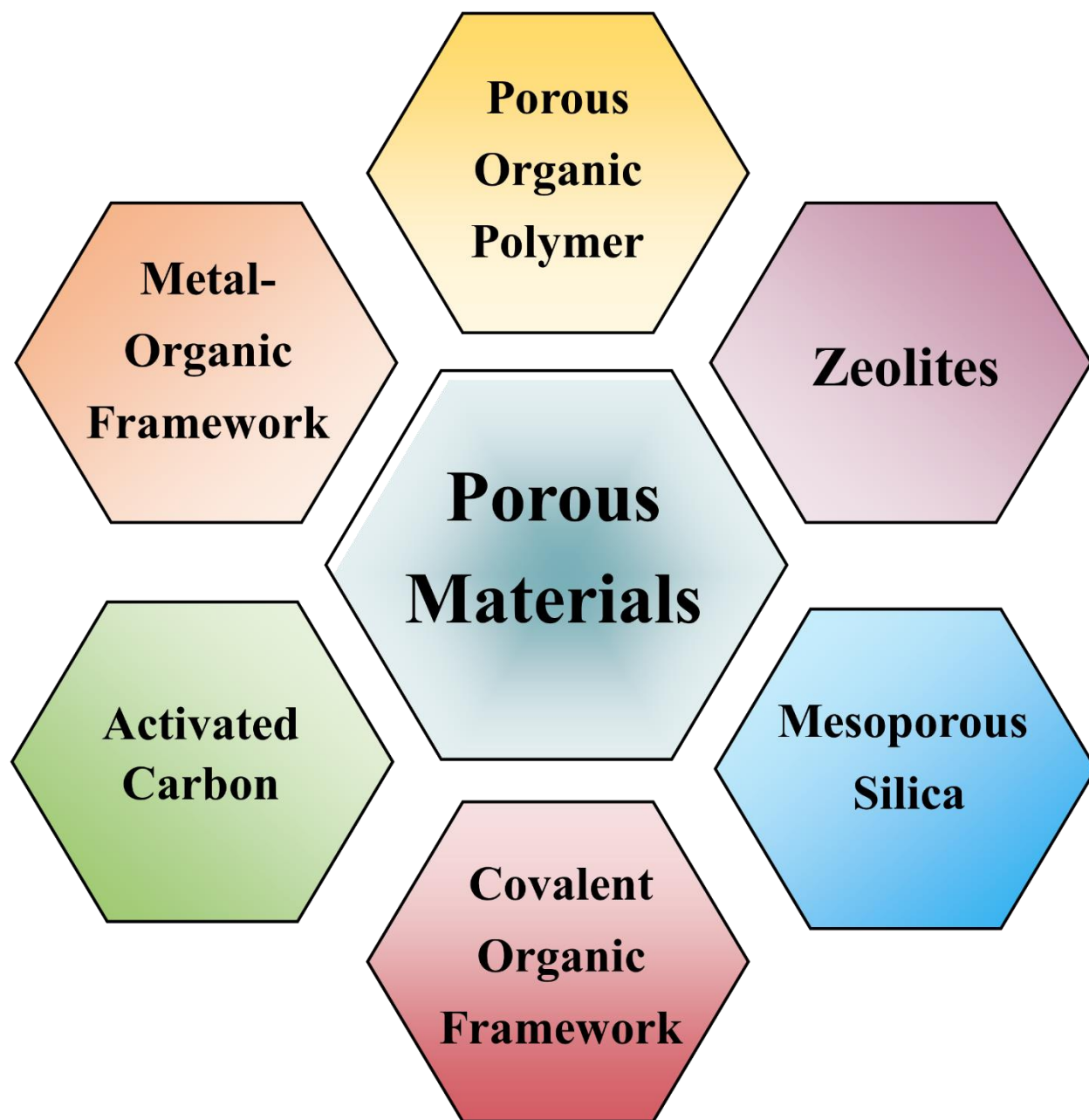


Fig. 1.2 Schematic representation for the classification of porous materials.

specific surface area in combination with functionality tailored pores can be precisely designed and synthesized. Additionally, these APMs can be made processable by transforming them into monolithic aerogels, molecular beads or thin films pertaining to their compatibility toward practical applications. Additionally, it is possible to create stimuli-responsive APMs that can reversibly switch between the open to closed porous form in response to an external stimulus. Most importantly, their superiority over other conventional porous solids is due to the wide range of simple synthetic routes available toward developing

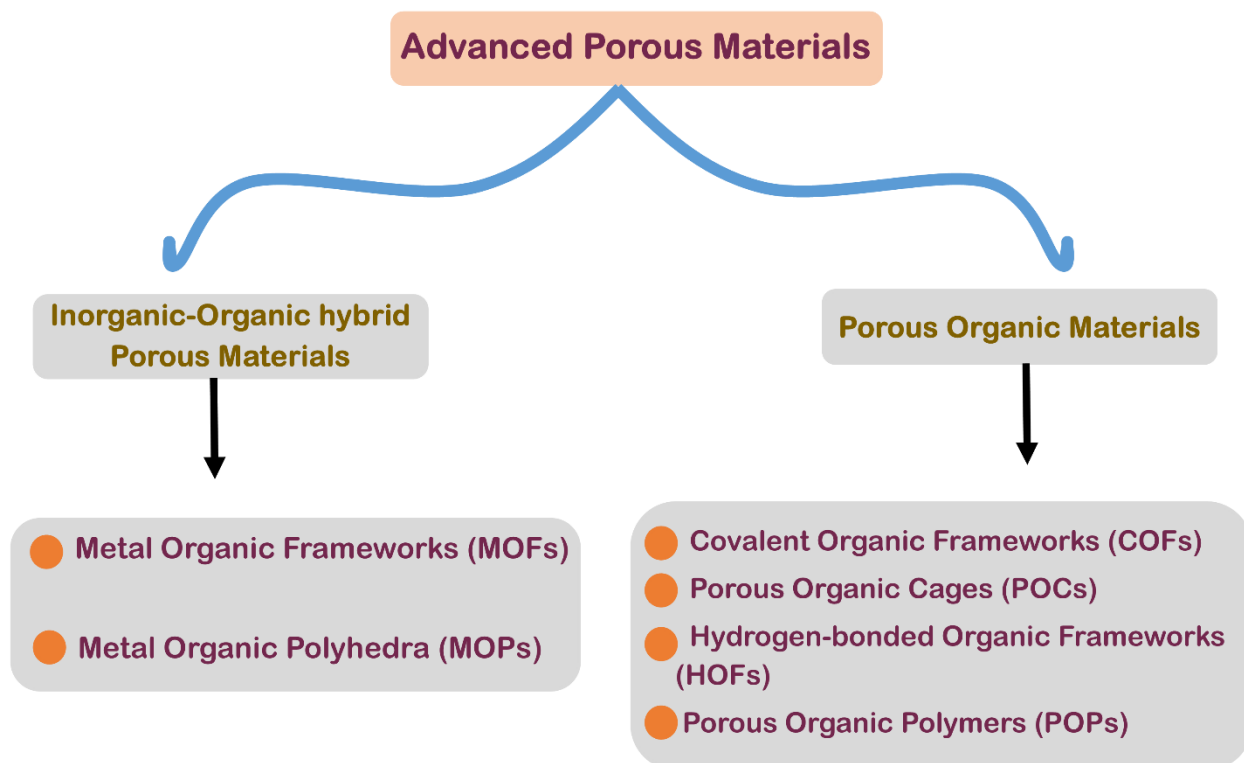


Fig. 1.3 Schematic representation for classification of different types of advanced porous materials.

APMs. These distinctive characteristics are not seen in conventional porous solids. Typically, there are two methods to construct APMs, a) crafting organic-inorganic hybrid porous architectures using functional organic synthons and inorganic metal nodes b) utilisation of purely organic functionalized molecular blocks to generate metal-free porous organic materials by linking them through covalent bonds and noncovalent interactions (Figure 1.3). Metal-organic structures such as metal-organic frameworks (MOFs), metal-organic polyhedra (MOPs), and metal-organic gels (MOGs) are included in the first category, whereas functionalized porous organic materials (POMs) comes in the latter. ^[17-22] Additionally, POMs represent a broad class of materials consisting of amorphous porous organic frameworks that include various types of porous organic polymers (POPs) as well as crystalline porous organic architectures like covalent-organic Frameworks (COFs), hydrogen-bonded organic Frameworks (HOFs), porous organic cages (POCs). ^[23-26] The main benefit of using the aforementioned strategies is that they enable careful selection of functional moieties for synthesizing of APMs, rendering task-specific nature to such materials. The building blocks are designed with application-specific functionality added to the framework backbone to create a porous scaffold that is interactive and functional according to the application.

1.3 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 are 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.^[27-31] 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). These materials are briefly introduced in this section.

1.3.1 Covalent Organic Framework (COF)

Covalent organic frameworks (COFs), a fascinating class of crystalline POM synthesized by the utilization of organic building blocks. Typically, COFs are crafted by the condensation reaction of various monomers bearing multiple reactive sites which eventually generates a porous crystalline polymeric network.^[32] The crux of synthesizing COFs fundamentally relies on the principle of dynamic covalent chemistry in which chemical reactions that are reversible in nature is employed to realize thermodynamically stable polymer networks. The advantage of such technique comes with the boon of generating highly ordered crystalline porous architectures assisted by bond breaking and mending. Amorphous porous polymers and crystalline COFs differ mainly in their reaction pathway; the former produces a product that is kinetically controlled, whereas the latter produces a product that is thermodynamically controlled.^[33] The choice of the building blocks and the reaction conditions are the two factors that dictate the synthetic methodology for the preparation of COFs. While the monomers used in COFs are of distinct symmetry, the synthetic process for the same involve solvothermal, ionothermal, microwave as well as mechanochemical techniques. These symmetry-induced monomers produces COFs with different topologies and symmetry based on various organic reactions.^[34] A combination of well-defined ordered structures, exceptional thermal and chemical stabilities, tunable pore size, and high porosity of COFs make them a very attractive class of materials. Furnished with the above mentioned features COFs have found their applicability in a wide spectrum of applications lately, i.e., molecular sieving, catalysis, drug delivery, gas storage, environmental remediation,

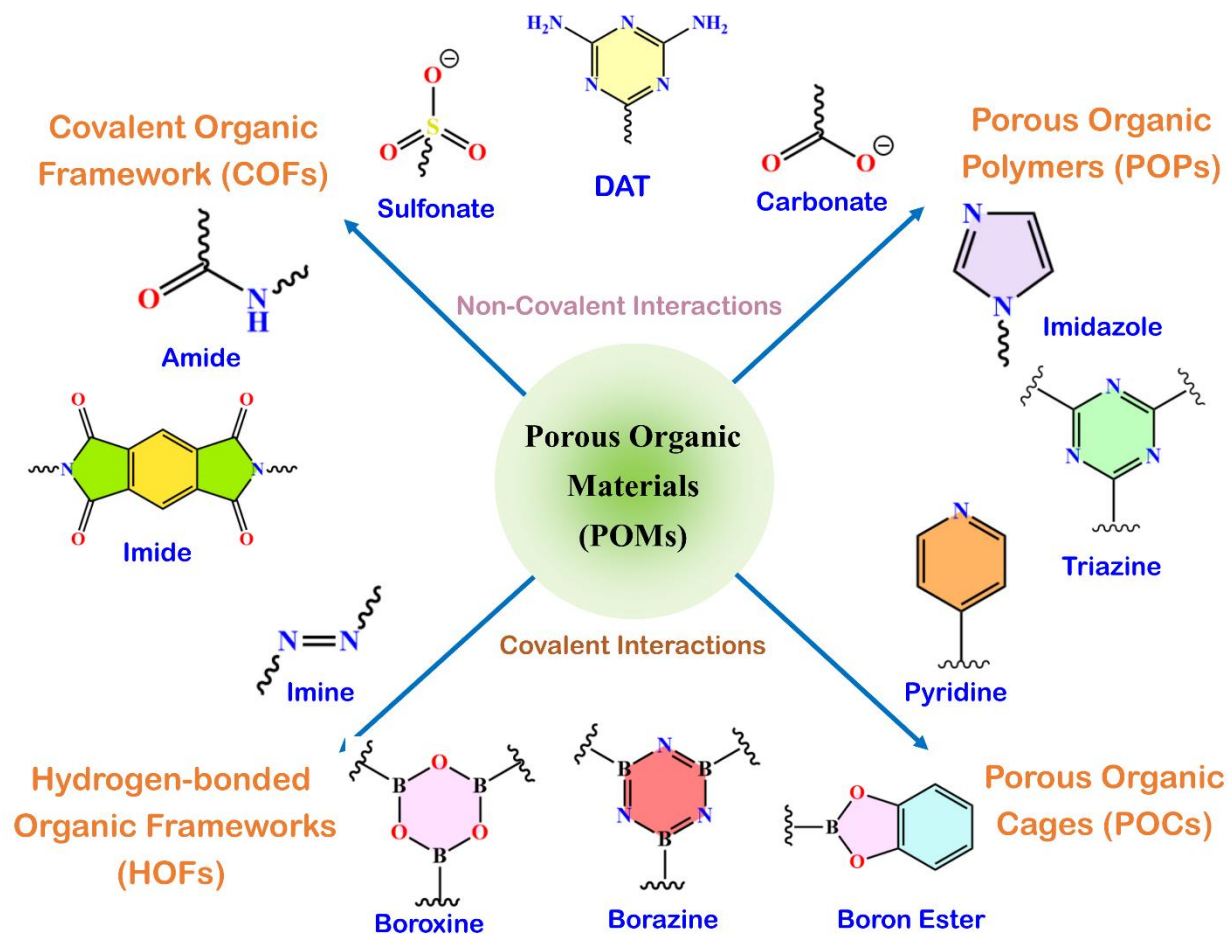


Fig. 1.4 Schematic representation for different types of porous organic materials along with the important functional building blocks utilized for synthesis

clean energy, electronics etc. [35-42] Numerous COFs have been synthesized till date by the formation of B-O-B, B-O-Si, B-N, C=N etc. linkages. Based on their choice of monomers, COFs can be divided into 2 or 3 dimensional architectures depending on their dimensionality. Strong supramolecular π bonding and ordered columnar stacking of the layered frameworks in the 2D COFs makes it easier for charge carriers to move in the direction of the stacking directions. The potential for 2D COFs in π -electronics as well as potent materials for optoelectronic and photovoltaic applications is therefore very high. Generally, tetrahedral units involving sp^3 carbons or silane-based linkages are present in 3D COF structural units to aid in the propagation of the polymeric structure in all three dimensions. [43] Due to the abundance of noncovalent interactions between the various layers, COFs exhibit structural robustness and are stable in a variety of chemical environments, including water and acidic and basic conditions. [44-45] Additionally, post-synthetic modification (PSM) is also employed to create task-specific COFs. [46]

1.3.2 Hydrogen-bonded Organic Framework (HOF)

HOFs are another crystalline member of POMs that have emerged recently. HOFs are mainly constructed from organic building blocks where the framework is stabilized by hydrogen bonding as well as noncovalent interactions.^[47-50] Monomers bearing a hydrogen bond donor and acceptor moiety are used to build HOFs.^[51] Functional groups such as diaminotriazine (DAT), guanidinium-organosulphonate moieties, carboxylic acid and amide-based moieties, and nitrogen heterocyclic moieties are generally used in the construction of HOFs. The fundamental idea behind creating HOFs is governed by the stability and control of hydrogen bonds during network propagation.^[52] In order to access the porous voids created after guest solvent removal, the hydrogen bond aided supramolecular architecture must remain stable after the construction of HOFs with permanent porosity. All of these aspects work in tandem to create functional HOFs for molecular recognition and clean energy-based applications. Till date HOFs have been used in the field of gas molecule separation, especially in separating of hydrocarbons and carbon dioxide from nitrogen.^[53-54] Additionally, HOFs have been utilized for applications focused on clean energy, such as proton conduction, as well as for the sensing and capture of various molecules, including enzyme encapsulation.^[55]

1.3.3 Porous Organic Cage (POC)

Another important class of porous solids known as porous organic cages (POCs) are created from organic constituents by virtue covalent and noncovalent interactions.^[56] POCs have inherent porosity because the solid-state packing of the building blocks creates a porous cavity inside the structure.^[57] Additionally, the POCs' discreteness aids in the enhancement of their solution Processability.^[58] The geometry of the parent molecules, the balance between rigidity and flexibility in the bonds that form the cage, the selection of the proper reaction conditions, including solvent, temperature, and the stoichiometry of the reactant materials, are all significant factors that affect the synthesis of POCs.^[59] Organic reactions, such as formation reversible imine bonds or irreversible C-C bond formation by organometallic coupling reactions, and crystallization reactions at both low and high temperatures, are used to synthesize cages. For POCs to maintain their permanent porous nature, their stability is very crucial. It is crucial to get rid of the guest solvents from inside the POCs in order to access the voids, which are already occupied by guest molecules. It's crucial that POCs maintain their structural integrity during the desolvation process, which is made possible by tight packing of the molecules, having rigid bonds within the architecture, and having stabilizing noncovalent interactions. Additionally, pre-synthesized POCs can undergo post-synthetic modifications to produce functional POCs with improved porosity, stability, and task-specific properties.^[60] POCs are used toward molecular recognition of gases and small molecule separation.^[61]

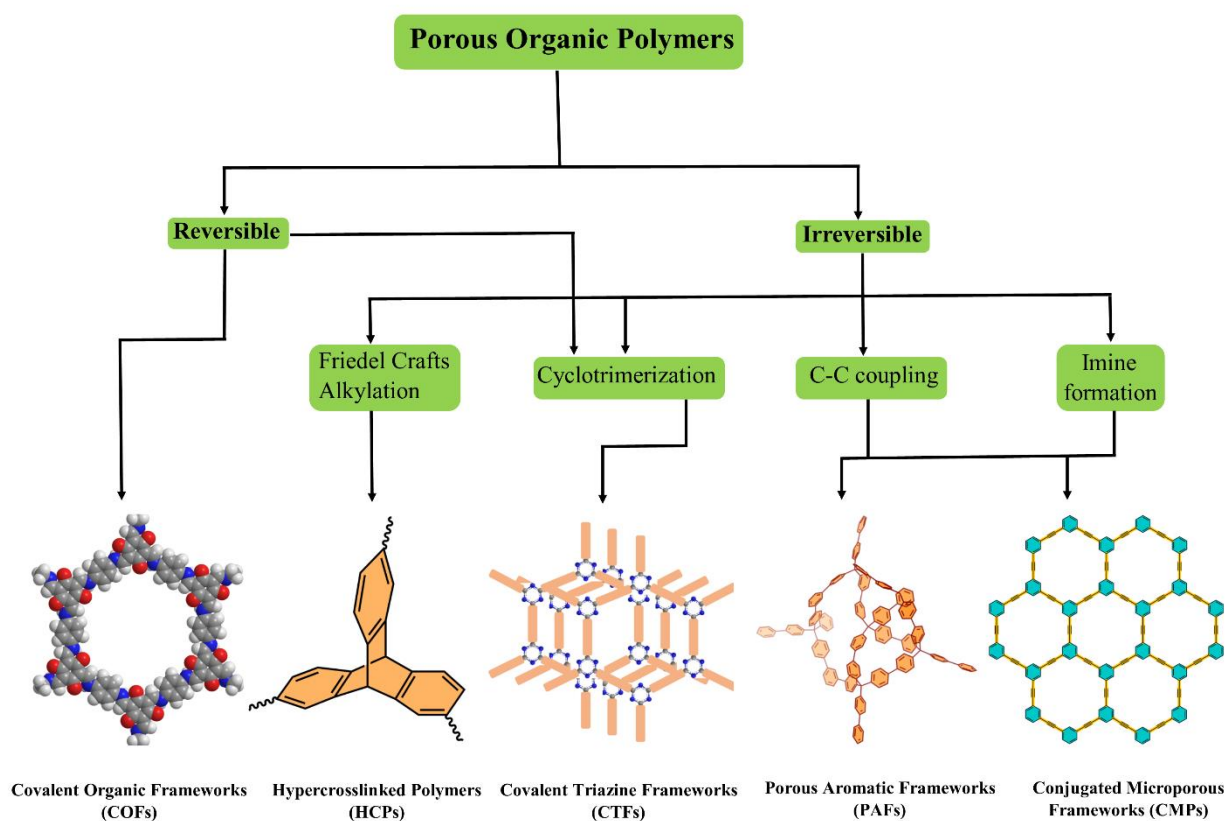


Fig. 1.5 Different types of porous organic polymer frameworks and their coupling formation reactions.

1.3.4 Porous Organic Polymer (POP)

Representing an extensive class of amorphous APMs known as porous organic polymers (POPs) are polymeric architectures crafted by covalently attaching functional organic moieties such as heterocycles, macrocycles, and fused aromatic systems.^[62] POPs offering advantages such as amenability of design & synthesis, large surface area and on demand tuneable pore surfaces etc. provide an edge for such covalently tethered porous materials to be very useful and important amongst contemporary porous materials.^[62-68] Porous organic polymers exhibits significantly more physiochemical stability than its congener MOFs due to their construction with stronger covalent bonds. A wide category of materials such as porous aromatic frameworks (PAFs), conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), hyper crosslinked polymers (HCPs) are regarded as POPs (Figure 1.5). Typically, POPs are found to be mostly amorphous in nature. Having said that, it should also be pointed out that their robust nature and excellent physiochemical stability allow them to be ideal sorbent materials for applicability in real time

stability is a fundamental criterion. In such applications such as wastewater remediation, “performance-property correlation” becomes more critical than “structure-property correlation”.^[69-70] 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.^[71-73] 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 building blocks and the freedom of rotation of the hanging chemical bonds.^[74] 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.^[75-76] Reaction conditions and parameters, which include the starting material concentration, solvent amount and catalyst (if used), and temperature, can have a subtle impact on the porosity of the generated POPs. POPs are recognized for having a large surface area, which accounts for excellent porosity, and a robust nature, pertaining to high stability in a variety of harsh chemical environments.

1.3.4.1 Ionic Porous Organic Polymer (iPOP)

In addition to neutral POP networks, charged polymeric frameworks bearing free counter ions can also be designed and constructed in these organic materials by carefully choosing synthetic pathways and building blocks (Figure 1.6).^[77-80] In general, there are two ways to impart desired functionality and charge over the extended networks of porous organic polymers: pre-synthetic and the post-synthetic modification (PSM) route.^[81-83] The judicious selection of the molecular building blocks as well as synthetic routes has been found to be crucial in the pre-synthetic route for imparting charged functionality inside the porous network. However, since pre-synthetic functionalization of porous polymers is not always straightforward and easily accessible, post-synthetic modification has been found to be a significant tool toward designing task-specific porous organic polymers. It is imperative to mention that post-synthesis structural engineering has come forth as an approach of great interest lately as desired functionality and electrostatic charge can be incorporated to the POPs for tailor made applications.^[84-85] However, ionic porous organic polymers (iPOPs) that represent a sub group of the broad POP family are very less probed and explored than its neutral congener.

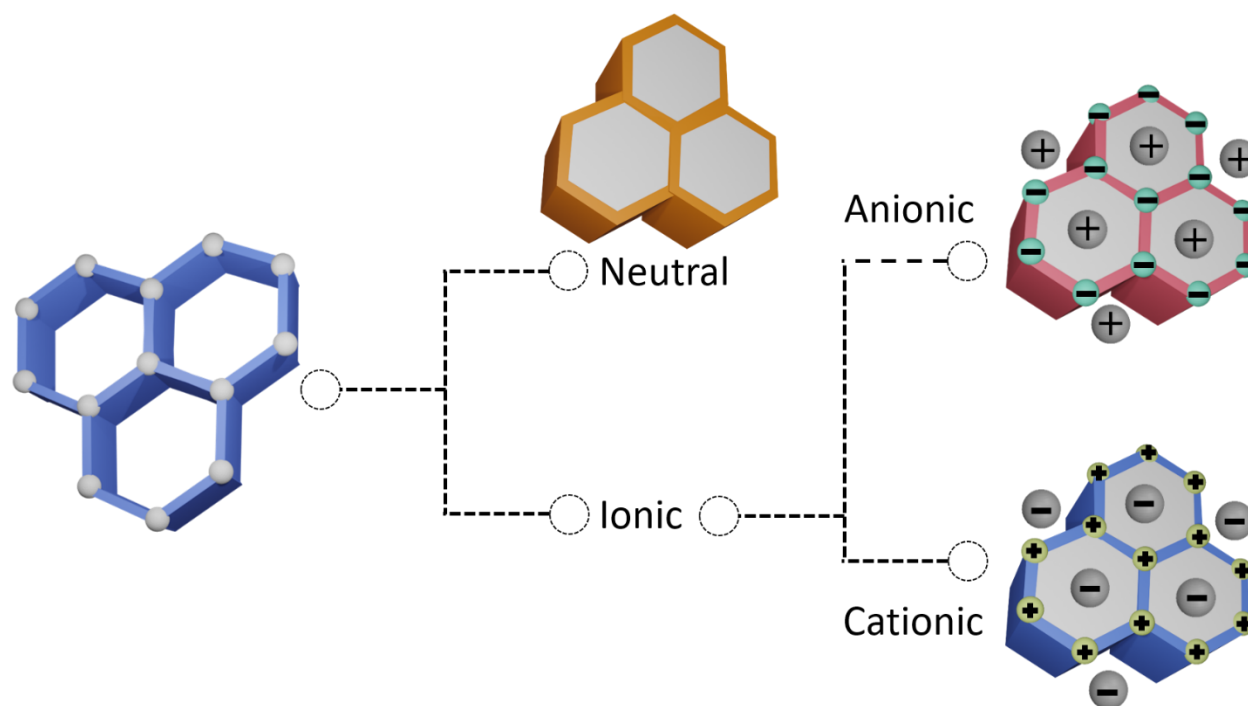


Fig. 1.6 Classification of POPs on the basis of the charge of the framework backbone.

1.4 Application of POPs:

Porous organic polymers have rapidly developed in the last few decades in terms of both synthetic strategy and morphology control. POPs with tunable porous structures or unique functionalities can now be successfully designed at the molecular level and prepared through copolymerization with multifunctional building blocks as well as post functionalization.^[86-88] Consequently, these materials are promising candidates for potential applications in gas storage, catalysis, water remediation, molecular separation, sensing, drug delivery etc. due to their adaptable physical and chemical properties.^[89-90] Similar to MOFs, POPs have found their utility in storage of several gases, such as hydrogen and methane, as well as the separation of carbon dioxide from other gases.^[91-92] Additionally, introducing tunable porosity in POPs to maximize the accessible surface area is an effective way to increase the amount of physisorption adsorption. In order to harness strong chemisorption between guest molecules and porous polymers, the pore environment can be engineered by adding functional units to the pore walls resulting in enhanced gas adsorption performance. POPs are also used as suitable support matrix for heterogeneous catalysis because they are structurally stable, have excellent reusability, and feature large pores that can accommodate functional molecules necessary for catalytic applications. The uniform spatially isolated dispersion and

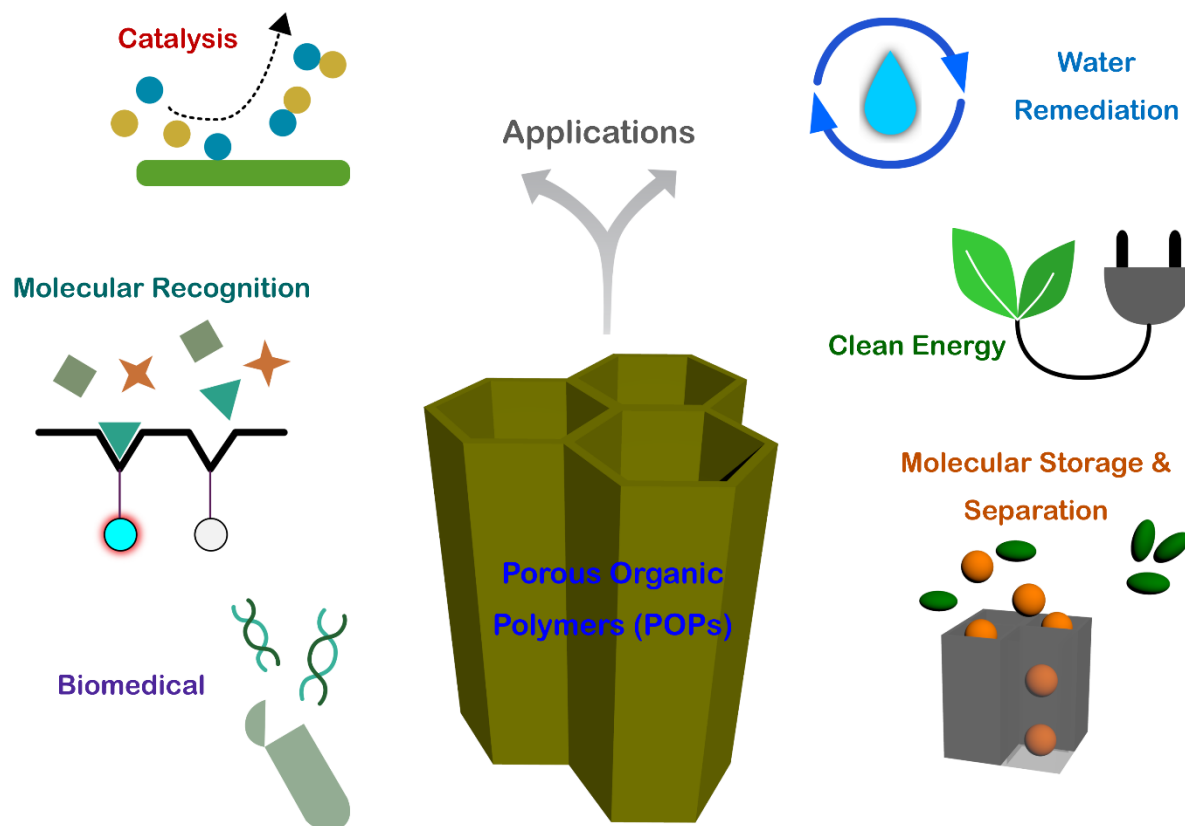


Fig. 1.7 Schematic representation for different applications of POPs.

high density of catalytically active sites make POPs promising candidate in heterogeneous catalysis. ^[93-95] By virtue of incorporating hydrophilic or hydrophobic functional moieties within the pores may result in the easy diffusion of both type of incoming guest molecules. This eventually allow POPs to be useful toward molecular recognition, including the molecular separation, toxic analyte sensing, and selective capture of a targeted molecules from both water and organic medium (Figure 1.7). ^[96-97] In addition, extended conjugation within POPs backbones aids in the development of various photo physical and light-harvesting applications, and the deliberate addition of the right functional moieties boost the use of these materials in a variety of electrochemical applications.

1.5. Heterogeneous Catalysis by POPs: Modern life is unimaginable without catalysis, which has emerged as a necessary technology for the rudimentary necessities of life. ^[98] Traditionally, heterogeneous catalyst is distinguished by its ease of segregation from the products, convenience of handling, reduced catalyst cost and its adaptability to continuous flow processes. A trend toward the crafting chemically homogeneous yet physically heterogeneous catalysts is the immobilization of a homogeneous catalyst into a heterogeneous support. ^[99-102] However, this method suffers from pitfalls like diminished catalytic efficiency, instability and increased catalyst cost that serve as bottlenecks toward the industrial utilization of anchored molecular catalysts. ^[103] The compromised catalytic efficiency may be reasoned to the declined accessibility of active sites and change of chemical environment. Also, to employ catalyst immobilization it often requires prefunctionalization of the precursor or supporting medium which is generated through tedious multi-step synthesis. Additionally, the aforementioned methodology require use of expensive and complex catalyst making it less feasible. Combining all these factors, it consequently increases the cost and diminishes the benefits of heterogenized homogeneous molecular catalyst toward chemical synthesis. Taking all the aforementioned parameters into account, heterogenation via immobilization of homogeneous catalysts should be employed strategically. Having said that, the developed approach should be synthetically feasible,

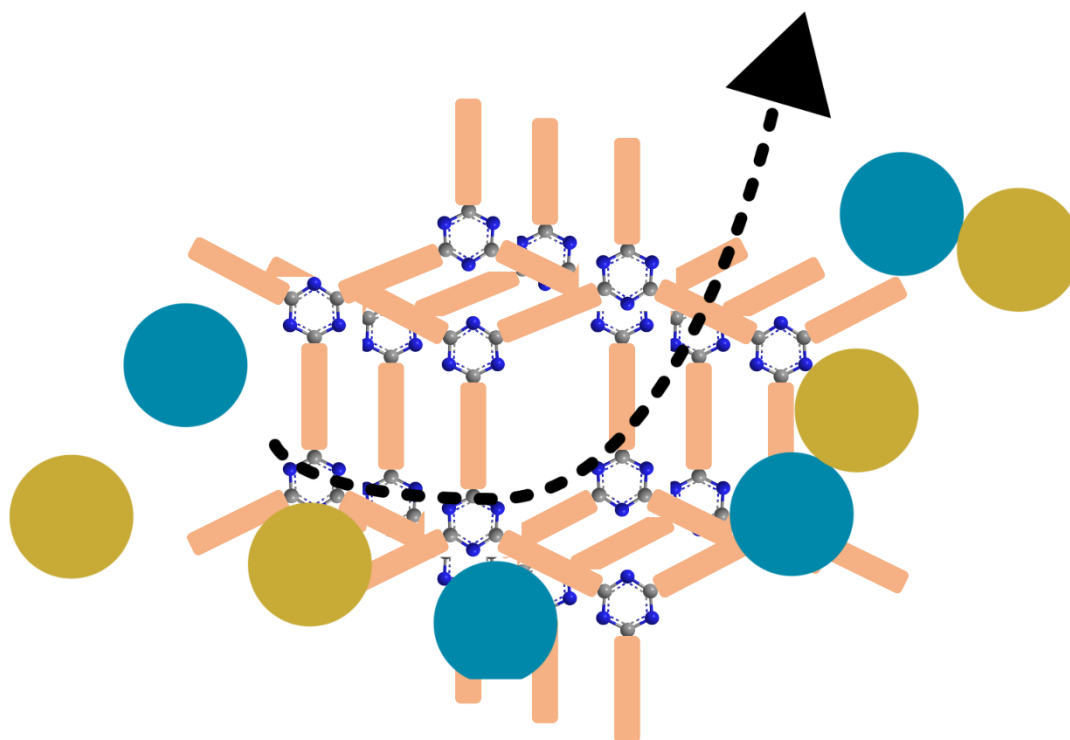


Fig. 1.8 Schematic representation of heterogeneous catalysis by POPs

cost-effective with high catalytic activity and amenable to design. Another important factor is that after anchoring of active catalysts onto solid support matrix the overall stability of the heterogeneous catalyst should be maintained or increased to keep the catalytic efficiency unaffected. However, the rapid growth and evolution of material chemistry allow us to search for suitable alternative solutions to tackle this issues. [104-105]

In this context, porous organic polymers (POPs) have earned great amount of research spotlight on account of their attractive features and synthetic ease. Combined with properties like large specific surface area, high physiochemical stability, pore size & surface tunibility, scalable synthesis these materials have triggered researchers interest in the field of heterogeneous catalysis (Figure 1.8). [106-109] Having said that, the main dictating constraint of polymer-supported heterogeneous catalysts is their cost-issue. The main reason for the high cost is their tedious synthetic protocol involving the post-immobilization process, as well as the below par catalyst loadings leading to poor efficiencies. [110] Bottom-up synthetic approach of porous organic polymers, on the other hand, provides simple and straightforward heterogeneous catalyst synthesis, featuring enhanced catalyst loading along with large surface area, and considerably high catalytic activity. This approach enables the development of highly stable and task-specific polymeric frameworks with abundance of high density catalytically active sites. Coupled with the advantage of catalyst reusability, POPs can be a viable solution to this long standing pitfall of solid catalysts. Bottom-up approaches also allow for the on-demand tailoring of porous polymers with customized porous structure and tuneable surface chemistry, as well as the design of function-led polymer frameworks bearing varied functionalities to be used as catalysts. Their high specific surface area, well-defined pore surfaces, and structurally engineered framework make them ideal toward heterogeneous catalysis. Although, there has been a progress toward the design & synthesis of POPs as solid reagent catalysts, most of them suffers from one or more drawbacks such as complex synthesis, use of toxic solvent, high operating temperature that transcend the purview of green chemistry. Hence, it becomes critical and topical to develop potent POP-based heterogeneous catalysts that can drive organic transformations under mild reaction conditions using environmentally benign green solvents. Additionally, the synthetic protocol should be straightforward and scalable. The above mentioned factors have been the pillars of design rationale in crafting efficient heterogeneous POP catalysts for eco-friendly transformations in the current thesis work.

1.6. Water Pollutants Remediation by POPs:

Water is an essential resource of survival to all living organisms, and the United Nations (UN) predicts that water consumption will rise by 20-55% by 2050. [111] The continual escalation in environmental

pollution has risen as one of the most pressing global issue, and significant attention has been paid worldwide to pollutant remediation. ^[112-113] Skyrocketing growth in world population, combined with rising energy and commodity consumption, endangers future generation's sustainable life on earth. ^[114] Water pollution has recently emerged as a major source of concern among all types of pollution. Lately, increasing water pollution and extensive utilization of fresh water have had a greater negative impact on the Earth's water system. To point out, wastewater effluents from various industries along with discharged radioactive nuclear power plant waste, is one of the leading causes of water pollution. ^[115-116] Furthermore, nearly 2 million people around the globe die each year from waterborne diseases such as poor hygiene, diarrhea, and so on, which are mainly caused by widespread water pollution. The Safe Drinking Water Act (SDWA) defines water pollutants or contaminants broadly into chemical, physical, or biological organisms or substances found in water. ^[117] Water pollution can be largely classified into physical water pollution, chemical water pollution, pathogen pollution, etc. that are distinctly prevailing and have major consequences. Water pollution caused by several types of toxic and noxious chemical species has been identified as one of the most dangerous and life threatening to living beings. Chemical water pollution has been gradually increasing as polluted wastewaters from various industrial sources are discharged directly into effluents. Furthermore, chemical water contaminants can be sub-divided into inorganic and organic contaminants. For organic pollutants, this subgroup of water pollutants includes a broad assorted range of organic chemicals. Different organic dye molecules, personal care products, polyaromatic hydrocarbons, herbicides/pesticides, oils, detergents, pharmaceutical products etc. are included amongst well-known ones. Organic pollutants are generally released from a variety of domestic activities, industries, agricultural activities, and so on. Toxic metal cations such as mercury (Hg^{2+}), cadmium (Cd^{2+}) and lead (Pb^{2+}) along with cationic radionuclides such as uranium (UO_2^{2+}), strontium (Sr^{2+}) and caesium ions (Cs^+) fall in the category of inorganic cationic contaminants. The anionic counterpart features oxo-anions of heavy-metal such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), arsenate (AsO_4^{3-}), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}), including various radioactive anions such as pertechnetate ($^{99}\text{TcO}_4^-$). ^[118-121] Several of these water pollutants are listed in the "Priority pollutant list" of the United States Environmental Protection Agency (US EPA). ^[122] It is worth mentioning that in comparison to organic pollutants, inorganic pollutants last much longer in the environment which makes them very lethal. Furthermore, inorganic pollutants are extremely difficult to degrade as well as conversion into non-toxic species. Most of these water contaminants both organic and inorganic are highly toxic, and carcinogenic by nature. Safe disposal of such pollutants is therefore of utmost scientific interest because all of these toxic and hazardous pollutants pose a severe threat to the ecological symbiosis.

Access to clean drinkable water is crucial for survival, so recycling and purification of water serves as a highly effective alternative method to mitigate water pollution. Along this line, efficient sequestration of toxic water contaminants can be regarded as a top priority scientific problem that needs immediate

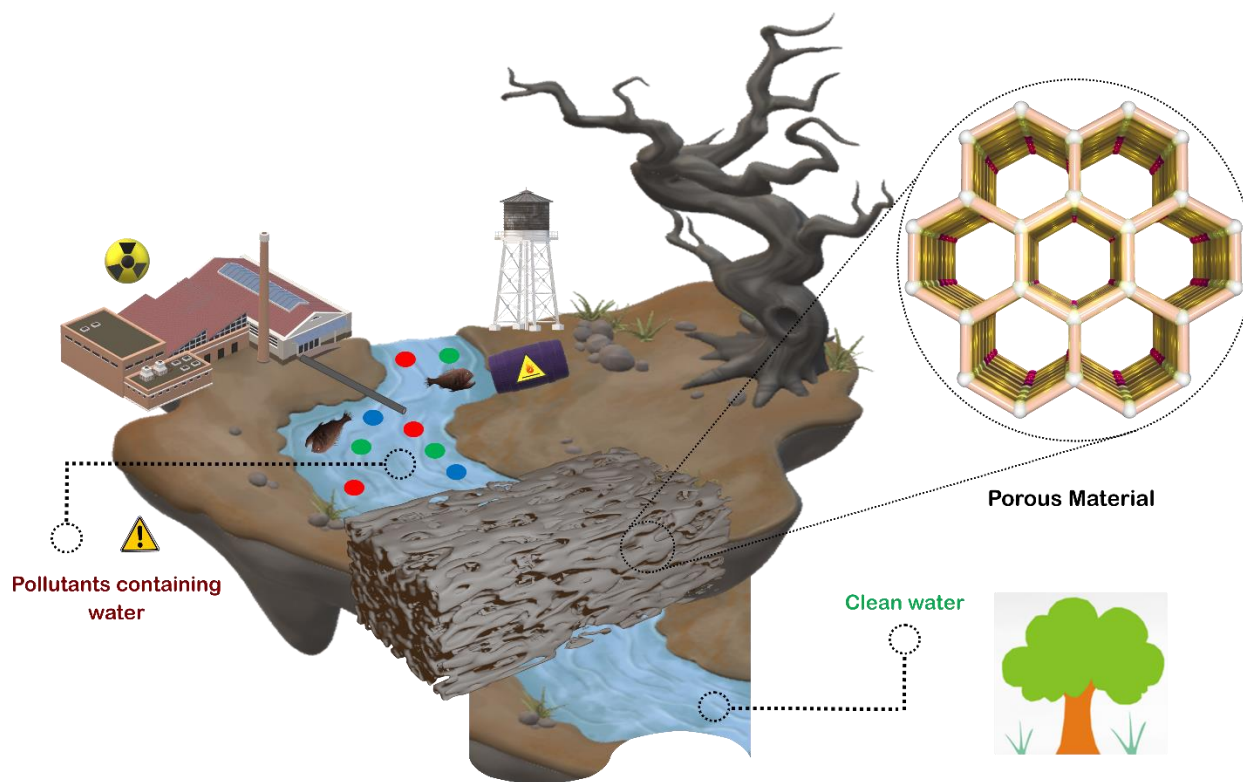


Fig. 1.9 Schematic representation illustrating remediation of toxic and hazardous water pollutants by POPs.

attention. Toward the removal of water pollutants there are two fundamental factors to keep in mind. First, the methods employed for the targeted application should be straightforward, potent, and rapid & efficient response to the target analyte. On the other hand, the material under investigation must be durable and stable in water for longer duration while maintaining high selectivity for the desired pollutant. To achieve this, an effective and affordable adsorption-driven pollutant trapping comes in handy instead of membrane-based separation, sedimentation, coagulation, precipitation etc. to selectively segregate toxic water pollutants.^[123-124] Therefore, it becomes very topical to develop potent adsorbent materials for the aforementioned application. Amongst context-current materials, zeolites, inorganic clays, activated carbons (AC), layered double hydroxides (LDHs), resins etc. have been employed as adsorbents, but these materials fail to meet the standard in terms of selectivity, capacity & kinetics.^[125] In this regard, porous organic polymers (POPs) have emerged as a promising material in combatting water pollution. POPs feature the combined benefits

of advanced porous materials like metal-organic frameworks (MOFs) as well as those of conventional adsorbents. Additionally, POPs, being crafted from entirely organic moieties through robust covalent bonding also present the advantages of tunability and desired chemical functionalization. Lately, ion-exchange based sorbent materials operating on electrostatics driven adsorption of toxic pollutants have shown promising potential toward detoxification of water. Having said that, the development and employment of such materials in wastewater remediation in highly efficient capacity is still in the nascent stage (Figure 1.9). The current thesis work tries to build on this window of opportunity in the rational design of task-specific ionic porous organic polymers (iPOPs) to fast-track and harness their immense potential in highly potent selective water contaminants sequestration.

1.7 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 porous organic polymers (POPs) as well their composites aimed at eco-friendly heterogeneous catalysis and potent water remediation applications. Function-led design of task-specific iPOPs 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 POPs 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 describe POPs being used strategically as the ideal support matrix to generate superior heterogeneous catalysts. Following this, the second part focuses on development & investigation of ionic porous organic polymer (iPOP) composites to combat water pollution, a pressing global problem that calls for immediate mitigation.

The second chapter (Chapter-2), deals with post-synthesis structural engineering enabled easy incorporation spatially isolated catalytically active Pd-NHC units in a composite polymer was employed toward eco-friendly Suzuki-Miyaura coupling reaction (SMC) at room temperature. This work catches the advantages of both worlds, i.e., being a heterogeneous solid catalyst, and also displaying robust stability in the reaction medium along with par excellence catalytic activity. Thus constructed polymer catalyst showed conceptual feasibility in terms of scope, scalability, sustainability along with processability. Along this line, the knowledge acquired from this work in terms of design & synthesis of robust functional iPOPs was propagated in the follow up work to incorporate site-isolated incompatible antagonistic catalytic sites in a cationic POP to drive one-pot cascade deacetylation-Knoevenagel condensation reaction using water as a

solvent under mild condition (Chapter-3). Additionally, the *i*POP displayed excellent catalytic performance toward Cyanosilylation (acid catalyzed) & Knoevenagel condensation (base catalyzed) reactions over wide variety of substrates. Pertaining to practical applicability, the cascade catalysis could also be carried out under flow conditions without compromising in the catalytic efficiency.

On our effort in crafting task-specific POPs, we continued our endeavour zeroing on another pressing global problem “water pollutants remediation”. To accomplish this we tapped into *i*POPs that feature electrostatics driven adsorptive removal of water contaminants as environmentally benign, energy economic and cost-effective methodology. In the fourth chapter (Chapter-4), we employed an ionic composite polymer bearing free exchangeable anions along with its magnetic nature, toward sequestration of wide range organic micropollutants from water (dye molecules, pharmaceuticals, plasticizers and aromatic compounds etc.). The composite polymer showed swift kinetics toward all the pollutants along with significant uptake capacity, comparable to the best-known values in the literature. The practical applicability was explored with real-world water samples, wherein, excellent pollutant trapping efficiency was observed for all the tested pollutants along with exceptional reusability performance to validate its sustainability. Furthermore, its magnetically retrievable nature made it convenient for post-adsorption extraction of the sorbent compared to otherwise available energetically taxing centrifugation or time-consuming filtration technique. Further in the fifth chapter (Chapter-5), we turned to Mother Nature to harness biological antagonism driven synergistic detoxification of water by tapping into Hg-Se antagonism abundant in biota. Judicious selection of silica nanoparticles templated synthetic methodology in combination with strategic post-synthetic modification was employed to introduce interconnected macropores along with functional anions inside a cationic polymer composite. The developed cationic macroporous polymer performed exceptionally well in removing Hg^{2+} from water with quick kinetics and a large uptake capacity. Additionally, ultrafast kinetics of simultaneously removing of Hg^{2+}/Se (VI) and Hg^{2+}/Se (IV) was accomplished. Selective sequestering the toxic pollutants in the presence of excess interfering ions & in real water samples pertaining to conceptual viability and practical relevance were established. This study exemplifies one of the few instances of using a cationic sorbent material to trap both cationic and anionic pollutants.

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Part-I

Function-led Design and Syntheses of Porous Organic Polymers as Superior Heterogeneous Catalysts

Present-day life is unimaginable barring catalysis and has become central to our elementary needs of life. The booming world economy and ever increasing population calls for an immediate need to establish an efficient & sustainable chemical industry through greener approaches of chemical transformations. Developing novel catalysts exhibiting efficiency in terms of product yield and selectivity and thereby lowering the cost is one way of achieving that. The design rationale behind developing catalysts lies in crafting materials bearing homogeneously exposed active sites to promote selective reaction to attain the desired product. ^[1] In contrast to its homogeneous counterpart, in spite of featuring plentiful active sites, historically, have needed more trial-and-error experimentation toward producing various catalysts. However, they often display critical advantages over homogeneous catalysts such as convenience of separation, recyclability and sustainability. ^[2-3] In this context, POPs have found catalytic applicability as ideal supports for metal nanoparticles or complexes as well as metal free organocatalysts. The inherent robust nature and excellent porosity of POPs make them attractive as heterogeneous catalysts. ^[4-5] Additionally, the convenience to introduce ligands within the frameworks of POPs allowing the feasibility of designing single-atom catalysts. POPs comprising of well-defined isolated active metal centers serve as the bridge between homogeneous and its heterogeneous counterpart. From green chemistry perspective, developing POP based heterogeneous catalysts to drive organic transformations under mild and eco-friendly condition is very important. However, in most cases the developed catalysts require high reaction temperature or use of toxic organic solvents. POPs with suitable choice of monomers as well as strategic post-synthesis engineering can be fabricated into potent heterogeneous catalysts to carry out chemical transformations under eco-friendly reaction conditions.

This section contain two chapters i.e. chapter 2 and chapter 3. In chapter 2, a potent POP based heterogeneous catalyst bearing catalytically active isolated Pd-NHC units was synthesized by judicious post-synthesis modifications to drive eco-friendly Suzuki–Miyaura coupling (SMC). Additionally in chapter 3, an all organic ionic POP based potent catalyst featuring incompatible Lewis acid-base sites was synthesized toward one-pot cascade catalysis under flow.

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Chapter 2

Palladium anchored N-Heterocyclic Carbene in a Porous Organic Polymer (POP): An Efficient Heterogeneous Composite Catalyst for Eco-Friendly Suzuki-Miyaura Coupling

2.1 Introduction

The present-day life is unthinkable without catalysis which has come forth as an indispensable technology toward the fundamental requisites of life such as energy, food, and water. Catalysis lies at the very heart of chemical products and the industries thereof constituting a rudimentary branch of contemporary scientific research with tremendous importance and conceptual bottlenecks.^[1] With thriving economy and an upsurge in global population together with downsizing of raw materials, manufacturing via a more sustainable and greener approach is of paramount importance where catalysis has a pivotal role to play. This is further punctuated in the 9th principle of green chemistry stated as “Catalytic reagents, as selective as possible, are superior to stoichiometric reagents”.^[2] Organometallic catalysis using metal-containing complexes to drive an organic transformation has become a significant area of research in organic chemistry. In particular, the Suzuki–Miyaura coupling (SMC) reaction, since its inception in 1979, has emerged as one of the potent, versatile, and straightforward methodologies for crafting carbon–carbon (C–C) bonds and has intrigued both industry and academia.^[3–6] Over the years, the SMC reaction has been successfully employed toward the selective construction of C–C bonds in pharmaceuticals, natural product synthesis, materials science, supramolecular chemistry, as well as various advanced functional materials.^[7–12]

Hitherto, in recent times, numerous palladium-based (Pd) homogeneous catalysts inclusive of palladium chloride along with palladium–phosphine complexes, ancillary ligands such as N-containing complexes, N-heterocyclic carbenes (NHCs), acyclic diaminoboranes (ADCs) as well as bipyridines have been documented for the SMC reaction.^[13–18] These catalysts usually proceed efficiently in harmful organic solvents under inert conditions. In general, homogeneous catalytic systems furnished with uniform and systematic active sites display quality performance, excellent yields, and great selectivity along with a high turnover frequency (TOF).^[19,20] However, utilization of costly ligands, complexity in the isolation of the catalyst and product, and metal leaching combined with toxic Pd contamination in the reaction products have greatly muted their application in academia and chemical industry.^[21,22] To circumvent these impediments, substantial efforts have been made worldwide in developing heterogeneous Pd-based catalysts. Palladium immobilization onto the insoluble support matrix serves as a viable solution offering superiority such as high catalyst stability, simple separation, ease of purification, and great reusability. Alternatively, the pursuit for greener, environmentally benign, safe, as well as sustainable competent technologies maximizing atom economy and energy efficiency while cutting down waste has found strong pertinence in current scientific research.^[23–27]

Thus far, Pd-based catalysts have been grafted onto different solid support matrices, for example, inorganic zeolites, carbon based materials, mesoporous silica, and so forth.^[28–32] Along the same direction, integrating metal catalysts inside nanoporous cavities enables harnessing the unique chemistry of “catalysis in

confinement” offering variation in the energetics and kinetics of the catalytic procedure, leading to improved yield and product selectivity.^[33] Porous architectures, namely, metal–organic frameworks, covalent organic frameworks, and porous organic polymers (POPs), have also surfaced as strong candidates in the area of heterogeneous catalysis lately.^[34–37] Among them, POPs have shown enormous potency as a novel heterogeneous catalyst support featuring a large surface area and superior stability along with porosity and functionality tailored nanospace.^[38–41] Microporous hyper-cross-linked polymers (HCPs) as a relatively new category of POPs, have invoked substantial research attraction on account of their superior structural robustness, high surface area, ease of designable task-specific functionality, permanent porosity, and cost-effective facile synthesis.^[42,43] Furnished with these unique properties, HCPs have emerged as an ideal support matrix in seeking a suitable heterogeneous catalyst, showcasing excellent performance and sustainability.^[44,45]

In general, methodologies adopted in fabricating a Pd-based heterogeneous catalyst are achieved via incorporating Pd nanoparticles onto the support material as well as anchoring Pd as the spatially isolated catalyst. The latter strategy with homogeneous spatial distribution of active sites can accomplish the highest theoretical efficiency and is more desirable. NHCs possessing similar coordination properties have a better electron-donating property with a robust metal–ligand bond making them stable and efficacious in heterogeneous catalysis.^[46,47] In this context, supported NHCs have been documented toward efficient heterogeneous organocatalysis in different materials.^[48–54] Having said that, often, their synthetic procedure is tedious or requires abundance of specific functionalities in the NHC monomer, which limit their applicability.^[55–57] Hence, it becomes topical to introduce catalytically active NHCs as suitable catalysts by a facile preparation method that allows simple structural modification to tune their electronic properties. While powder materials display efficient activity, their full potential in development toward practical applications is still hindered as they are difficult to process, shape, and even to be reused after utilization. Also, the aggregating nature of these materials often reduces the exposed active sites of a catalyst as well as limits the mass transport rate. One way of bypassing the bottlenecks is to make them processable by shaping them into monoliths, aerogels. In this work, we report a simple and facile synthesis of the NHC-tethered stable composite polymer, viz., 120-EI@Pd NHC, illustrating exceptional activity toward SMC in an aqueous medium at room temperature (RT). Post-synthesis structural engineering enabled easy incorporation of active Pd(II)–NHC units throughout the HCP matrix that could catalyze the SMC reaction across a wide spectrum of aryl halide derivatives and boronic acids with superior efficiency. Additionally, the heterogeneous catalyst could be recycled with unaltered efficiency as well as could be utilized in a large-scale SMC reaction. Furthermore, catering to the need of practical feasibility, a covalently cross-

linked macroscopic 3D composite aerogel cup-based reactor was also devised to readily carry out the SMC reaction at RT in a gram-scale quantity.

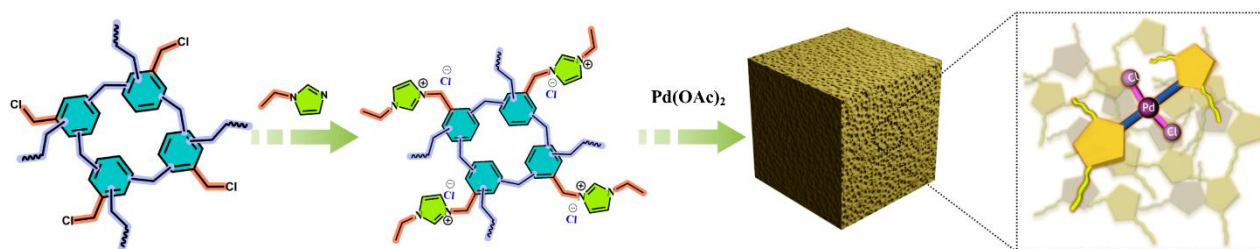


Figure 2.1. Schematic diagram of HCP 120-Cl and 120-EI & schematic illustration of 120-EI@Pd NHC.

2.2 Experimental

2.2.1 Materials and Measurements.

Unless otherwise mentioned, all reagents and solvents were available commercially and were used without any further purification procedure.

2.2.2 Synthesis.

Synthesis of HCP 120-Cl: HCP 120-Cl was synthesized from cross-coupling of benzyl chloride (Scheme-1) by following our previous report.^[57] A flame dried round bottom flask was charged with benzyl chloride (300 mg, 1.7625 mmol), to that 20 ml of anhydrous 1,2- dichloroethane ($C_2H_4Cl_2$) was added. Next, formaldehyde dimethyl acetal (470 μ l, 5.288 mmol) and anhydrous $FeCl_3$ (860 mg, 5.288 mmol) were added respectively. Following this, the reaction mixture was heated in an oil bath at 50 $^{\circ}C$ for 5 h and then was allowed to reflux at 80 $^{\circ}C$ for 18 h (Scheme-S1). Upon completion of the reaction, dark brown precipitate was obtained which was then filtered off and washed extensively with various solvents like DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained brown amorphous powder material was further purified via Soxhlet extraction with chloroform and tetrahydrofuran for 24 h respectively to remove any unreacted monomers along with any metal catalyst residues. To remove the guest solvent molecules, the polymer was heated at 120 $^{\circ}C$ under vacuum for 24 h to obtain activated HCP-120 with which further works have been carried out. Yield: 335 mg (~87%).

Synthesis of HCP120-MI: Desolvated HCP-120 (200 mg) was taken in a round bottom flask and to that 20 ml of acetonitrile (ACN) was added (Scheme-S2). Then to the reaction mixture 2 mL (2.05 g, 25 mmol) of 1-methyl imidazole (MI) was added dropwise allowed stir for 48 hrs. at reflux temperature in an oil bath.

On completion of the reaction dark brown coloured precipitate was filtered off and washed with water for several times to remove excess MI. Then the precipitate was again washed with DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained dark brown coloured solid material (HCP 120-MI) was subject to Soxhlet extraction in MeOH for 24 h to remove the unreacted molecules from the porous network of HCP 120-MI. Then the solvent exchanged phase of HCP@MI was heated at 140 °C under vacuum to obtain the guest free activated material and with this phase further works have been carried out. Yield: 243 mg (~93%).

Synthesis of HCP120-EI: HCP 120-EI was synthesized by using 1-ethyl imidazole following the same procedure discussed for HCP 120-MI. Yield: 227 mg (~89%).

Synthesis of HCP120-MI@Pd NHC: The Pd²⁺ immobilized heterogeneous organometallic catalyst was synthesized by anchoring Pd²⁺ ions with NHC bearing HCP. Briefly, HCP 120-MI (500 mg) was added to a THF solution (15 mL) containing Pd(OAc)₂ (56 mg 0.25 mmol) and stirred under reflux in an oil bath under N₂ atmosphere at 80 °C for 12 h. The solid was separated centrifugally, washed repeatedly with copious amount of acetone to remove the Pd²⁺ species physisorbed on the surface of the polymer. The final catalyst was dried at 80 °C under vacuum, and the as-prepared catalyst is denoted as HCP@MI-NHC-Pd. Yield: 443 mg (~88%).

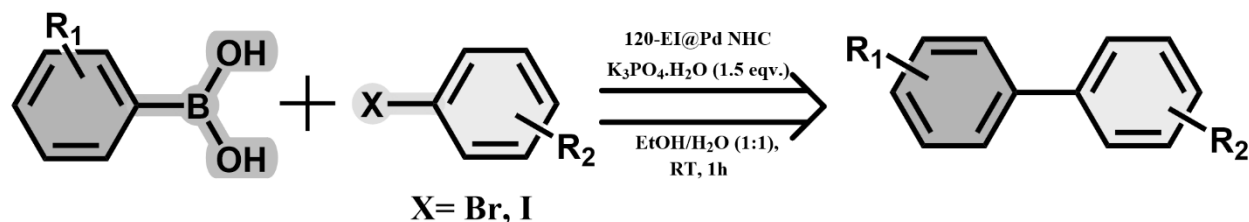
Synthesis of HCP120-EI@Pd NHC: HCP 120-EI@NHC Pd was synthesized using the same protocol mentioned above except for HCP 120-EI was taken instead of HCP 120-MI. Yield: 435 mg (~87%).

2.2.3 Physical Measurements.

High resolution solid-state NMR spectrums were collected at ambient pressure on a 500 MHz Bruker AVANCE III spectrometer. ¹H NMR spectra were recorded using a JEOL 400 MHz or Bruker 400 MHz spectrometer. The surface morphology of the polymers was probed by scanning electron microscopy using FEI Quanta 3D dual beam FESEM at 30 KV. HRTEM images were acquired on JEOL USA JEM-2200 FS Transmission Electron Microscope. Fourier transform infrared spectroscopy (FT-IR) spectra were measured on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets in 400-4000 cm⁻¹ range. The powder X-ray diffraction patterns were recorded with a Bruker D8 Advance X-ray diffractometer at room temperature (rt) using Cu K α radiation (λ = 1.5406 Å). XPS analysis was performed using K-Alpha⁺ model (Thermo Fischer Scientific, UK) with Al K α source Thermogravimetric Analyses (TGA) were performed in the temperature range of 30–800 °C on a PerkinElmer STA 6000 analyzer under a N₂ atmosphere at a heating rate of 10 °C min. The surface area and pore size distribution analyses of polymers were acquired on a BelSorp-max instrument from Bel Japan, using N₂ adsorption and desorption at 77 K. Before

performing adsorption measurements, the samples were activated at 120 °C under vacuum for 12 hours using BelPrepvacII.

2.2.4 General Procedure for the Suzuki-Miyaura Coupling Reaction Catalyzed by 120-EI@Pd NHC at Room Temperature:



In a typical catalytic run, to an oven-dried reaction vessel were sequentially added aryl boronic acid (0.45 mmol), base (0.6 mmol), aryl halide (Ar-I or Ar-Br) and the catalyst (5 mg) were dispersed in 4 mL EtOH-H₂O (1:1) solvent mixture. The reaction mixture was then stirred at room temperature (RT) for designated time. After completion of the reaction (monitored by TLC), the reaction mixture was centrifuged to separate the catalyst. The combined organic phase was then washed with water in order to remove any base residue. Then, the organic phase was dried over anhydrous sodium sulfate and evaporated under vacuum leaving the crude product, which was purified by flash chromatography with 1% ethyl acetate over silica gel to obtain the final product.

2.2.5 Recyclability Experiment:

After the completion of coupling reaction between p-Tolylboronic acid and bromobenzene, the NHC Pd catalyst easily separated by centrifugation. After centrifugation, the solid catalyst was washed with CH₂Cl₂ and the combined organic solution was concentrated under reduced pressure followed by flash chromatography to give the desired product. The recovered catalyst was then washed with water and EtOH and dried at 80 °C under vacuum for 6h before using for the next catalytic cycle.

2.2.6 Fabrication of HCP-based Hybrid Aerogels:

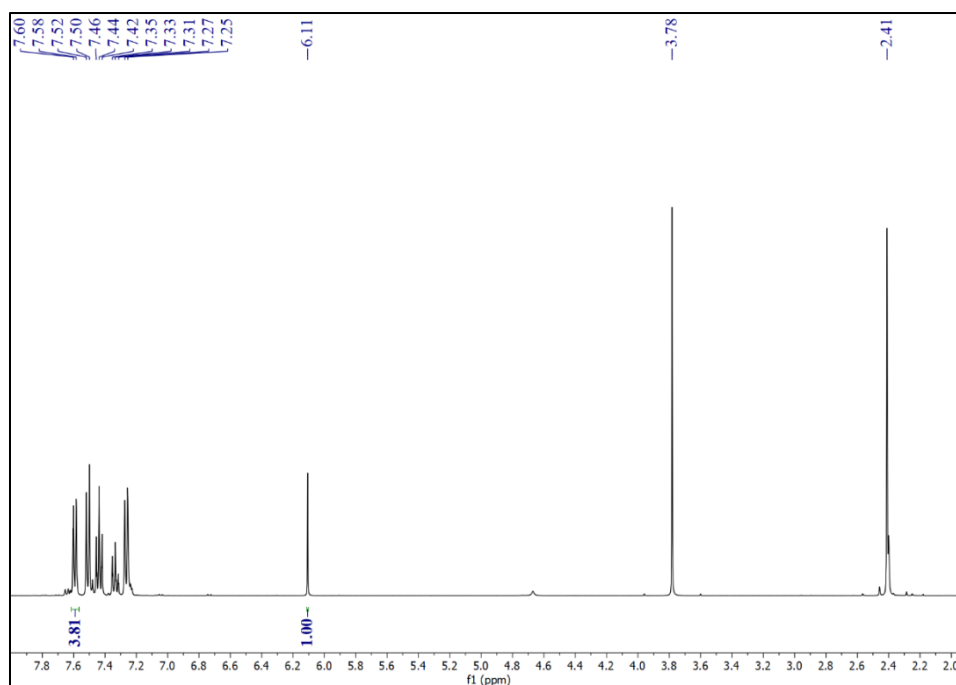
The aerogels were prepared following a reported protocol.^[71] Briefly, 0.2 g of chitosan powder was dissolved in 10 mL of deionized water added with 120 µL of acetic acid with stirring, until formation of a transparent solution. After that, 0.2 g of HCP 120-EI@Pd NHC was added into the chitosan solution. Following strong stirring and ultrasonic shaking, 480 µL of 1,4-Butanediol diglycidyl ether was added to the mixture as the cross-linker. Then, the obtained composite solution was immediately transferred into the desired mold. The mold containing the solution was allowed stand undisturbed for ca. 10 h until a stable

hydrogel was formed. Thus obtained hydrogel was slowly transferred into a cooler for 12 h to generate the ice crystals. Finally, the frozen sample was freeze-dried at minus 50 °C for approximately 24 h in a freeze-dryer to give the dry HCP-chitosan aerogel monolith with 50 wt% of HCP loading.

2.2.7 ICP Analysis to Determine Pd Content:

The Pd content in the porous polymer catalysts were determined by inductively coupled plasma atomic emission (ICP-AES) measurement. For this, a certain amount of the polymer catalyst was digested and the corresponding Pd content was measured from ICP-AES analysis. The obtained Pd content for 120-EI@Pd NHC & 120-MI@Pd NHC were 4.41 and 4.62 wt% respectively.

2.2.8 Calculation of Yield of the C-C Coupling Reaction:



The yield of the C-C coupling reaction was calculated using ¹H NMR spectroscopy with respect to 1,3,5-trimethoxybenzene as the internal standard (I.S.). The 3H peak ($\delta = 6.12$, s) of internal standard and the 2H peak ($\delta = 7.59$, d) of product was taken as the reference peak for calculating the reaction yield. A typical example for the calculation of the yield for NMR spectrum is estimated below. The 2H peak ($\delta = 7.59$, d) peak of product was integrated with respect to the internal standard.

The integrated value of 2H peak corresponding to the product = 3.81

The integrated ratio between I.S. and Product:

$$\frac{r_{Product}}{r_{I.S.}} = \frac{3.81/2}{1/3} = 5.715$$

The amount used of I.S. to determine yield = 11.79 mg

Moles of internal standard present in the reaction = 11.79 mg/ 168.19 = 0.07 mM

So, the moles of product form = 0.07 × 5.715 = 0.400 mM

The Theoretical expected yield of the reaction = 0.4 mM

So, the yield of the reaction is = (0.4/ 0.4) × 100 = 100 %

2.3 Results and Discussion

Catalyst Synthesis and Structural Characterization: As illustrated in Figure 2.1, the catalyst was synthesized via post-polymerization structural modification of the parent polymer. We synthesized the precursor polymer, namely, HCP 120-Cl, following a protocol previously reported by our group.^[57] Subsequently, 1-methyl imidazole and 1-ethyl imidazole were reacted with dissolved 120-Cl in acetonitrile under the refluxing condition to produce 120-MI and 120-EI, respectively. In the next step, Pd–NHC units were anchored onto the HCP backbone by treating with Pd(OAc)₂ to fabricate the organometallic polymer catalyst (see experimental section for details). It is worthwhile mentioning that the post-synthetic modifications carried out were facile and effective. All the polymers were insoluble in common organic solvents including water.

Following their successful synthesis, all the HCPs were thoroughly characterized and corroborated of their polymeric structures via Fourier transform infrared (FTIR) spectroscopy, solid-state cross-polarization magic-angle spinning (CP/MAS), ¹³C NMR spectroscopy, powder X-ray diffraction (PXRD), nitrogen adsorption/desorption isotherms, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The FTIR spectra of all the resulting HCPs displayed consistent peaks attributed to the proposed polymeric networks (Figures 2.2a, Appendix 2.1-2.2). A comparison between 120-Cl, 120-MI, and 120-EI shows peaks at ca. 1670 cm⁻¹, corresponding to the C=C bands of the aromatic skeleton. Peaks at ca. 2923 cm⁻¹ and 1452 cm⁻¹ were assigned to the C–H stretching and bending vibrations of the –CH₂– bonds, while two peaks arising at ca. 1600 and 1162 cm⁻¹ corresponded to the C=N and C–N stretching frequencies of the imidazolium ring, validating the successful post-synthetic modification in both 120-EI and 120-MI (Appendix 2.1). Additionally, significant attenuation in the C=N stretching was observed for both 120-EI@Pd NHC and 120-MI@Pd NHC, confirming the NHC-coordination complex unit formation in the organometallic polymer catalyst (Figures 2.2a and Appendix 2.2). Solid-state ¹³C CP/MAS NMR spectroscopic analysis was also performed to disseminate the chemical constitution of the polymers (Figures 2.2b and Appendix 2.3-2.6). Broad peaks centered around 36 ppm, 129 ppm, and 135 ppm for all the polymers were corroborated with the methylene cross linkage along with non-substituted (i.e., hydrogen-bearing) and aromatic-substituted carbons, respectively, consistent with the literature reports.^[58] In addition, 120-EI@Pd NHC and 120-MI@Pd NHC displayed the appearance of an additional peak at 169 ppm that substantiated the abundance of carbene carbons in the modified polymers (Figures 2.2b, Appendix 2.5-2.6). Thermal stability was investigated by performing TGA under a N₂ atmosphere that disclosed an initial weight loss up to 100 °C for all the pristine polymers, indicating loss of occluded solvent molecules

inside the network (Figures 2.2c and Appendix 2.7-2.11). Beyond the initial loss, the polymers showed very high thermal stability with no gradual loss till 400 °C.

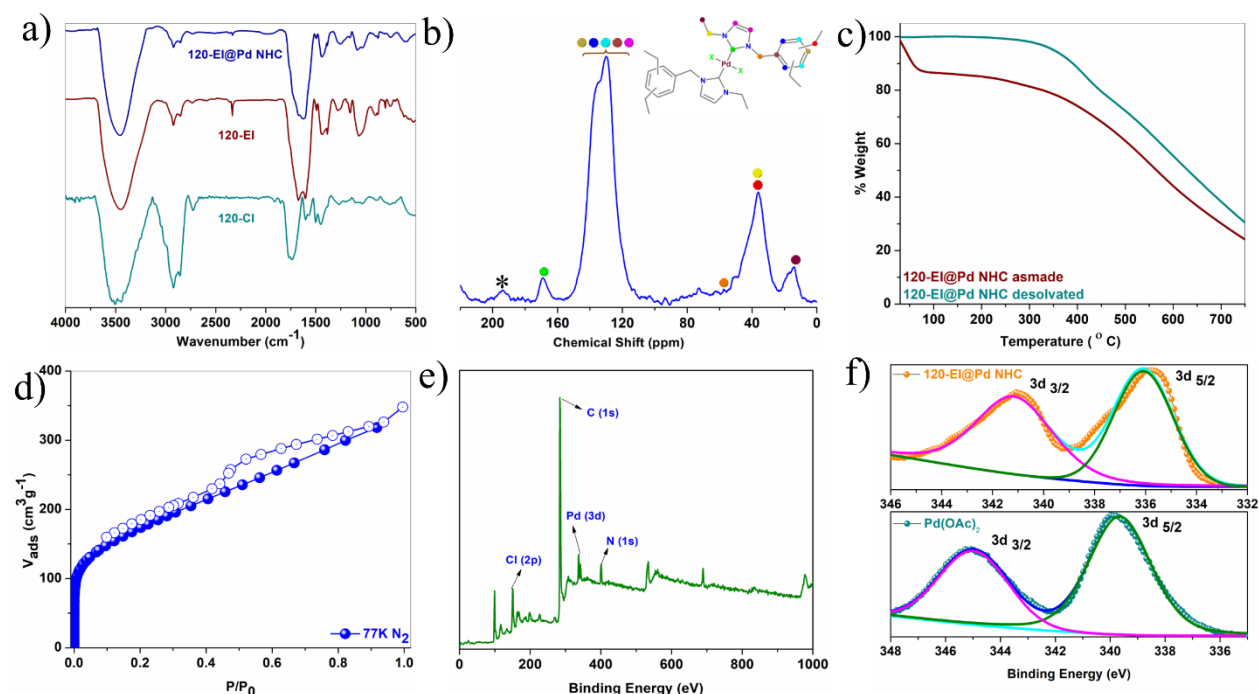


Figure 2.2. (a) FT-IR spectra of 120-Cl (cyan), 120-EI (wine), and 120-EI@Pd NHC (blue). (b) Solid-state ¹³C CP/MAS NMR spectrum of polymer 120-EI@Pd NHC. (c) TGA profile of 120-EI@Pd NHC (Under N₂ atmosphere). (d) N₂ adsorption curves of 120-EI@Pd NHC. (e) XPS survey scan of 120-EI@NHC Pd. (f) High resolution XPS spectra of palladium 3d for 120-EI@Pd NHC.

Similar thermal stability was also observed for the catalyst polymers. This elevated thermal robustness can be ascribed to a higher degree of cross-linking throughout the polymer backbone and rigid aromatic monomer. Furthermore, permanent porosity of these polymers was established with low-temperature (77 K) N₂ adsorption. The parent polymer 120-Cl and modified networks (120-MI and 120-EI) illustrated a type-II isotherm with the presence of the H3-hysteresis loop coherent with predominantly a large number of micropores and a certain degree of mesopores, making them hierarchical porous networks (Appendix 2.12-2.17). The Pd-modified NHC polymers displayed similar N₂ isotherm profiles, while the uptake amount showed a declining trend for the post-synthetically modified polymers owing to partial pore blocking associated with the successful chemical modifications (Figures 2.2d and Appendix 2.15-2.17). The surface area analysis showed a similar trend where the Brunauer–Emmett–Teller (BET) surface areas of 1044 m² g⁻¹ for 120-Cl, 814 m² g⁻¹ for 120-EI, and 620 m² g⁻¹ for 120-EI@Pd NHC were calculated

from their N₂ adsorption profiles. It should be pointed out that all the polymers showed high specific surface areas even after post-synthetic structural modulations (Appendix Table 2.1).

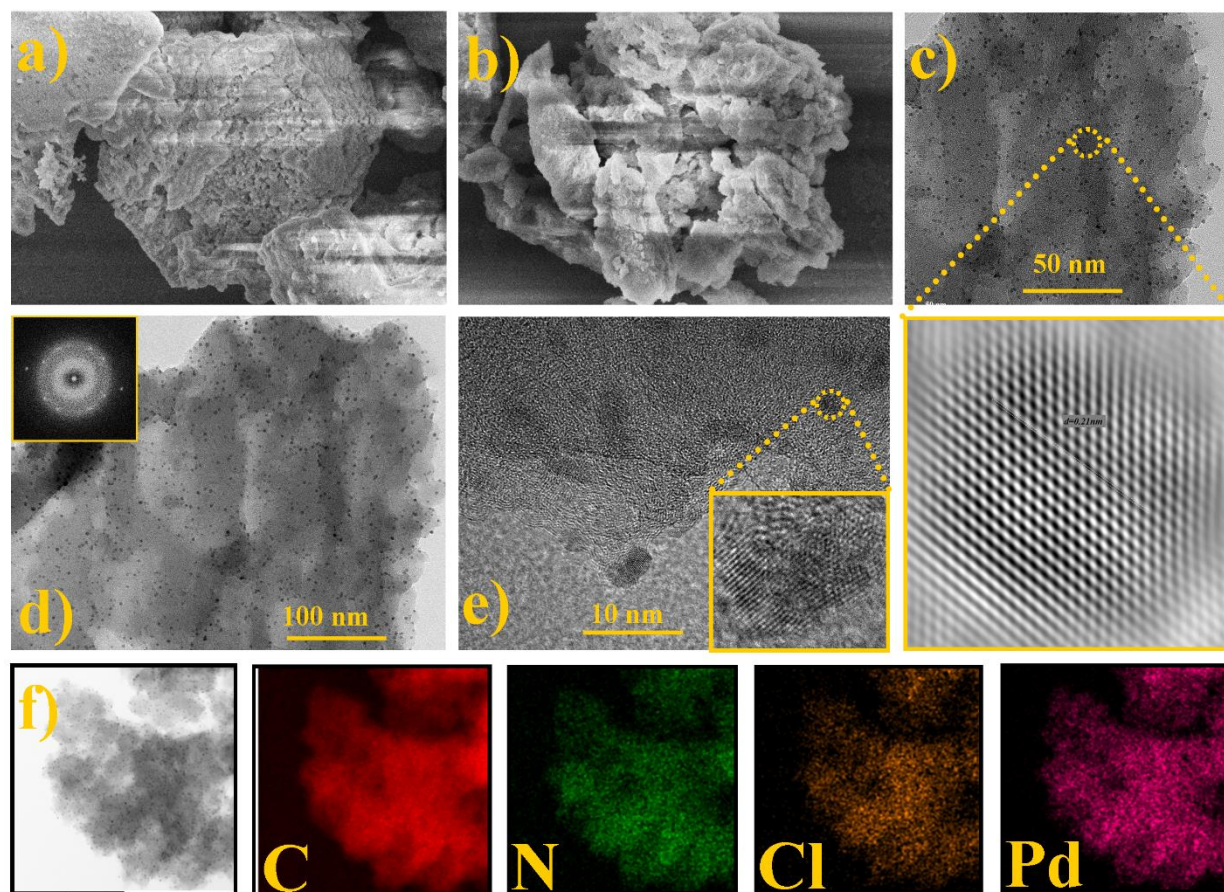


Figure 2.3. The morphological analysis of the surface of 120-EI@Pd NHC (a), (b) FESEM images. (c), (d), (e) TEM & HRTEM images at different magnification, the inset shows the selected area electron diffraction (SAED) pattern and lattice fringes. (f) STEM–EDS mapping profile of composition elements in 120- EI@Pd NHC.

To gain insight into the electronic state of the anchored palladium inside the polymer scaffold, XPS was utilized (Figure 2.2e, f). Figure 2.2f shows the presence of mainly two broad peaks at binding energies of 342.3 eV and 337.2 eV, respectively, in 120-EI@Pd NHC. These peaks were attributed to the Pd 3d_{5/2} and Pd 3d_{3/2} energy levels, indicating the +2 oxidation state of Pd, which is also consistent with the literature reports of the Pd (II)–NHC complex documented earlier.^[59–61] It is crucial to point out that compared to free Pd(OAc)₂ (344.9 and 338.9 eV), a negative shift was observed in the Pd²⁺-binding energies of 2.6 and 1.7 eV, respectively. This negative shift can be reasoned as the consequence of strong coordination between

Pd^{2+} and the NHC unit immobilized inside the polymer catalyst. Furthermore, the amount of Pd loaded inside the composite polymer was quantified by the inductively coupled plasma–atomic emission (ICP–AES) measurement that revealed 4.41 and 4.62 wt % of the Pd content for 120-EI@Pd NHC and 120-MI@Pd NHC, respectively. The PXRD pattern of the catalyst polymers showed broad peaks, attributed to their amorphous nature (Appendix 2.18). The microscopic structure of all the synthesized polymers as well as bulk morphology was probed via FESEM and HRTEM measurements. The FESEM images of the parent polymer illustrated aggregated dense irregular particles at the micrometer scale (Appendix 2.19). Additionally, no pronounced morphological changes were observed for the modified as well as Pd-incorporated polymers (Appendix 2.19 and Figures 2.3a, b). Elemental mapping along with EDX spectra revealed the presence of all the concerned elements in the respective polymers in a homogeneous manner, further validating successful structural modification and Pd introduction (Appendix 2.20–2.26). TEM images revealed that palladium species were well-dispersed throughout the catalyst polymer matrix of 120-EI@Pd NHC and 120-MI@Pd NHC (Appendix 2.27–2.28). A closer look at HRTEM images of 120-EI@Pd NHC verified the crystalline phase of the Pd species, distinctly verified from its lattice fringes (Figure 2.3c–e), while the selected area electron diffraction (SAED) pattern demonstrated a polycrystalline nature of palladium along with characteristic diffraction rings (Figure 2.3c, d).^[62] In addition, STEM-EDS elemental mapping supported the composition of the NHC-polymer catalyst wherein all the necessary elements were evenly distributed throughout the polymer (Figure 2.3f). Also, the preceding observation of evenly dispersed Pd suggests successful fabrication of isolated catalytic sites in the polymer.

Optimization and catalytic performance toward Suzuki–Miyaura Coupling (SMC) reaction: After carrying out in-depth structural characterization of the composite polymer catalysts 120-EI@Pd NHC and 120-MI@Pd NHC, their catalytic performance toward the SMC reaction was evaluated. Initially, reaction conditions were optimized using *p*-tolylboronic acid and bromobenzene as model substrates for the SMC reaction with 5 mg (0.002 mmol of Pd) of 120-EI@Pd NHC as the catalyst. A series of control experiments involving various reaction parameters, for example, base, solvent, and temperature, were varied to arrive at the best optimized condition. Often, reactivity is promoted by the polarity of the solvents and solvent mixtures utilized to solubilize reactants and bases. As is seen in entries 2–7 and 12–13 of Appendix Table 2.2, EtOH–H₂O (1:1) produced the best yield among the screened solvent combinations. Considering the underlying mechanism of the SMC reaction, the type as well as solubility of bases present strongly dictates the activity of SMCs as base plays the role of a co-reactant along with the promoting agent in initiating the trans-metalation step and facilitating the reductive elimination process, respectively.^[63–65] Under similar conditions taking bases as the single variable, 120-EI@Pd NHC displayed the best catalytic activity using K₃PO₄·3H₂O in EtOH–H₂O (1:1) at 25 °C in open air (Appendix Table 2.2, entries 6 and 8–10). However,

it should be noted that no desired product could be obtained (Appendix Table 2.2, entries 1 and 14) without using base or the catalyst, advocating the need for the base and composite polymer catalyst in achieving

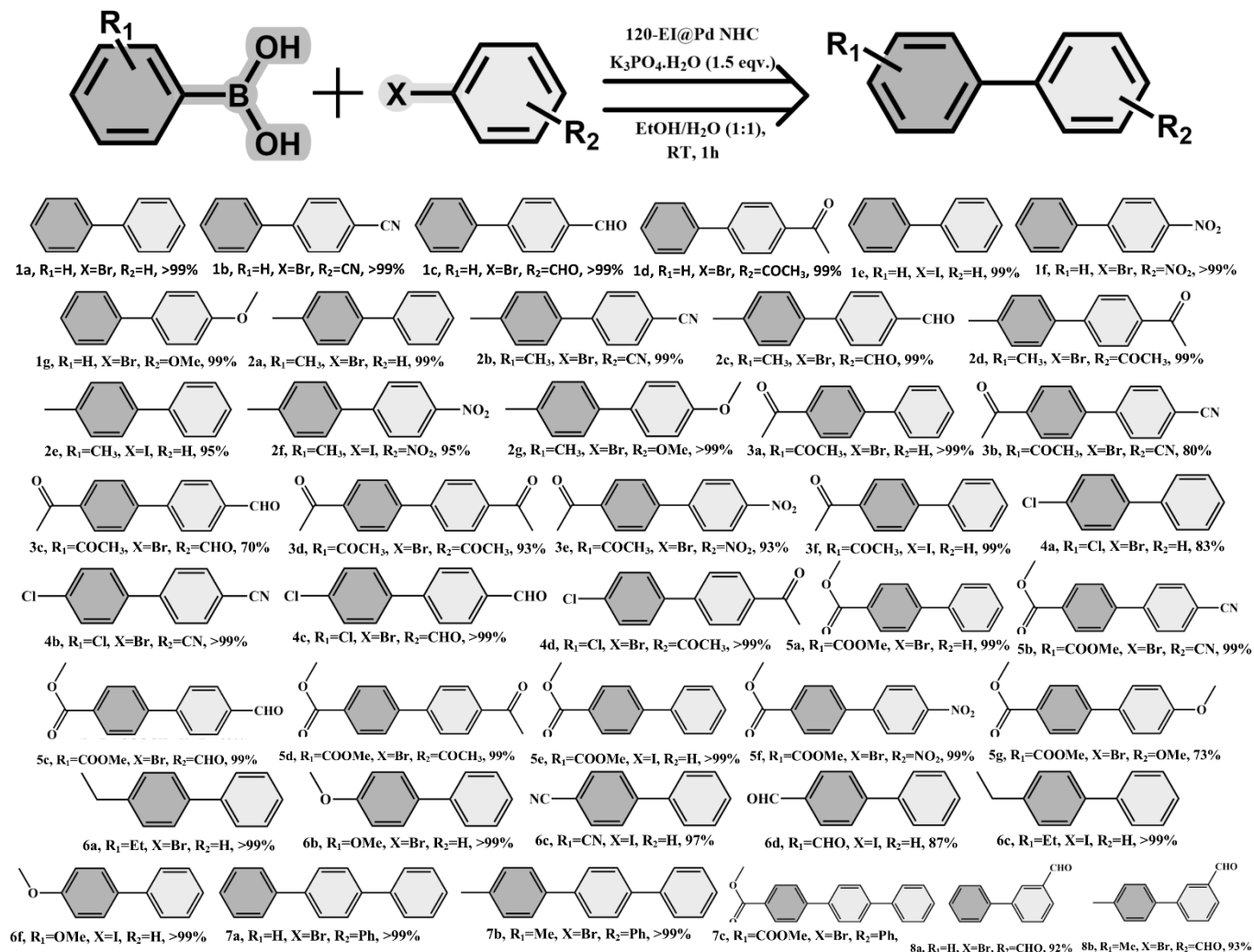


Table 2.1. 120-EI@Pd NHC catalyzed SMC reaction at room temperature Reaction Conditions: 0.45 mmol of aryl Boronic acid, 0.4 mmol aryl halide and 0.6 mmol base and 5 mg (0.002 mmol of Pd) catalyst was stirred in 4 mL EtOH/H₂O (1:1) solvent mixture for 1 h; Yield determined from ¹H NMR.

biaryl derivatives via the SMC reaction. Alternatively, a supernatant solution of 120-EI@Pd NHC and K₃PO₄·3H₂O suspended in the EtOH–H₂O (1:1) mixture failed to display any kind of catalytic activity even when kept for a longer period of time (Appendix Table 2.2, entry 15), indicating no leaching of the active catalytic species from the polymer composite. This observation further testifies the heterogeneous nature of the catalytic reaction taking place. While at higher temperature 120-EI@Pd NHC showed almost the

quantitative yield (Appendix Table 2.2, entry 5), similar performance was observed under milder conditions at RT with reduced time (Appendix Table 2.2, entry 6) and thus was chosen as the best optimal condition.

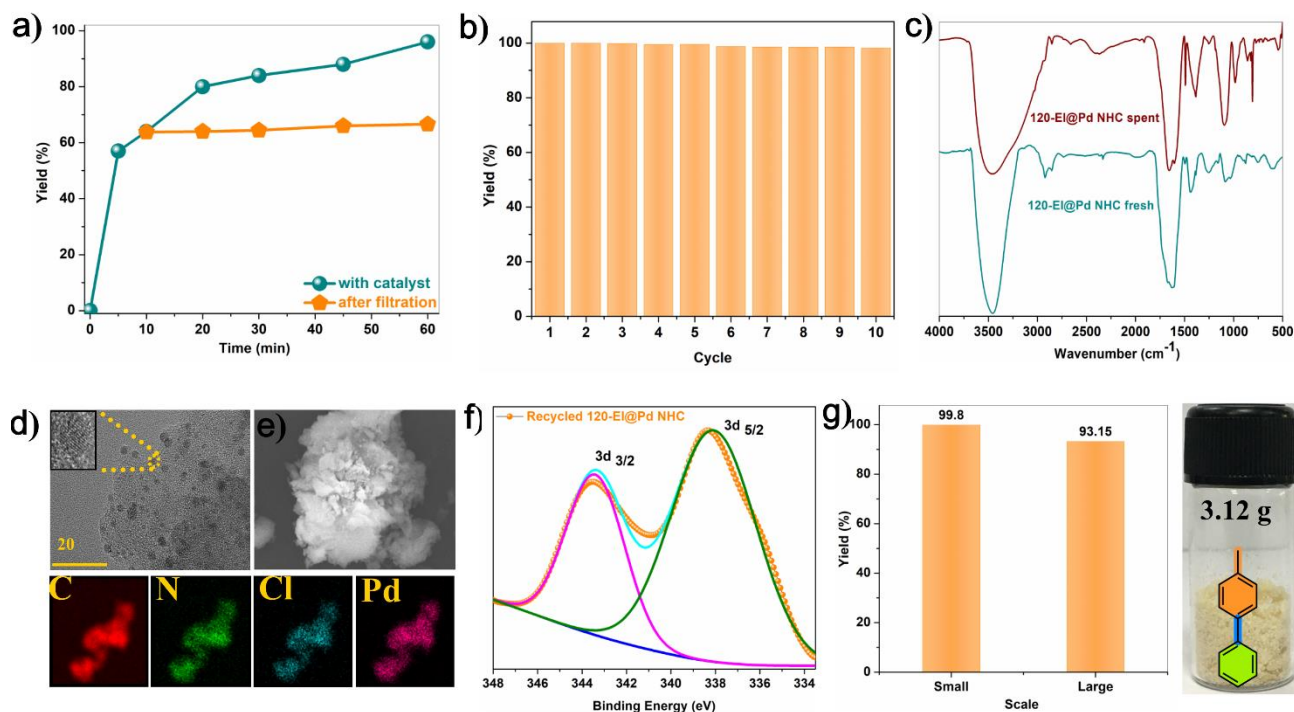


Figure 2.4. (a) Kinetic profile of p-Tolylboronic acid and bromobenzene (cyan); Hot filtration test (orange). (b) Catalytic recycling test of 120-EI@Pd NHC with p-Tolylboronic acid & bromobenzene. (c) FT-IR spectra of fresh 120-EI@Pd NHC catalyst (cyan), spent 120-EI@Pd NHC catalyst (brown). (d) HRTEM image & STEM-EDS mapping profile of composition elements in spent 120-EI@Pd NHC after 10 cycles of catalysis. (e) FESEM image of spent 120-EI@Pd NHC. (f) High resolution XPS spectra of palladium 3d spent 120-EI@Pd NHC after 10 catalytic cycles. (g) Reaction Yield comparison with the scale-up synthesis with a photograph of the isolated pure product.

Additionally, for comparison, 120-MI@Pd NHC bearing the less bulky methyl group as the substituent was employed under the optimal condition and showed less catalytic efficiency compared to 120-EI@Pd NHC (Appendix Table 2.2, entries 6 and 11). This difference in catalytic activity may be attributed to the difference in the electron-donating capability of substituents on the NHC where the other catalyst bearing a bulkier ethyl substituent showed better efficiency.^[66–68] This observation suggests the important role of tuning the electronic and steric environment around the NHC to regulate its stability and catalytic activity. It should be mentioned that with the aryl chloride derivative, chlorobenzene, we observed moderate

catalytic activity compared to that of other aryl derivatives (Ar–I and Ar–Br) where 61% yield was achieved even after the extended reaction time of 6 h (Appendix Table 2.2, entries 6, 17, and 18). With optimized reaction conditions and the superior catalyst 120-EI@Pd NHC in hand, its catalytic efficiency toward the SMC reaction was further evaluated using a series of aryl halides as well as boronic acid derivatives bearing a wide spectrum of electronically diverse substituents. As summarized in Table 2.1, 120-EI@Pd NHC displayed remarkable competence in affording the cross-coupling biaryl products with excellent yields (up to >99%) when screened for more than 40 substrates. The potent catalytic efficiency over such a broad substrate scope further highlighted the wide generality along with high functionality tolerance of the thus-developed 120-EI@Pd NHC heterogeneous catalyst. To our delight, boronic acid derivatives bearing either electron-withdrawing functionality (such as –CN, –COCH₃, –COOMe, –CHO, –Cl, Table 2.1 entries 6c, 3f, 5a, 6d, and 4b) or electron-donating functionality (–CH₃, –CH₂CH₃, –OCH₃, Table 2.1, entries 2a, 6a, and 6b) afforded very high to excellent product yields. Similarly, we have also investigated the efficiency of 120-EI@Pd NHC with aryl halides with different electronic functionalities. The reactions proceeded smoothly in all the cases to produce the desired biaryl products in nearly quantitative yields (Table 2.1, entries 1b, 1d, 1f, and 1g). To our delight, we also found that when reacted with a larger aryl halide 4-bromobiphenyl, we obtained a near quantitative yield for the desired biaryl product bearing three phenyl rings in all the cases (Table 2.1, entries 7a, 7b, and 7c). This can be attributed to the presence of flexible methylene (–CH₂–) linkages spread across the polymer skeleton that not only benefits in realizing a high specific surface area but also facilitates the diffusion of larger reactant molecules inside the catalyst matrix. The high surface area of the polymer plays a vital role in realizing highly efficient catalytic reactions under mild conditions. Furthermore, ¹H NMR spectra of all the targeted compounds in Table 2.1 confirmed their purity (details in the Appendix 2.37).

Figure 2.4a shows the sigmoidal kinetic profile of the SMC reaction of p-tolylboronic acid and bromobenzene catalyzed by 120-EI@Pd NHC. It should be noted that each data point was duplicated, and the average yields obtained were used for kinetics determination. The typical model reaction showed that an increment in the product yield as a function of increasing reaction time with a maximum yield of 99% was achieved after only 1 h. Furthermore, to validate the heterogeneity of the 120-EI@Pd NHC catalyst, the hot filtration technique was employed using p-tolylboronic acid and bromobenzene as model substrates (Figure 2.4a). After 10 min, the catalyst was removed from the reaction mixture via filtration, and the filtrate was allowed to further react under similar conditions for the designated time. It was observed that there was no change in the % yield with passing of time without the solid catalyst, indicating that the catalytically active Pd species did not leach out of the support polymer matrix and the catalysis taking place was heterogeneous in nature.

Sustainability, Stability & Conceptual Feasibility: Recovery and recyclability of a heterogeneous catalyst are not only crucial but of a priori necessity toward sustainability. After each catalytic cycle, the catalyst was readily recovered by centrifugation and washed with water and ethanol, followed by drying in vacuo at 100 °C for 6 h before being used for the next cycle of reaction. As seen in Figure 2.4b, 120-EI@Pd

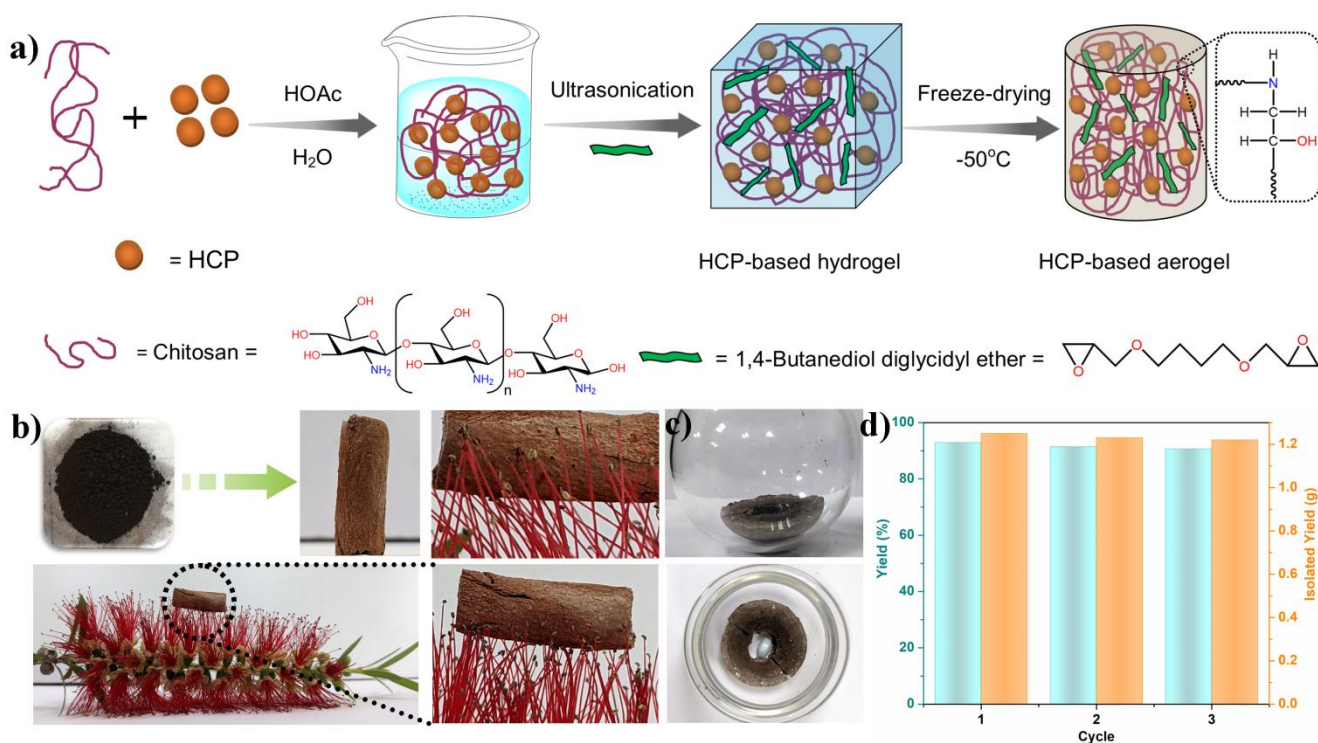


Figure 2.5. (a) Schematic illustration of fabricating HCP-Chitosan hybrid aerogel monoliths. (b) HCP 120-EI@Pd NHC-Chitosan covalently cross-linked hybrid aerogel monolith; Ultralight nature and extremely low density, as illustrated by the photograph of the mono-lith resting on top of crimson bottlebrush. (c) Side and top view of HCP-Chitosan based cup-reactor. (d) Recyclability of the cup-based reactor.

NHC exhibited exceptional reusability with unaltered catalytic efficiency up to 10 cycles (yield > 98%). This result underlines the robust and sustainable nature of the composite polymer catalyst. At this point, it should be mentioned that very few heterogeneous catalysts have been documented in the literature, showcasing such catalytic efficiency retention over 10 cycles. The catalyst recovered after performing the SMC reaction was thoroughly analyzed via FESEM, TEM, FTIR, XPS, N₂ gas adsorption, ICP-AES, etc., to substantiate the stability of the catalyst under optimized reaction conditions. While there were no noticeable changes of morphology observed in the post-catalysis FESEM images of 120-EI@Pd NHC

(Figures 2.4e and Appendix 2.29), TEM images showed the abundance of well-distributed Pd species contained in the polymer network similar to that of the fresh catalyst (Figures 2.4d and Appendix 2.29). Additionally, the FTIR measurement revealed no dissimilarity in the characteristic stretching frequencies with the parent catalyst (Figure 2.4c). Retention of permanent porosity in the spent catalyst was also verified with N_2 gas adsorption studies (Appendix 2.30). The superior stability of the composite polymer was further punctuated from the minimal metal leaching, as revealed by ICP-AES analysis where the Pd content of 4.17 wt % as compared to 4.41 wt % of the fresh catalyst was found in the spent catalyst. XPS analysis affirmed the presence of Pd in the +2 oxidation state with corresponding binding energies of 343.5 eV and 338.3 eV for Pd $3d_{5/2}$ and Pd $3d_{3/2}$ energy levels, respectively, indicating the absence of metallic Pd(0) particles even after several catalytic cycles (Figure 2.4f).

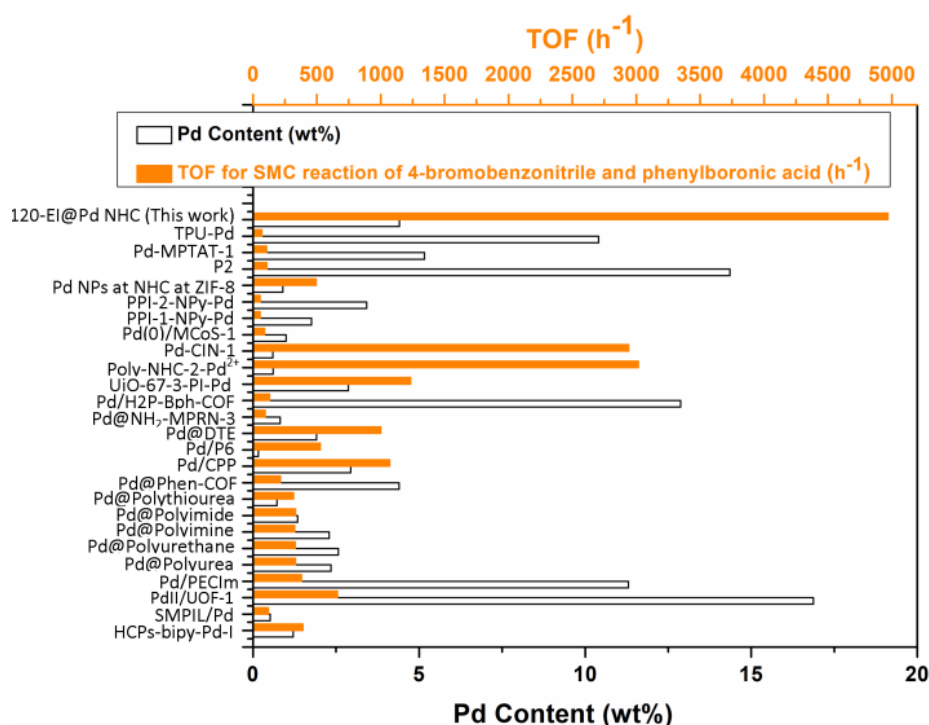


Figure 2.6. Pd loading and the catalytic performances in the Suzuki– Miyaura coupling reaction of 120-EI@Pd NHC and other reported porous materials immobilized Pd catalysts (with <20 wt% Pd loading), Ref. Appendix Table 2.3.

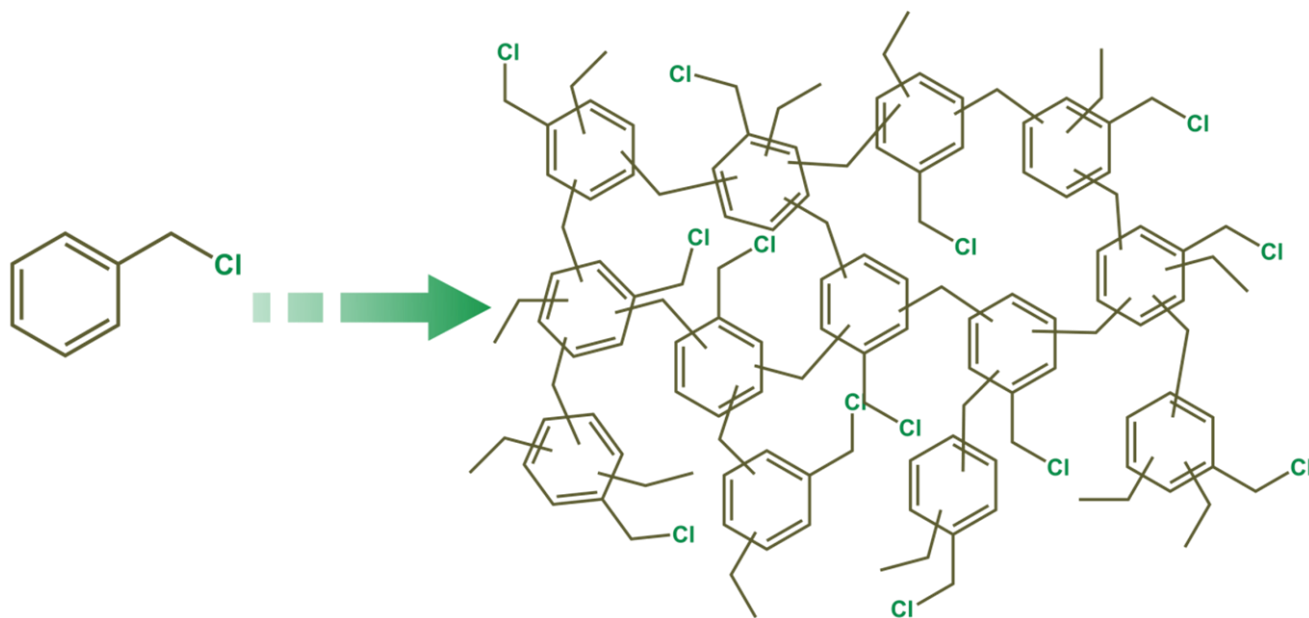
Inspired from the reusable potency and high stability of the 120-EI@Pd NHC catalyst, we zeroed our focus on the scaled up prospect with increased reactant amounts. We kept the same ratio but increased the reactant, catalyst, and solvent amount by 50 times. Satisfyingly, after performing the reaction at RT, we

were able to isolate 3.12 g of pure product with 93% yield (Figure 2.4g) within only 1 h, illustrating the ease of scalability with 120-EI@Pd NHC for gram-scale quantity making it a superior heterogeneous catalyst. Furthermore, we delved into the conceptual feasibility of the developed polymer catalyst toward practical relevance. Along this direction, we tapped into organic aerogels - a potential fit between processability and macroscopic hierarchical porosity along with ultra-low density. These unique features promoting easier mass transport and diffusion have made them front runners in surpassing contemporary porous materials toward realizing superior performance.^[69–72] Chitosan was chosen as the matrix support on account of its low cost, biocompatibility, as well as biodegradability along with its high abundance. Toward converting 120-EI@Pd NHC into a processable form and shape, a chitosan-based covalently cross-linked 3D aerogel monolith was prepared along with the subsequent crafting of a 120-EI@Pd NHC_Chitosan aerogel-based fixed bed cup-like reactor (Figure 2.5a–c) for practical applicability. The successful emergence of the $\text{–NH–CH}_2\text{–CH(OH)–}$ linkage along with conjugation between 1,4-butanediol diglycidyl ether and the amine group from chitosan in the aerogel was established from FTIR spectra (Appendix 2.33). The composite aerogel was also investigated for surface morphology with FESEM (Appendix 2.32). As shown in Figure 2.5d, taking p-tolylboronic acid and bromobenzene as reactants at 20 times higher scale, we were able to isolate 92.9% yield (1.25 g) of the biaryl product after 1 h of performing the reaction in a prototype aerogel cup-like microreactor (50 wt % 120-EI@Pd NHC loading) at RT. Additionally, the 120-EI@Pd NHC_Chitosan catalyst reactor could be easily reused after washing with water and ethanol and vacuum drying, followed by the product separation. The cup-like reactor was found to be stable under reaction conditions and showed excellent activity retention (yield >90%) even after three catalytic cycles (Figure 2.5d). This accounts for excellent reusability of the aerogel cup-based reactor. Thus, the prepared aerogel monolith herein has proven to be maneuverable as well as highly potent toward the heterogeneous SMC reaction at RT, also serving as an effective alternative to bypass the pitfalls of catalyst recovery and product segregation. Additionally, to realize the full potential of our catalyst, we carried out the catalysis with less amount of the catalyst (1 mg, corresponding to 0.04 mol % of Pd) and a higher amount of reactants (1 mmol aryl halide). It is noteworthy to mention that even at low dosage, the catalyst displayed excellent efficiency with a TOF value reaching up to 4970 h^{-1} for the reaction between 4-bromobenzonitrile and phenylboronic acid (Appendix Table 2.4, Figure 2.6). A literature comparison on Pd contents versus TOF values of reported porous materials is summarized in Figure 2.6. It was observed that 120-EI@Pd NHC stands tall among the reported TOF values proving its superiority as a potent heterogeneous catalyst (Appendix Table 2.3). The observed catalytic activity can be rationalized with the spatial isolation of catalytically active sites along with the remnant porosity of the polymer after the introduction of the catalytic sites.

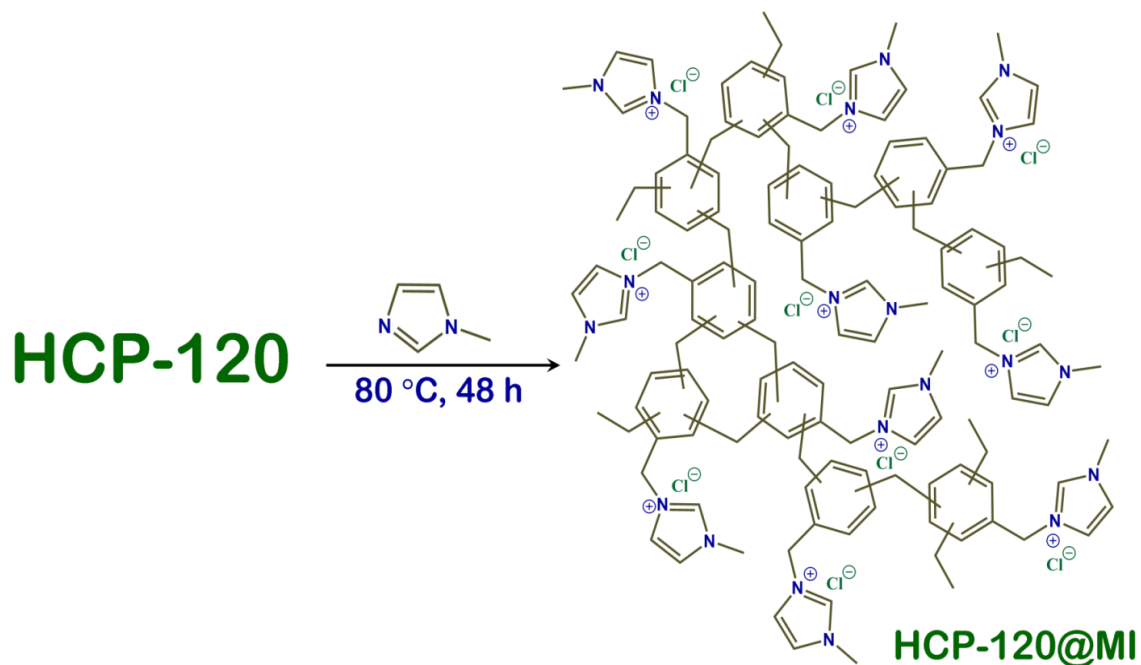
2.4 Conclusion

To summarize, we have successfully developed a NHC containing heterogeneous composite polymer catalyst based on post-synthesis structure modulation. Thus, the prepared polymer catalyst was thoroughly characterized with spectroscopy as well as electron microscopy. Owing to highly dispersed catalytically active NHC units, 120-EI@Pd NHC displayed excellent potency toward catalyzing SMC at RT and in green solvents. At a low Pd loading (4.41 wt %), the substrate scope illustrated by the synthesized catalyst over 40 substrates with varying electronic factors is exceptional and rarely reported. Furthermore, 120-EI@Pd NHC displayed superior stability under catalytic conditions and outstanding reusability over 10 catalytic cycles without compromising its catalytic efficiency. The catalyst also illustrated unaltered efficiency for scaled-up reactions (50 times higher) in producing the desired biaryl product. Pertaining to conceptual feasibility toward practical implementation, a 3D macroscopic covalently cross-linked chitosan-based aerogel was also devised, which showed similar catalytic performance resulting in the isolation of gram-scale product over three cycles. Strategic structural modification by the tethering spatially isolated NHC moiety and strong electron donation prevent palladium aggregation along with keeping the Pd species firmly held to eliminate metal leaching.

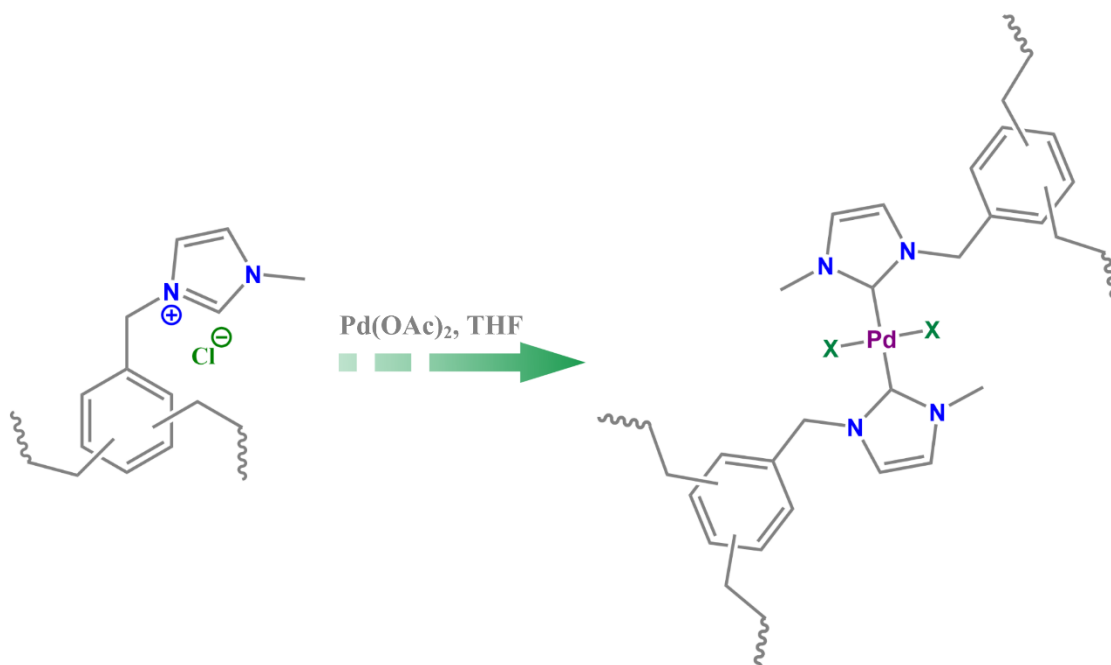
2.5 Appendix section



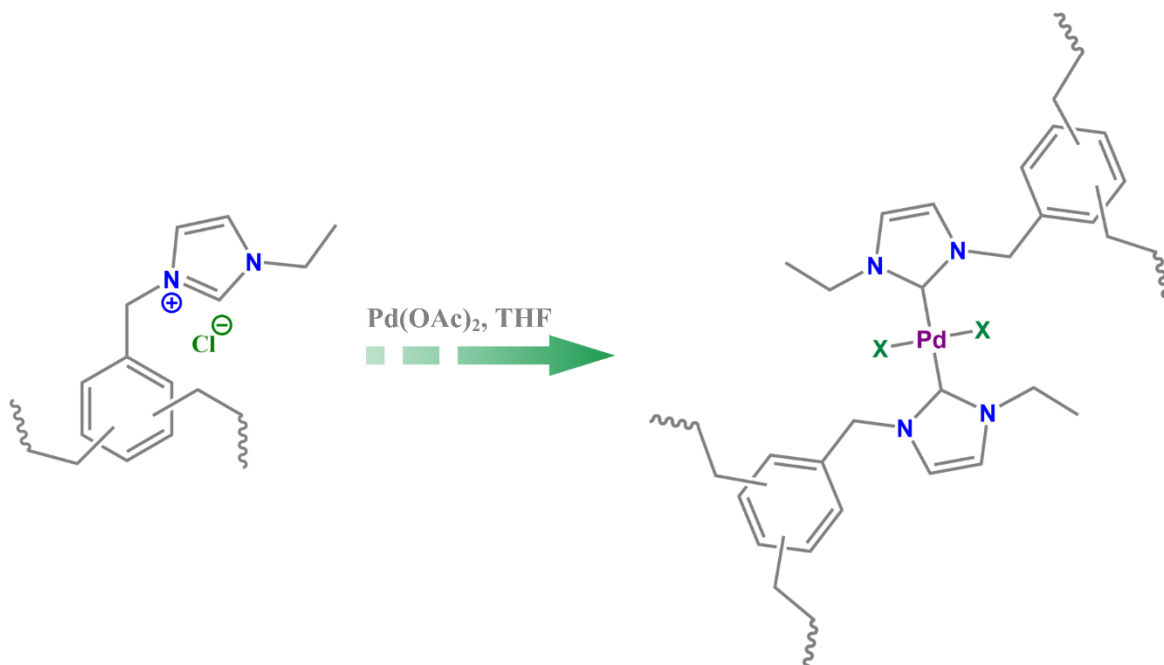
Appendix Scheme 2.1. Synthesis of HCP-120 Cl.



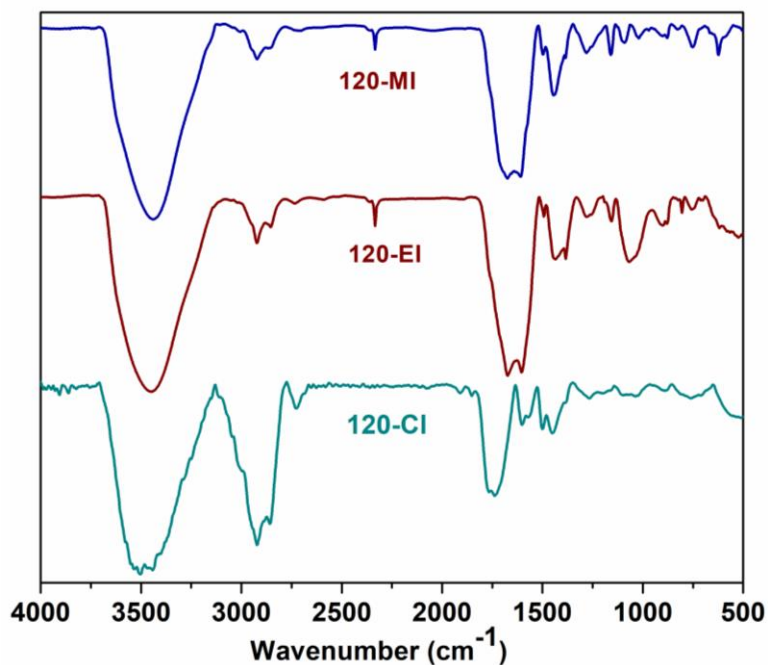
Appendix Scheme 2.2. Synthesis of HCP 120-MI.



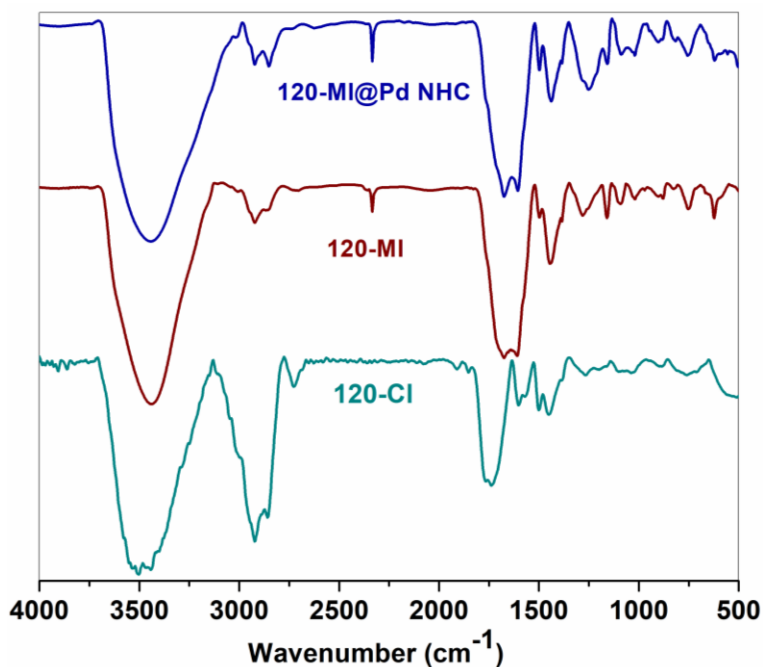
Appendix Scheme 2.3. Synthesis of HCP120-MI@Pd NHC.



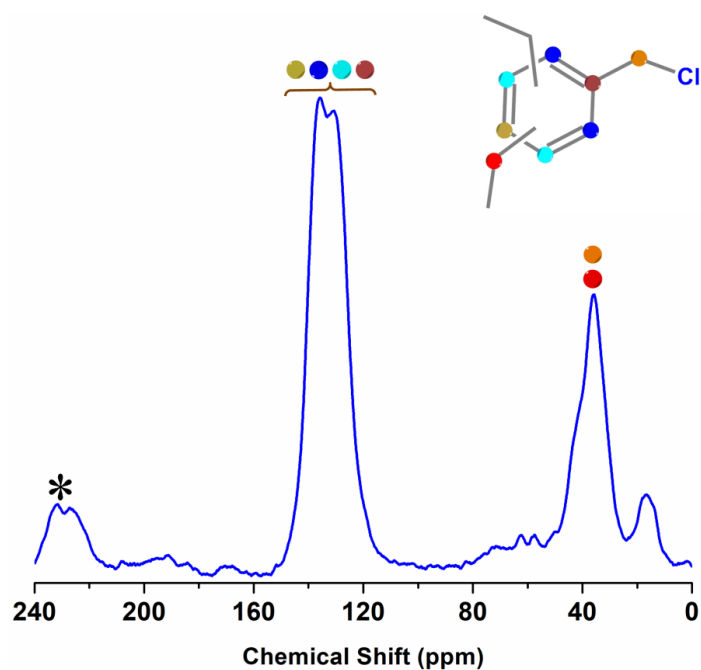
Appendix Scheme 2.4. Synthesis of Synthesis of HCP120-EI@Pd NHC.



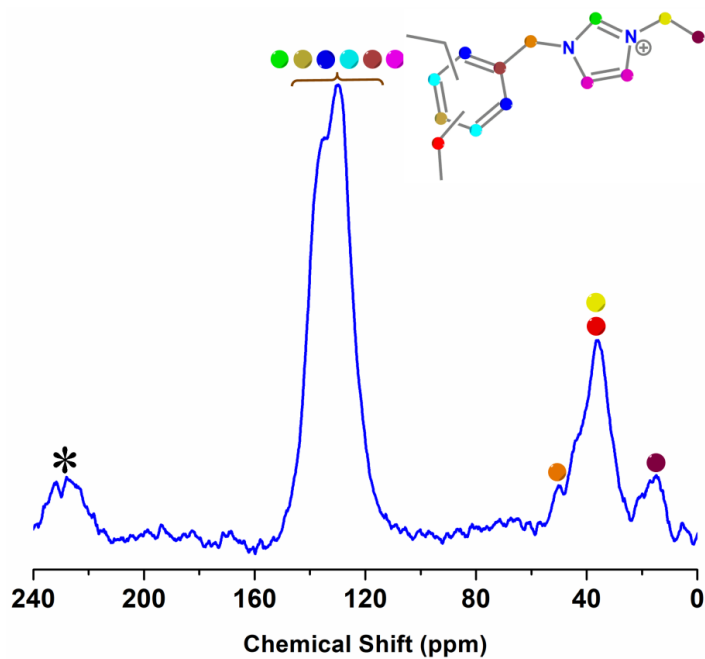
Appendix Figure 2.1. Infra-red (IR) spectra of 120-Cl (cyan), 120-EI (wine) and 120-MI (blue).



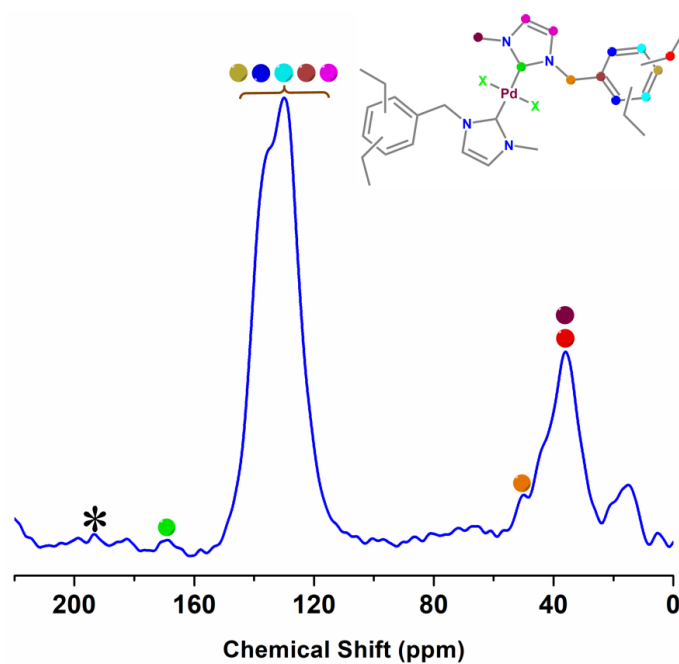
Appendix Figure 2.2. : Infra-red (IR) spectra of 120-Cl (cyan), 120-MI (wine) & 120-MI@NHC Pd (blue).



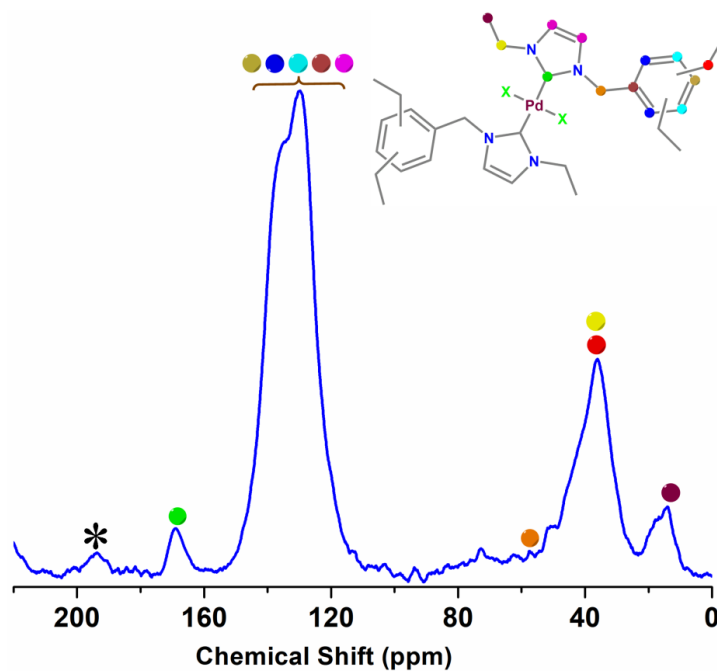
Appendix Figure 2.3. Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-Cl.



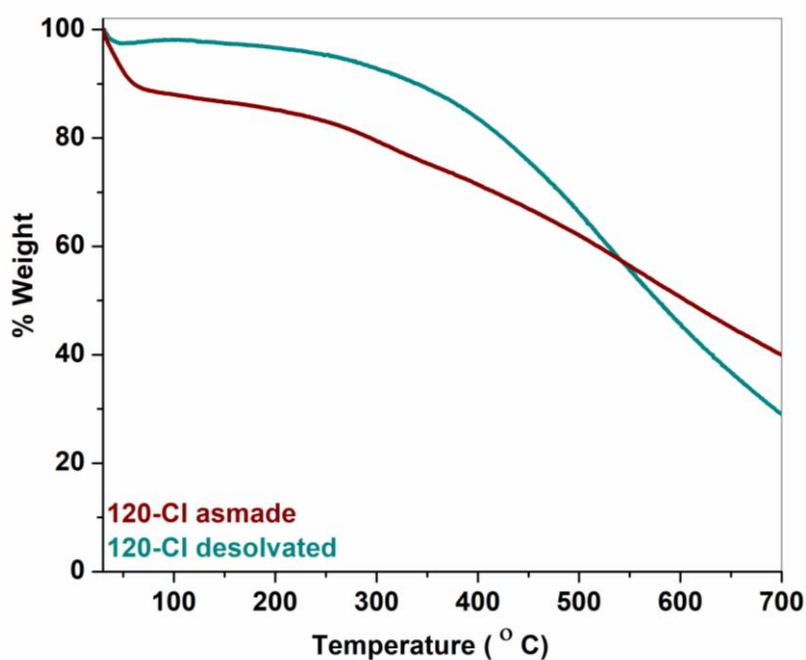
Appendix Figure 2.4. Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-EI.



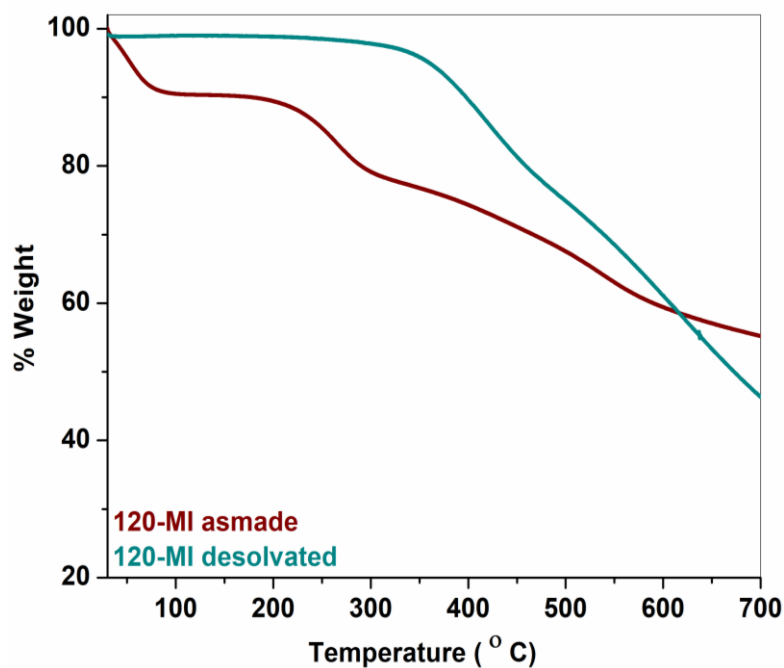
Appendix Figure 2.5. Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-MI@Pd NHC.



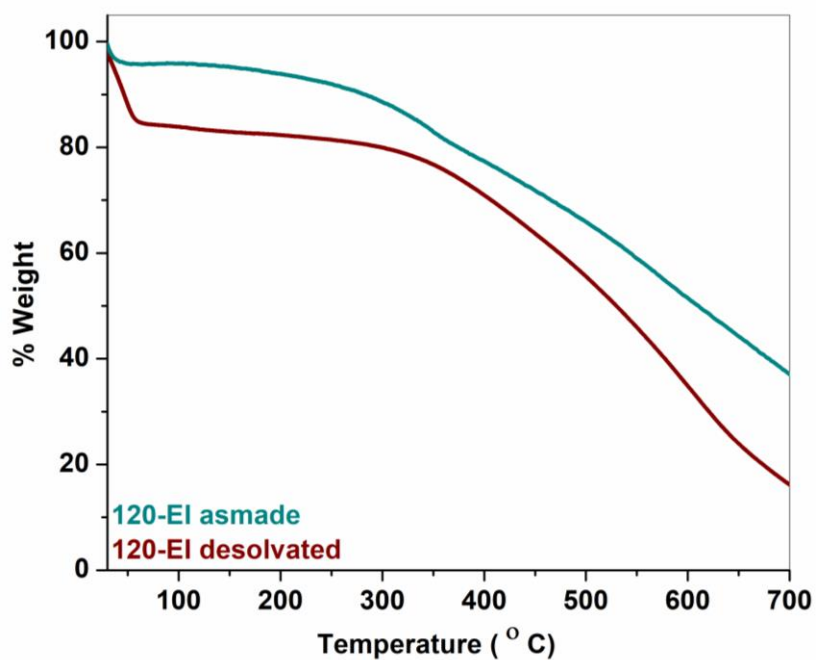
Appendix Figure 2.6. Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-EI@Pd NHC.



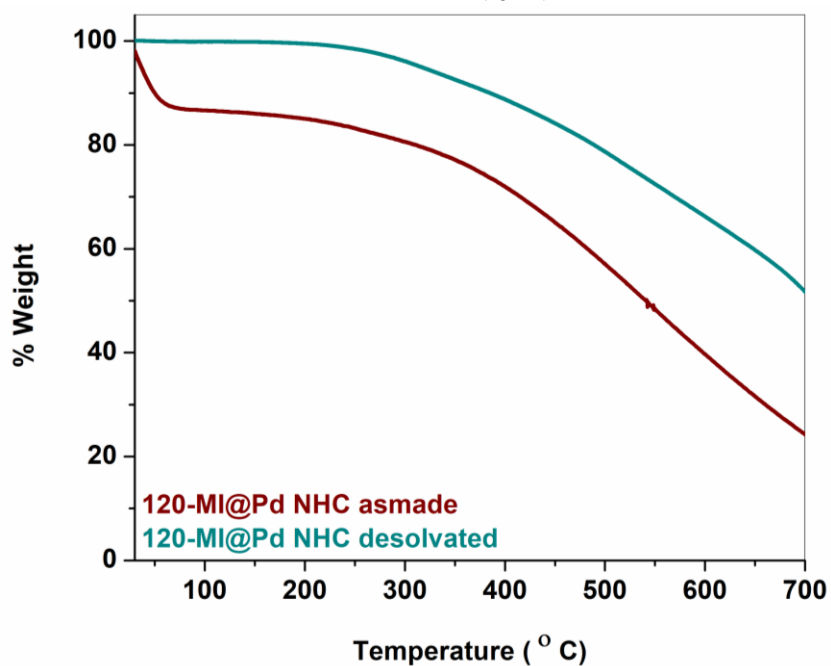
Appendix Figure 2.7. Thermogravimetric profiles (under N₂ atmosphere) for pristine 120-Cl (wine) and activated 120-Cl (cyan).



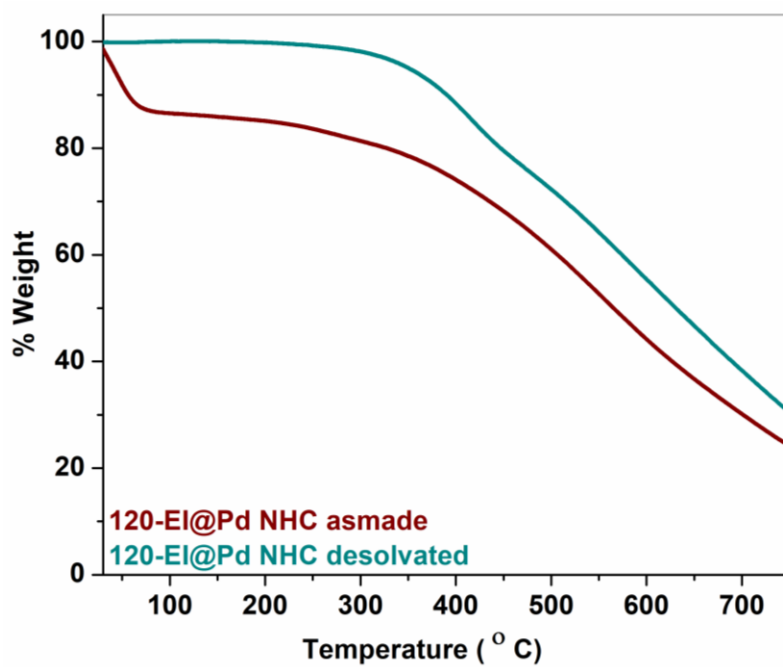
Appendix Figure 2.8. Thermogravimetric profiles (under N₂ atmosphere) for pristine 120-MI (wine) and activated 120-MI (cyan).



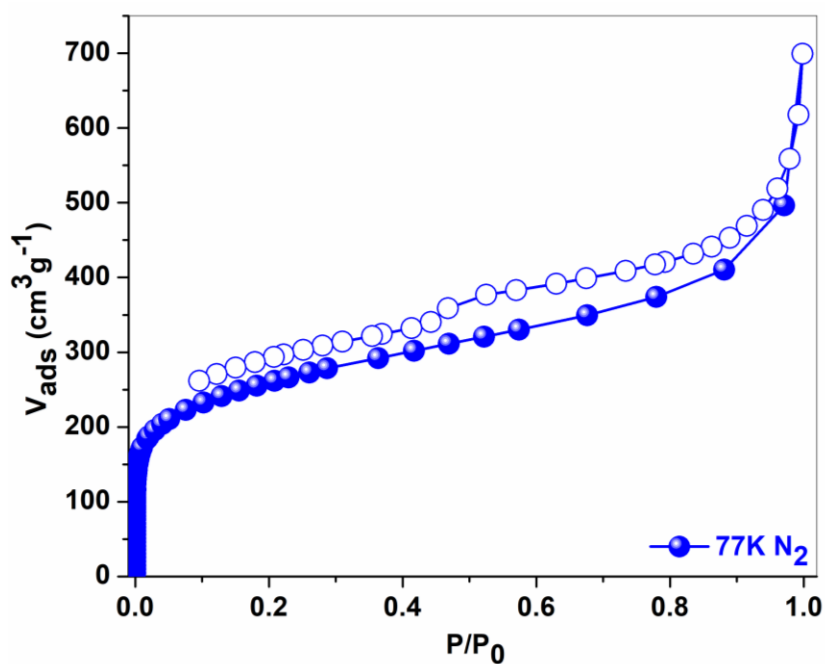
Appendix Figure 2.9. Thermogravimetric profiles (under N₂ atmosphere) for pristine 120-EI (wine) and activated 120-EI (cyan).



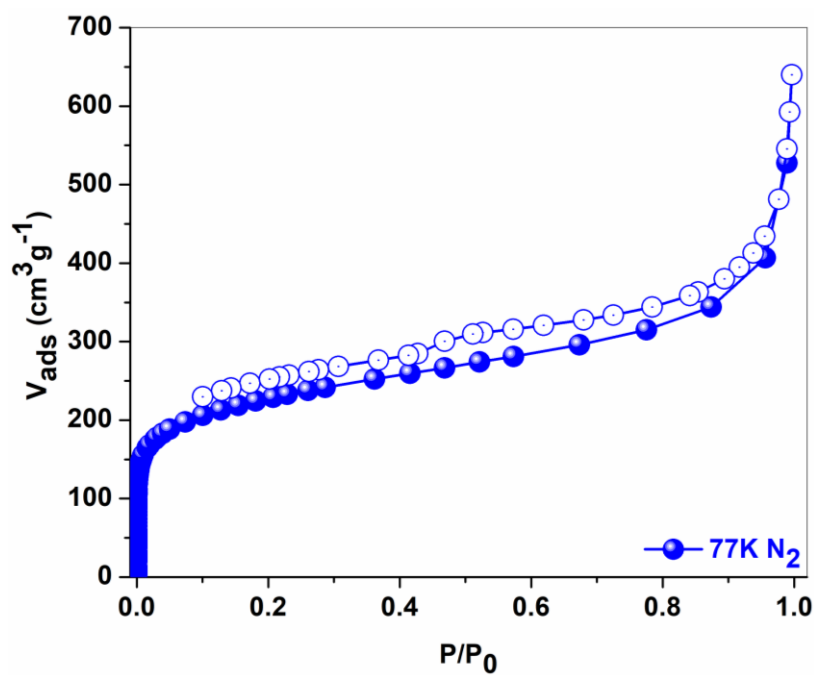
Appendix Figure 2.10. Thermogravimetric profiles (under N₂ atmosphere) for pristine 120-MI@NHC Pd (wine) and activated 120-MI@Pd NHC (cyan).



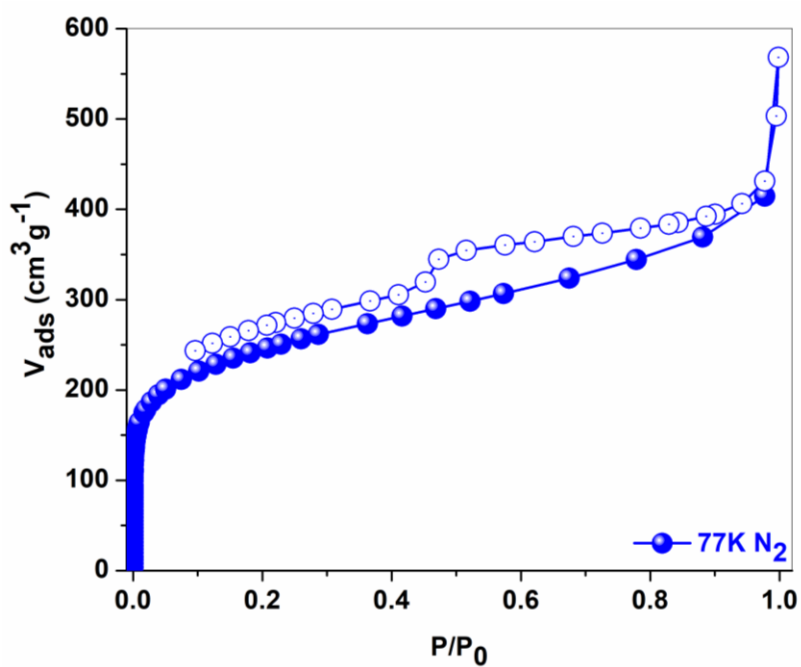
Appendix Figure 2.11. Thermogravimetric profiles (under N_2 atmosphere) for pristine 120-EI@NHC Pd (wine) and activated 120-EI@Pd NHC (cyan).



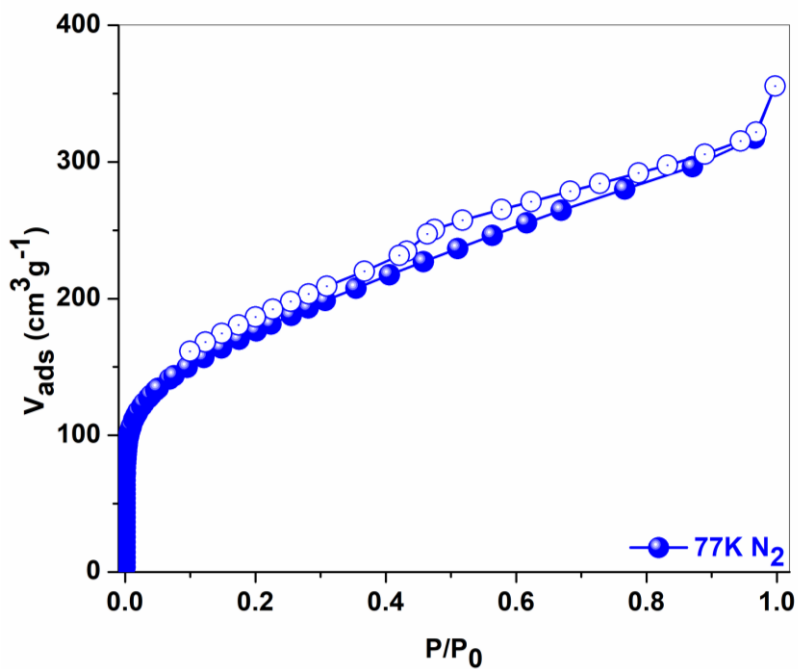
Appendix Figure 2.12. N_2 adsorption profile at 77 K for 120-Cl.



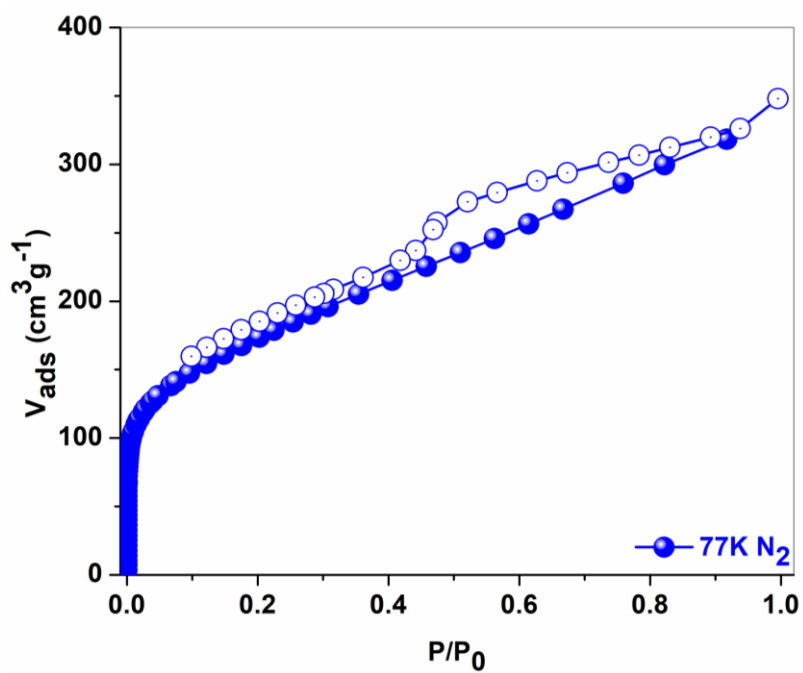
Appendix Figure 2.13. N₂ adsorption profile at 77 K for 120-MI.



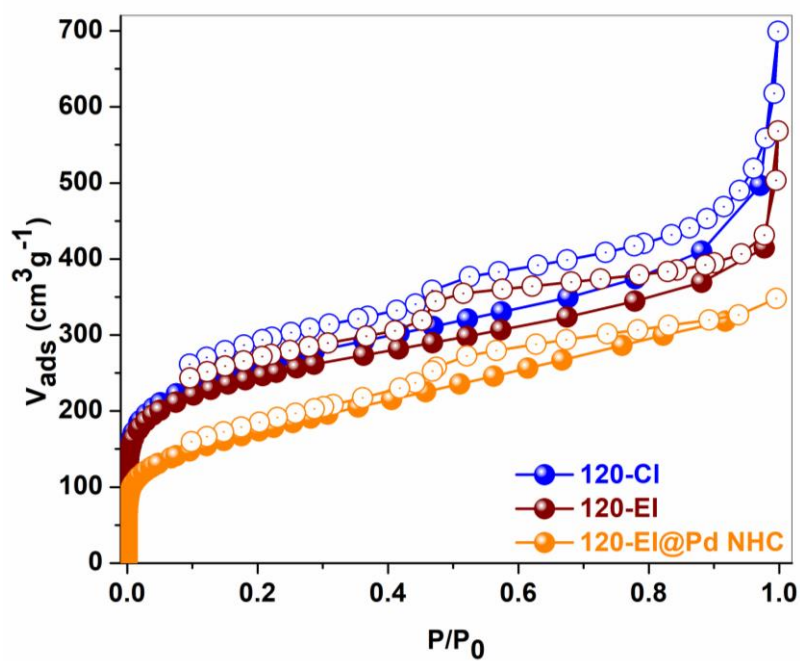
Appendix Figure 2.14. N₂ adsorption profile at 77 K for 120-EI.



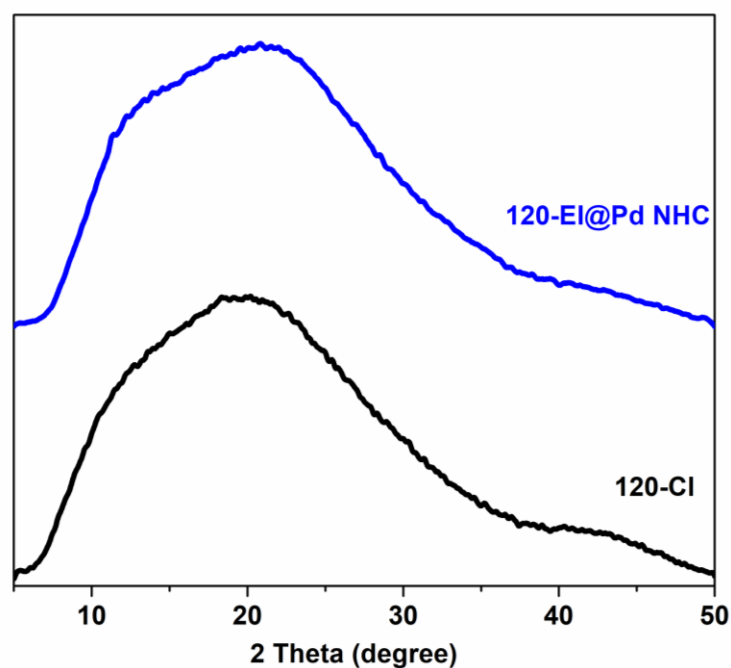
Appendix Figure 2.15. N₂ adsorption profile at 77 K for 120-MI@Pd NHC.



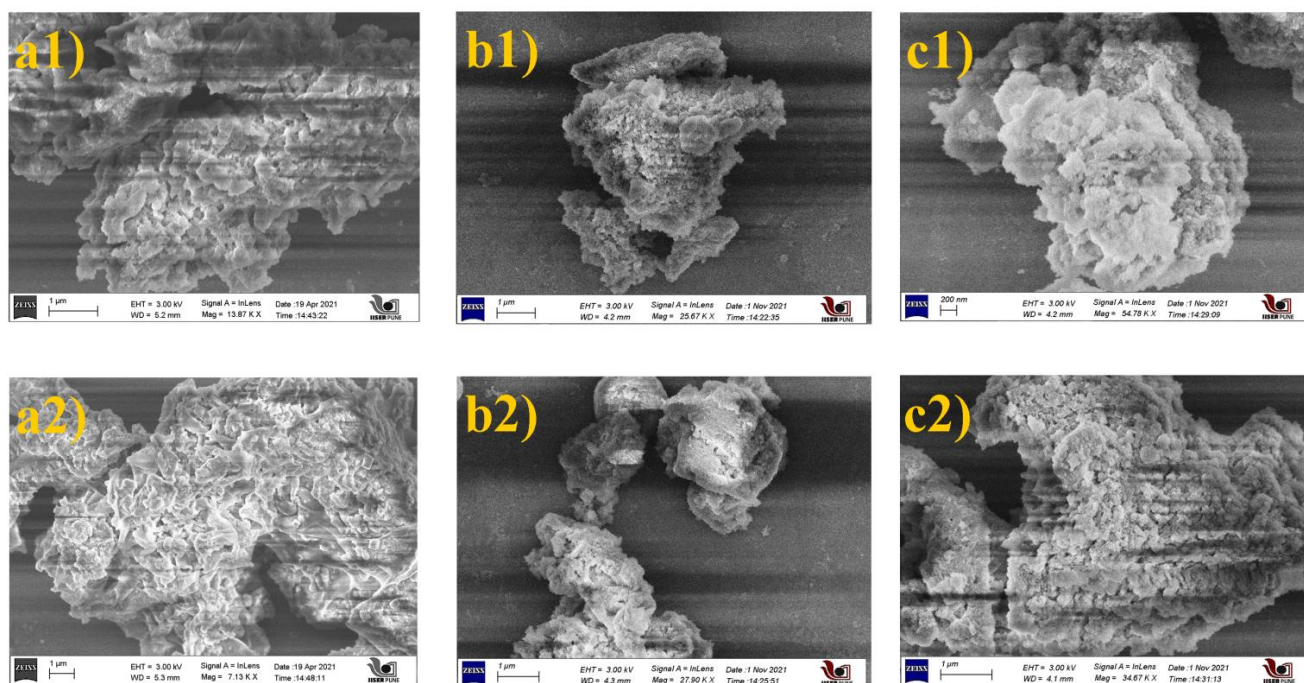
Appendix Figure 2.16. N₂ adsorption profile at 77 K for 120-EI@Pd NHC.



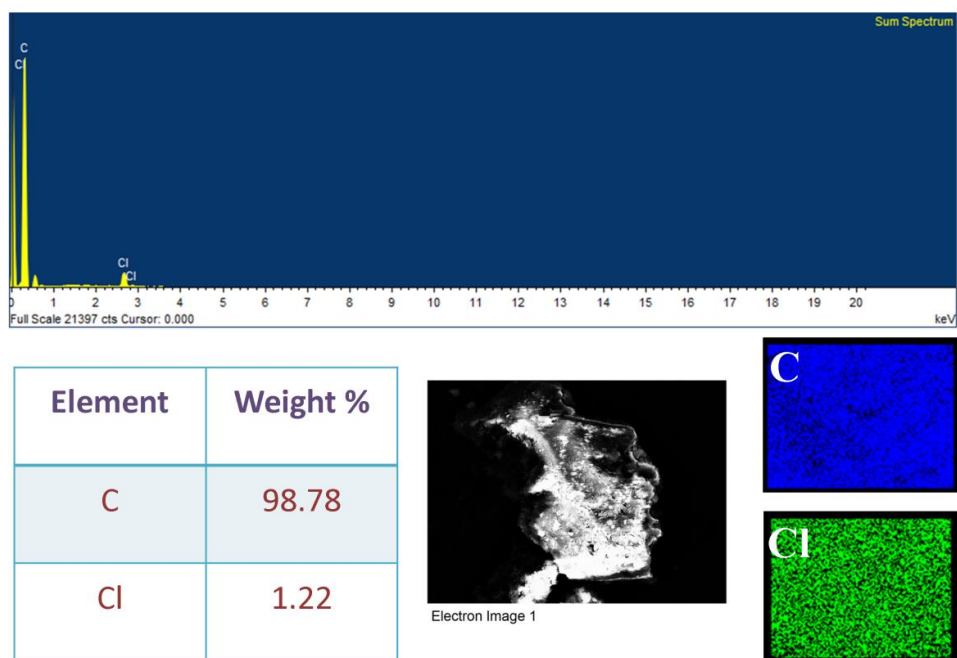
Appendix Figure 2.17. Comparative N₂ adsorption profiles at 77 K for 120-Cl (blue), 120-EI (wine) and 120-EI@Pd NHC.



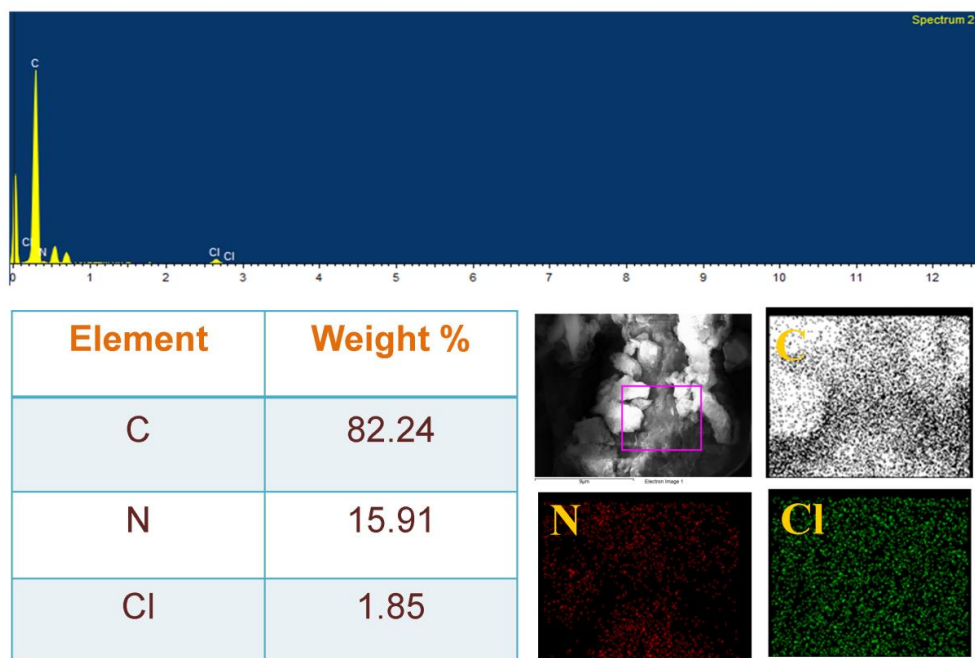
Appendix Figure 2.18. PXRD pattern of polymer 120-Cl (black) and 120-EI@Pd NHC.



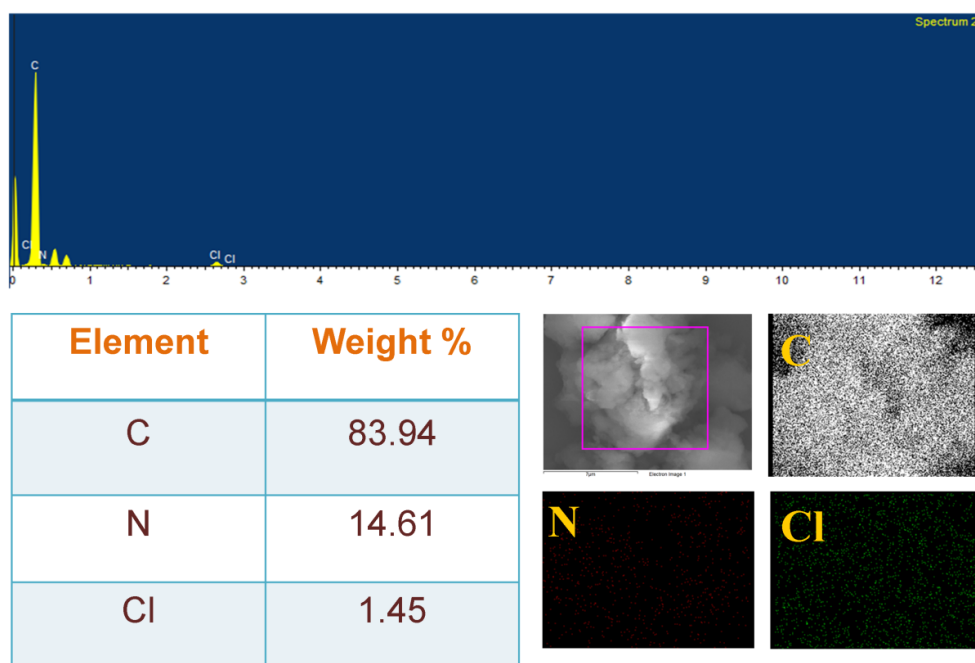
Appendix Figure 2.19. Magnified FESEM images of (a1-a2) 120-Cl, (b1-b2) 120-MI and (c1-c2) 120-EI, scale bar = 1-2 μm .



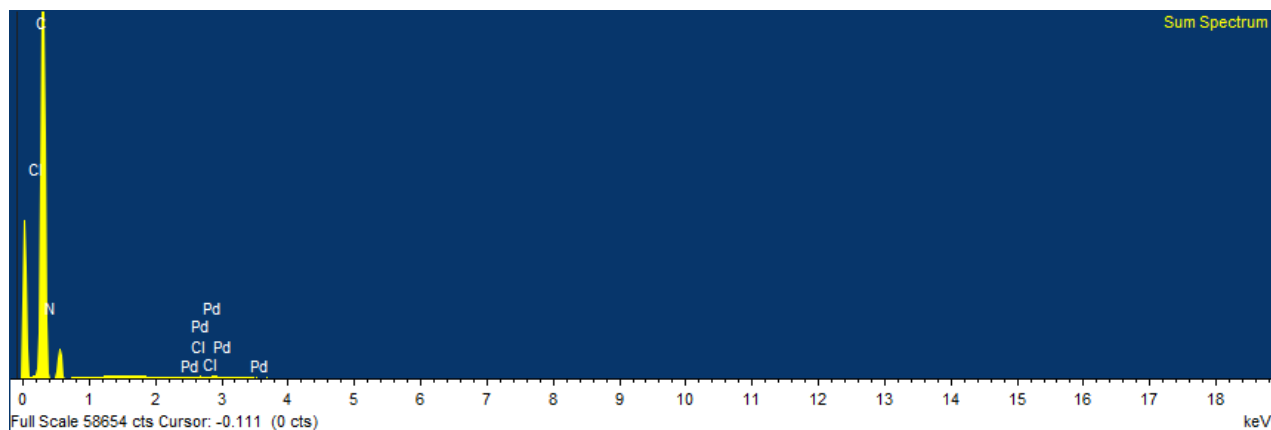
Appendix Figure 2.20. EDX analysis and elemental mapping of 120-Cl.



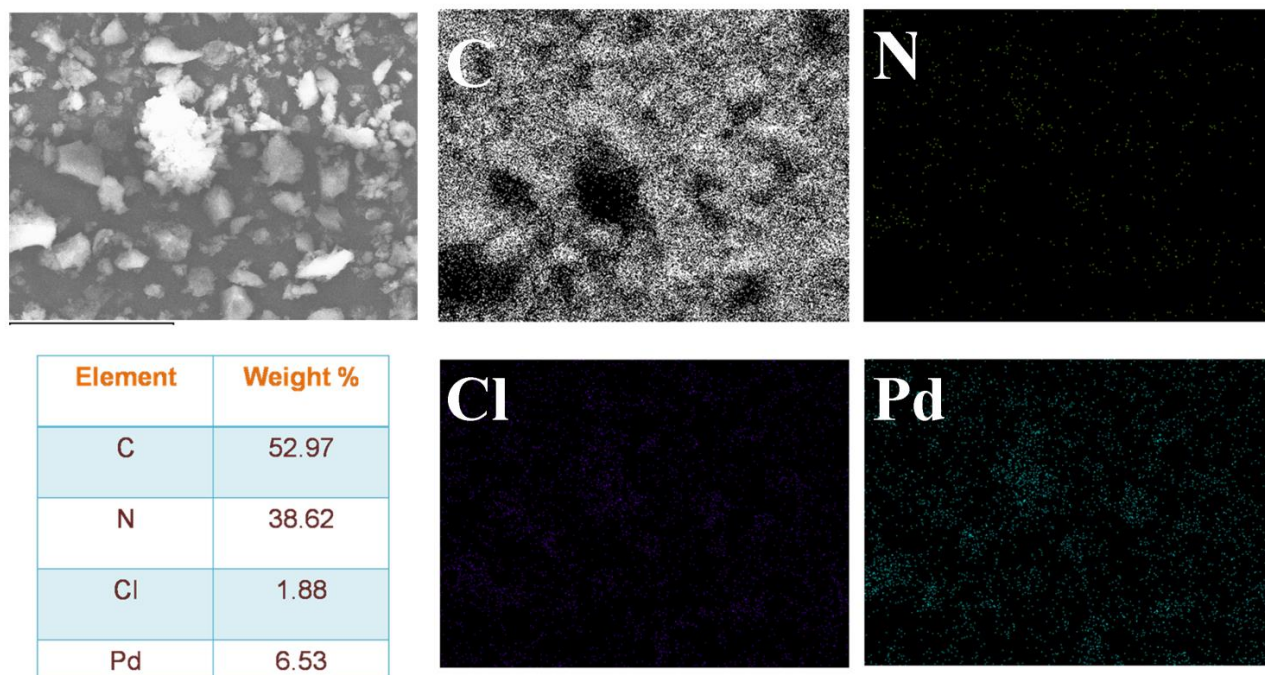
Appendix Figure 2.21. EDX analysis and elemental mapping of 120-MI.



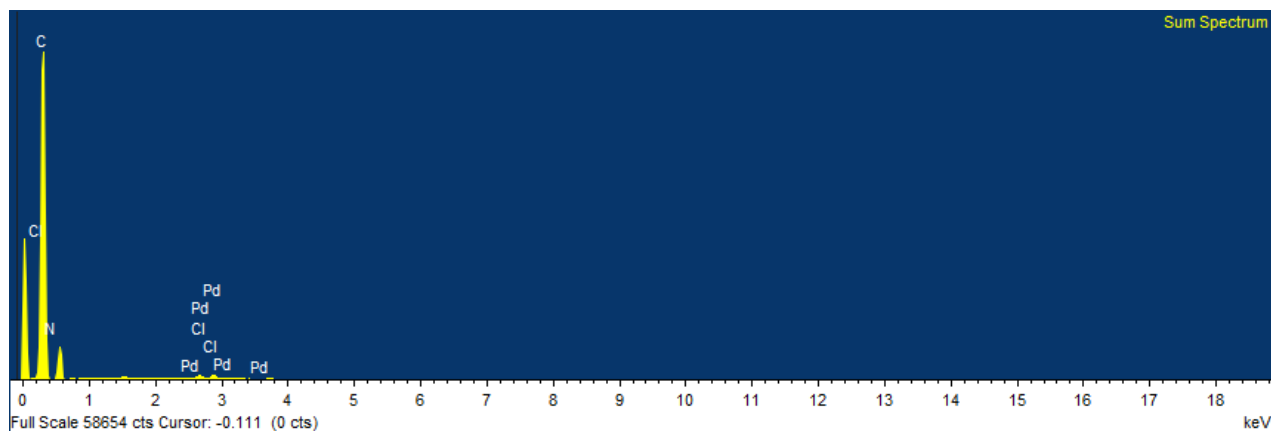
Appendix Figure 2.22. EDX analysis and elemental mapping of 120-EI.



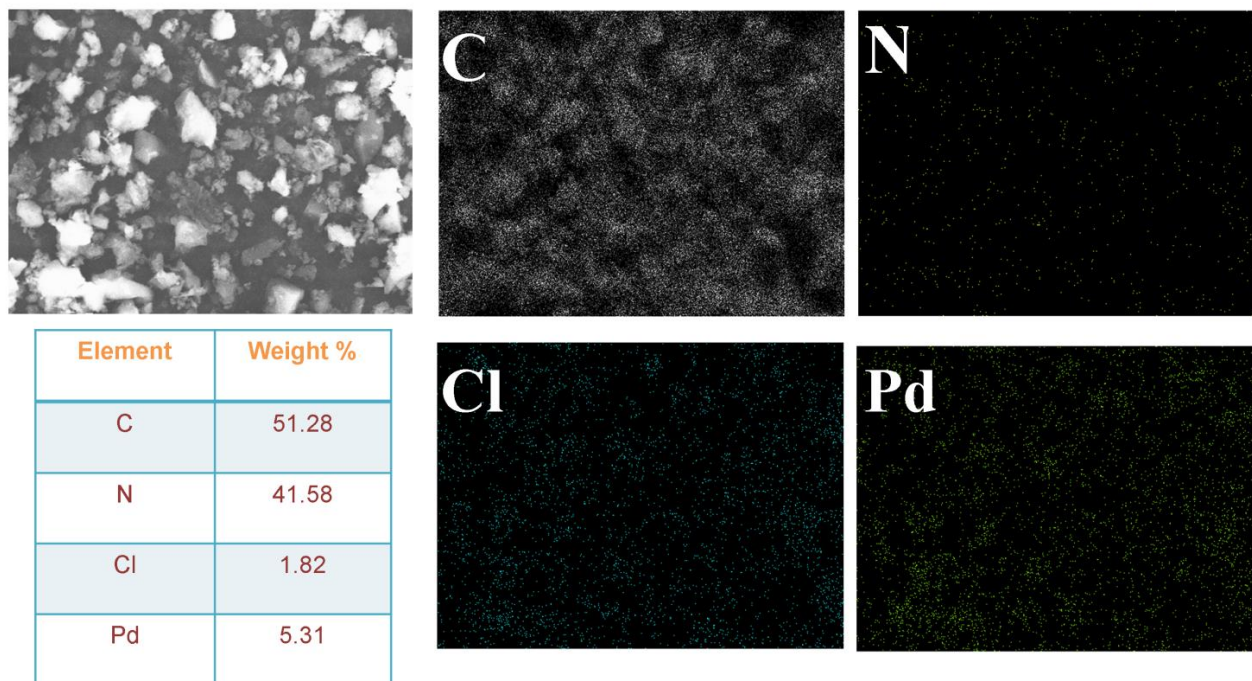
Appendix Figure 2.23. EDX analysis of 120-MI@Pd NHC.



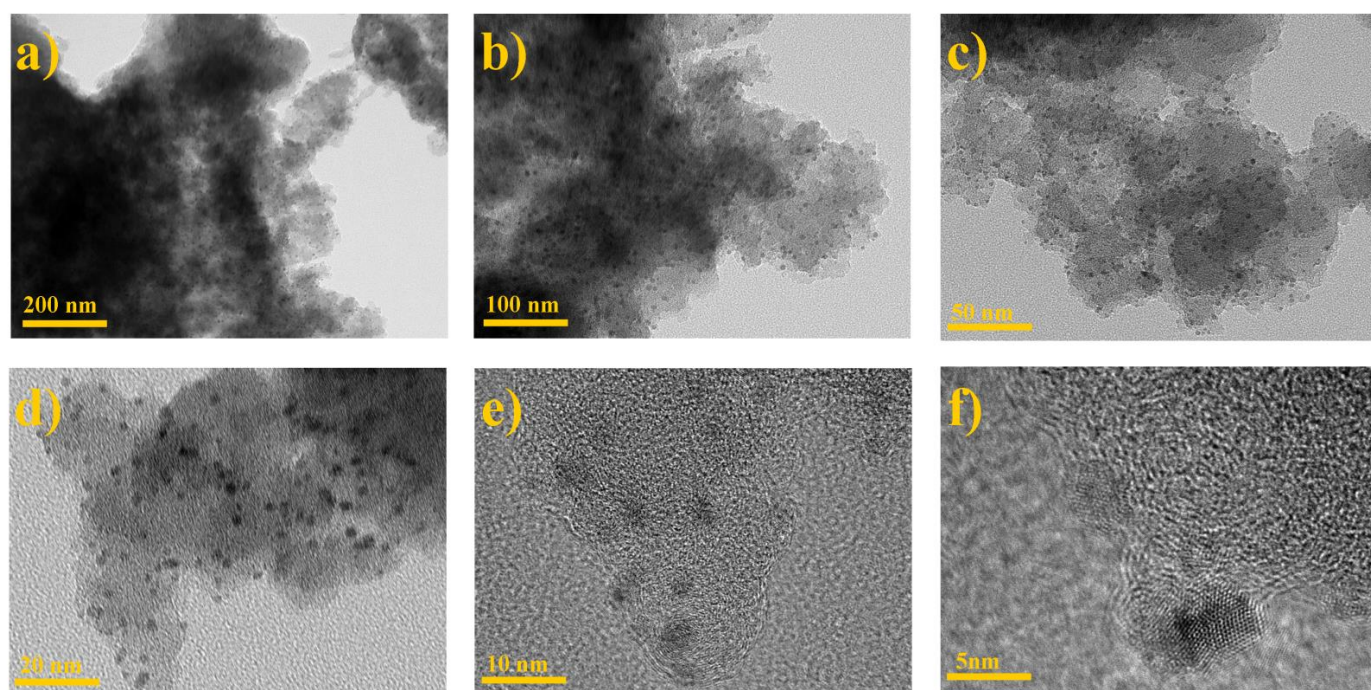
Appendix Figure 2.24. Elemental mapping of 120-MI@Pd NHC.



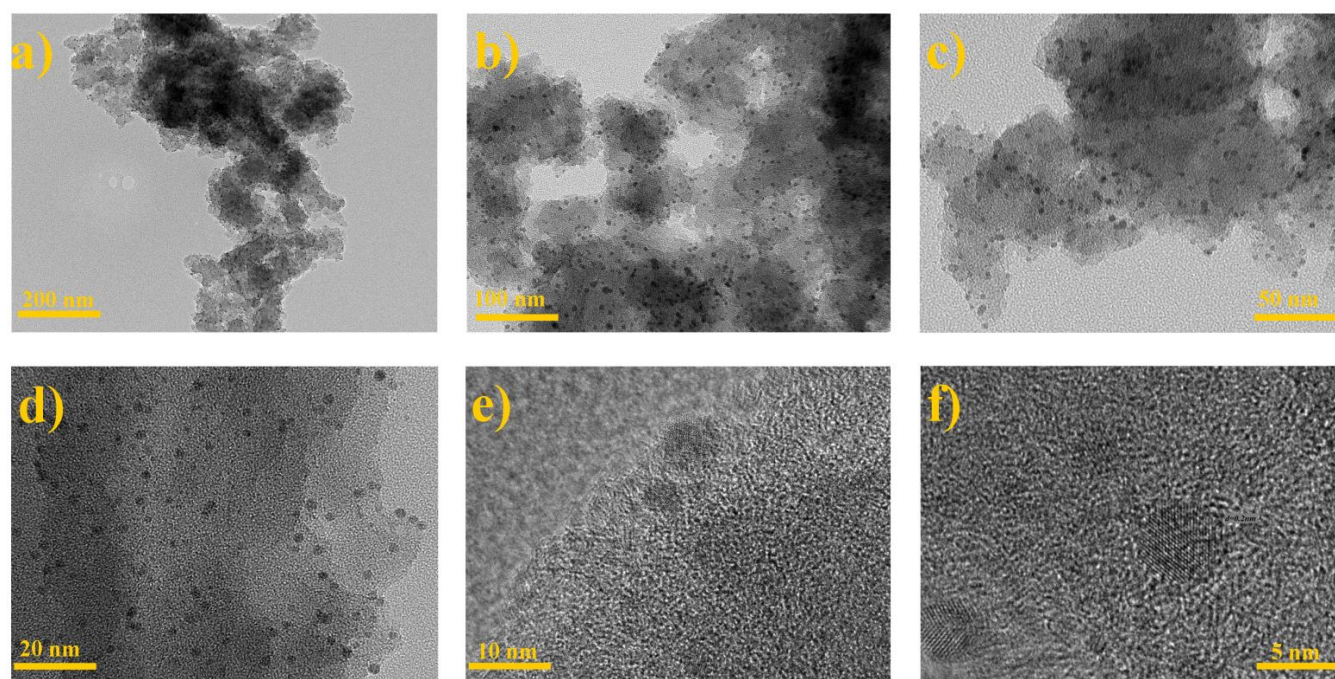
Appendix Figure 2.25. EDX analysis of 120-EI@Pd NHC.



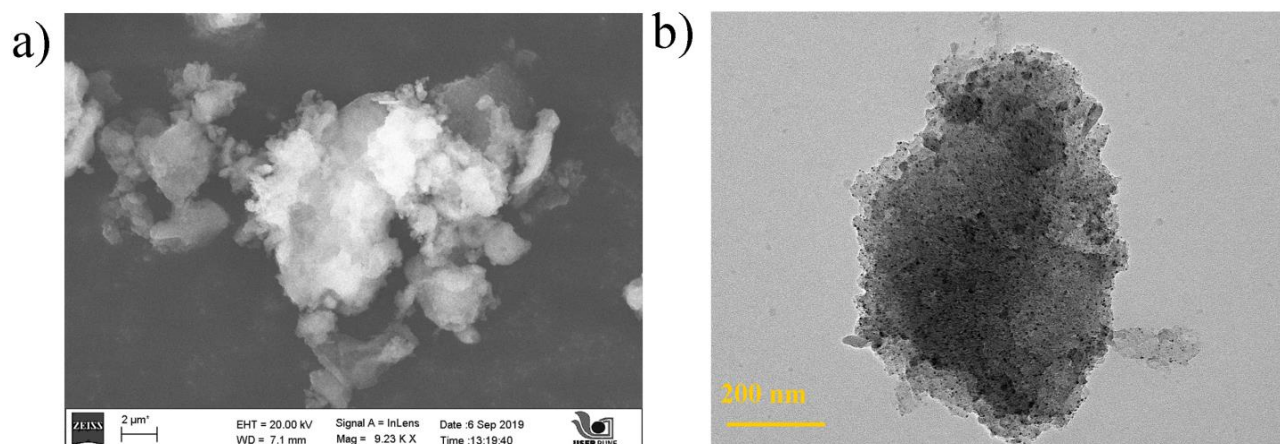
Appendix Figure 2.26. Elemental mapping of 120-EI@Pd NHC.



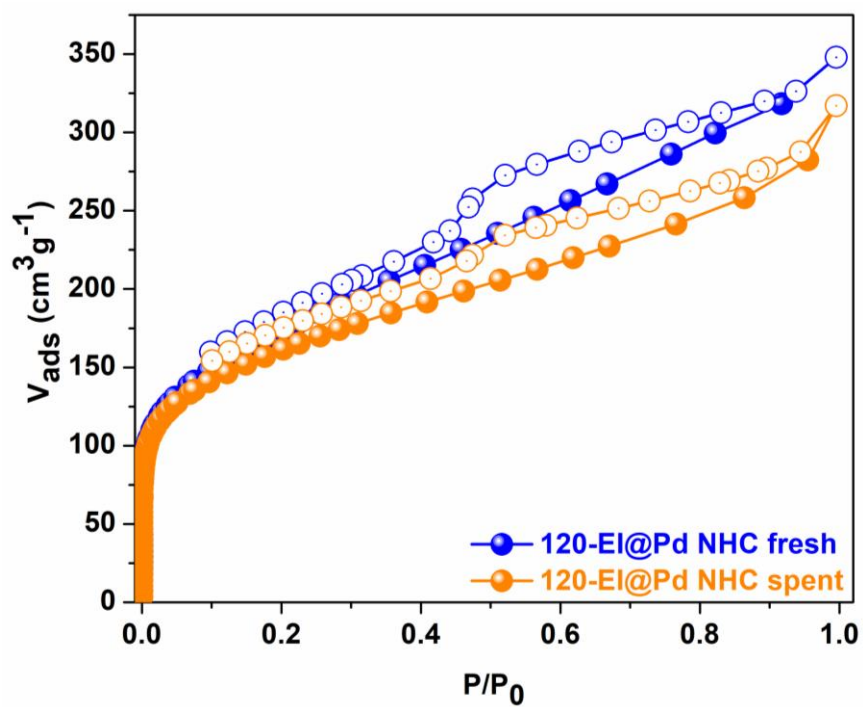
Appendix Figure 2.27. TEM & HRTEM images of 120-MI@Pd NHC.



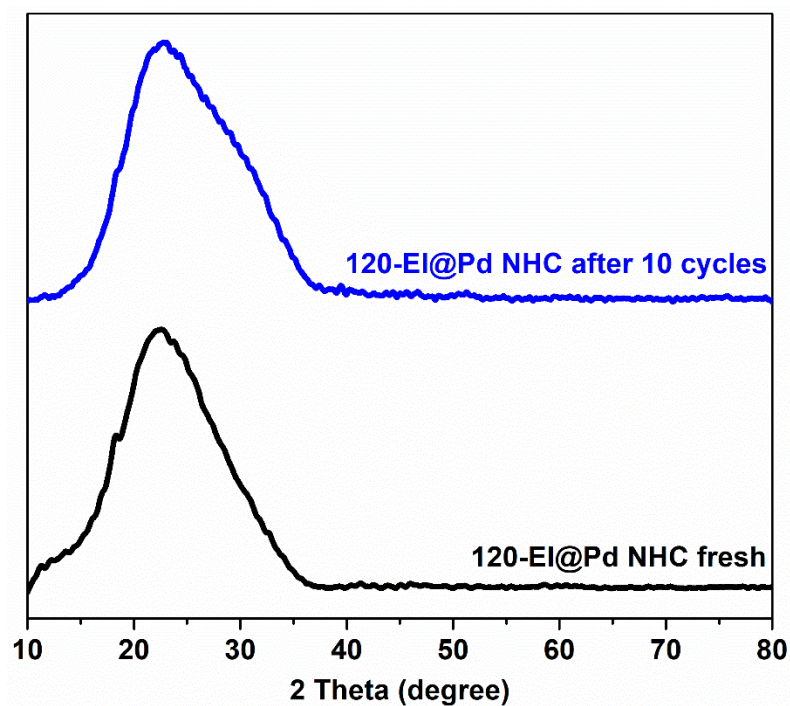
Appendix Figure 2.28. TEM & HRTEM images of 120-EI@Pd NHC.



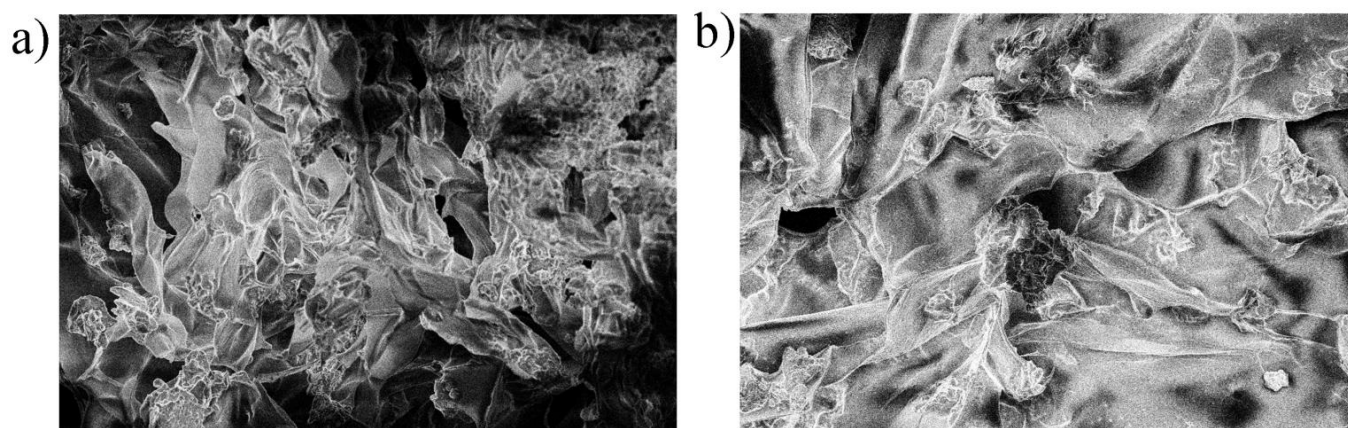
Appendix Figure 2.29. FESEM (a) and TEM (b) images of spent 120-EI@NHC Pd catalyst after 10 catalytic cycles.



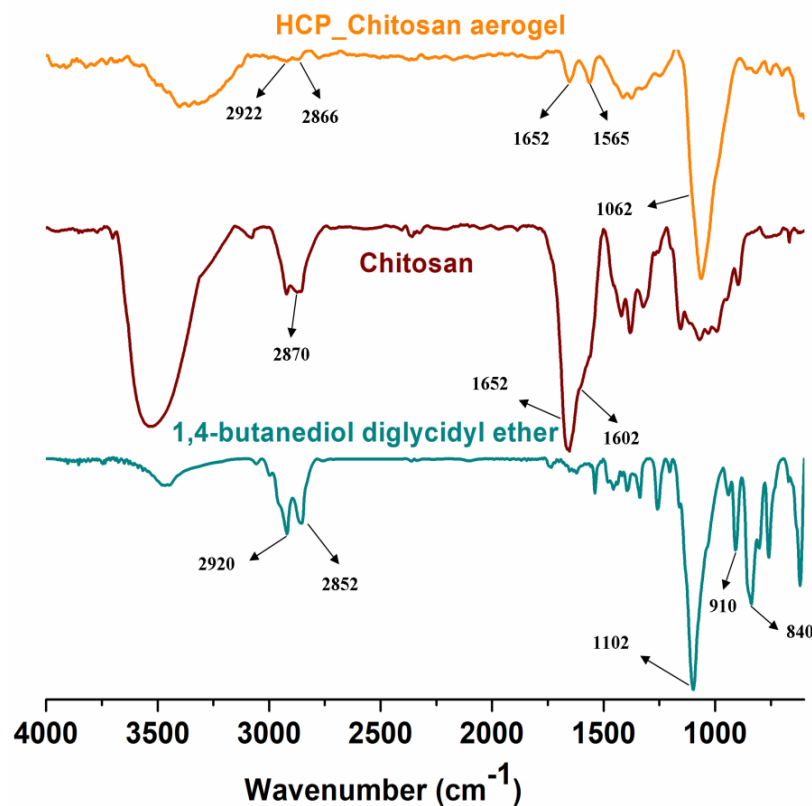
Appendix Figure 2.30. N_2 adsorption profile at 77 K for fresh 120-EI@Pd NHC (blue) and spent 120-EI@Pd NHC (orange) after 10 catalytic cycles.



Appendix Figure 2.31. PXRD pattern of fresh 120-EI@Pd NHC (black) & 120-EI@Pd NHC after 10 catalytic cycles (blue).

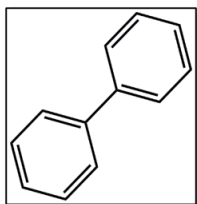


Appendix Figure 2.32. FESEM images of 120-EI@NHC Pd_chitosan aerogel.

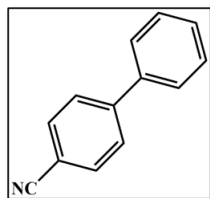
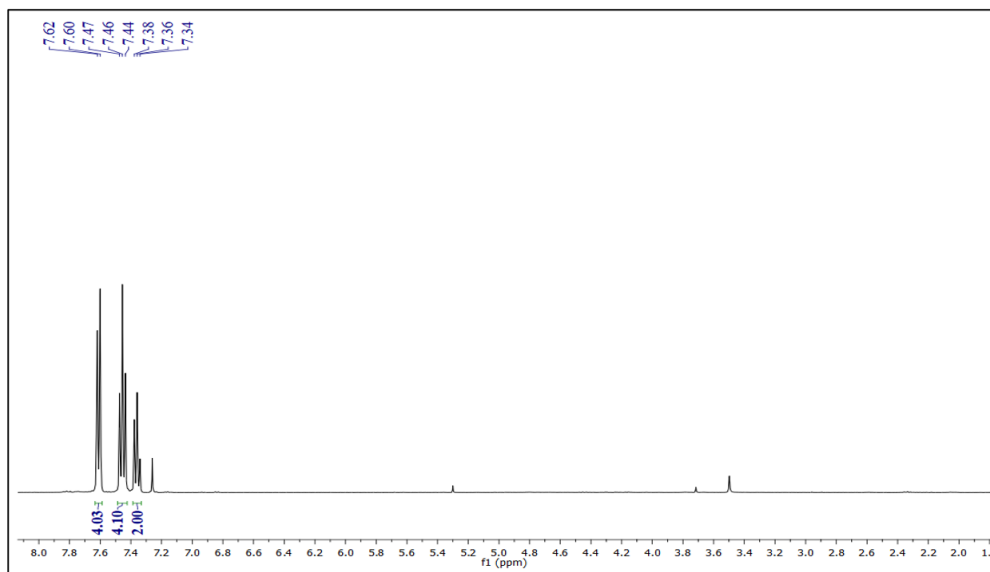


Appendix Figure 2.33. Infra-red (IR) spectroscopy of 1,4-butanediol diglycidyl ether (cyan), chitosan (95% degree of deacetylation) and HCP_chitosan aerogel (orange). As indicated in Fig. S32, the characteristic peaks appearing at 840 and 910 cm^{-1} corresponding to the epoxy group of 1,4-butanediol diglycidyl ether basically disappeared in the spectrum of HCP_chitosan-aerogel. However, the peaks at 2922 and 2866 cm^{-1} attributed to the methylene group along with the peak at 1102 cm^{-1} for C-O-C band were still seen in the spectrum of HCP_chitosan-aerogel. Additionally, the peak at 1602 cm^{-1} corresponding to the primary amine group on chitosan was found shifted to 1565 cm^{-1} , and the peak area was significantly attenuated in the spectrum for HCP_chitosan-aerogel. Hence, the FTIR analysis validated the successful conjugation of 1,4-butanediol diglycidyl ether to the amine group of chitosan. Also, the peak at 1652 cm^{-1} corresponds to the residual amide moiety of commercial chitosan.

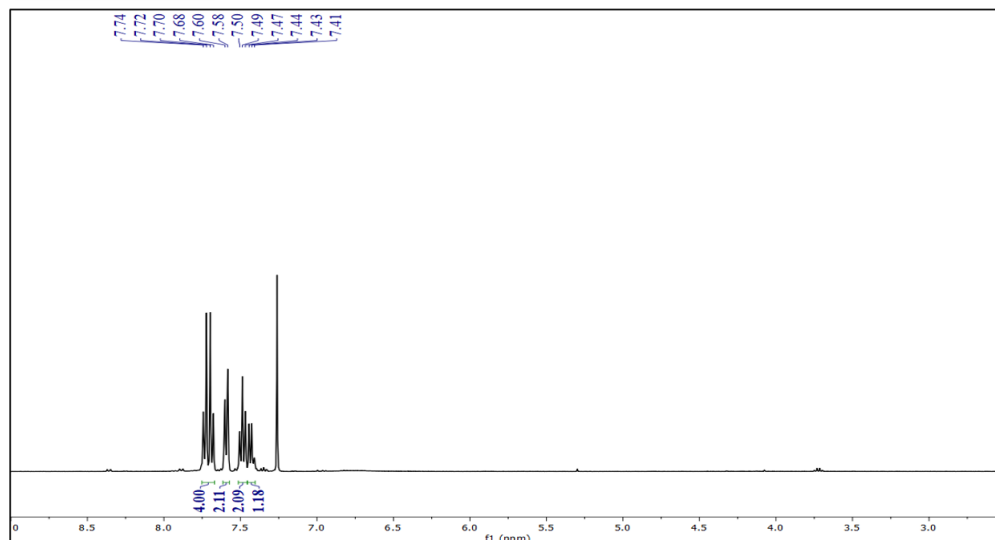
Appendix 2.37. NMR Spectra of compounds.

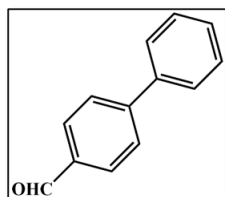
**Biphenyl (1a):**

^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.61 (d, $J = 8$ Hz, 4H, ArH), 7.46 (t, $J = 8$ Hz, 4H, ArH), 7.36 (t, $J = 8$ Hz, 2H, ArH).

**[1,1'-biphenyl]-4-carbonitrile (1b):**

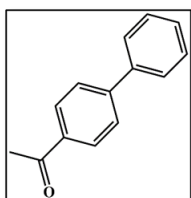
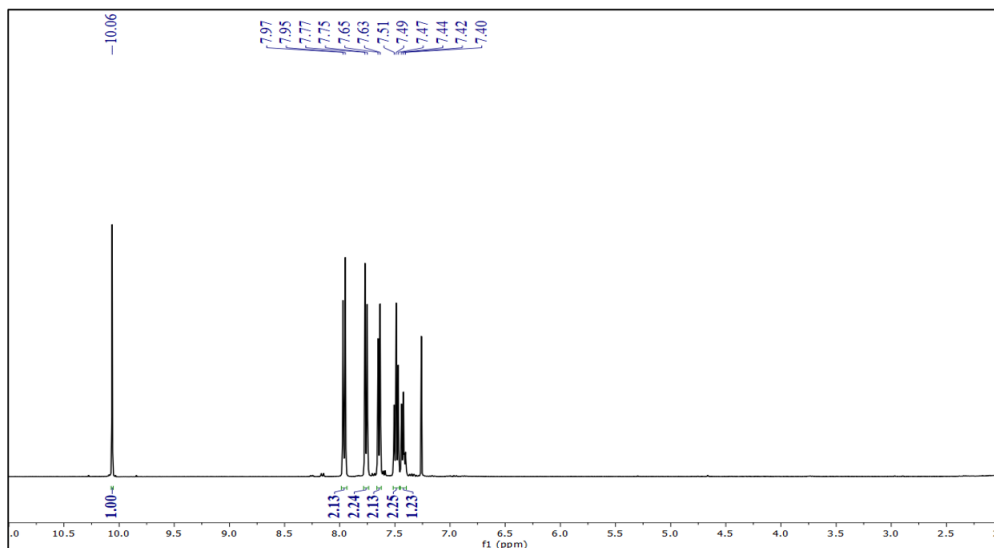
^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.71 (dd, $J = 8$ Hz, 4H, ArH), 7.59 (d, $J = 8$ Hz, 2H, ArH), 7.49 (t, $J = 8$ Hz, 2H, ArH), 7.43 (t, $J = 8$ Hz, 1H, ArH).





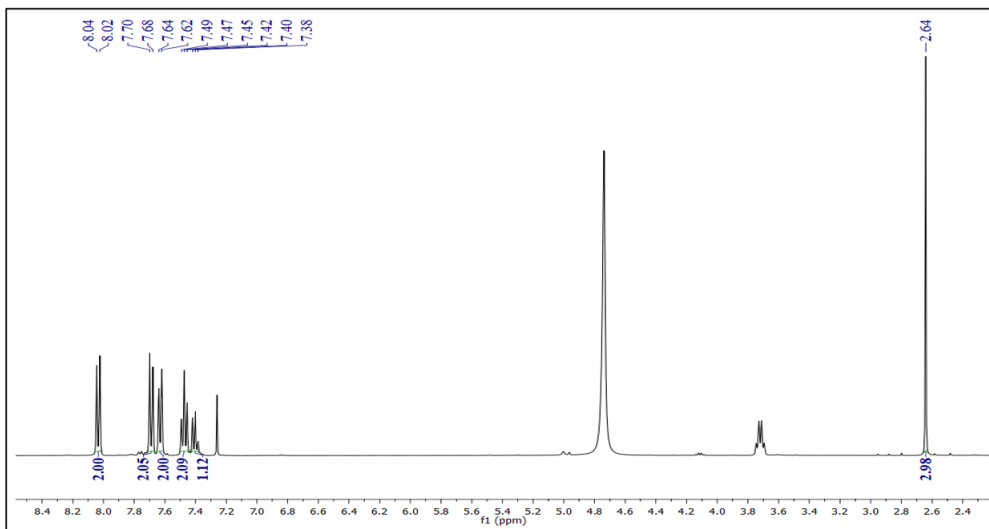
[1,1'-biphenyl]-4-carbaldehyde (1c):

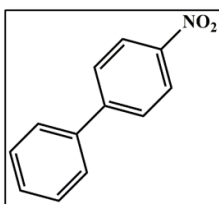
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.06 (s, 1H, ArH), 7.96 (d, $J=8$ Hz, 2H, ArH), 7.76 (d, $J=8$ Hz, 2H, ArH), 7.64 (d, $J=8$ Hz, 2H, ArH), 7.49 (t, $J=8$ Hz, 2H, ArH), 7.42 (t, $J=8$ Hz, 1H, ArH).



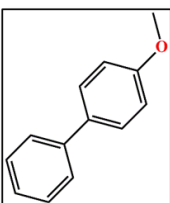
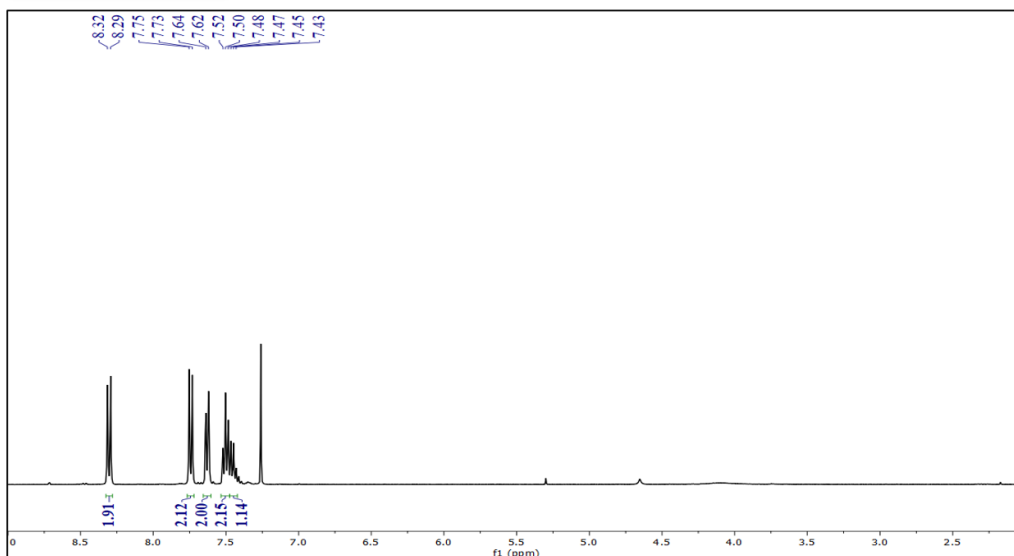
1-([1,1'-biphenyl]-4-yl)ethan-1-one (1d):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.03 (d, $J=8$ Hz, 2H, ArH), 7.69 (d, $J=8$ Hz, 2H, ArH), 7.63 (d, $J=8$ Hz, 2H, ArH), 7.47 (t, $J=8$ Hz, 2H, ArH), 7.40 (t, $J=8$ Hz, 1H, ArH), 2.64 (s, 3H, AliH).

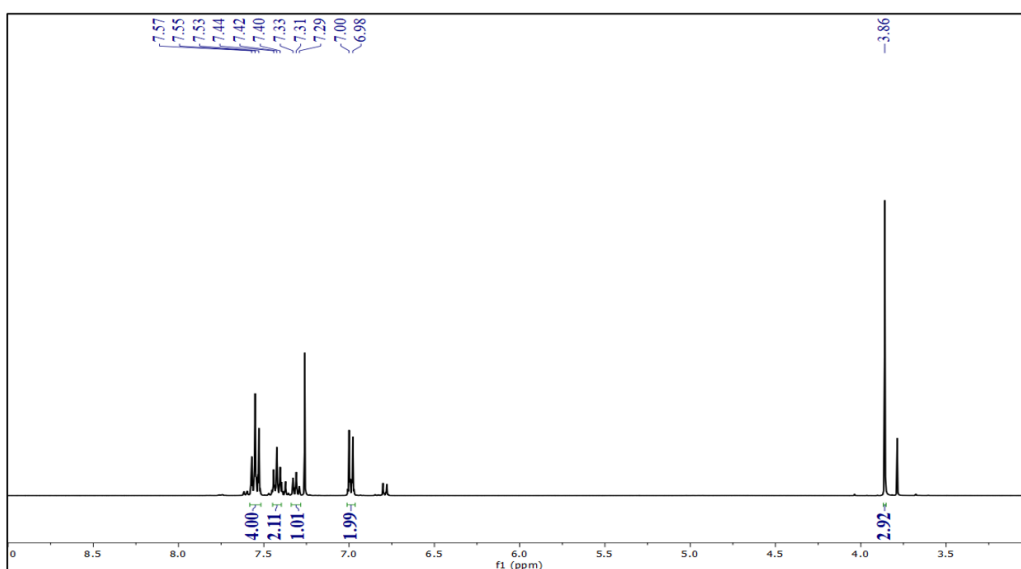


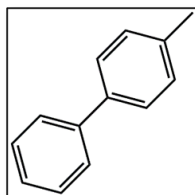

4-nitro-1,1'-biphenyl (1f):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.31 (d, $J = 8$ Hz, 2H, ArH), 7.74 (d, $J = 8$ Hz, 2H, ArH), 7.63 (d, $J = 8$ Hz, 2H, ArH), 7.50 (t, $J = 8$ Hz, 2H, ArH), 7.45 (t, $J = 8$ Hz, 1H, ArH).


4-methoxy-1,1'-biphenyl (1g):

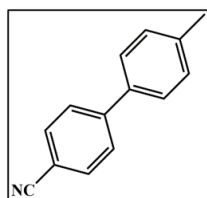
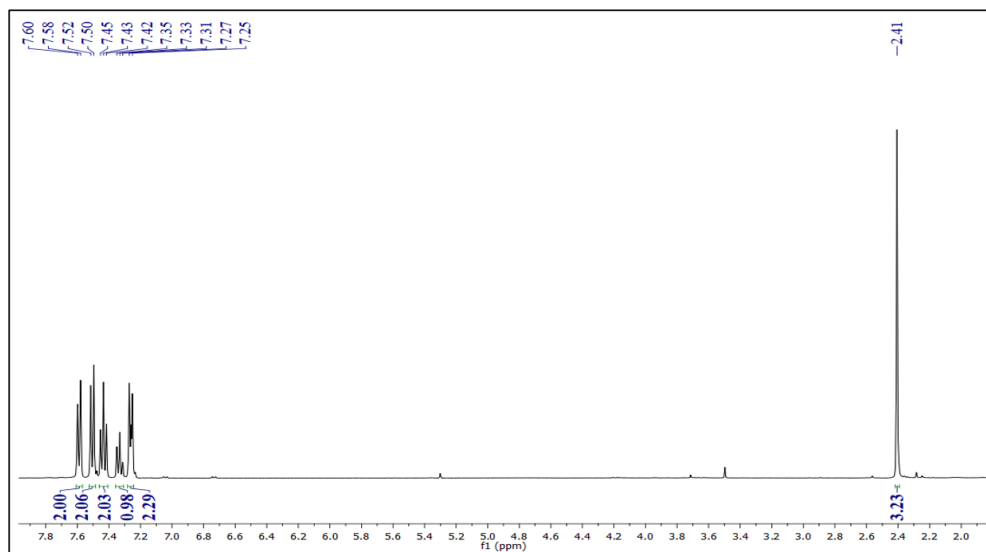
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.55 (t, $J = 8$ Hz, 4H, ArH), 7.42 (t, $J = 8$ Hz, 2H, ArH), 7.31 (t, $J = 8$ Hz, 1H, ArH), 6.99 (d, $J = 8$ Hz, 2H, ArH), 3.86 (s, 3H, ArH).





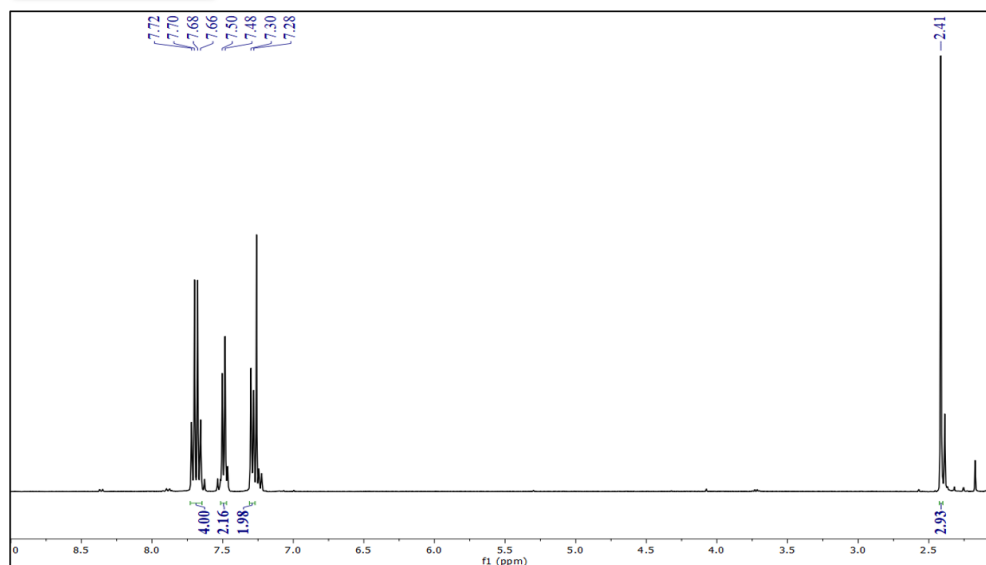
4-methyl-1,1'-biphenyl (2a):

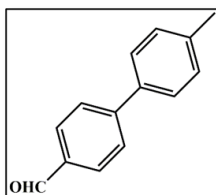
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.59 (d, $J = 8$ Hz, 2H, ArH), 7.51 (d, $J = 8$ Hz, 2H, ArH), 7.43 (t, $J = 8$ Hz, 2H, ArH), 7.33 (t, $J = 8$ Hz, 1H, ArH), 7.26 (d, $J = 8$ Hz, 2H, ArH), 2.41 (s, 3H, AliH).



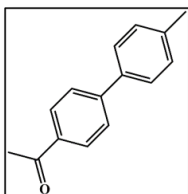
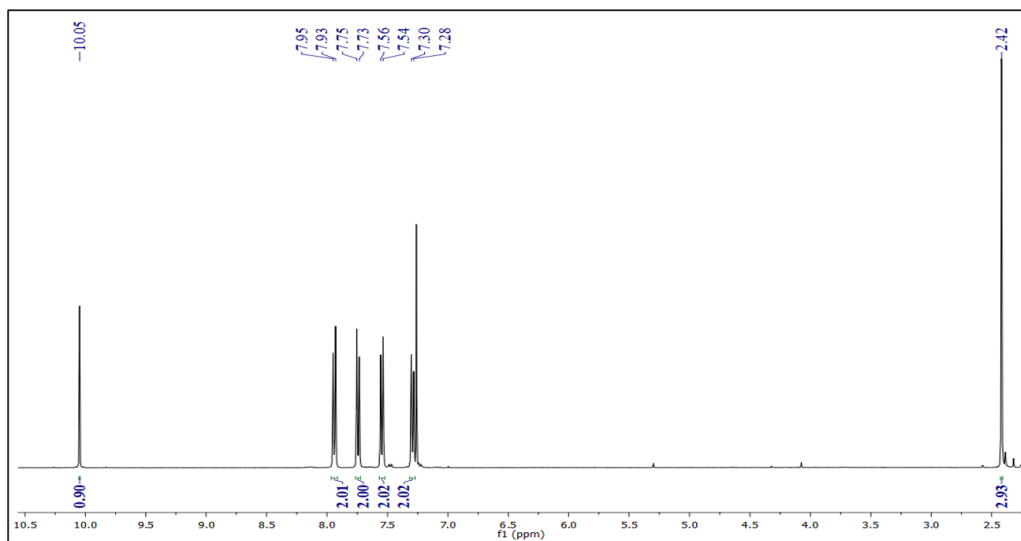
[1,1'-biphenyl]-4-carbonitrile (2b):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.69 (dd, $J = 8$ Hz, 4H, ArH), 7.49 (d, $J = 8$ Hz, 2H, ArH), 7.29 (d, $J = 8$ Hz, 2H, ArH), 2.41 (s, 3H, AliH).

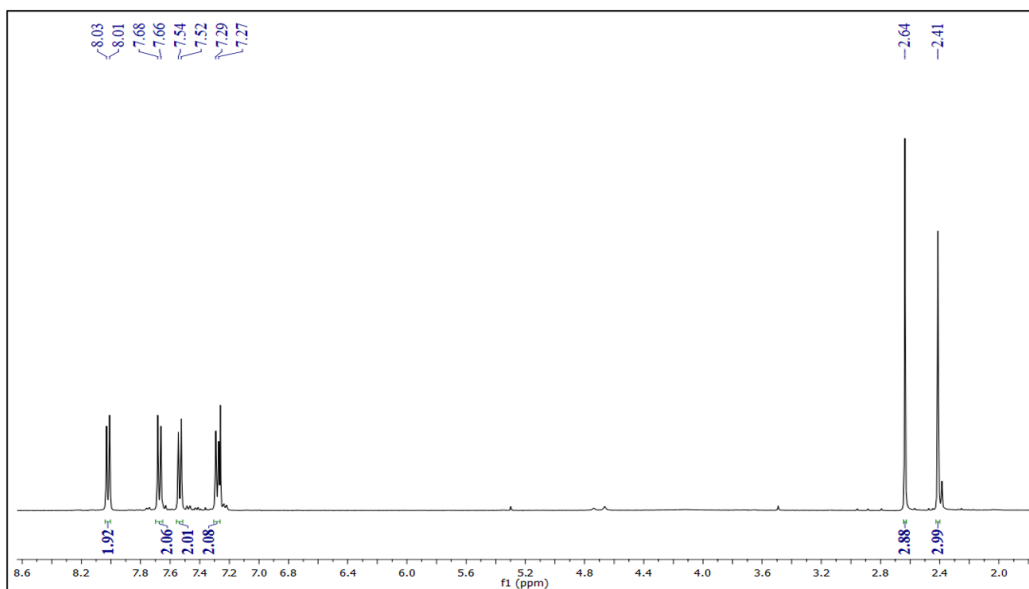


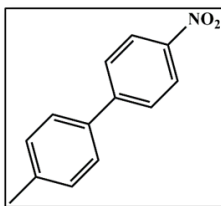

4'-methyl-[1,1'-biphenyl]-4-carbaldehyde (2c):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.05 (s, 1H, ArH), 7.94 (d, $J = 8$ Hz, 2H, ArH), 7.74 (d, $J = 8$ Hz, 2H, ArH), 7.55 (d, $J = 8$ Hz, 2H, ArH), 7.29 (t, $J = 8$ Hz, 2H, ArH), 2.42 (s, 3H, AliH).

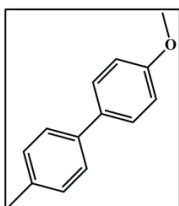
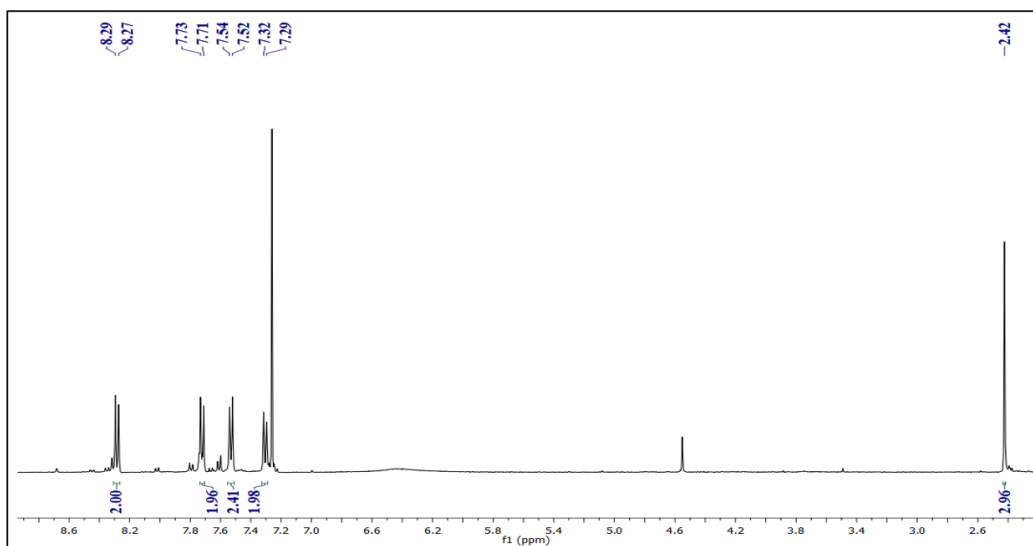

1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (2d):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.02 (d, $J = 8$ Hz, 2H, ArH), 7.67 (d, $J = 8$ Hz, 2H, ArH), 7.53 (d, $J = 8$ Hz, 2H, ArH), 7.28 (d, $J = 8$ Hz, 2H, ArH), 2.64 (s, 3H, AliH), 2.41 (s, 3H, AliH).

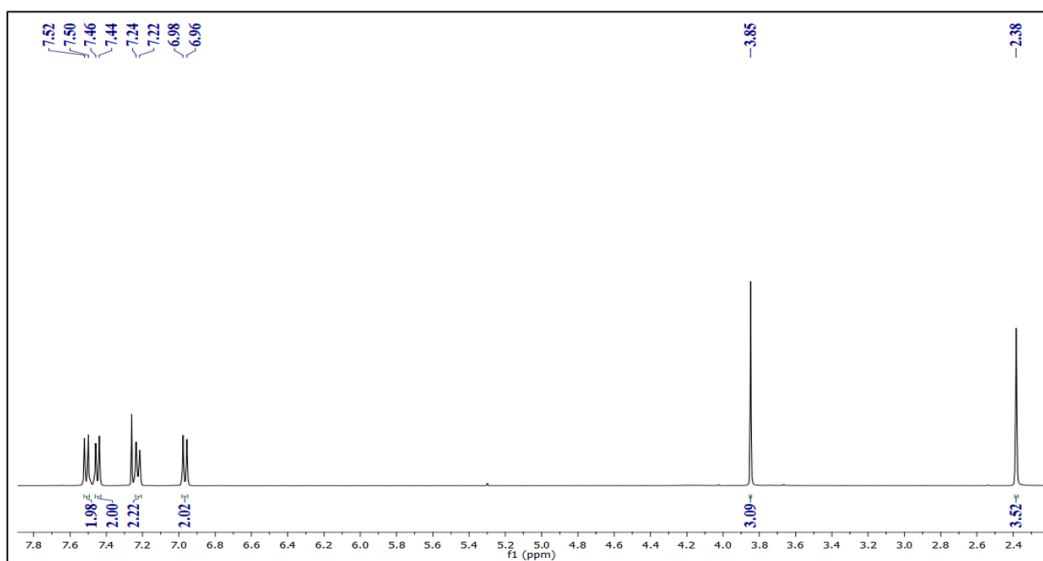


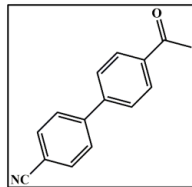
**4-nitro-1,1'-biphenyl (2f):**

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.28 (d, $J = 8$ Hz, 2H, ArH), 7.72 (d, $J = 8$ Hz, 2H, ArH), 7.53 (d, $J = 8$ Hz, 2H, ArH), 7.30 (d, $J = 8$ Hz, 2H, ArH), 2.42 (s, 3H, AliH).

**4-methoxy-4'-methyl-1,1'-biphenyl (2g):**

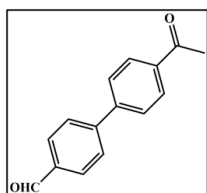
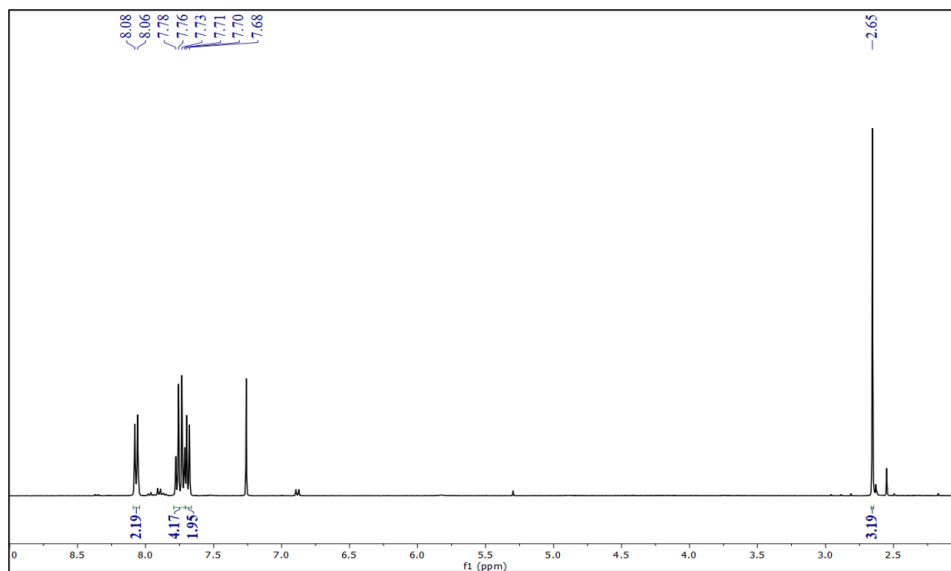
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.51 (d, $J = 8$ Hz, 2H, ArH), 7.45 (d, $J = 8$ Hz, 2H, ArH), 7.23 (d, $J = 8$ Hz, 2H, ArH), 6.97 (d, $J = 8$ Hz, 2H, ArH), 3.85 (s, 3H, AliH), 2.38 (s, 3H, AliH).





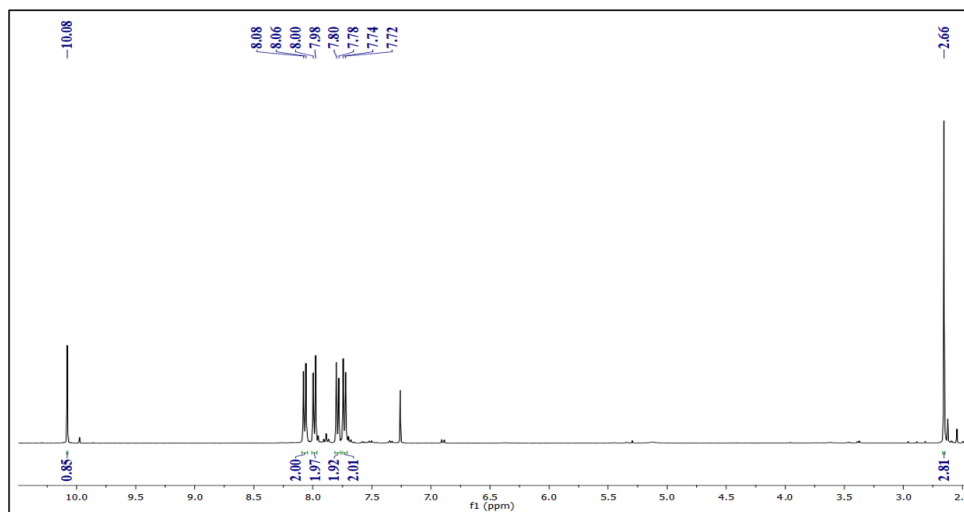
4'-acetyl-[1,1'-biphenyl]-4-carbonitrile (3b):

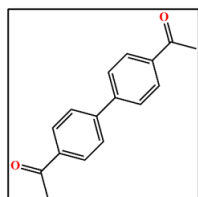
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.07 (d, $J = 8$ Hz, 2H, ArH), 7.75 (dd, $J = 8$ Hz, 4H, ArH), 7.69 (d, $J = 8$ Hz, 2H, ArH), 2.65 (s, 3H, AliH).



4'-acetyl-[1,1'-biphenyl]-4-carbaldehyde (3c):

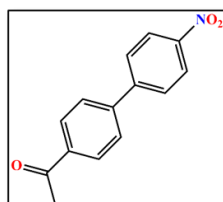
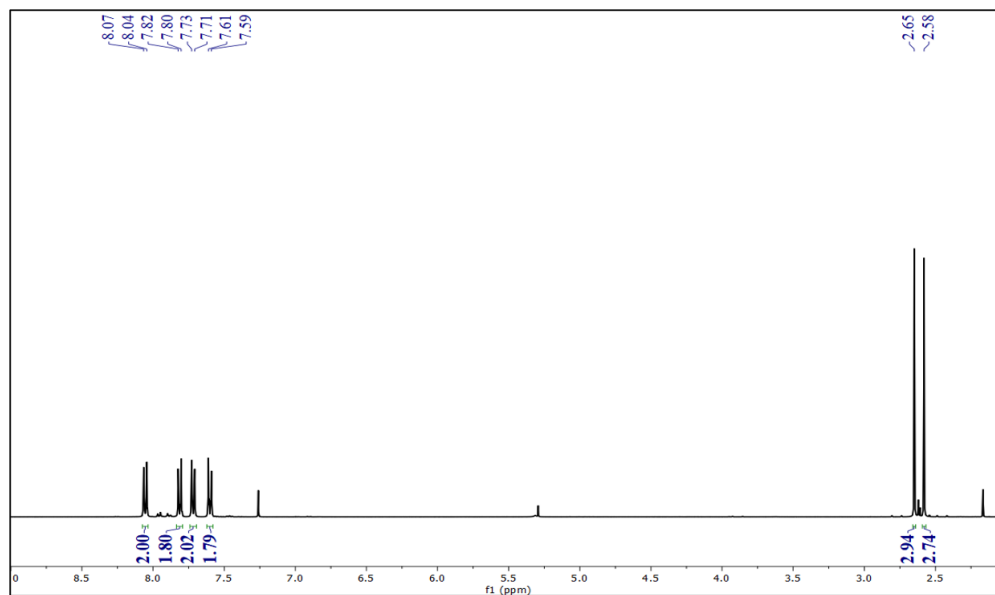
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.08 (s, 2H, ArH), 8.07 (d, $J = 8$ Hz, 2H, ArH), 7.99 (d, $J = 8$ Hz, 2H, ArH), 7.79 (d, $J = 8$ Hz, 2H, ArH), 7.73 (d, $J = 8$ Hz, 2H, ArH), 2.66 (s, 3H, AliH).





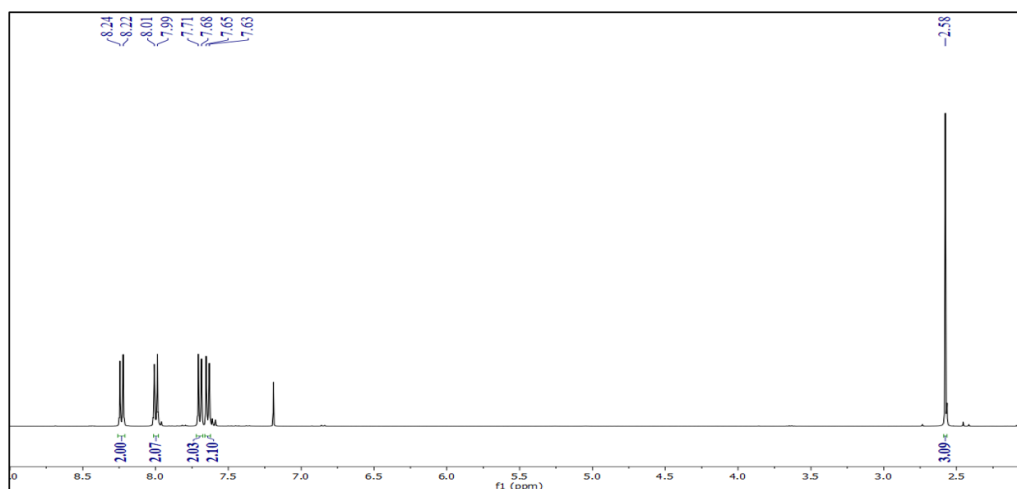
1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one) (3d):

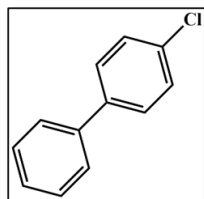
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.05 (d, $J = 8$ Hz, 2H, ArH), 7.81 (d, $J = 8$ Hz, 2H, ArH), 7.72 (d, $J = 8$ Hz, 2H, ArH), 7.60 (d, $J = 8$ Hz, 2H, ArH), 2.65 (s, 3H, AliH), 2.58 (s, 3H, AliH).



1-(4'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one (3e):

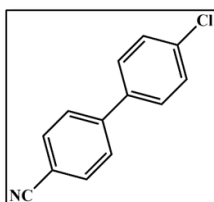
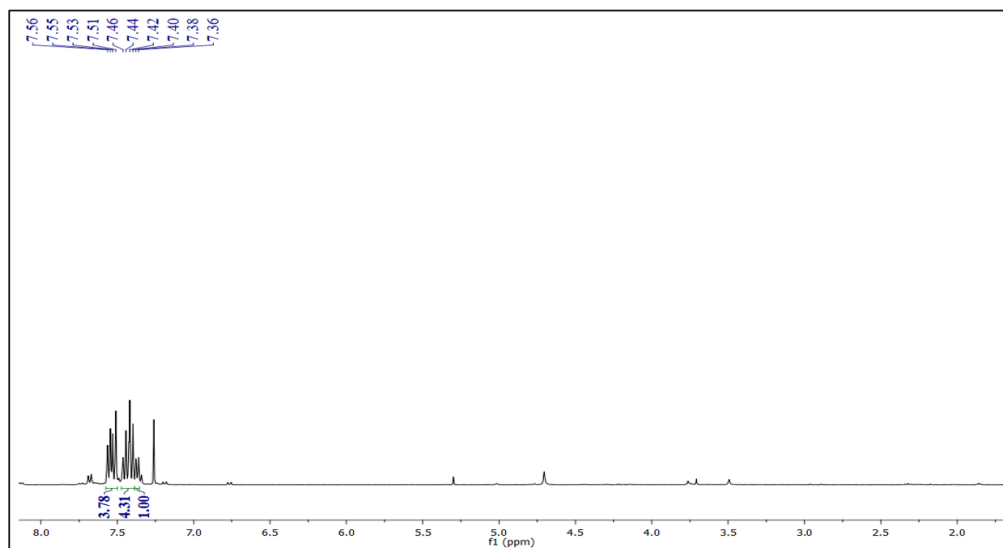
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.23 (d, $J = 8$ Hz, 2H, ArH), 8.00 (d, $J = 8$ Hz, 2H, ArH), 7.69 (d, $J = 8$ Hz, 2H, ArH), 7.64 (d, $J = 8$ Hz, 2H, ArH), 2.58 (s, 3H, AliH).





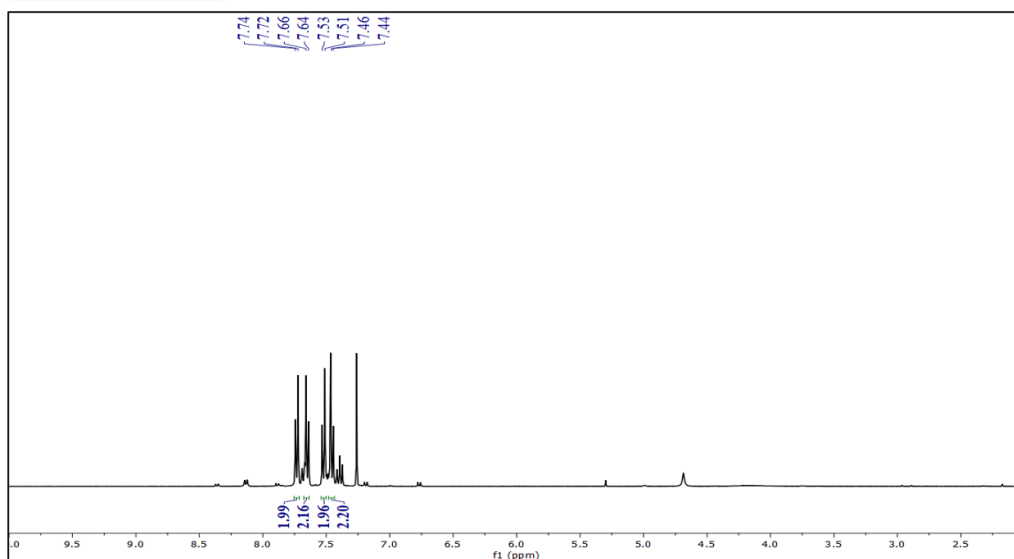
4-chloro-1,1'-biphenyl (4a):

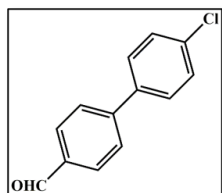
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.54 (m, $J = 8$ Hz, 4H, ArH), 7.43 (m, $J = 8$ Hz, 4H, ArH), 7.36 (t, $J = 8$ Hz, 1H, ArH).



4'-chloro-[1,1'-biphenyl]-4-carbonitrile (4b):

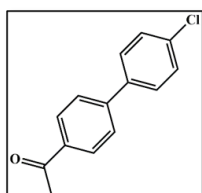
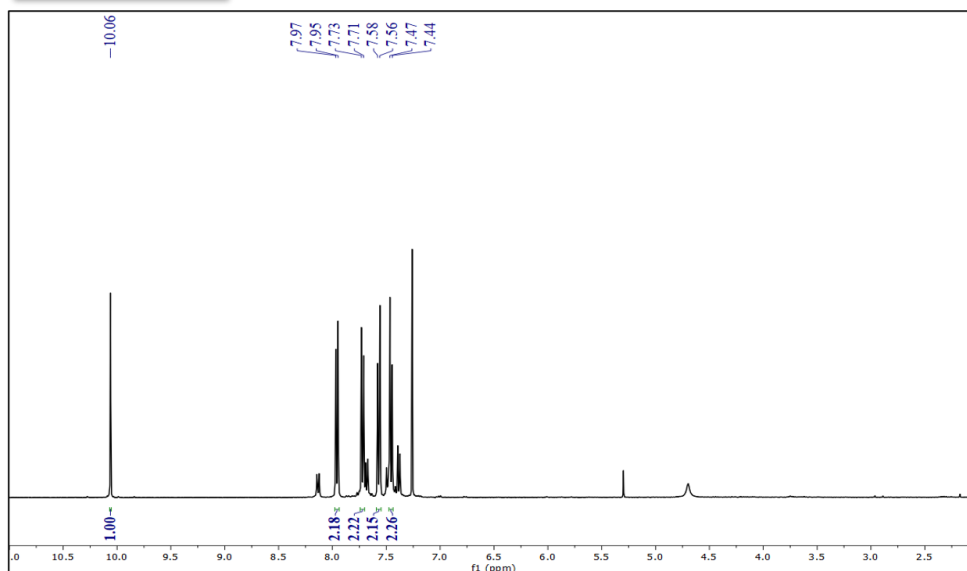
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.73 (d, $J = 8$ Hz, 2H, ArH), 7.65 (d, $J = 8$ Hz, 2H, ArH), 7.52 (d, $J = 8$ Hz, 2H, ArH), 7.45 (d, $J = 8$ Hz, 2H, ArH).





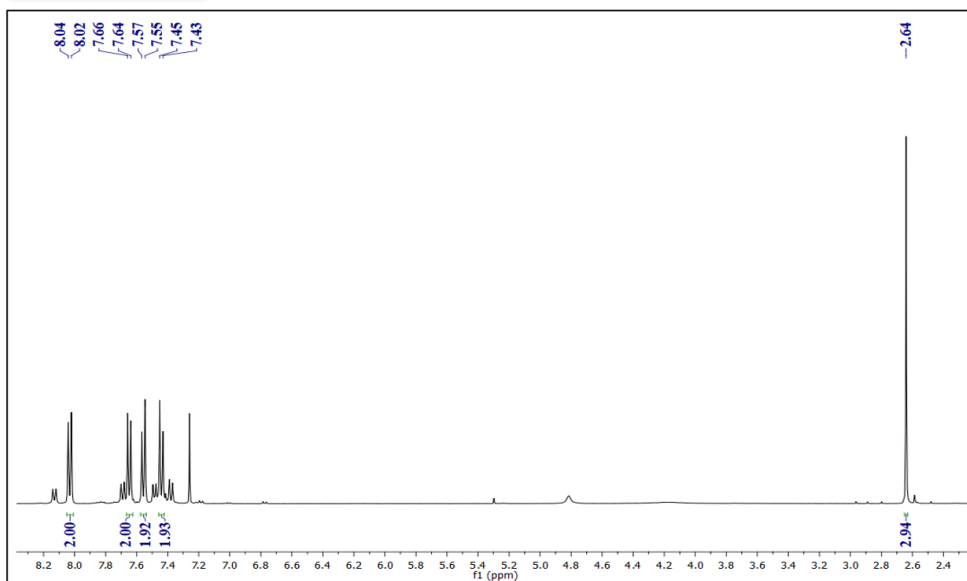
4'-chloro-[1,1'-biphenyl]-4-carbaldehyde (4c):

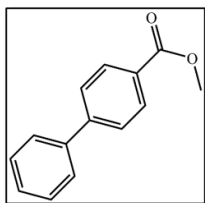
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.06 (s, 1H, ArH), 7.96 (d, $J=8$ Hz, 2H, ArH), 7.72 (d, $J=8$ Hz, 2H, ArH), 7.57 (d, $J=8$ Hz, 2H, ArH), 7.45 (d, $J=8$ Hz, 2H, ArH).



1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (4d):

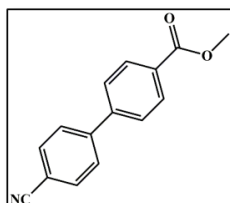
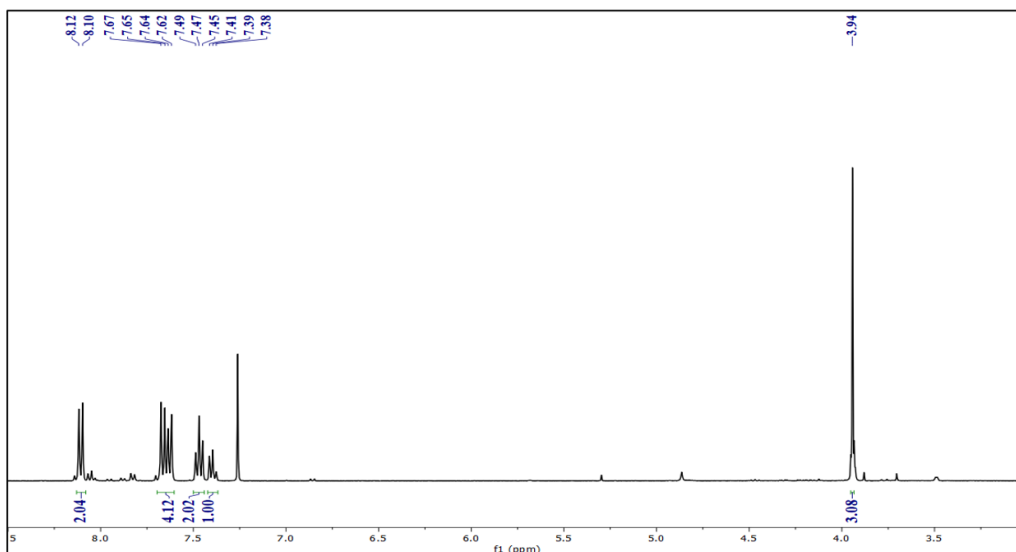
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.01 (d, $J=8$ Hz, 2H, ArH), 7.65 (d, $J=8$ Hz, 2H, ArH), 7.56 (d, $J=8$ Hz, 2H, ArH), 7.44 (d, $J=8$ Hz, 2H, ArH), 2.64 (s, 3H, ArH).





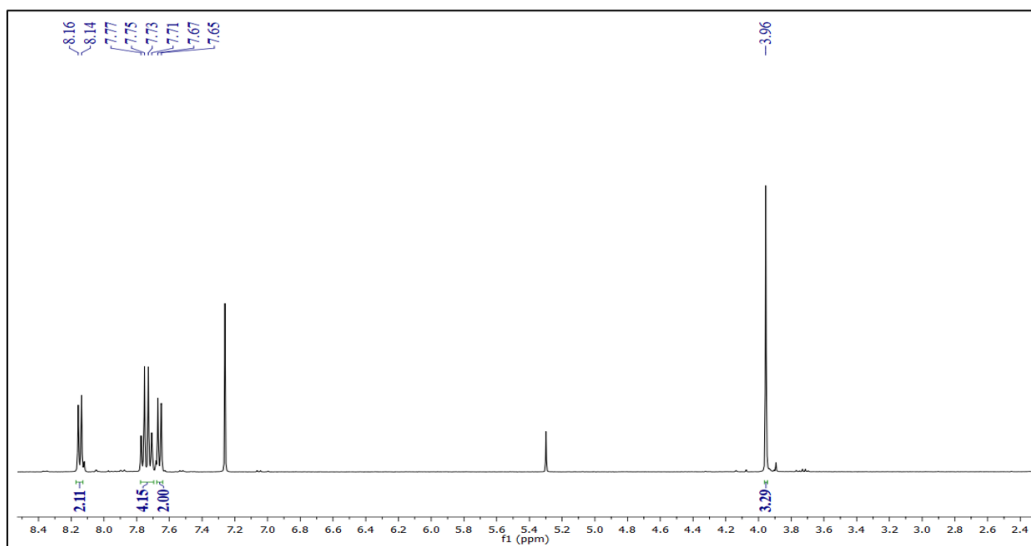
Methyl [1,1'-biphenyl]-4-carboxylate (5a):

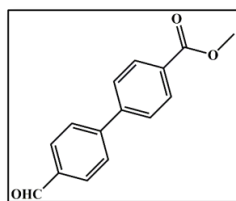
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.11 (d, $J = 8$ Hz, 2H, ArH), 7.65 (m, $J = 8$ Hz, 4H, ArH), 7.47 (t, $J = 8$ Hz, 2H, ArH), 7.39 (t, $J = 8$ Hz, 1H, ArH), 3.94 (s, 3H, AliH).



Methyl 4'-cyano-[1,1'-biphenyl]-4-carboxylate (5b):

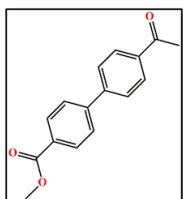
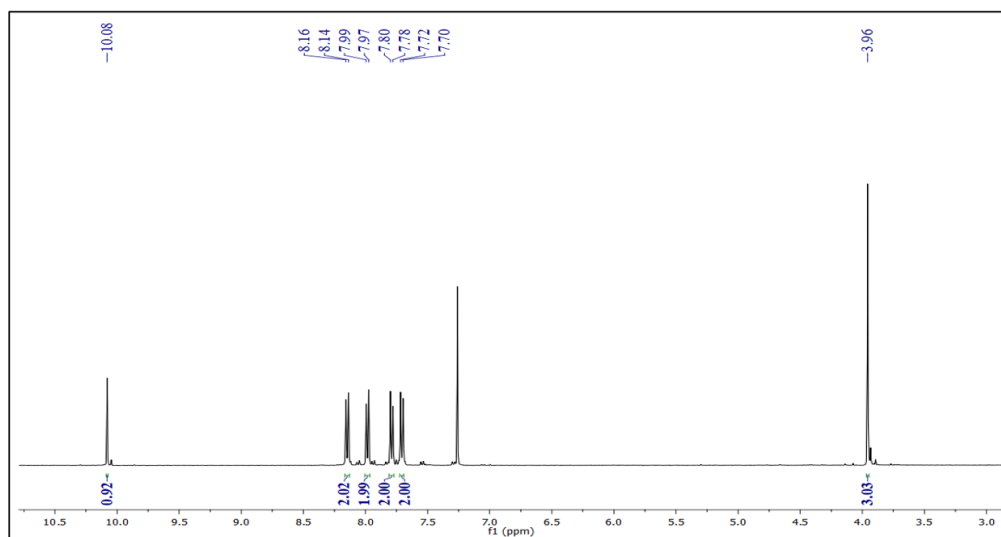
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.15 (d, $J = 8$ Hz, 2H, ArH), 7.74 (dd, $J = 8$ Hz, 4H, ArH), 7.66 (d, $J = 8$ Hz, 2H, ArH), 3.96 (s, 3H, AliH).





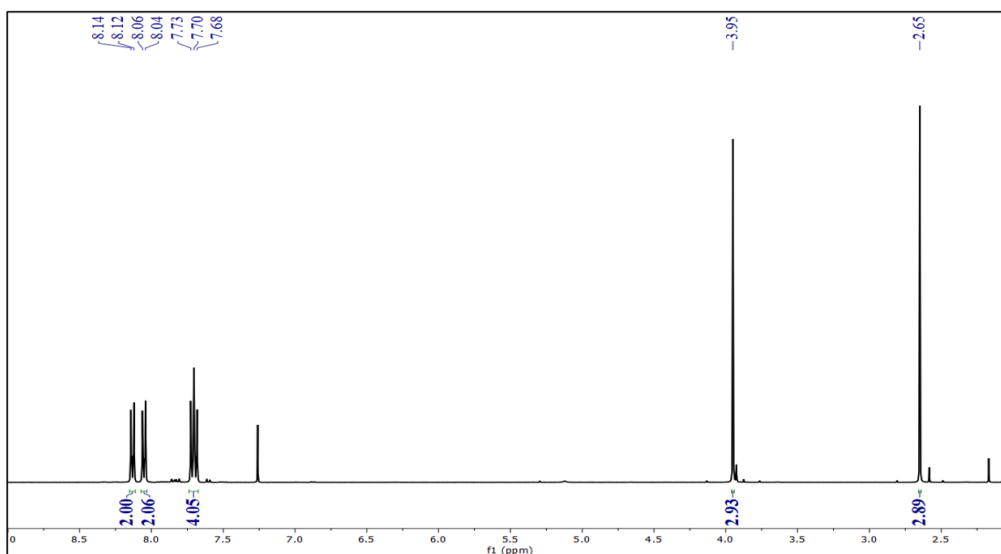
Methyl 4'-formyl-[1,1'-biphenyl]-4-carboxylate (5c):

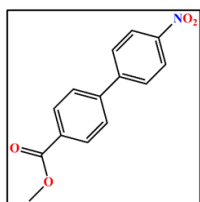
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.08 (s, 2H, ArH), 8.15 (d, $J = 8$ Hz, 2H, ArH), 7.96 (d, $J = 8$ Hz, 2H, ArH), 7.79 (d, $J = 8$ Hz, 2H, ArH), 7.71 (d, $J = 8$ Hz, 2H, ArH), 3.96 (s, 3H, AliH).



Methyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate (5d):

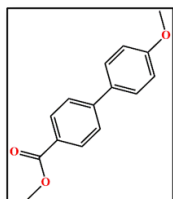
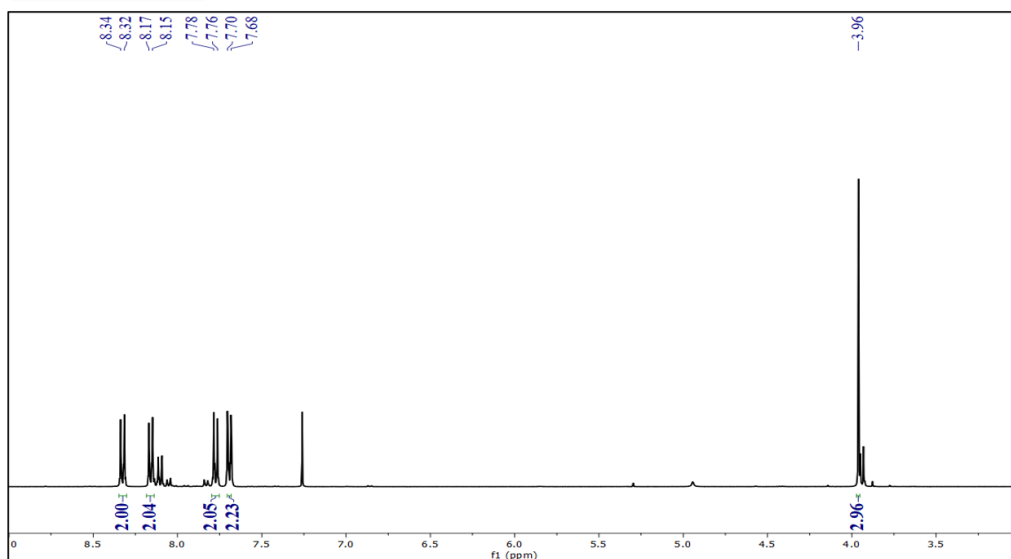
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.13 (d, $J = 8$ Hz, 2H, ArH), 8.05 (d, $J = 8$ Hz, 2H, ArH), 7.70 (t, $J = 8$ Hz, 4H, ArH), 3.95 (s, 3H, AliH), 2.65 (s, 3H, AliH).





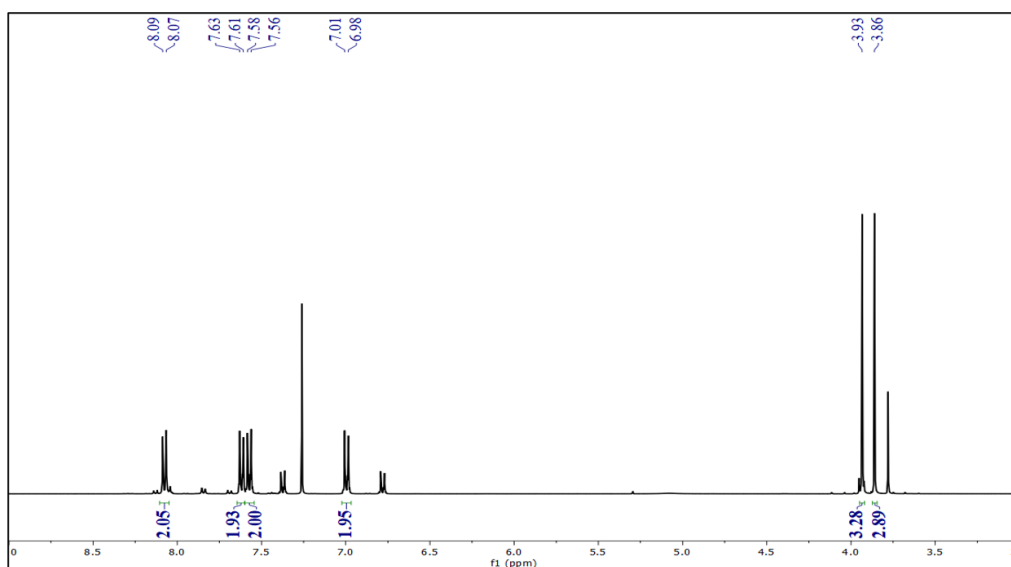
Methyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate (5f):

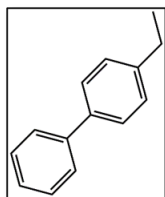
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.33 (d, $J = 8$ Hz, 2H, ArH), 8.16 (d, $J = 8$ Hz, 2H, ArH), 7.77 (d, $J = 8$ Hz, 2H, ArH), 7.69 (d, $J = 8$ Hz, 2H, ArH), 3.96 (s, 3H, AliH).



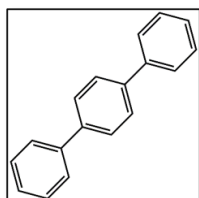
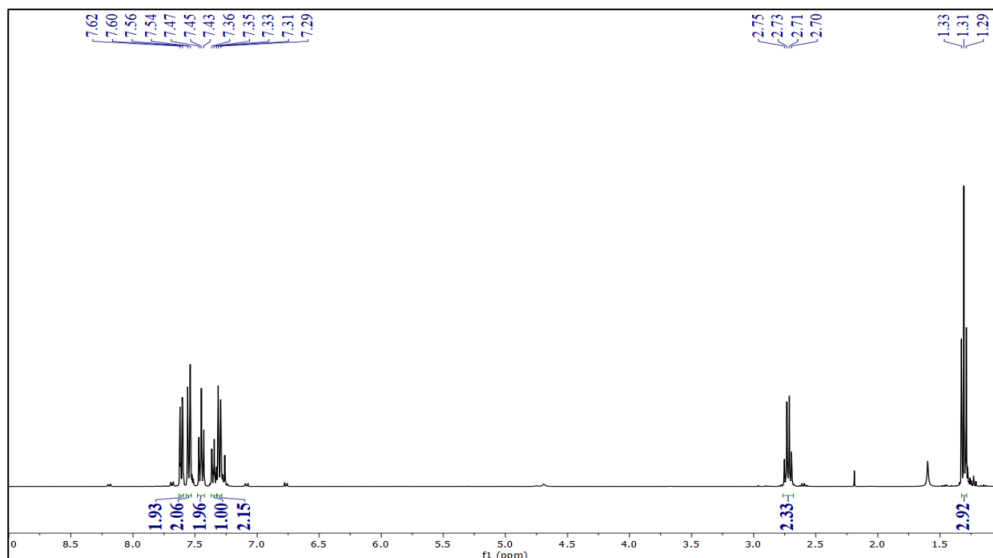
Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (5g):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.08 (d, $J = 8$ Hz, 2H, ArH), 7.62 (d, $J = 8$ Hz, 2H, ArH), 7.57 (d, $J = 8$ Hz, 2H, ArH), 6.99 (d, $J = 8$ Hz, 2H, ArH), 3.93 (s, 3H, AliH), 3.86 (s, 3H, AliH).

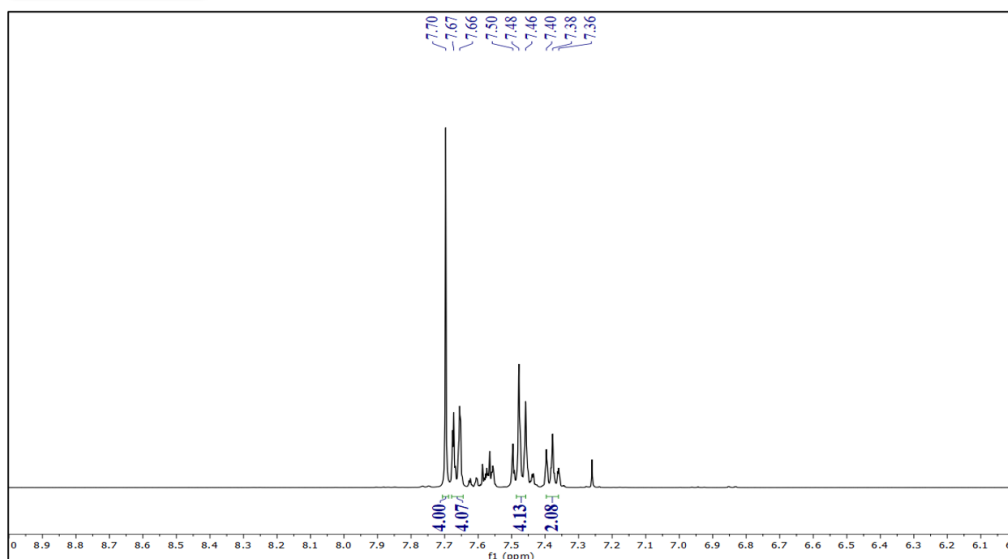


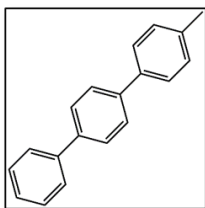

4-ethyl-1,1'-biphenyl (6a):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.61 (d, $J = 8$ Hz, 2H, ArH), 7.55 (d, $J = 8$ Hz, 2H, ArH), 7.45 (t, $J = 8$ Hz, 2H, ArH), 7.35 (t, $J = 8$ Hz, 1H, ArH), 7.30 (d, $J = 8$ Hz, 2H, ArH), 2.72 (q, 2H, AliH), 1.31 (t, 3H, AliH).

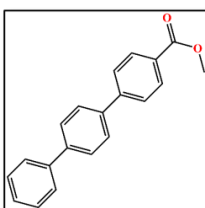
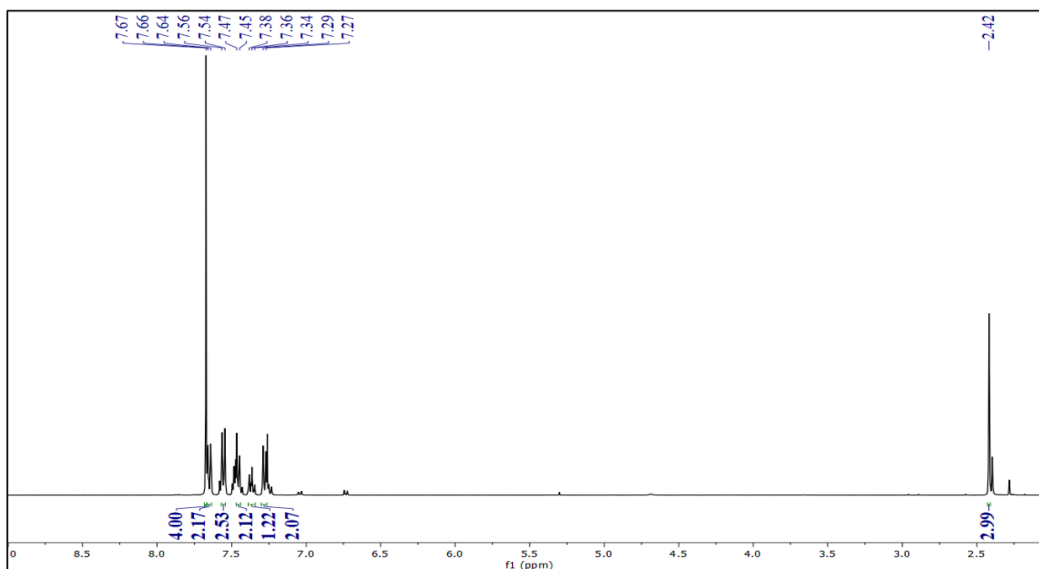

1,1':4',1''-terphenyl (7a):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.70 (s, 4H, ArH), 7.66 (d, $J = 8$ Hz, 4H, ArH), 7.48 (t, $J = 8$ Hz, 4H, ArH), 7.38 (t, $J = 8$ Hz, 2H, ArH).

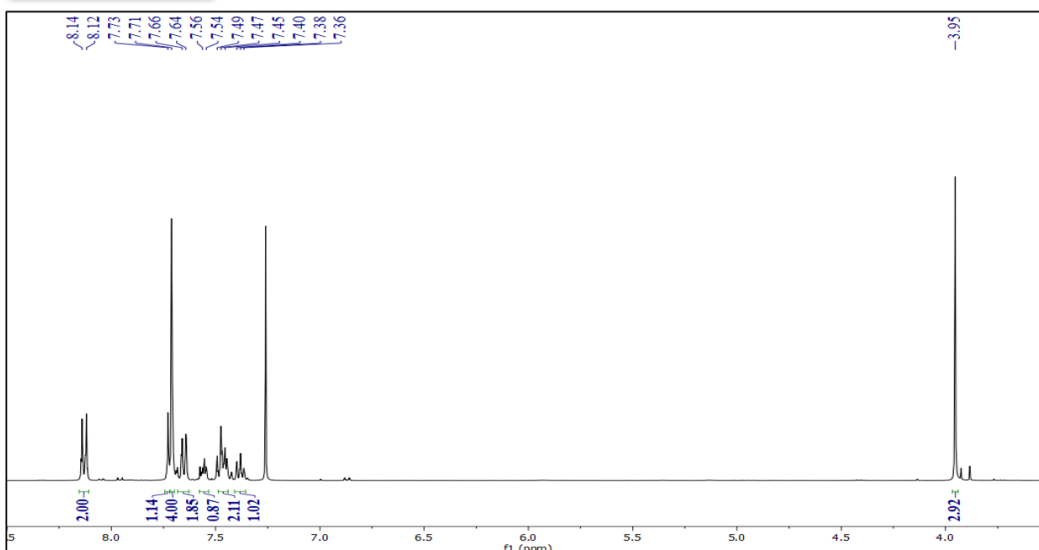


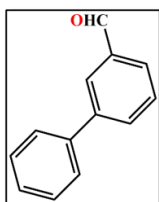

4-methyl-1,1':4',1''-terphenyl (7b):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.67 (s, 4H, ArH), 7.65 (d, $J=8$ Hz, 2H, ArH), 7.55 (d, $J=8$ Hz, 2H, ArH), 7.46 (d, $J=8$ Hz, 2H, ArH), 7.36 (t, $J=8$ Hz, 1H, ArH), 7.28 (d, $J=8$ Hz, 2H, ArH), 2.42 (s, 3H, AliH).


1-([1,1':4',1''-terphenyl]-4-yl)propan-1-one (7c):

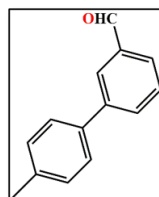
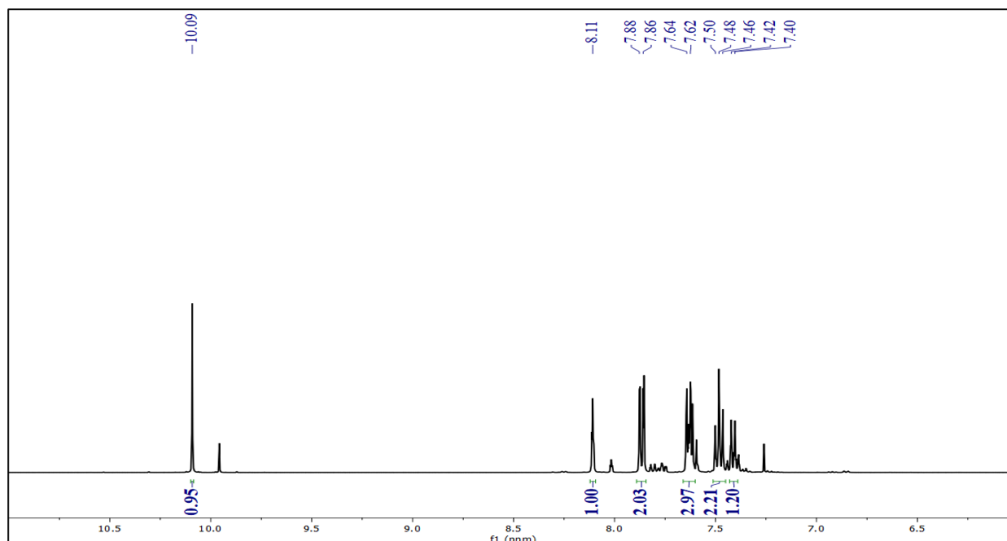
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.13 (d, $J=8$ Hz, 2H, ArH), 7.73 (s, 1H, ArH), 7.71 (s, 4H, ArH), 7.63 (d, $J=8$ Hz, 2H, ArH), 7.54 (t, $J=8$ Hz, 1H, ArH), 7.46 (m, $J=8$ Hz, 2H, ArH), 7.38 (t, $J=8$ Hz, 1H, ArH), 3.95 (s, 3H, AliH).





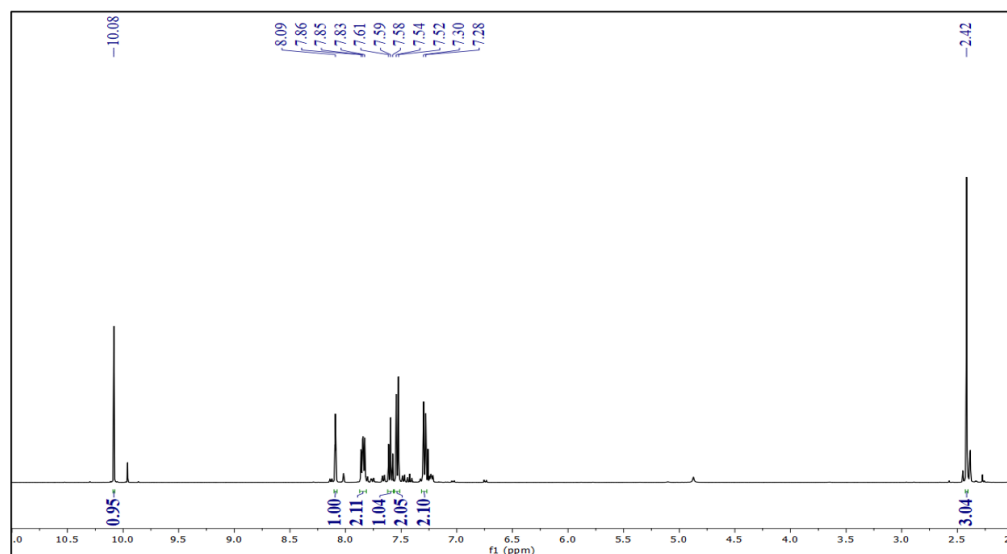
[1,1'-biphenyl]-3-carbaldehyde (8a):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.09 (s, 1H, ArH), 8.11 (s, $J = 8$ Hz, 1H, ArH), 7.87 (d, $J = 8$ Hz, 2H, ArH), 7.63 (d, $J = 8$ Hz, 3H, ArH), 7.48 (t, $J = 8$ Hz, 2H, ArH), 7.41 (d, $J = 8$ Hz, 1H, ArH).



4'-methyl-[1,1'-biphenyl]-3-carbaldehyde (8b):

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 10.08 (s, 1H, ArH), 8.09 (s, $J = 8$ Hz, 1H, ArH), 7.85 (t, $J = 8$ Hz, 2H, ArH), 7.59 (t, $J = 8$ Hz, 1H, ArH), 7.53 (d, $J = 8$ Hz, 2H, ArH), 7.29 (d, $J = 8$ Hz, 2H, ArH), 2.42 (s, 3H, ArH).



Appendix Table 2.1. Porosity parameters of 120-Cl, 120-MI, 120-EI, 120-MI@Pd NHC & 120-EI@Pd NHC.

	S_{BET} (m²g⁻¹)	Pore volume (cm³g⁻¹)	Pore width (nm)
120-Cl	1044	0.98	0.89
120-MI	867	0.83	0.88
120-EI	814	0.78	0.87
120-MI@NHC Pd	631	0.53	1.04
120-EI@NHC Pd	620	0.53	1.03
120-EI@NHC Pd after 10 Catalytic cycles	576	0.48	0.92

Appendix Table 2.2. Optimization Table for 120-EI@NHC Pd catalyzed Suzuki-Miyaura Coupling (SMC) reaction.

Entry	Catalyst	Solvent	Base	Temp. (°C)	Time	Yield ^b
1.	120-EI@Pd NHC	EtOH	No Base	80	2h	0
2.	120-EI@Pd NHC	EtOH	K ₂ CO ₃ (1.5 eqv)	80	2h	92
3.	120-EI@Pd NHC	EtOH-H ₂ O (4:1)	K ₂ CO ₃ (1.5 eqv)	80	2h	90
4.	120-EI@Pd NHC	EtOH-H ₂ O (1:1)	K ₂ CO ₃ (1.5 eqv)	80	2h	83
5.	120-EI@Pd NHC	EtOH-H ₂ O (1:1)	K ₃ PO ₄ (1.5 eqv)	80	2h	>99
6.	120-EI@Pd NHC	EtOH-H ₂ O (1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	99
7.	120-EI@Pd NHC	H ₂ O	K ₃ PO ₄ (1.5 eqv)	RT	1h	88
8.	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	TEA (1.5 eqv.)	RT	1h	78
9.	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	K ₂ CO ₃ (1.5 eqv)	RT	1h	98
10.	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	NaOH (1.5 eqv)	RT	1h	78
11.	120-MI@Pd NHC	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	94
12.	120-EI@Pd NHC	ACN-H ₂ O (1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	18
13.	120-EI@Pd NHC	DMF-H ₂ O (1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	18
14.	No Catalyst	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	0
15 ^c .	Supernatant Liquid	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	80	6h	0
16 ^d .	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	93
17 ^e .	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	RT	6h	61
18 ^f .	120-EI@Pd NHC	EtOH-H ₂ O(1:1)	K ₃ PO ₄ (1.5 eqv)	RT	1h	>99

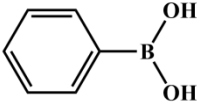
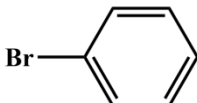
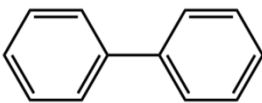
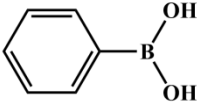
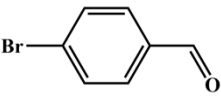
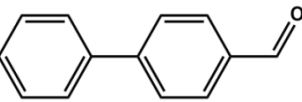
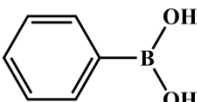
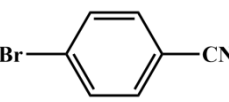
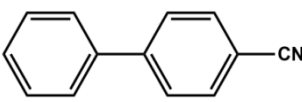
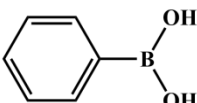
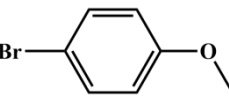
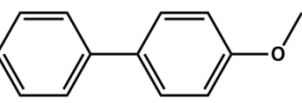
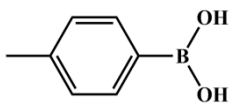
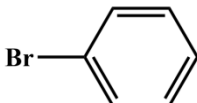
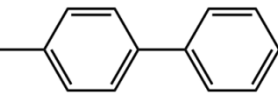
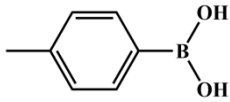
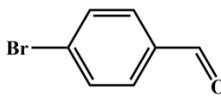
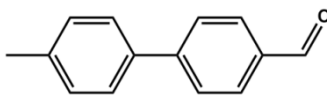
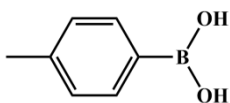
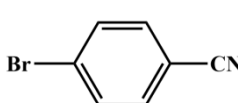
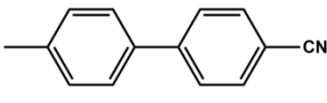
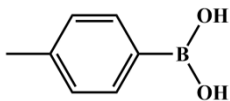
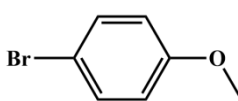
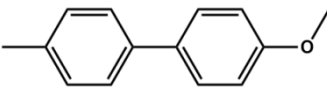
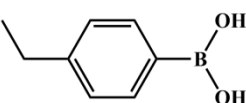
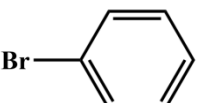
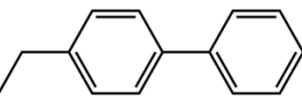
^a Reaction conditions (Unless otherwise mentioned): a solution of 1a (0.4 mM), p-tolylboronic acid (0.45 mM), Base (0.6 mM), and (5 mg, 0.002 mmol of Pd) catalyst (for entry 13, no catalyst was added) in 4 mL of solvent and was stirred at the indicated temperature for noted time duration. ^b Yield determined from ¹H-NMR. ^c 5 mg of 120-EI@Pd NHC and K₃PO₄ (0.6 mM) were stirred in 4 mL (1:1) EtOH-H₂O at 80 °C for 2h, after centrifugation 0.4 mM 1a and 0.45 mM p-tolylboronic acid and 0.6 mM K₃PO₄ was added and the resulting mixture was stirred at 80 °C for 6h. ^d The reaction scale was 4 mM of 1a. ^e Chlorobenzene (0.4 mM) was used as the aryl halide. ^f Iodobenzene (0.4 mM) was used as the aryl halide

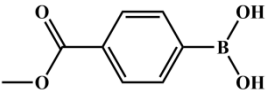
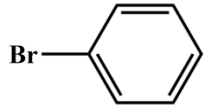
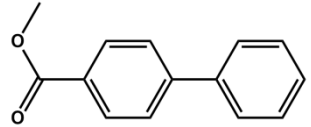
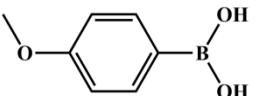
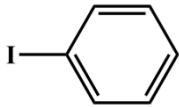
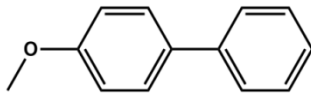
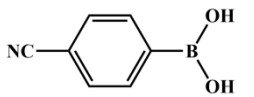
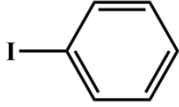
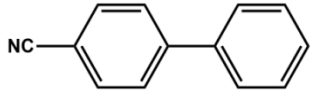
Appendix Table 2.3. Comparison with previously reported other porous materials Pd

Immobilized catalysts.

Catalyst	Pd (wt%)	Catalyst amount (mol%)	Reaction condition	Duration (h)	TOF (h ⁻¹)	Reference
120-EI@Pd NHC	4.41	0.04	RT, EtOH: H₂O (1:1, v/v)	0.5	4970	This Work
HCPs-bipy-Pd-I	1.21	0.23	80 °C, EtOH	1	392	74
SMPIL-Pd	0.52	0.08	80 °C, EtOH: H ₂ O (3:1, v/v)	10	121	3
PdII/UOF-1	16.87	0.05	60 °C, H ₂ O	3	660	4
Pd/PECIm	11.3	0.5	60 °C, iPrOH/H ₂ O	0.5	380	5
Pd@Polyurea	2.35	0.3	60 °C, H ₂ O	1	334	6
Pd@Polyurethane	2.57	0.3	60 °C, H ₂ O	1	330	6
Pd@Polyimine	2.29	0.3	60 °C, H ₂ O	1	327	6
Pd@Polyimide	1.34	0.3	60 °C, H ₂ O	1	334	6
Pd@Polythiourea	0.72	0.3	60 °C, H ₂ O	1	317	6
Pd@Phen-COF	4.4	0.027	Rt, iPrOH-H ₂ O	16	216	7
Pd/CPP	2.94	0.55	RT, EtOH: H ₂ O (3:2, v/v)	1	1070	8
Pd/P6	0.16	0.003	Blue light, Methanol:H ₂ O (3:2, v/v)	12.5	527	9
Pd@DTE	1.91	0.1	50 °C, EtOH: H ₂ O (1:1, v/v)	1	1000	10
Pd@NH ₂ -MPRN-3	0.82	0.5	80 °C, EtOH: H ₂ O (2:1, v/v)	2	96	11
Pd/H ₂ P-Bph-COF	12.87	0.5	110 °C, Toluene	1.5	130	12
UiO-67-3-PI-Pd	2.87	0.054	80 °C, EtOH: H ₂ O (4:1, v/v)	1.5	1235	13
Poly-NHC-2-Pd ²⁺	0.61	0.57	80 °C, EtOH: H ₂ O (3:2, v/v)	0.5	3018	14
Pd-CIN-1	0.60	0.01	80 °C, DMF	0.5	1470	15
Pd(0)/MCoS-1	1.0	0.18	70 °C, H ₂ O	6	91	16
PPI-1-NPy-Pd	1.76	0.8	100 °C, H ₂ O	5	57	17
PPI-2-NPy-Pd	3.42	0.5	100 °C, H ₂ O	7	55	17
Pd NPs at NHC at ZIF-8	0.9	0.08	90 °C, EtOH: H ₂ O (1:1, v/v)	2.5	495	18
P2	14.36	0.3	RT, EtOH: H ₂ O (1:1, v/v)	3	110	19
Pd-MPTAT-1	5.16	0.8	85 °C, DMF: H ₂ O (1:5, v/v)	10	107	20
TPU-Pd	10.4	0.48	RT, Ethanol	3	69	21

Appendix Table 2.4. TOF values obtained for SMC reactions with 120-EI@Pd NHC.

Boronic acid	Aryl halide	Product	TOF (h ⁻¹)
			4550
			4965
			4970
			4960
			4200
			4980
			4970
			3800
			3500

			4000
			4620
			4765

2.6 References

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Chapter 3

A Bi-catalytic site-isolated Porous Polymer Featuring Incompatible Lewis pairs for Antagonistic Cascade Catalysis in water

3.1 Introduction

Cascade catalytic reactions ($A \rightarrow B \rightarrow C \dots$) have emerged as an eloquent and efficacious technique to achieve one-pot multi-step organic transformations. Lately, cascade catalysis have commanded sizeable research attention on account of its simplified synthetic route bypassing costly and time intensive isolation as well as purification of reaction intermediates. Additionally, cascade reactions provide an edge with reduced waste generation, overall shortened reaction and decreased operation cost.^[1-4] Having said that, progress in one-pot tandem catalysis is thwarted by difficulties in mainly two aspects. Firstly, the rational design of catalyst compatible with one-pot tandem modus operandi is arduous, particularly those comprising successive organic transformations demanding synergistic catalytically active sites bearing antagonistic properties without mutual intrusion, i.e, acidic sites in step 1 ($A \rightarrow B$) and basic sites in step 2 ($B \rightarrow C$) such as deacetalization-Henry reaction, deacetalization-Aldol reaction, deacetalization-Knoevenagel condensation reaction etc.^[5-8] Secondly, tethering antagonistic sites necessitate rigid heterogeneous nanoarchitecture, core-shell type or yolk-shell nanomaterials as prerequisite but often prove suboptimal due to limited active site accessibility.^[9-13] However, nature has found its unique way to mitigate this problem via compartmentalization, i.e, spatial isolation of catalysts in the nano-terrain of organelles prevailing in living cells. This spatial partitioning inhibit cross-reactions in catalysts (as well as substrates) allowing them to engage in specific order of reaction steps leading to the desired product of the catalytic reaction.^[14] Taking inspiration from this catalyst site-isolation existing in nature, researchers around the globe have tried to revamp catalyst design by separately storing catalysts in distinct repositories^[15] that include linear polymers^[16], polymeric nanostructures (e.g. micelles^[17], polymersomes^[18-19], hydrogels^[20], bottlebrushes^[21], pickering emulsions^[22-23], graphene oxide^[24], silica particles (yolk-shell^[25], double shell^[26], mesoporous silica^[27-28]). One of the initial reports of combining two star polymers containing both acid and base catalyst as an elegant approach to drive one-pot cascade deacetalization-Henry reaction in DMF.^[29] On the other hand, diminishing the reactants diffusion path from one catalytic centre to the adjacent one and thus, likely lowering the reaction time, more research attention were directed in combining dual catalysts in the same material residing in few nanometer of interspace.^[30-32] It should be emphasized that although some reports have achieved to successfully combine antagonistic acid-base catalytic sites in a single material to showcase cascade one pot catalysis, there still remain pitfalls toward practical application. In particular, complicated and tedious synthetic routes that demand protection and deprotection methodologies to avoid acid-base neutralization as well as usage of particular pore-forming agents to render easy mass transfer of reactants.^[33] Consequently, these factors surely reduce efficiency of the reaction and increase the cost. Other catalyst supports, e.g., metal organic frameworks (MOFs), graphene oxide, silica are difficult for on demand post-synthesis functionalization owing to their bulk rigidity as well as lack of

suitable silane precursors. Additionally, mesoporous silica is unstable in strong alkaline medium and most of the MOFs decompose in acidic conditions.^[34] Hence, it is imperative to explore and develop potent heterogeneous bifunctional catalysts showcasing efficient activity and robustness albeit include simple synthesis and facile post-structural functionalization to harness cooperative catalysis.

In comparison to inorganic materials, porous organic polymers (POPs) have emerged as an intriguing class of amorphous polymers bearing exceptional physiochemical stability and large surface areas. Additionally, POPs present leverage in diversity of chemical composition, desired functionality, ease of post-synthesis engineering as well as control over pore size and volume. Owing to these properties, they have established their utility in varied applications such as gas storage & separation^[35], environmental remediation^[36-37], heterogeneous catalysis^[38-39] etc. In heterogeneous catalysis, POPs feature advantages such as: (1) Diverse functional groups can be integrated in POPs skeleton through chemical reactions^[40-42], (2) The nanoscale confinement both in terms of space and electronic aspect in POPs render them enhanced activity that is reflected in yield and selectivity of the product^[43], (3) POPs are generally insoluble, stable and allow easy recovery^[44]. Hyper-cross-linked microporous polymers (HCPs), belonging to a sub-class of POPs have drawn great research attention owing to their unique structural features, i.e., high stability, convenience of tailored functionality, facile & cost-effective synthesis, large permanent porosity and so on.^[45-46] These exquisite properties have made them a fitting choice as support matrix in crafting potent heterogeneous catalysts exhibiting enhanced performance and recyclability.^[47-48]

Synthesizing fine chemicals in continuous mode has attracted much attention lately.^[49] To this end, continuous flow cascade catalysis comes forth as a step-change way of upgrading stepwise synthesis of fine chemicals encompassing cumulative convenience of cascade reaction and continuous flow combined with better reaction efficiency, downsized energy utilization, evasion of separating reaction intermediate and propitious shift in the reaction equilibrium.^[50-53] In the current work, aiming at the above mentioned fundamental goal we report straightforward fabrication of an efficient heterogeneous polymer catalyst, viz., 120-MI@OH, to successfully execute one-pot cascade deacetalization-Knoevenagel condensation in a continuous flow manner under mild condition. The particular cascade reaction serves its usefulness in preparing coumarins and related derivatives that are crucial intermediates toward synthesizing pharmaceuticals, perfumes, cosmetics etc.^[54] Satisfyingly, 120-MI@OH displayed excellent performance in cascade catalysis under both batch and flow conditions. Additionally, owing to their structural trait of encompassing site-isolated antagonistic sites, the catalyst polymer outstanding activity toward cyanosilylation (acid catalyzed) and Knoevenagel condensation (base catalyzed) reaction respectively.

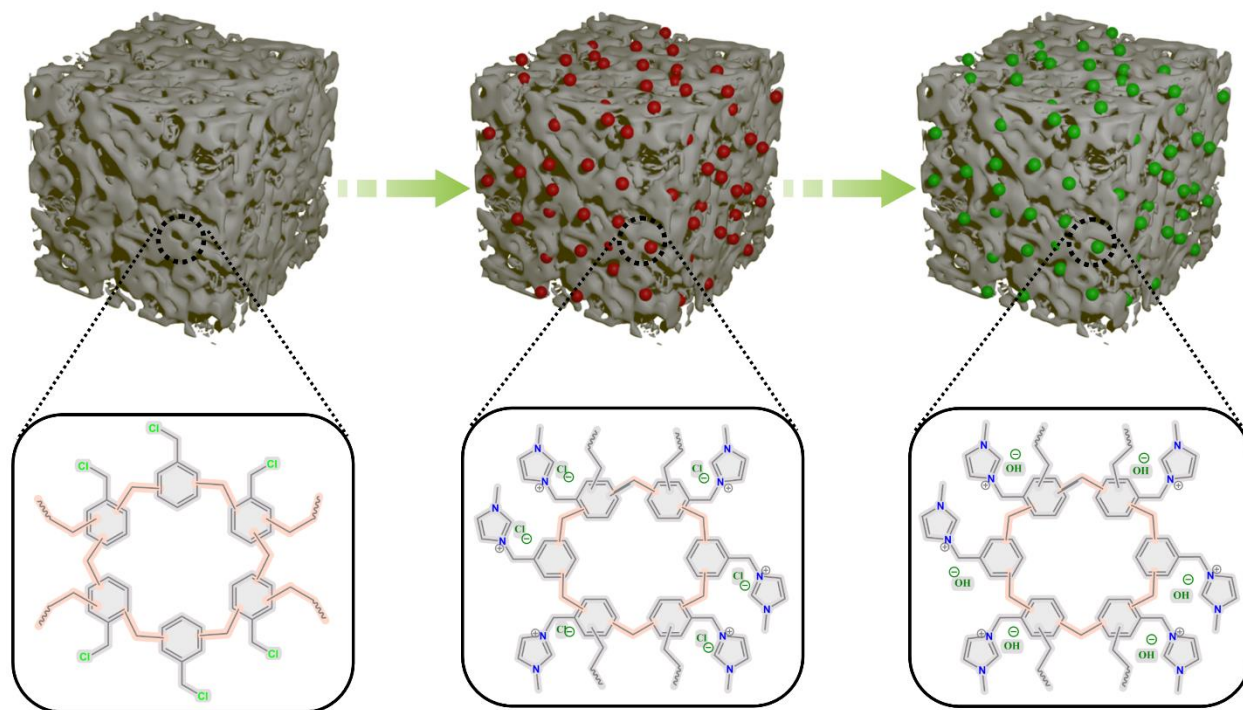


Figure 3.1. Schematic illustration and diagrams of HCP 120, 120-MI@Cl and 120-MI@OH.

3.2 Experimental

3.2.1. Materials: Starting materials, Benzyl chloride, FeCl_3 , formaldehyde dimethyl acetal (FDA), 1-Methylimidazole, were purchased from Sigma-Aldrich. NaOH, THF, 1,2-Dichloroethane (DCE) and remaining solvents were purchased locally. These chemicals were utilized without any further purification.

3.2.2 Physical Measurements:

3.2.2.1 Fourier Transform Infrared Spectroscopy (FT-IR): The IR spectra were recorded in the 550-4000 cm^{-1} range using NICOLET 6700 FT-IR spectrophotometer using KBr pellet.

3.2.2.2 Thermogravimetric Analysis (TGA): Thermogravimetric analyses of all the samples were conducted using Perkin-Elmer STA 6000 TGA analyzer by heating the samples from 40 to 800 $^{\circ}\text{C}$ under N_2 atmosphere at a 10 $^{\circ}\text{C}$ per min heating rate.

3.2.2.3 Field Emission Scanning Electron Microscopy (FESEM): The morphological analysis 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

mm2 (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 >600s.

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

3.2.2.5 Solid-state 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).

3.2.2.6 Proton (^1H) Nuclear Magnetic Resonance (NMR) Spectroscopy: All ^1H spectra were recorded either on Bruker 400 MHz and Jeol 400 MHz spectrometers. The chemical shifts (δ) in ppm were referenced to the residual signal of deuterium solvents (^1H NMR CDCl_3). The multiplicities of the peaks are s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet).

3.2.2.7 Powder X-ray Diffraction (PXRD): Powder X-ray diffraction (PXRD) patterns 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 $0.5^\circ \text{ min}^{-1}$ and a step size of 0.01° in 2θ .

3.2.2.8 Nitrogen Adsorption-Desorption Isotherm Measurements: N_2 gas adsorption measurements were performed using BelSorp-Max instrument (Bel Japan). Prior to adsorption measurements, the activated samples were heated at 120°C under vacuum for 12 hours using BelPrepvacII.

3.2.2.9 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.

3.2.2.10 Temperature-Programmed Desorption (TPD) Measurements: The temperature programmed desorption (TPD) study was done using CHEMBETTM TPR/TPD, QUANTACHROME.

3.2.3 Synthesis

3.2.3.1 Synthesis of HCP 120-Cl:

HCP-120 was synthesized by following our previous report (Scheme-1).^[55]

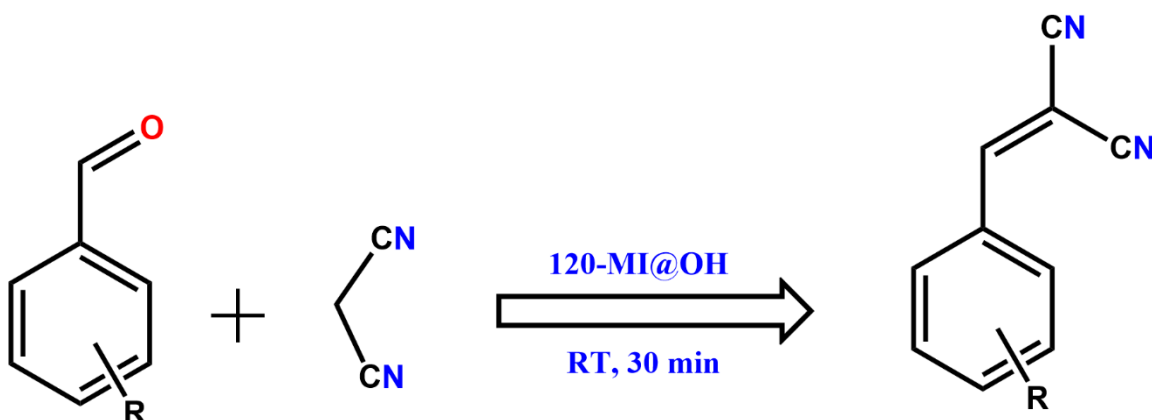
3.2.3.2 Synthesis of HCP 120-MI@Cl:

Activated HCP 120-Cl (300 mg) was taken in a round bottom flask and to that 30 ml of acetonitrile (ACN) was added (Scheme-3). This was followed by dropwise slow addition of 3 mL 1-methyl imidazole (MI) and further allowed to react under stirring for 48 hrs. at reflux temperature. After completion of the polymerization reaction, obtained brown precipitate was filtered and repeatedly washed with copious amount of water for several times to get rid of excess MI. Then the precipitate was again washed with water, DMF, methanol, chloroform, tetrahydrofuran (THF), and dichloromethane repeatedly. Thus obtained dark brown solid material (HCP 120-MI@Cl) was subject to Soxhlet extraction in MeOH for 24 h to eliminate the high boiling solvents from the polymer network of HCP 120-MI@Cl. After obtaining solvent exchanged HCP-120-MI@Cl was further heated at 140 °C under vacuum overnight to get the activated material and with this phase further experiments were performed. Yield: 352 mg (~ 92%).

3.2.3.3 Synthesis of HCP 120-MI@OH:

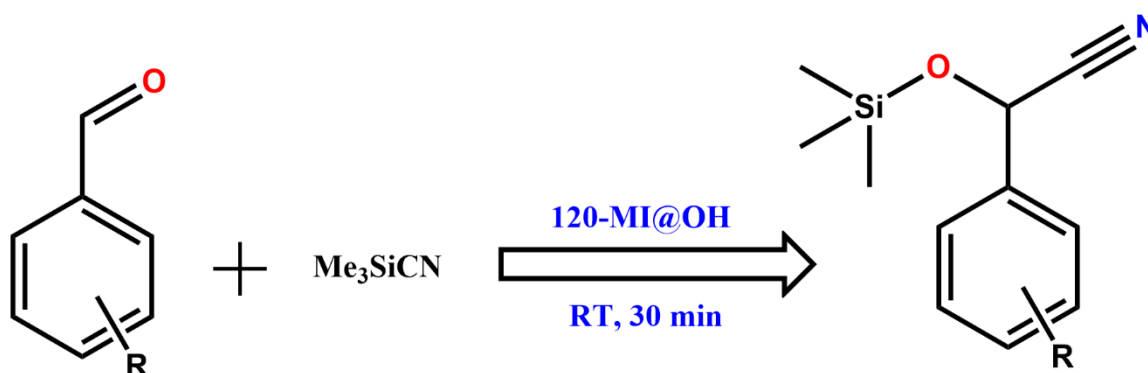
100 mg of activated 120-MI@Cl and 250 mg KOH were suspended in 10 mL H₂O. The resultant mixture was kept under stirring at room temperature for 72 h. The mixture was then filtrated off and the obtained solid was washed with H₂O until neutral. Afterwards, the solid was dried in vacuo at 120 °C to yield 120-MI@OH (92mg).

3.2.4. HCP 120-MI@OH Catalyzed Knoevenagel Condensation:



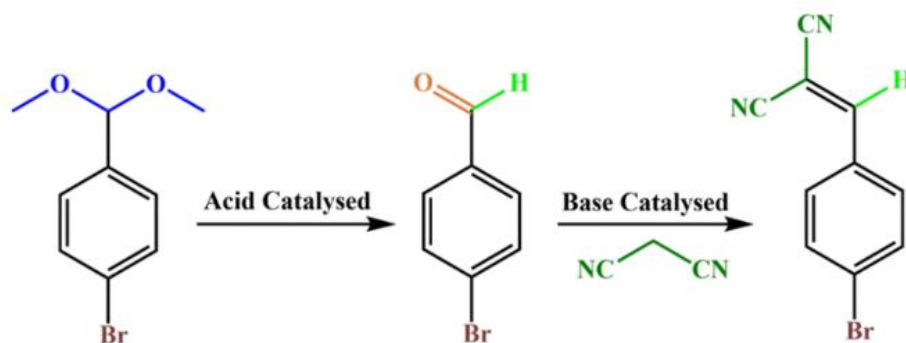
To a 10 mL reaction tube were sequentially added aldehyde (0.8 mmol, 1 equiv.), H₂O (4 mL), malononitrile (0.8 mmol, 1 equiv.), and the heterogeneous catalyst HCP 120-MI@OH (5 mg). The reaction mixture was then stirred at room temperature for 0.5 h. After extraction with CH₂Cl₂ (3 × 10 mL), the combined organic phase was dried over Na₂SO₄. After evaporation of the solvent under vacuum, the crude product was analyzed ¹H NMR using 1,3,5 trimethoxybenzene as the internal standard to determine product yield.

3.2.5. HCP 120-MI@OH Catalyzed Cyanosilylation:



Me₃SiCN (2.0 mmol), carbonyl substrate (1.0 mmol) and catalyst 120-MI@OH (5 mg) were placed into a screw cap vial. The reaction mixture was vigorously stirred at room temperature for 1h. After the reaction was completed, the crude product was extracted with CH₂Cl₂ (3 × 5 mL), and the solvent was evaporated. Finally, the conversion was determined by ¹H NMR using 1,3,5 trimethoxybenzene as the internal standard.

3.2.6. HCP 120-MI@OH Catalyzed One-Pot Cascade Catalysis Reaction:



The one-pot deacetalization-Knoevenagel condensation reaction was performed in a 10 mL reaction tube equipped with a temperature controller and magnetic drive. A typical process is as follows: 5 mg of HCP 120-MI@OH catalyst together with a mixture of 4-bromobenzaldehyde dimethyl acetal (0.5 mmol),

malononitrile (0.5 mmol) was put into the reactor. Then, 5 ml water (H_2O) was added as solvent and the reaction mixture was heated at 60 °C for 2 h. To test the reaction conversion, the compositions of starting reagent, intermediate product and the final product 3 were measured by ^1H NMR in CDCl_3 . 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 dimethyl acetal (5.35 ppm) and 4-bromobenzaldehyde (9.96 ppm), the conversions of the starting reagent acetal and the intermediate product aldehyde were calculated by ^1H NMR using 1,3,5 trimethoxybenzene as the internal standard (see the example in Appendix 3.15).

3.2.7. Scaled-up Cascade Catalysis:

The scaled up deacetalization-Knoevenagel condensation cascade catalysis was carried out by increasing the reactant, solvent as well as the catalyst amount. Typically, benzaldehyde dimethyl acetal (6.1 mL, 40 mmol), malononitrile (2.64 g, 40 mmol) and 150 mL water (H_2O) was added to a round bottom flask and was heated for 2 h at 60 °C. To test the reaction conversion, the formation of the final product and its purity ^1H NMR was performed in CDCl_3 . Isolated product yield 5.54 g (89%)

3.2.8. Continuous Flow-through Cascade Catalysis:

A mixture of benzaldehyde dimethylacetal (1.82 mL, 12.0 mmol), H_2O (5 mL), malononitrile (792.8 mg, 12.0 mmol) in $\text{C}_2\text{H}_5\text{OH}$ solution (40 mL) was pumped through the spiral transparent glass tube reactor which is evenly charged with a mixture of 120-MI@OH beads (0.2 g) at 60 °C with a flow rate of 0.4 mL min^{-1} .

3.3 Results and Discussion

Scheme 1 illustrates the synthesis of polymer catalyst, viz., 120-MI@OH through strategic post-synthesis functionalization. Precursor polymer 120-Cl was synthesized by our previously published method.^[55] Following this, imidazolium ionic liquid moieties were incorporated through nucleophilic substitution reaction by N-methylimidazole at the electrophilic chloromethyl centres to produce 120-MI@Cl. In the second step, a straightforward ion-exchange reaction to introduce hydroxyl anions (OH⁻) throughout the polymer network by treating 120-MI@Cl with KOH solution. These stepwise structural modifications resulted in immobilized imidazolium cations and hydroxyl anions as Lewis acid-base pair antagonistic catalytic sites in 120-MI@OH.

After successful synthesis, the polymers were comprehensively characterized and verified of their structures with various techniques such as Fourier transform infrared (FTIR) spectroscopy, solid-state NMR spectroscopy, low temperature nitrogen sorption isotherms (N₂ adsorption), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) etc. The recorded FT-IR spectrum of 120-MI@Cl verified the successful integration of imidazolium cations inside the polymer network. Peaks arising at ca. 1662 cm⁻¹ and 2922 cm⁻¹ are ascribed to the olefin C=C bonds from the aromatic rings whilst two peaks at around 1163 cm⁻¹ & 1598 cm⁻¹ were assigned to C-N & C=N bonds from the imidazole moiety respectively confirming the quaternization reaction. Appearance of an additional broad peak at ca. 3420 cm⁻¹ in 120-MI@OH can be attributed to the stretching frequency of the hydroxyl group indicating successful fabrication of the desired polymer catalyst (Figure 2.2a). It should be mentioned that both 120-MI@Cl and 120-MI@OH displayed distinct stretching frequencies at ca. 1460 cm⁻¹ and 2920 cm⁻¹ owing to the presence of crosslinking -CH₂- linkages throughout the polymer matrix that corresponds to C-H bending & stretching vibrations respectively. The structural composition was probed via solid-state ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy. Presence of three main broad peaks at 36 ppm, 129 ppm and 135 ppm were observed in 120-MI@Cl, which corroborates to the methylene carbon from the external crosslinker, C4/C5-carbons of imidazole ring and non-substituted aromatic carbons and C2-carbon of imidazolium ring along with substituted aromatic carbons respectively (Figure 2.2b).^[56-57] Additionally, a peak at 51 ppm was assigned to the adjacent carbon atom attached to the N atom of the imidazole ring and the resonance peak at 16 ppm was attributed to the methyl carbon of the imidazole moiety, further validating the post-synthesis modification. Porosity analysis was carried out by performing N₂ sorption at 77K. Both 120-MI@Cl and 120-MI@OH displayed swift nitrogen uptake at very low pressure (P/P₀ < 0.03) accompanied by continuous increase in uptake at high relative pressures indicating hierarchical porosity featuring both micropores as well as mesopores (Figure 2.2c).^[58] A similar pattern of

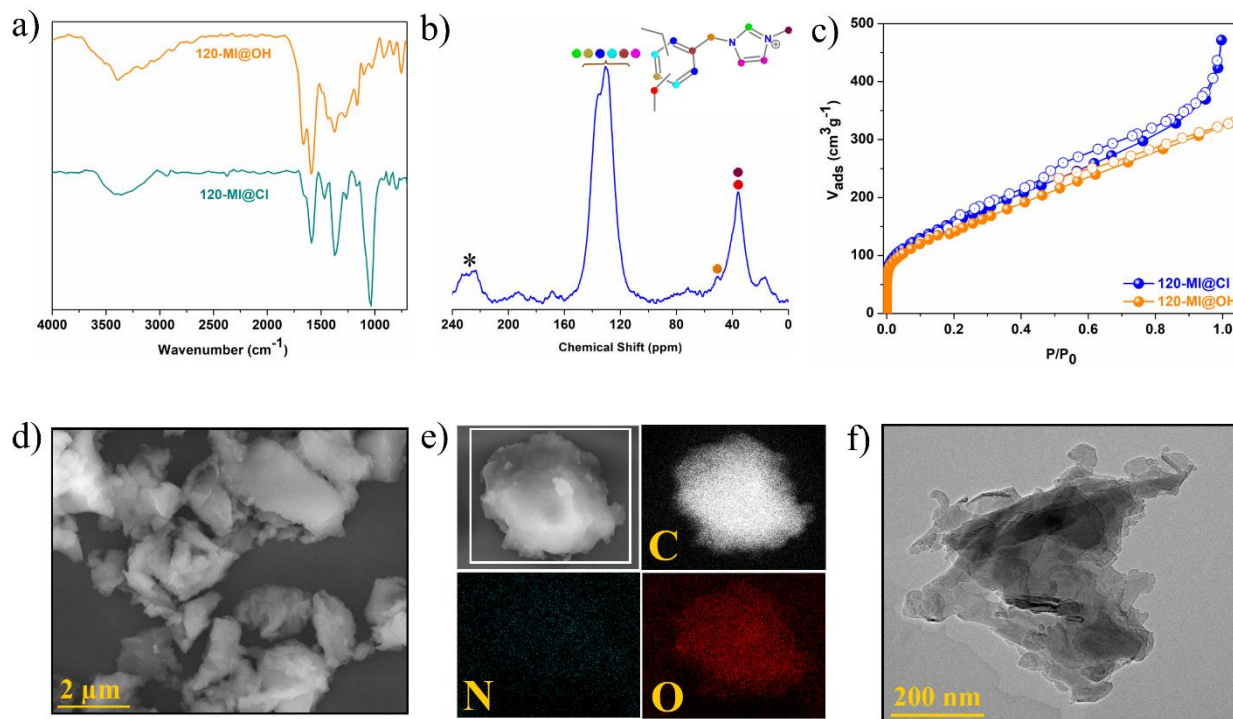


Figure 3.2. (a) FT-IR spectra of 120-MI@Cl (cyan), 120-EI (wine), and 120-MI@OH (orange). (b) Solid-state ^{13}C CP/MAS NMR spectrum of polymer 120-MI@Cl. (c) N_2 sorption curves of 120-MI@Cl (blue) and 120-MI@OH (orange). (d) FESEM image of 120-MI@OH. (e) Elemental mapping of 120-MI@OH. (f) TEM image of 120-MI@OH.

initial weight loss under 100 °C was seen in case of all the pristine polymers after which greater than 70 wt% retention up to ~400 °C advocated their thermal robustness (Appendix 3.3- Appendix 3.6). While the first weight loss was assigned to the removal of trapped solvent molecules, gradual loss after 400 °C accounts for the decomposition of the organic frameworks. Surface morphology of the polymers were evaluated via FESEM and TEM analysis. FESEM images revealed amorphous dense particles of irregular shape in case of the precursor polymer (Appendix 3.8). Furthermore, no significant change in the surface morphology was noticed in the modified polymers (Figure 3.2d, Appendix 3.8). The homogeneous presence of all the composition elements in all the polymers were confirmed by EDX analysis coupled with elemental mapping which additionally confirms the post-synthetic structural modifications (Figure 3.2e, Appendix 3.9- Appendix 3.11). TEM images of 120-MI@OH showed aggregated uneven sized nanoparticles similar to the FESEM images (Figure 3.2f, Appendix 3.12). The modified polymer 120-MI@OH was further structurally characterized in detail with X-ray photoelectron spectroscopy (XPS) analysis. The survey-scan spectra is shown in Figure 3.3a, demonstrating three signals approximately at 285.2, 401.1, 533.1 eV

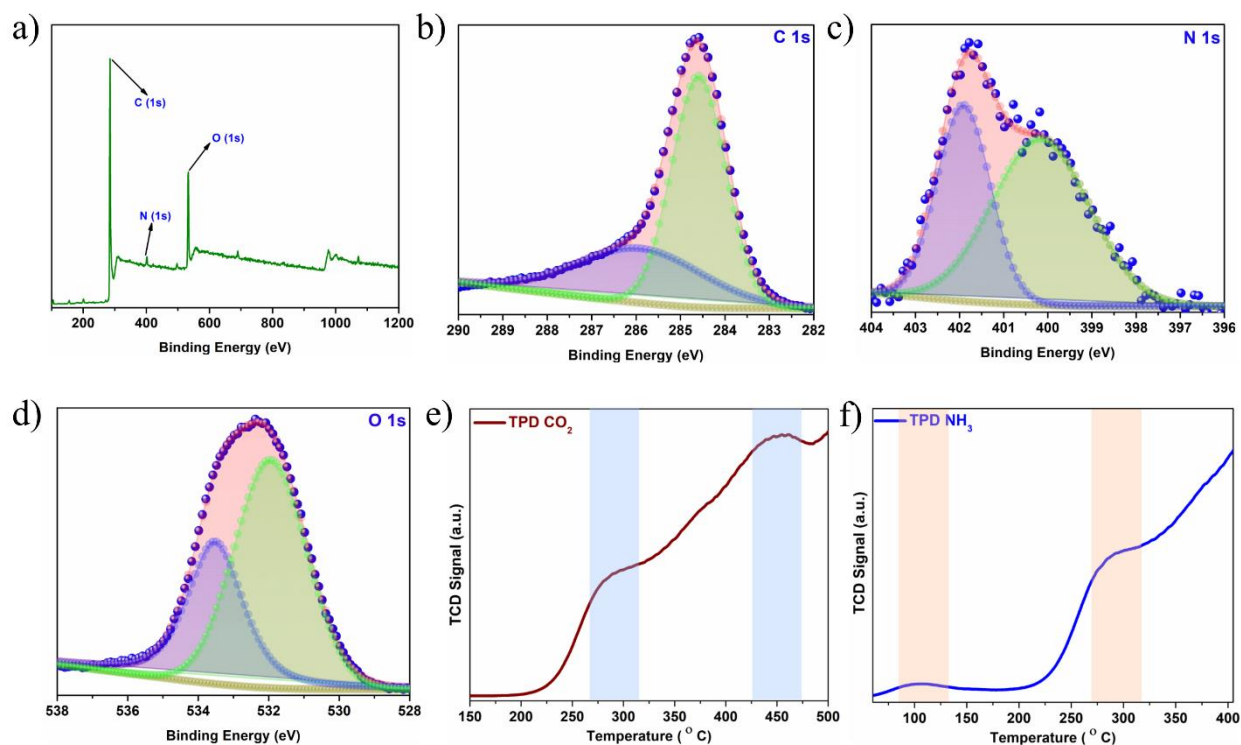
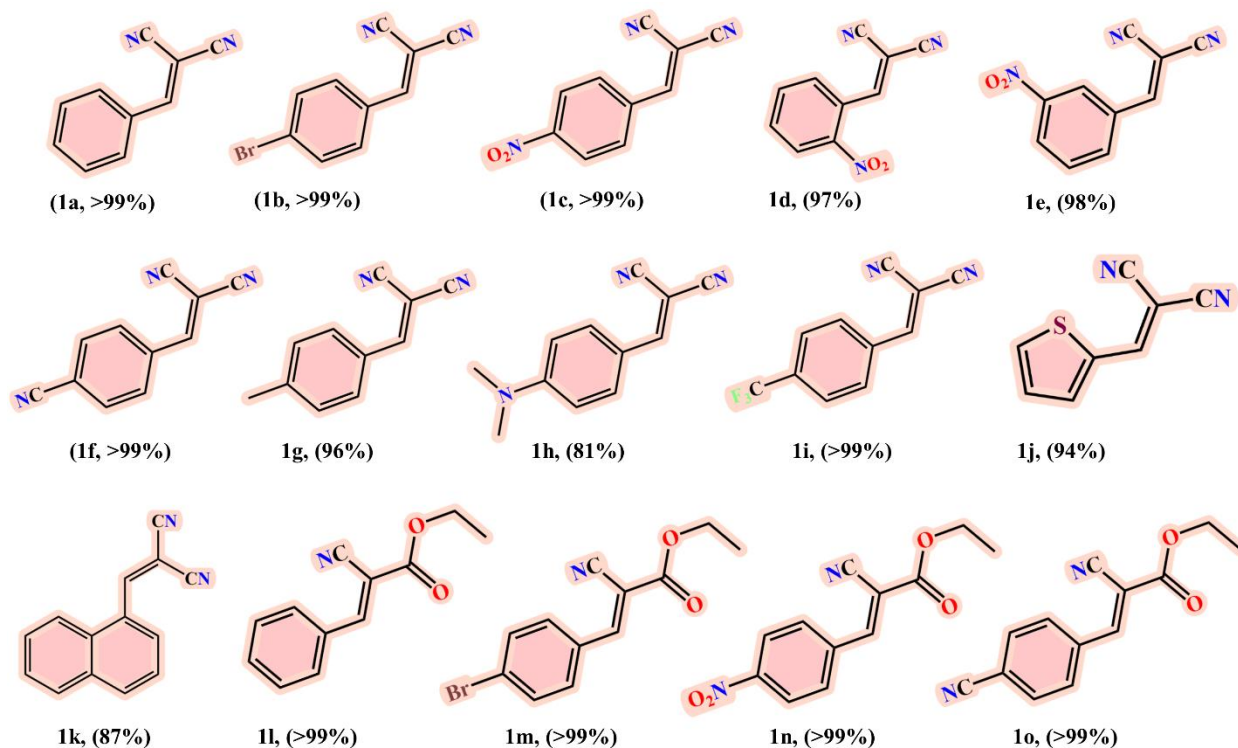


Figure 3.3. (a) XPS survey scan spectra of 120-MI@OH. (b) C 1s XPS spectrum of 120-MI@OH. (c) N 1s XPS spectrum of 120-MI@OH. (d) O 1s XPS spectrum of 120-MI@OH. (e) CO₂ TPD profile and (f) NH₃ TPD profile of 120-MI@OH.

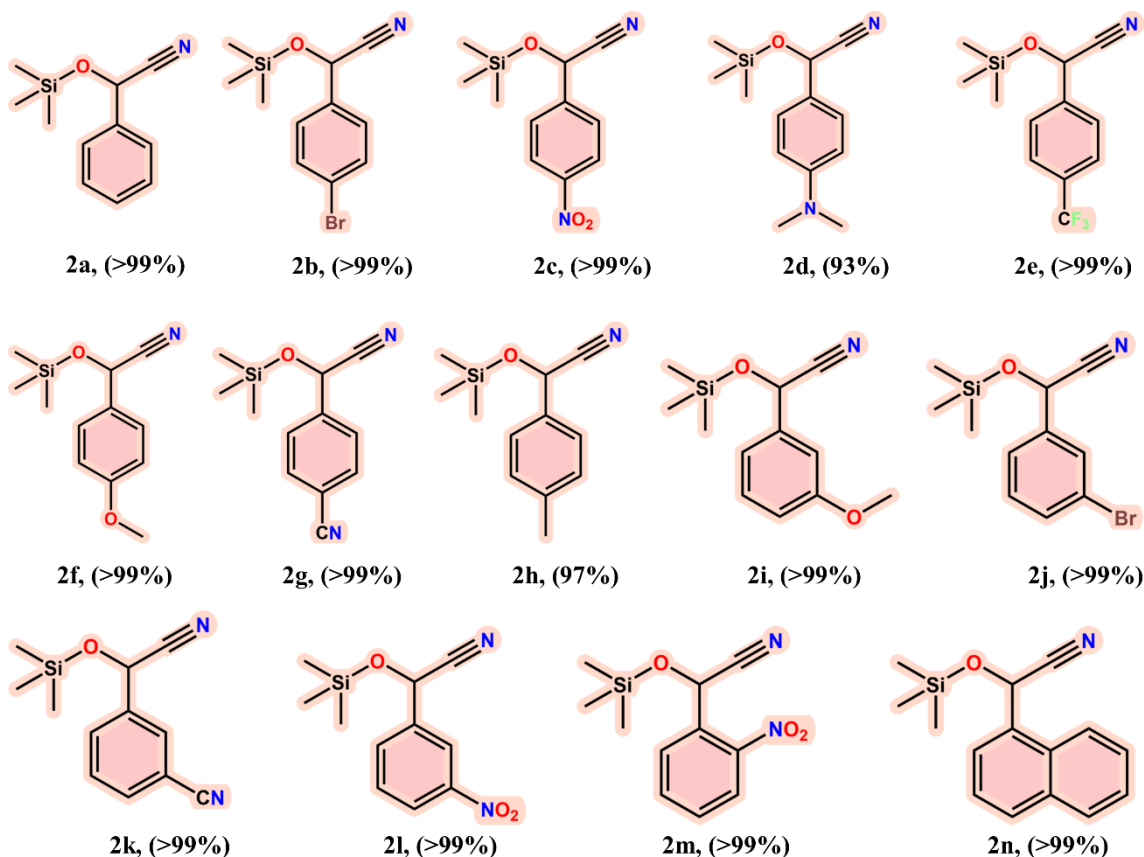
that corresponds to C 1s, N 1s and O 1s elements signifying structural modification enabled successful catalyst fabrication (Figure 3.3a-3.3c). Detailed analysis of high resolution N 1s spectra were deconvoluted to two distinct peaks implied the abundance of two types of N of the imidazolium unit (Figure 3.3c). Specifically, the peak at 401.8 eV corresponded to the cationic N⁺ atoms of imidazolinium fraction while the other peak at 400.1 eV was ascribed to the non-ionic N, respectively.^[59-61] C 1s XPS spectrum was fitted into two different peaks at 285.8 eV and 284.6 eV which were assigned to signals from C-N of imidazolium rings as well as methylene and phenyl carbons of 120-MI@OH (Figure 3.3b). These observations further confirm the integration of imidazolium units. The existence of Lewis acid and basic sites was investigated by performing temperature-programmed desorption (TPD) spectrometry. NH₃-TPD profile of 120-MI@OH displayed two definite peaks 104 °C & 300 °C attributable to moderate together with strong Lewis acidic sites respectively (Figure 3.3f). Similarly, CO₂-TPD analysis exhibited peaks at 276 °C & 455 °C corresponding to moderate as well as strong Lewis basicity (Figure 3.3e). These experimental observations confirms the simultaneous presence of antagonistic pairs in the fabricated catalyst.



Scheme 3.1. 120-MI@OH catalyzed Knoevenagel condensation reaction at room temperature. Conditions: 0.8 mmol of carbonyl compound, 0.8 mmol malononitrile and 5 mg of catalyst was stirred in 4 mL H_2O for 0.5 h; Yield determined from ^1H NMR.

Mild-Condition Knoevenagel condensation: Knoevenagel condensation of carbonyls and active methylene compounds is a typical $\text{C}=\text{C}$ bond forming reaction.^[62] Over the years, it has found utilization as a powerful and widely used reaction toward synthesizing fine chemicals, cosmetics, agrochemicals, pharmaceuticals along with biologically relevant heterocyclic compounds and so on.^[63-64] Generally, Knoevenagel condensation serves the purpose of a reference reaction for the heterogeneous basic catalysts.^[65] Motivated by the presence of Lewis basic sites in 120-MI@OH, we investigated its potential toward this reaction employing benzaldehyde and malononitrile as the model substrates. Initially, a set of control experiments were performed to arrive at the optimal reaction condition. As seen in Appendix Table 3.1, when 0.8 mmol benzaldehyde was allowed to react with 0.8 mmol of malononitrile in presence of 120-MI@OH (5 mg), benzylidenemalononitrile was isolated with an excellent yield up to 99% at room temperature (RT). It is also worth mentioning that amongst the tested solvents (H_2O , CH_2Cl_2 and MeOH), H_2O produced the best result (Appendix Table 3.1, entries 1,2,4) in only 30 minutes. Also, increasing the reaction time or catalyst amount did not have any significant effect in yield% (Appendix Table 3.1, entry 3). 120-MI@Cl was found to catalyze the reaction but with suboptimal yield (Appendix Table 3.1, entry

5). However, no significant conversion to the desired product was observed in absence of 120-MI@OH, advocating the role of the catalyst (Appendix Table 3.1, entry 6). Heterogeneous nature of the catalyst was confirmed by carrying out a control reaction with the supernatant of H₂O suspension of 120-MI@OH that yielded almost no conversion and also indicated no leaching of catalytically active components (Appendix Table 3.1, entry 7). These results clearly suggested the potency of 120-MI@OH as an efficient heterogeneous catalyst for Knoevenagel condensation reaction.



Scheme 3.2. 120-MI@OH catalyzed cyanosilylation reaction at room temperature. Conditions: Me₃SiCN (2.0 mmol), carbonyl substrate (1.0 mmol) and catalyst 120-MI@OH (5 mg) at RT for 1 h; Yield determined from ¹H NMR.

After arriving at the optimal reaction conditions, we evaluated the competency of 120-MI@OH a series of aromatic carbonyls to establish its universality. Scheme 3.1, illustrates exceptional substrate scope and functionality tolerance provided by the polymer catalyst when tested with various aldehydes. However, a slight decreased yield was observed for substrates with electron-donating groups (-CH₃, -N(CH₃)₂ etc.). On the other hand, substrates having electron-withdrawing groups produced excellent yields (up to >99%). When subjected to heterocyclic compounds (Scheme 3.1), high yield of 94% was achieved which

has profound importance in terms of biological relevance toward synthesizing bioactive compounds. Additionally, we observed similar catalytic performance even when the active methylene compound was changed to Ethyl cyanoacetate suggesting the versatile nature of our polymer catalyst.

Mild-Condition Cyanosilylation: Cyanohydrins have emerged as a critical and versatile intermediates in biology and industry on account of being precursor for β -hydroxy amino alcohols, α -hydroxy carboxylic acids, α -hydroxy aldehydes and various fine chemicals.^[66] To synthesize cyanohydrins that involve a nucleophilic addition with carbonyl compounds, trimethylsilyl cyanide (TMSCN) is employed replacing the usage toxic chemicals such as HCN, NaCN or KCN to generate C-C bond in a greener approach.^[67] Organic-inorganic salts^[68], nucleophilic catalysts^[69] or Lewis acids^[70-71] have been utilized to serve as electrophilic catalysts in order to activate various carbonyls for efficient cyanosilylation reaction. Considering the Lewis acidity shown by 120-MI@OH, we evaluated its potential toward catalytic cyanosilylation reactions. Reaction condition optimization was done by taking benzaldehyde (1 mmol), Me₃SiCN (2.0 mmol), and catalyst 120-MI@OH (5 mg) at room temperature (RT) without any solvent. After 1 h of carrying out the reaction, we observed >99% yield of the cyanohydrin trimethylsilyl ether product. This performance can be ascribed to the excellent potential of 120-MI@OH to act as Lewis acid solid catalyst. Motivated by this observation, we extended the substrate scope with various carbonyl compounds bearing diverse functionalities. It was observed that electron-withdrawing functionalities on benzaldehyde moiety (-NO₂, -CF₃, -CN, -Br) did not have any impact irrespective of their position (ortho, meta) by producing near quantitative yield (Scheme 3.2). Likewise, electron-donating groups displayed high to exception yields, validating the competence of 120-MI@OH as an efficacious heterogeneous catalyst for doing cyanosilylation reaction under mild conditions.

One-pot Cascade Deacetalization-Knoevenagel Condensation: After successfully verifying the potency of 120-MI@OH as a bifunctional acid-base heterogeneous catalyst, we went ahead to investigate its performance in one-pot cascade deacetalization-Knoevenagel condensation. As is known, this type of C-C coupling reaction is critical in fine chemicals synthesis.^[72-73] Benzaldehyde dimethyl acetal (0.5 mmol) and malononitrile (0.5 mmol) in 5mL H₂O were selected as the benchmark reaction while the catalyst amount of 120-MI@OH (5 mg) was kept fixed. Typically, the first step of this cascade catalysis include deacetalization reaction to yield benzaldehyde from benzaldehyde dimethyl acetal promoted by acidic sites. Second step consists of Knoevenagel condensation with malononitrile which is catalyzed by the basic sites to generate the unsaturated product, a crucial intermediate toward the synthesis of pharmaceuticals, natural products etc. After careful optimization of ideal reaction conditions, we discovered that 120-MI@OH is remarkably active toward the cascade catalysis as the desired benzylidenemalononitrile product was

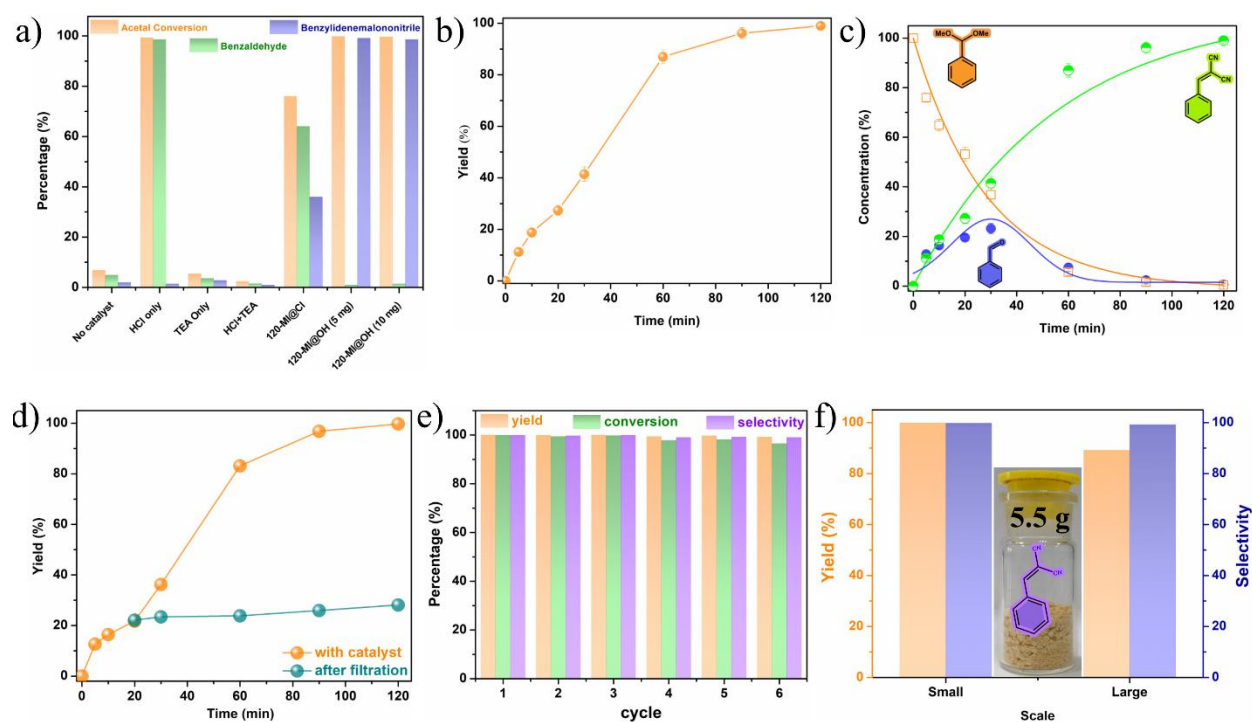


Figure 3.4. (a) Control experiments for one-pot deacetalization-Knoevenagel condensation with different catalysts. (b) Kinetic profile of cascade catalysis by 120-MI@OH. (c) Hot filtration test for one-pot deacetalization-Knoevenagel condensation. (d) Time-dependent catalytic performance of 120-MI@OH monitored over time by NMR. (e) Catalytic recycling test of 120-MI@OH for cascade reaction and (f) Reaction Yield comparison with the scale-up synthesis with a photograph of the isolated pure product.

obtained with 99% yield within just 2 hrs. at 60°C under aerobic conditions. Additionally, several control experiments were conducted to disseminate the reaction process (Figure 3.4a). As seen in Figure 3.4a, without addition of 120-MI@OH no desired product formation was observed, indicating the role of the catalyst polymer. Subsequently, increasing the catalyst amount to 10 mg did not have significant impact as best activity was observed using 5mg 120-MI@OH. Use of HCl (0.1 mmol) resulted in smooth deacetalization reaction but the Knoevenagel condensation did not proceed to give the ultimate product. On the contrary, using Triethylamine (TEA, 0.1 mmol) led to trace conversion of the acetal advocating the need for acidic sites. However, the mixture of HCl & TEA produced almost no conversion owing to their neutralization reactions leading to the annihilation of the antagonistic acid-base sites. ^1H NMR was utilized to determine product yield and conversion in all the cases. These control reactions further confirm that spatially separated acidic & basic sites within the polymer catalyst is imperative in order to accomplish

high performance cooperative catalysis. Additionally, 120-MI@Cl exhibited lower activity in comparison to 120-MI@OH which may be attributed to its weaker basicity compared to 120-MI@OH.^[74]

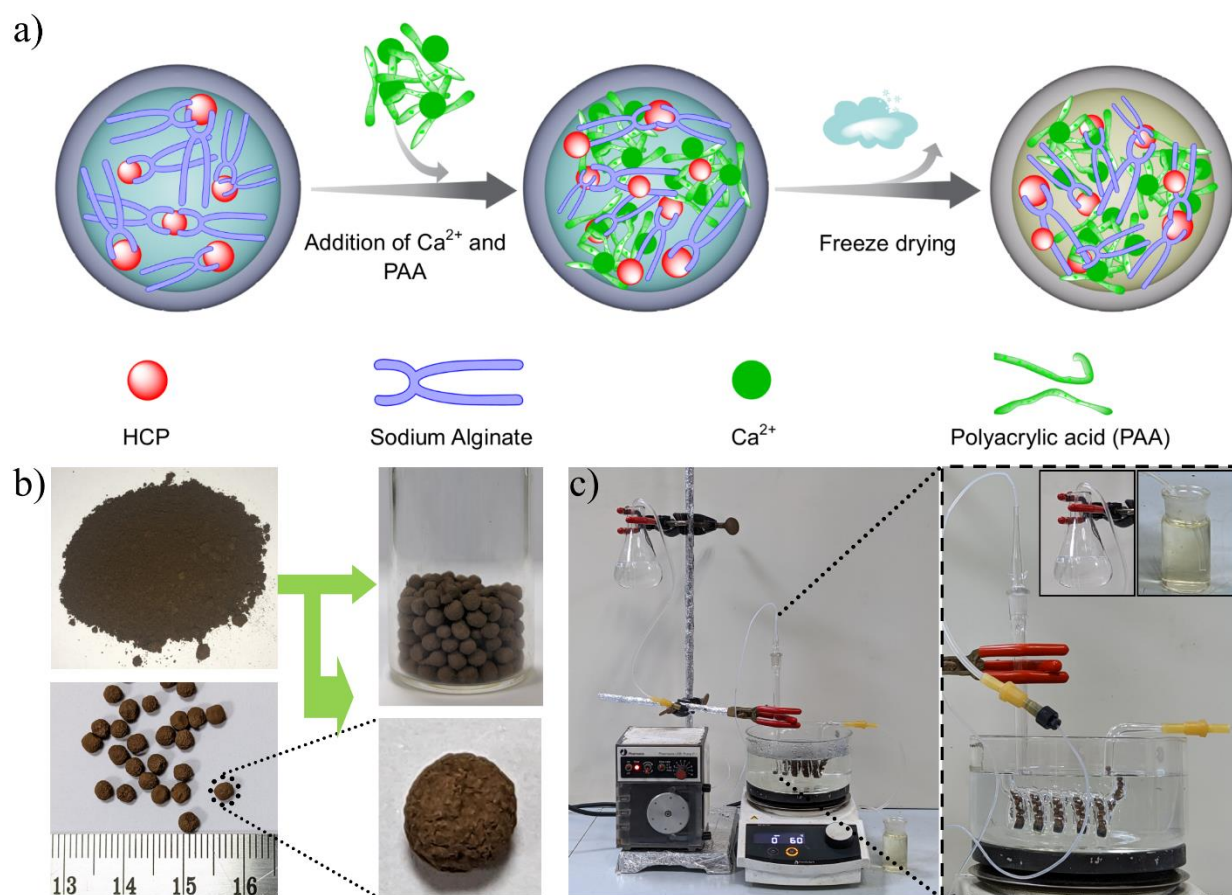


Figure 3.5. (a) Schematic illustration of PAA–Ca²⁺–alginate bead formation from 120-MI@OH powder. (b) Photographs of 120-MI@OH powder and beads respectively. (c) Photograph of the continuous-flow reactor for the synthesis of benzylidenemalononitrile at gram scale.

We also probed the kinetics of the reaction and determined the completion of the cascade catalysis. From Figure 3.4b, a continuous incremental trend in the yield was seen over the course of time with >99% product yield after only 2 h. Each kinetics data points were duplicated to get accurate results. Also, heterogeneity of 120-MI@OH was also tested by removing the polymer catalyst after 20 min through filtration. The reaction was further allowed to proceed with the supernatant liquid but no significant increase in % yield of the product was observed, indicating the reaction taking place in a heterogeneous manner (Figure 3.4d). To delve deeper into the cascade reaction, we also monitored time dependant conversion of the reaction via plotting consumption of benzaldehyde dimethyl acetal into the intermediate benzaldehyde all the way to

the final product benzylidenemalononitrile formation (Figure 3.4c, Appendix 3.14). This was carried out by taking out aliquots at predetermined time intervals from the reaction mix while the conversion was monitored by ^1H NMR spectroscopy. As illustrated in Figure 3.4c, in accordance to the kinetics graph, an exponential decrease in the starting material was from the start (orange trace). Within the first 20 min, ~50% of benzaldehyde dimethyl acetal was consumed which went up to ~95% after 60 min on account of deacetalization reaction facilitated by the imidazolium moiety. Accordingly, the amount of benzaldehyde intermediate (purple trace) was found to increase at the same duration of time (30 min). However, we observed exponential decrement of the intermediate after 30 min owing to its conversion to the final product. Additionally, the amount of benzylidenemalononitrile showed steady increase over the course of time until it reached a plateau as the starting material as well as intermediate approaching depletion.

Pertaining to sustainability, reusability of a catalyst is not only critical but is of priori necessity. After performing each cycle of cascade catalysis, the catalyst could be easily recovered via centrifugation, following which it was washed by water & methanol before drying at 80° for 6 h. 120-MI@OH demonstrated exceptional recyclability performance with >98% obtained of the final product after 6 catalytic cycles along with excellent conversion & selectivity (>99%) (Figure 3.4e). Scalability is another crucial aspect of a catalyst and is highly sought after. To test the competence of our catalyst at large scale (80 times higher scale) and isolated 5.5 g of the product after 2 h of the reaction with admirable yield (89%) punctuating its potency of scalability (Figure 3.4f). These results clearly highlight the superior nature of 120-MI@OH in terms of robustness, sustainability and remarkable catalytic activity.

Continuous Flow Cascade Catalysis: Inspired by its satisfying catalytic performance, we further tested the conceptual feasibility by performing the one-pot deacetalization-Knoevenagel condensation under continuous flow conditions. In this context, structuring of the polymer catalyst was done by converting 120-MI@OH powder into composite beads by a double-cross-linking strategy utilizing poly (acrylic acid) (PAA), Ca^{2+} ions and sodium alginate using H_2O as solvent (Appendix 3.13, Figure 3.5a-3.5b).^[75] 200 mg polymer beads were packed in a custom made fixed microreactor to carry out continuous flow catalysis. Under optimized reaction conditions, ethanolic solution (40 mL) of benzaldehyde dimethyl acetal (1.82 mL), malononitrile (792.8 mg) and 5 mL H_2O was allowed to flow at a flow rate of 0.4 mL/min to accomplish continuous conversion (Figure 3.5c). Delightfully, we obtained 96% yield of the final product benzylidenemalononitrile in gram scale (1.77 g). Additionally, a steady yield (>95%) of the desired product was obtained after performing 5 continuous flow catalytic cycles which corroborate to the excellent scope

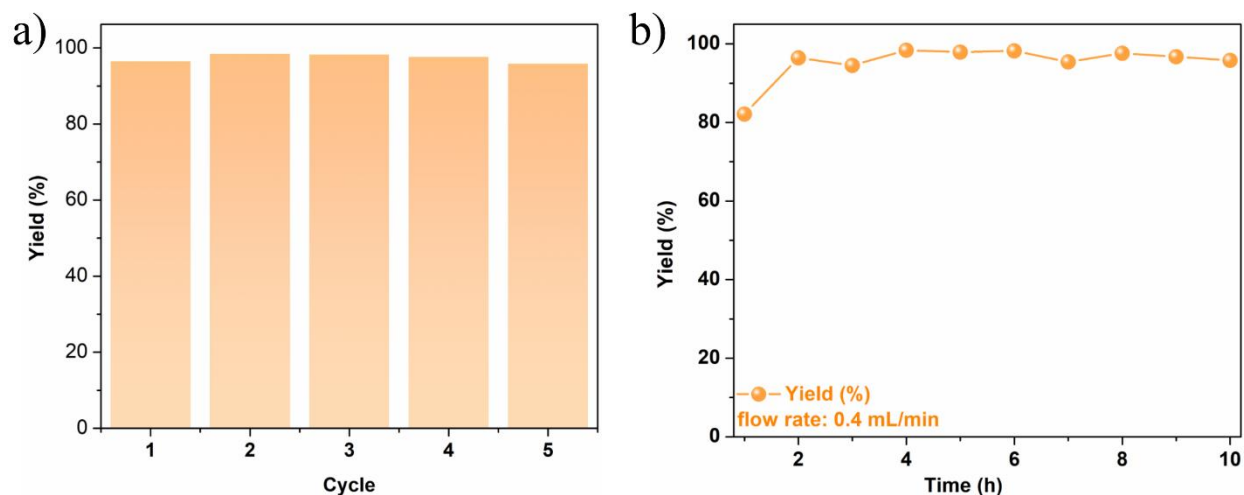


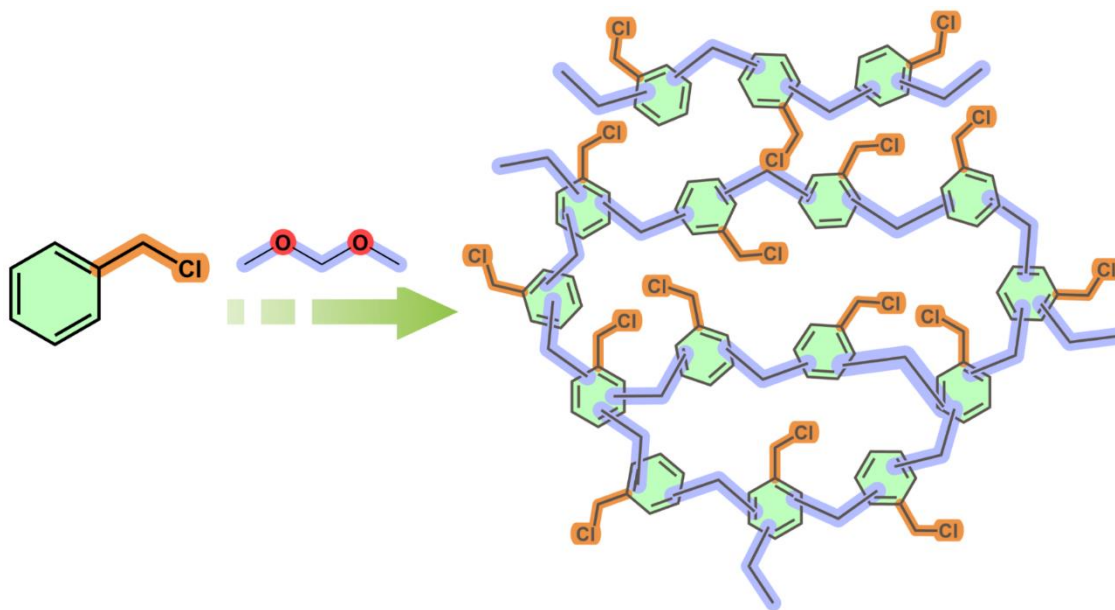
Figure 3.6. (a) Recyclability test for one-pot cascade catalysis under flow. (b) Yield over time of flow deacetalization-Knoevenagel condensation reactions under continuous flow condition.

of 120-MI@OH in flow catalysis (Figure 3.6).

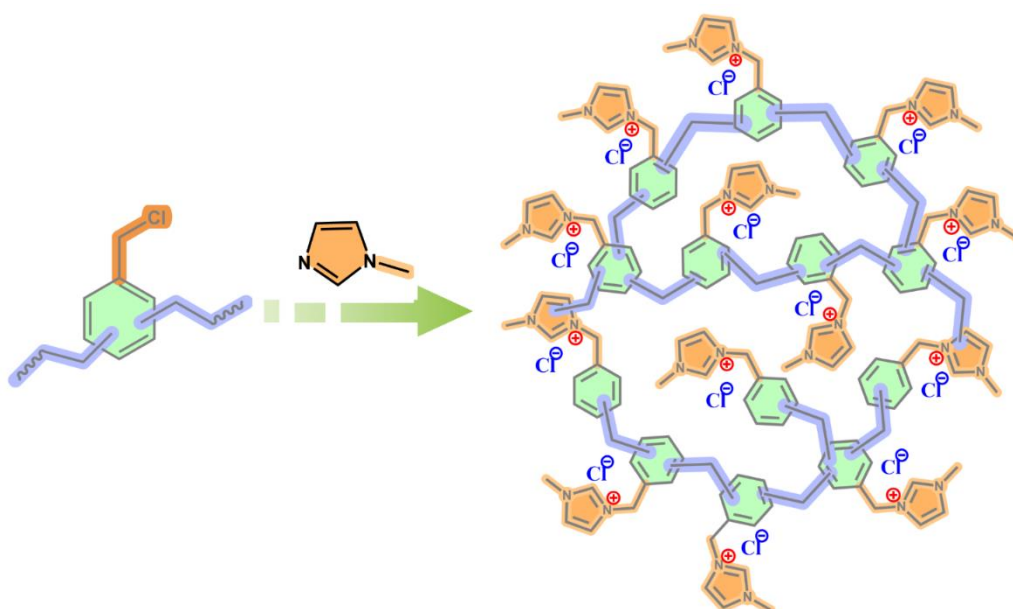
3.4 Conclusion:

In summary, the present study reports successful fabrication of a potent heterogeneous catalyst aided by strategic modifications post polymer synthesis. The developed catalyst, 120-MI@OH, featured antagonistic catalytic sites that were in close proximity spatial isolation. Owing to the presence of acidic as well as basic catalytically active sites, the polymer catalyst displayed outstanding performance in driving cyanosilylation (acid catalyzed) and Knoevenagel condensation (base catalyzed) under mild conditions. Additionally, the presence of antagonistic sites enabled 120-MI@OH to carry out one-pot deacetalization-Knoevenagel condensation cascade catalysis with great potency. The catalyst demonstrated intact efficiency upon reusability for 6 cycles as well as in large scale. Furthermore, practical relevance of the catalyst was established from its processability into composite beads to promote the cascade catalysis under continuous flow without compromising activity. This work may trigger strategic development of potent heterogeneous catalysts that offer effective structural modification coupled with cost-effectiveness aimed at function-led porous polymer catalysts.

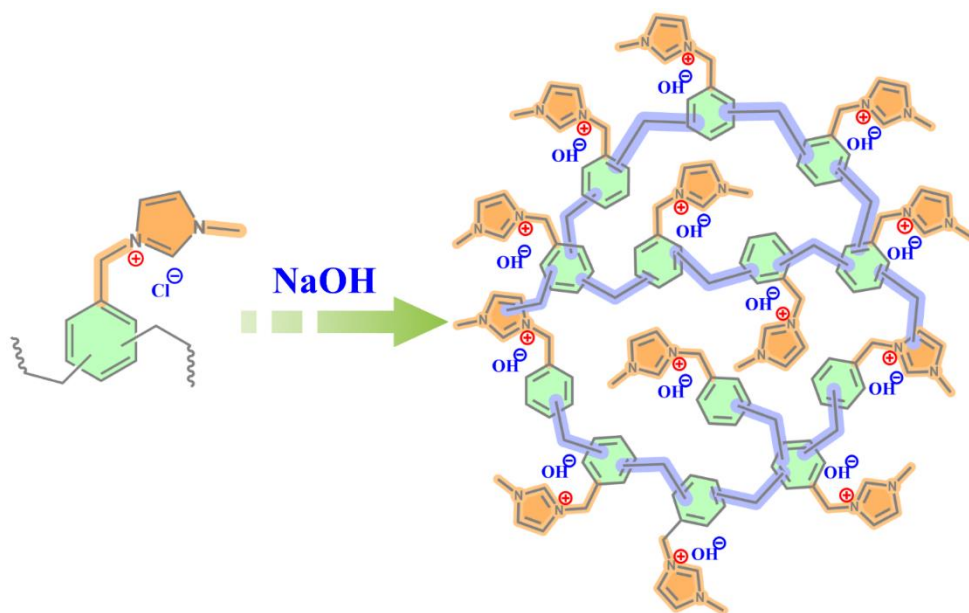
3.5 Appendix section



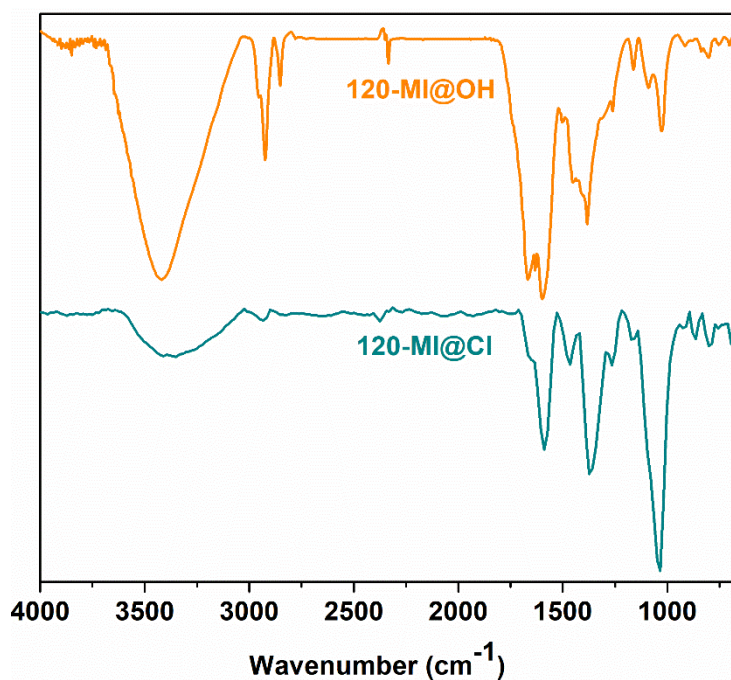
Appendix Scheme 3.1. Synthesis of HCP-120.



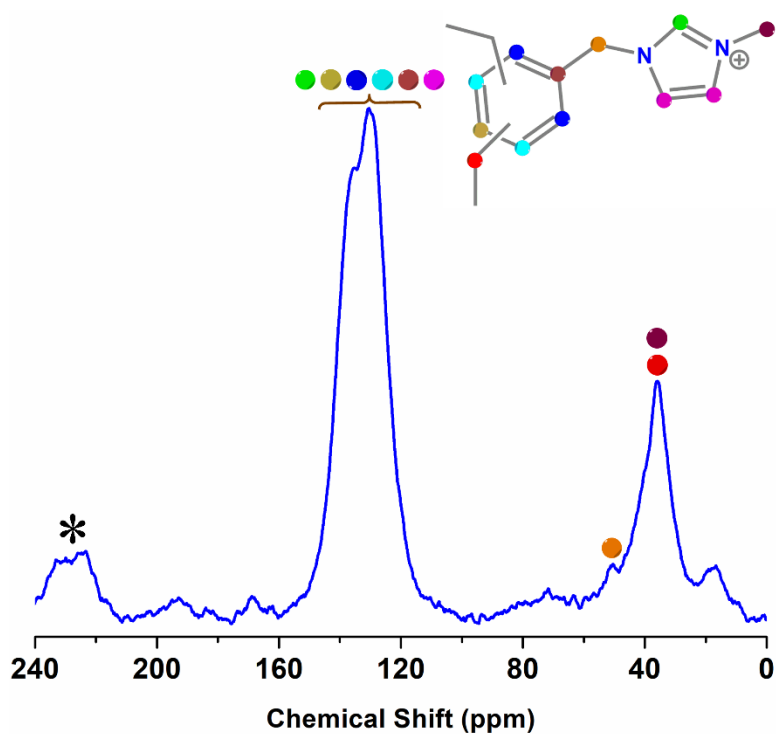
Appendix Scheme 3.2. Synthesis of HCP 120-MI@Cl



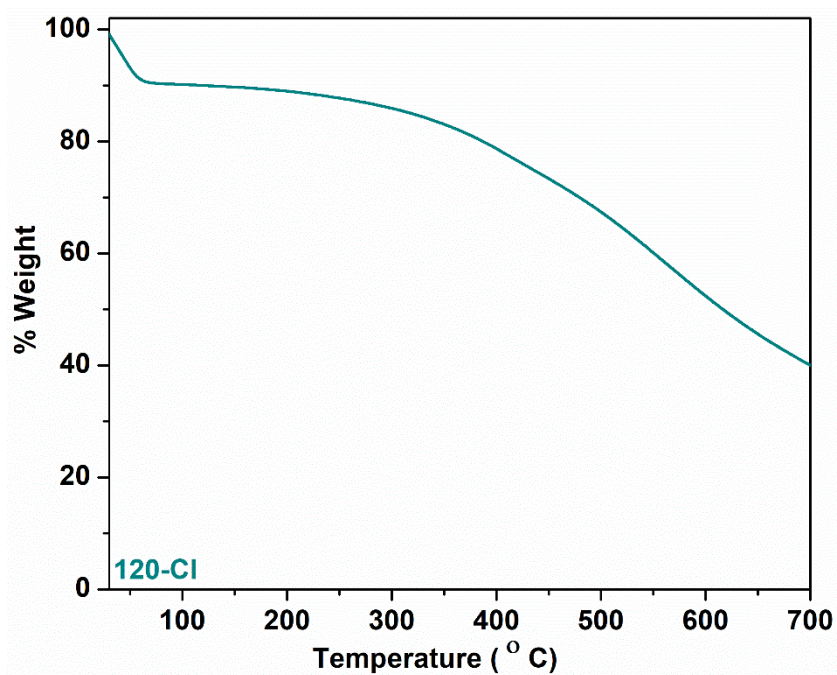
Appendix Scheme 3.3. Synthesis of HCP120-MI@OH.



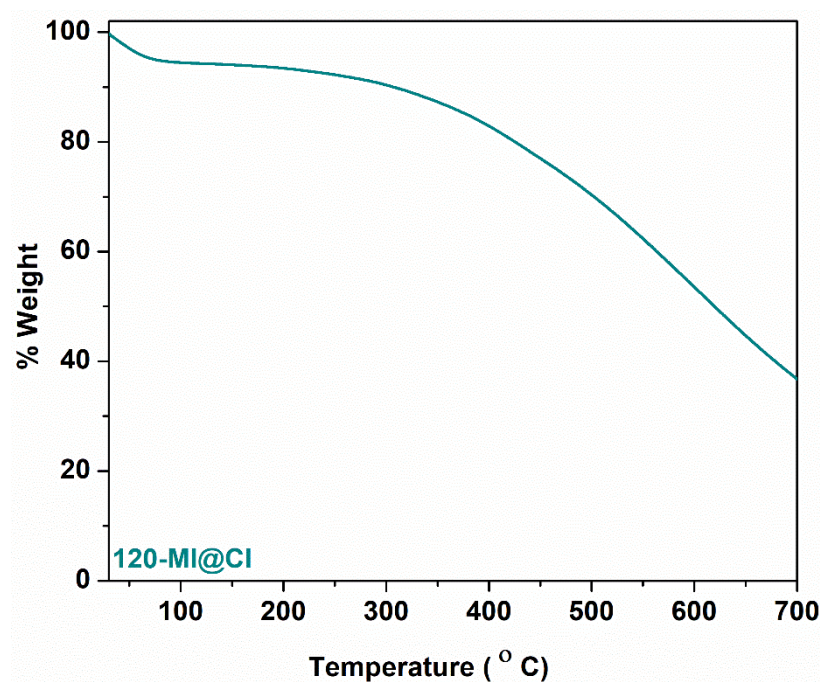
Appendix Figure 3.1. Infra-red (IR) spectra of 120-MI@Cl (cyan) and 120-MI@OH (orange).



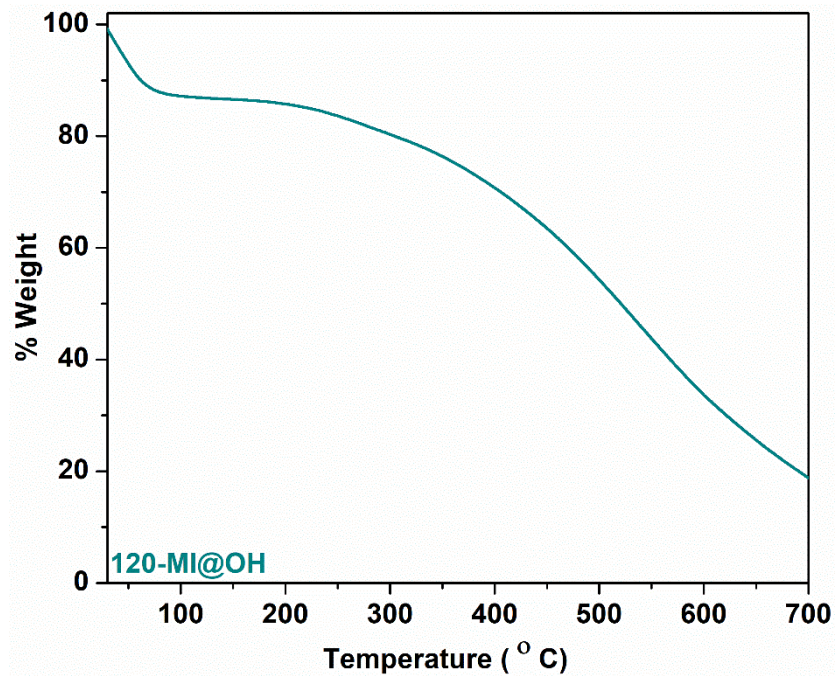
Appendix Figure 3.2. Solid-state ^{13}C CP-MAS NMR spectrum of polymer 120-MI@Cl.



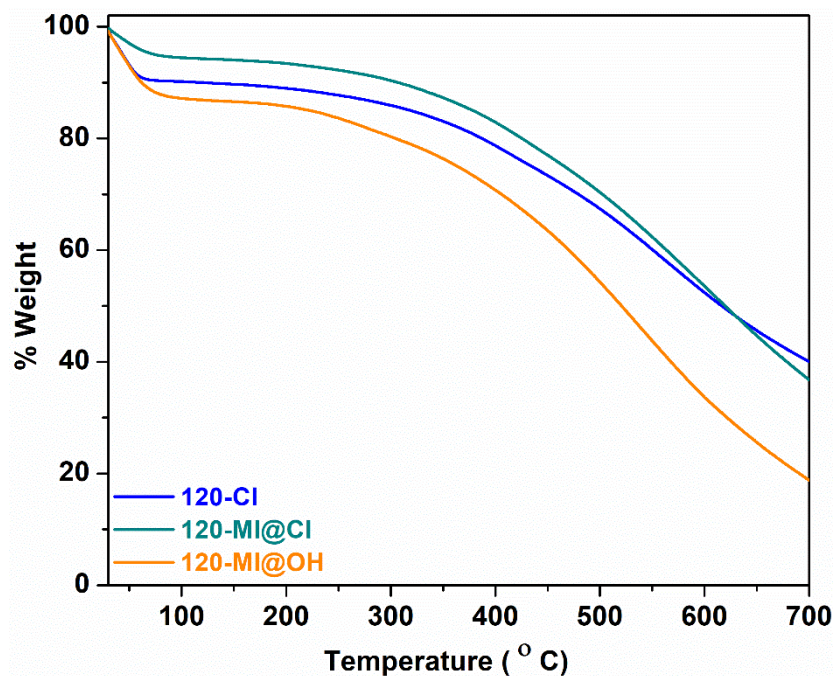
Appendix Figure 3.3. Thermogravimetric profile (Under N_2 atmosphere) for pristine 120-Cl (cyan).



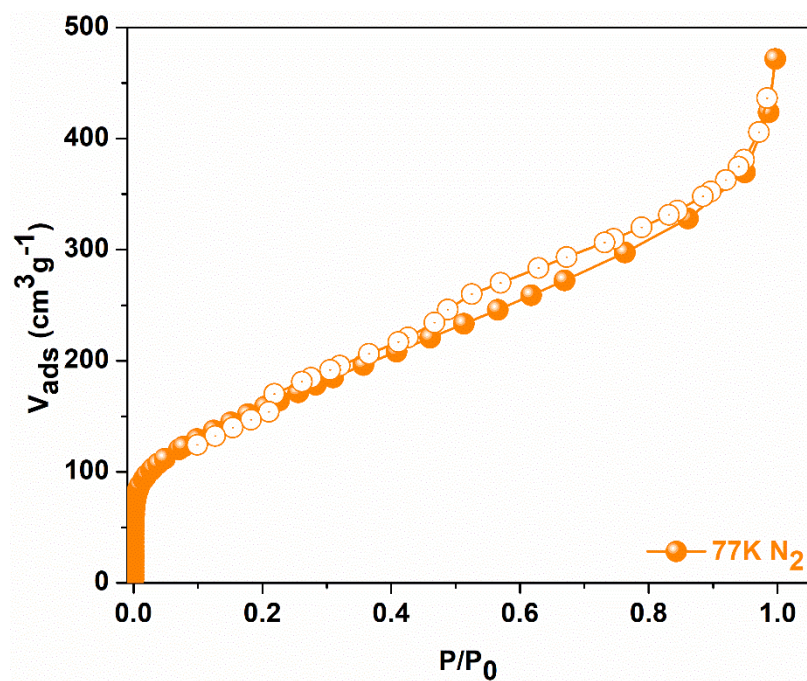
Appendix Figure 3.4. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-MI@Cl (cyan).



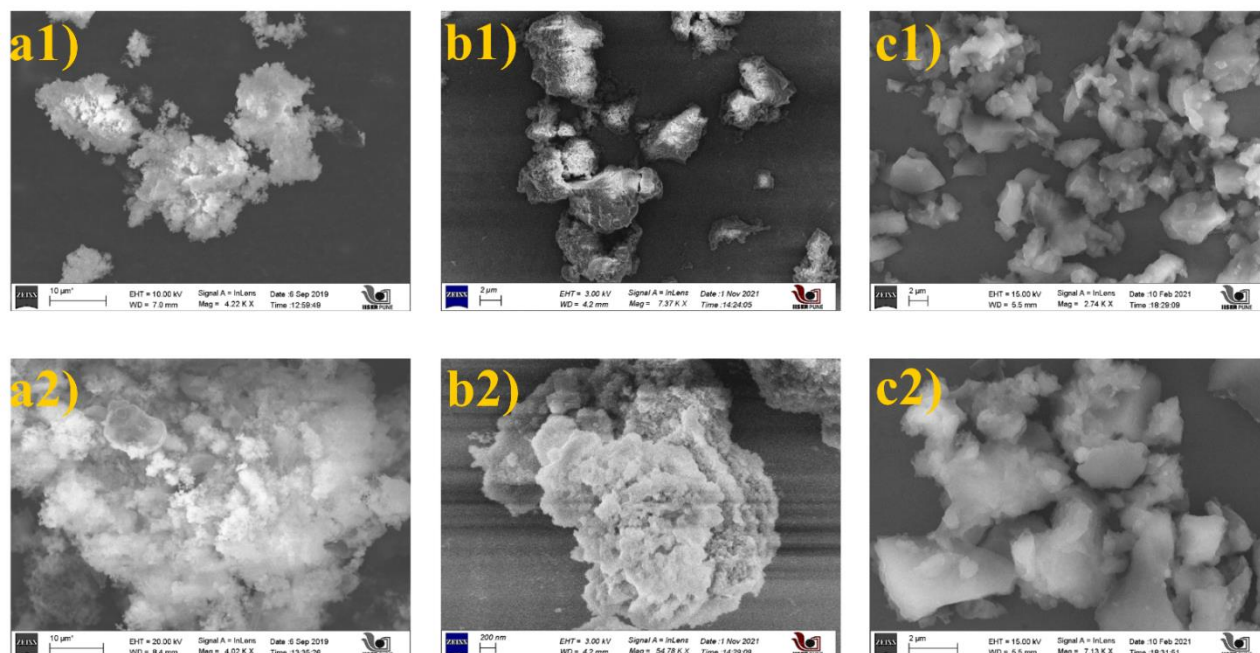
Appendix Figure 3.5. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-MI@OH (cyan).



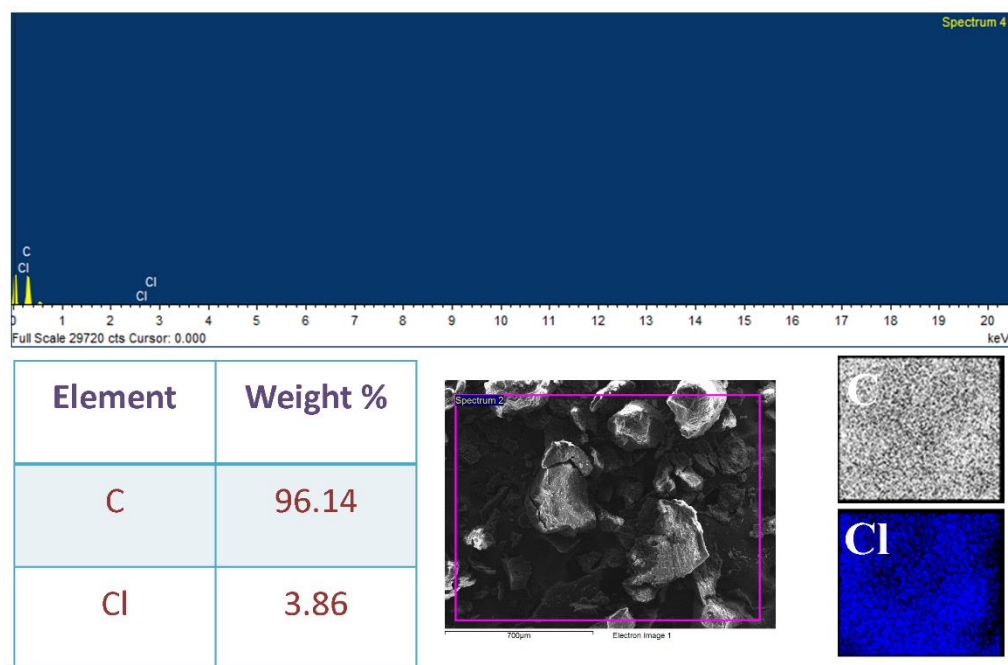
Appendix Figure 3.6. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-Cl (blue), 120-MI@Cl (cyan) and 120-MI@OH (orange).



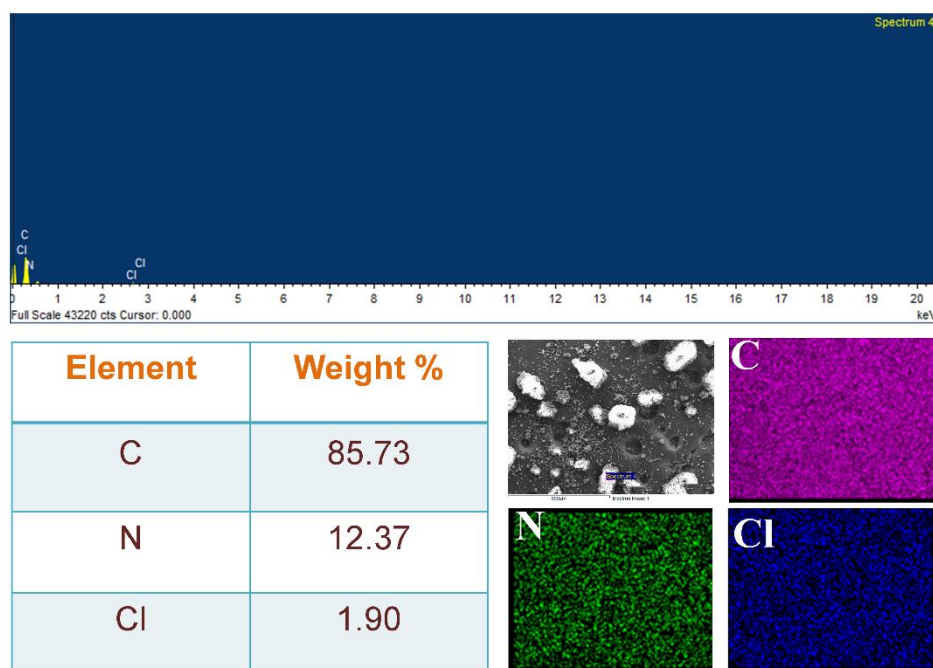
Appendix Figure 3.7. N₂ adsorption profile at 77 K for 120-MI@Cl.



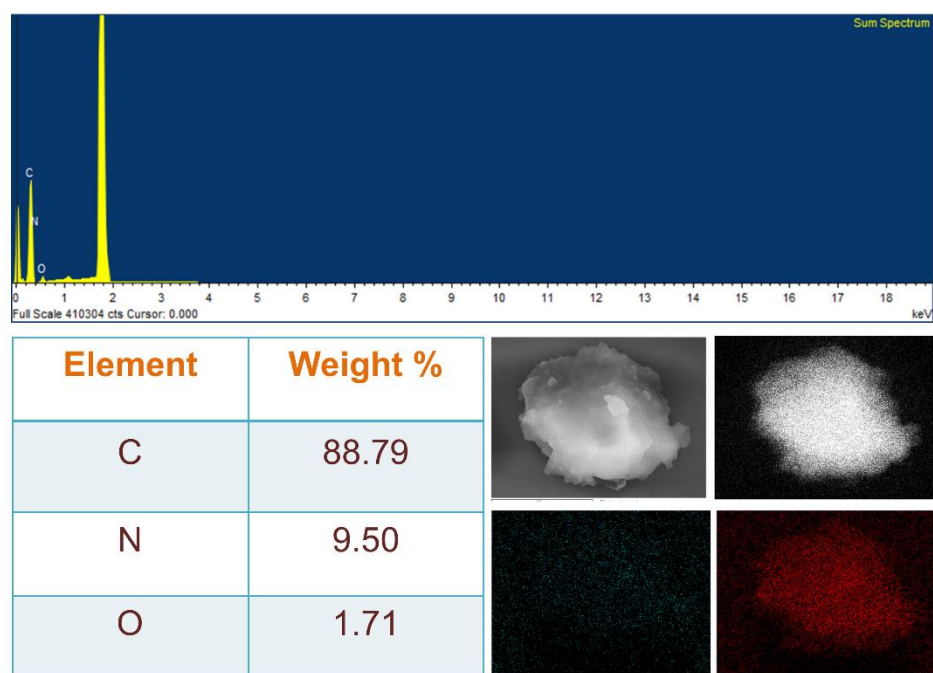
Appendix Figure 3.8. Magnified FESEM images of (a1-a2) 120-Cl, (b1-b2) 120-MI@Cl and (c1-c2) 120-MI@OH, scale bar = 1-2 μM .



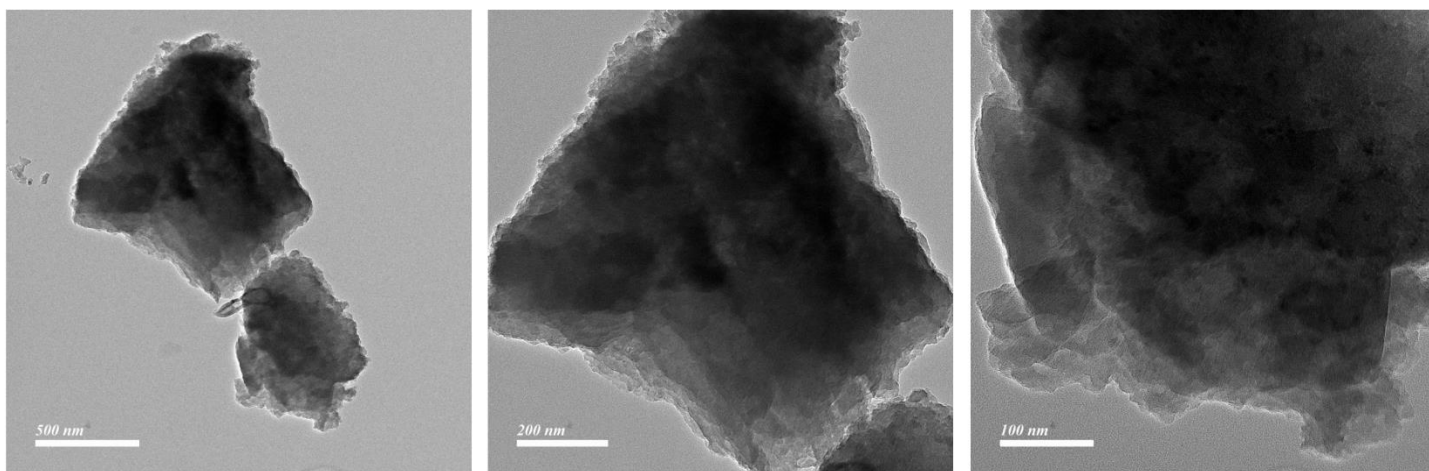
Appendix Figure 3.9. EDX analysis and elemental mapping of 120-Cl.



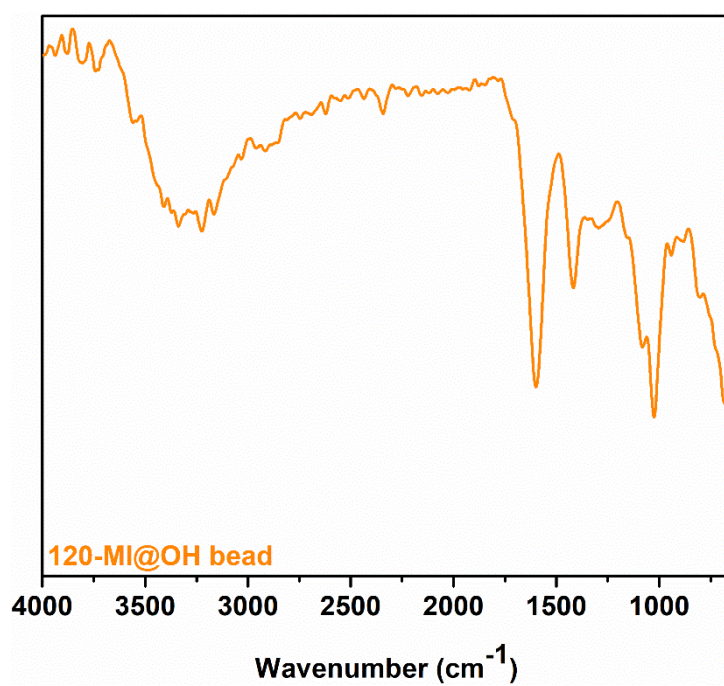
Appendix Figure 3.10. EDX analysis and elemental mapping of 120-MI@Cl.



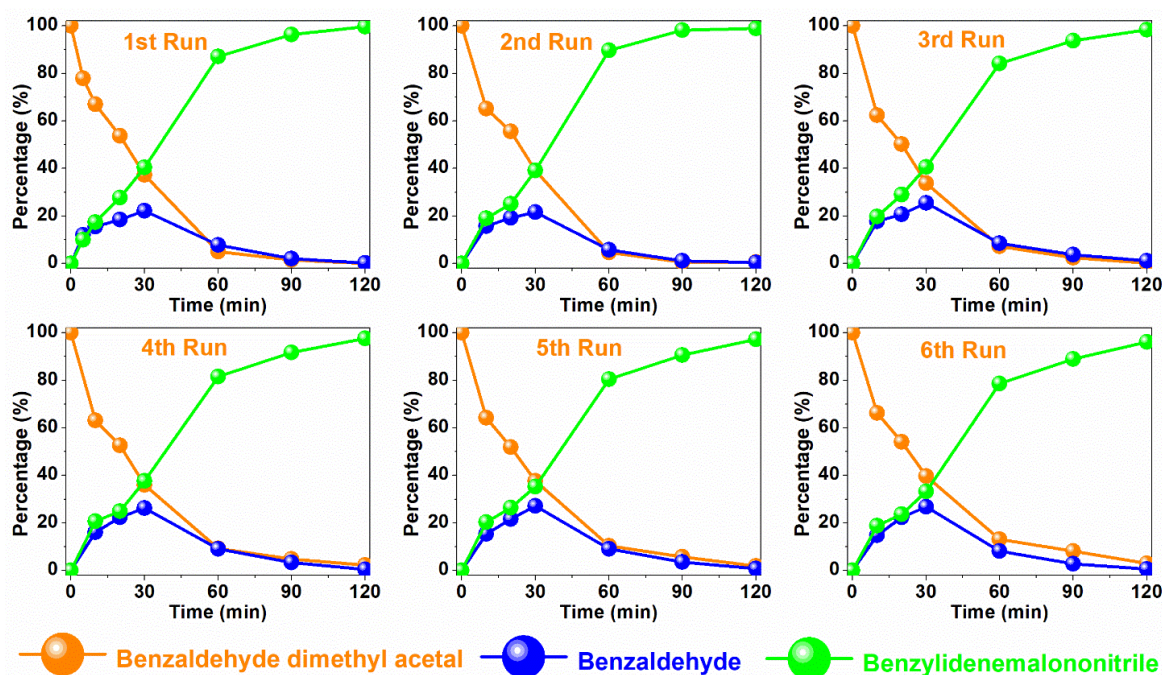
Appendix Figure 3.11. EDX analysis and elemental mapping of 120-MI@OH.



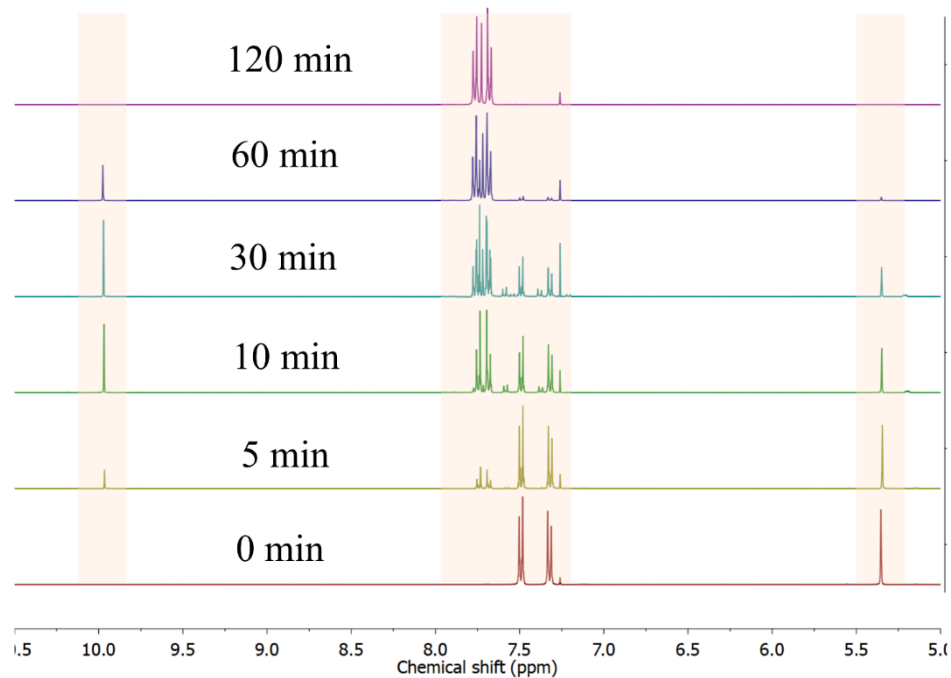
Appendix Figure 3.12. TEM images of 120-MI@OH.



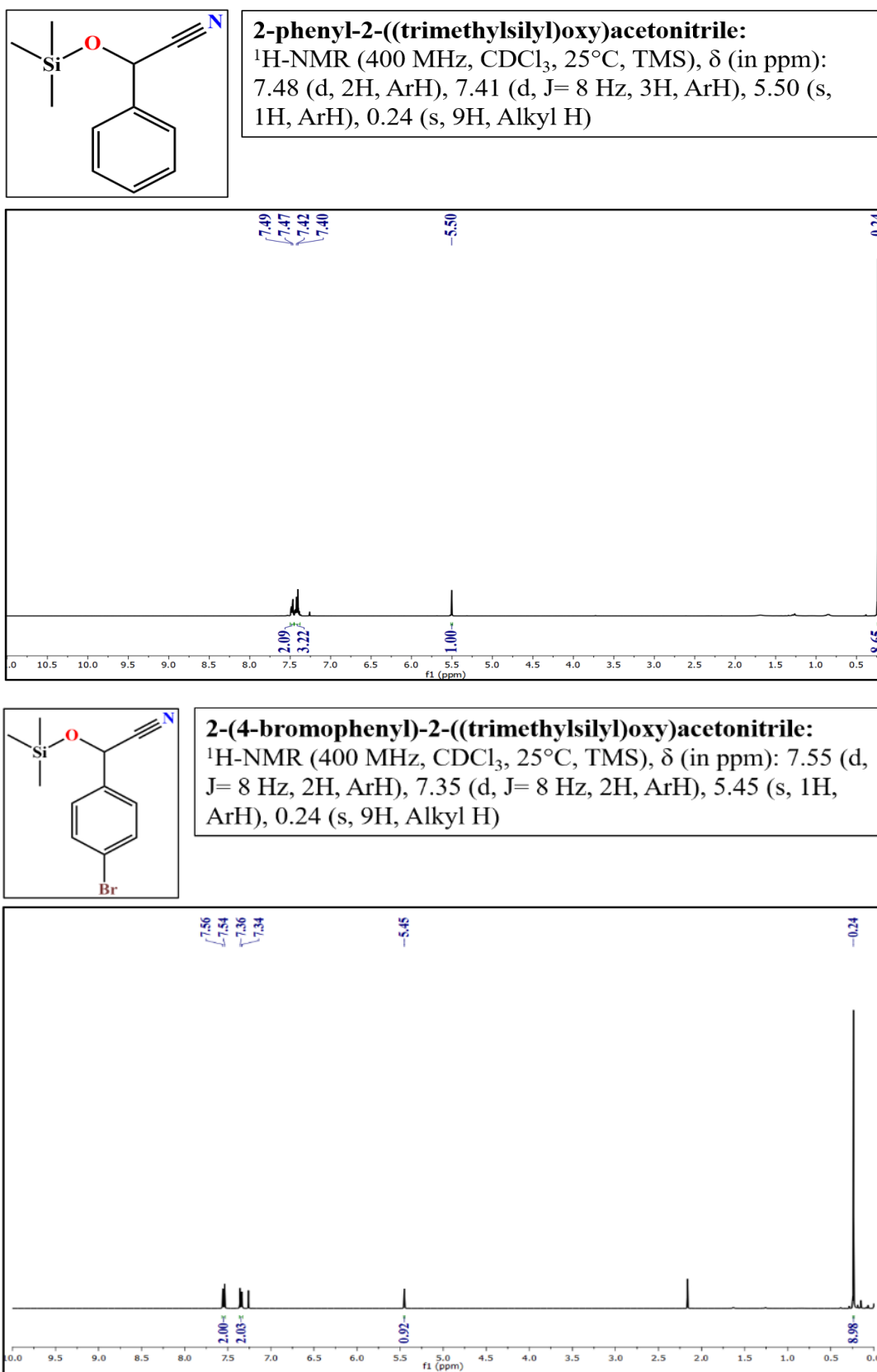
Appendix Figure 3.13. Infra-red (IR) spectrum of 120-MI@OH bead (orange).

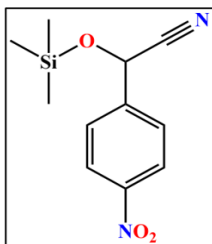


Appendix Figure 3.14. Kinetics monitoring of recyclable cascade catalytic reaction.

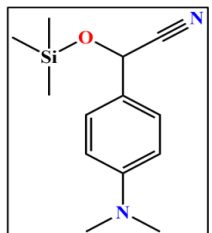
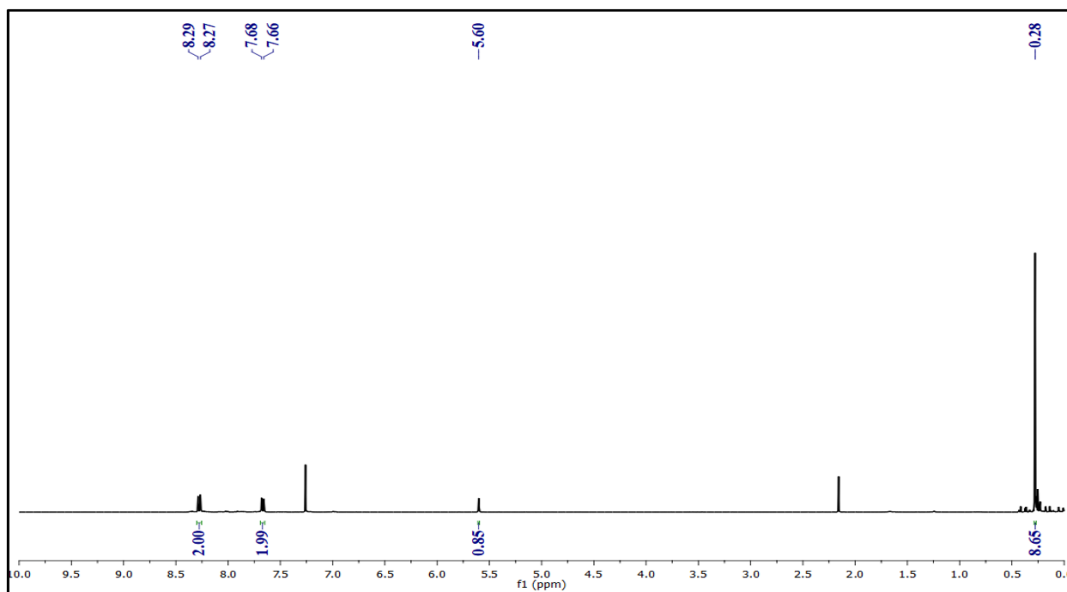


Appendix Figure 3.15. Partial ^1H NMR spectra (CDCl_3) of the cascade reaction at different times (0 min, 5 min, 10 min, 30 min, 60 min and 120 min).

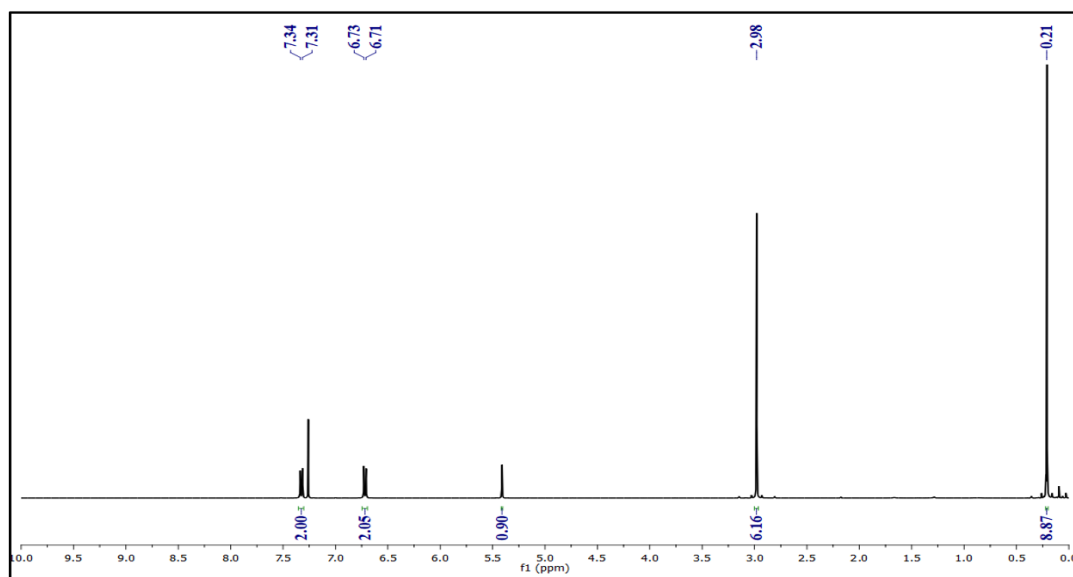
Appendix Figure 3.16. ^1H NMR Spectra of compounds.

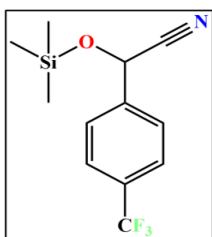

2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.28 (d, $J = 8$ Hz, 2H, ArH), 7.67 (d, $J = 8$ Hz, 2H, ArH), 5.60 (s, 1H, ArH), 0.28 (s, 9H, Alkyl H)


2-(4-(dimethylamino)phenyl)-2-((trimethylsilyl)oxy)acetonitrile:

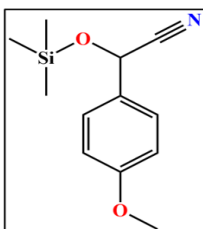
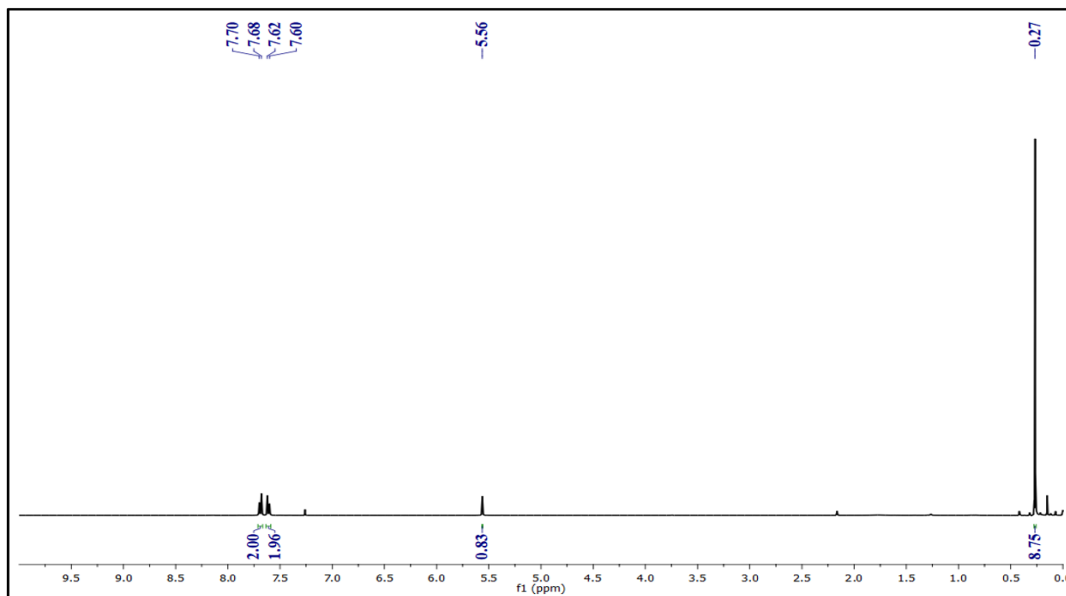
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.33 (d, $J = 8$ Hz, 2H, ArH), 6.72 (d, $J = 8$ Hz, 2H, ArH), 5.4 (s, 1H, ArH), 2.98 (s, 6H, Alkyl H), 0.21 (s, 9H, Alkyl H)





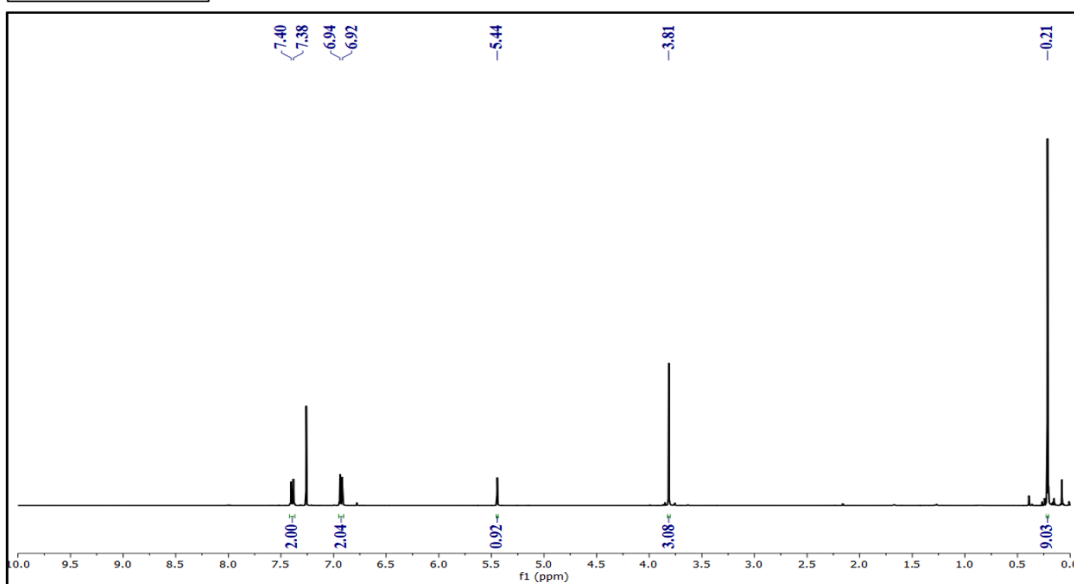
2-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)oxy)acetonitrile:

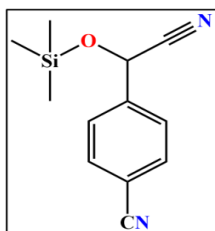
¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.69 (d, J= 8 Hz, 2H, ArH), 7.61 (d, J= 8 Hz, 2H, ArH), 5.56 (s, 1H, ArH), 0.27 (s, 9H, Alkyl H)



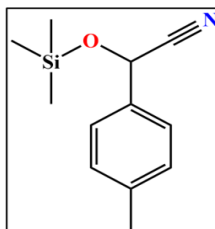
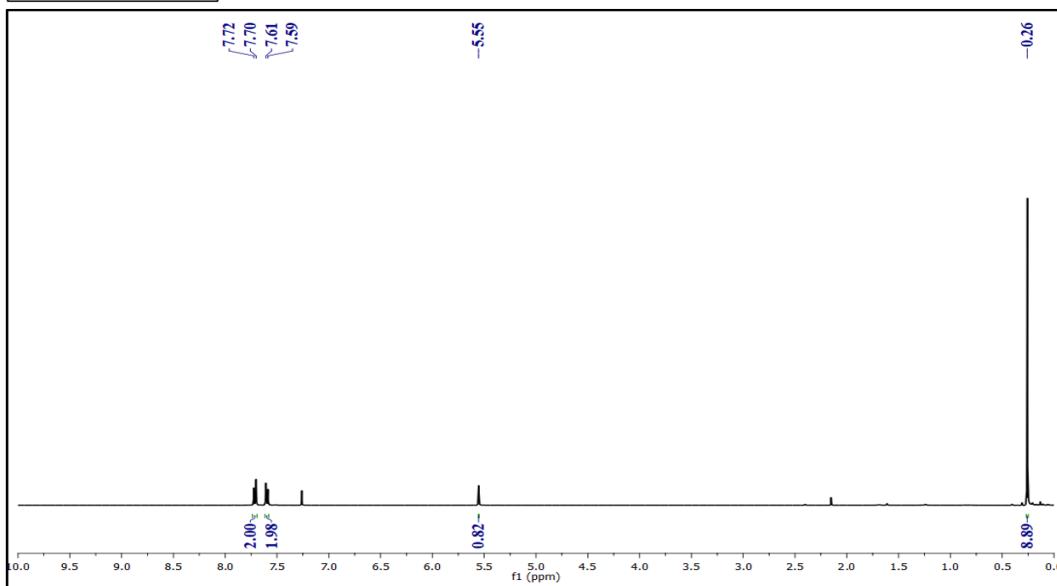
2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile:

¹H-NMR (400 MHz, CDCl₃, 25°C, TMS), δ (in ppm): 7.39 (d, J= 8 Hz, 2H, ArH), 6.93 (d, J= 8 Hz, 2H, ArH), 5.44 (s, 1H, ArH), 3.81 (s, 3H, Alkyl H), 0.21 (s, 9H, Alkyl H)

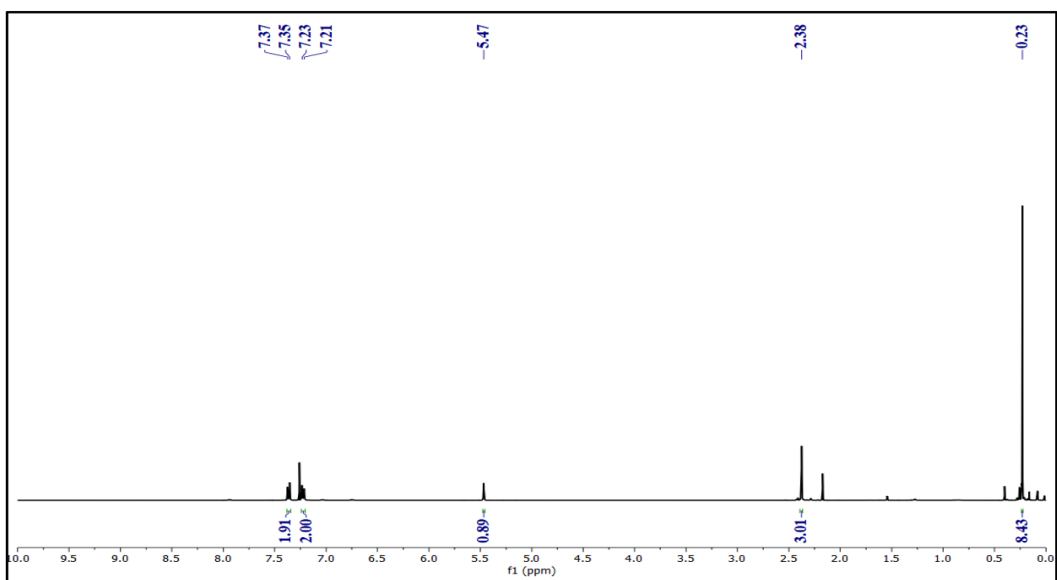


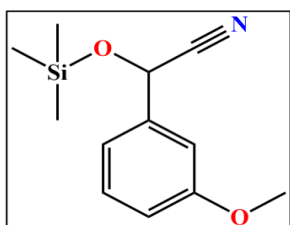

4-(cyano((trimethylsilyl)oxy)methyl)benzonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.71 (d, $J = 8$ Hz, 2H, ArH), 7.60 (d, $J = 8$ Hz, 2H, ArH), 5.55 (s, 1H, ArH), 0.26 (s, 9H, Alkyl H)


2-(p-tolyl)-2-((trimethylsilyl)oxy)acetonitrile:

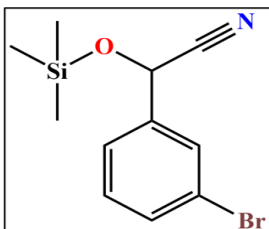
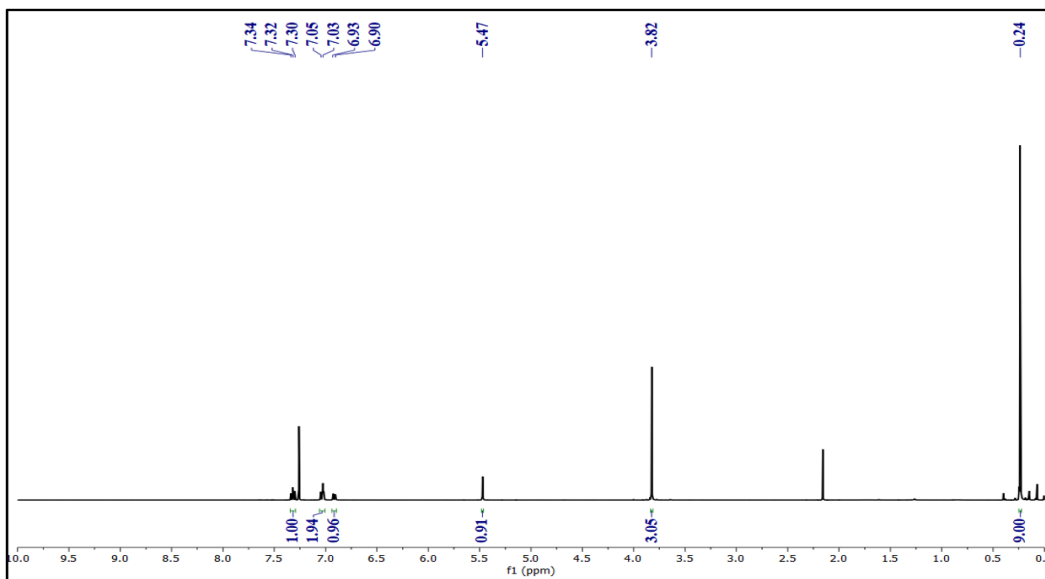
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.36 (d, 2H, ArH), 7.22 (d, $J = 8$ Hz, 2H, ArH), 5.47 (s, 1H, ArH), 2.28 (s, 3H, Alkyl H), 0.23 (s, 9H, Alkyl H)





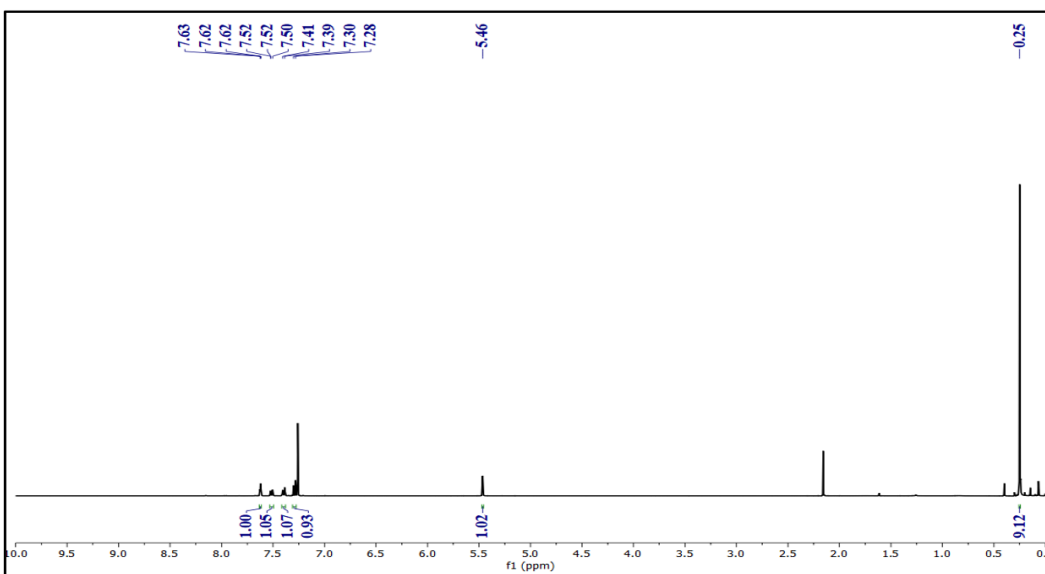
2-(3-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile:

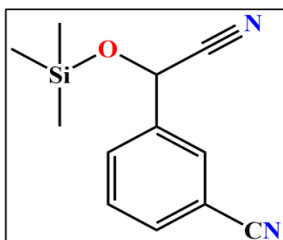
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 7.32 (t, $J = 8$ Hz, 1H, ArH), 7.04 (d, $J = 8$ Hz, 2H, ArH),
 6.91 (d, $J = 8$ Hz, 1H, ArH), 5.47 (s, 1H, ArH), 3.05 (s,
 3H, Alkyl H), 0.24 (s, 9H, Alkyl H)



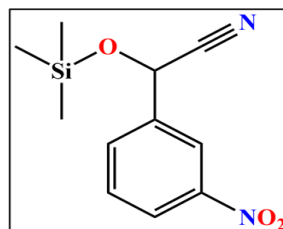
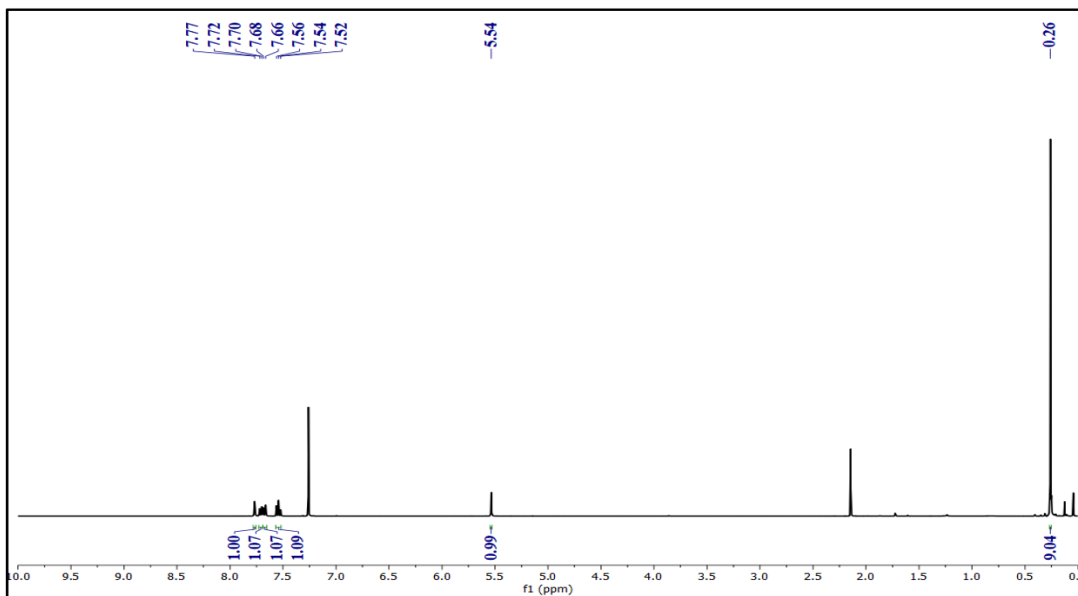
2-(3-bromophenyl)-2-((trimethylsilyl)oxy)acetonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 7.62 (t, $J = 8$ Hz, 1H, ArH), 7.51 (t, $J = 8$ Hz, 1H, ArH),
 7.40 (t, $J = 8$ Hz, 1H, ArH), 7.31 (d, $J = 8$ Hz, 1H, ArH),
 5.46 (s, 1H, ArH), 0.25 (s, 9H, Alkyl H)

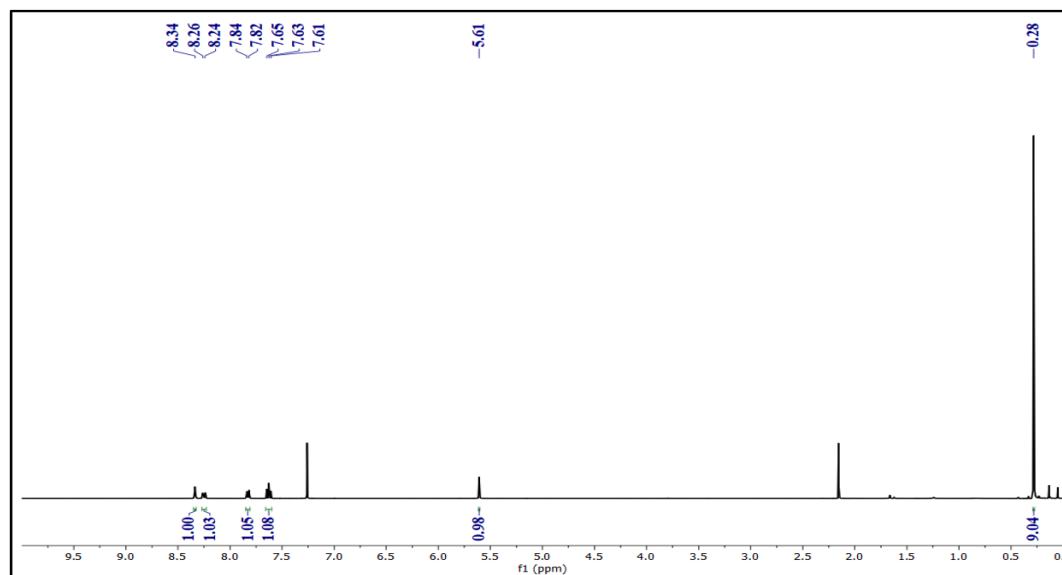


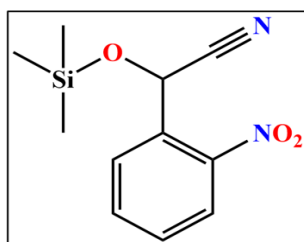

3-(cyano((trimethylsilyl)oxy)methyl)benzonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 7.77 (s, $J = 8$ Hz, 1H, ArH), 7.71 (d, $J = 8$ Hz, 1H, ArH),
 7.67 (d, $J = 8$ Hz, 1H, ArH), 7.54 (d, $J = 8$ Hz, 1H, ArH),
 5.54 (s, 1H, ArH), 0.26 (s, 9H, Alkyl H)

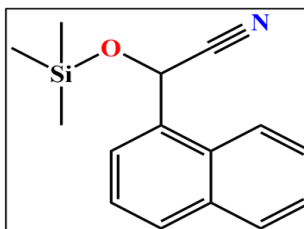
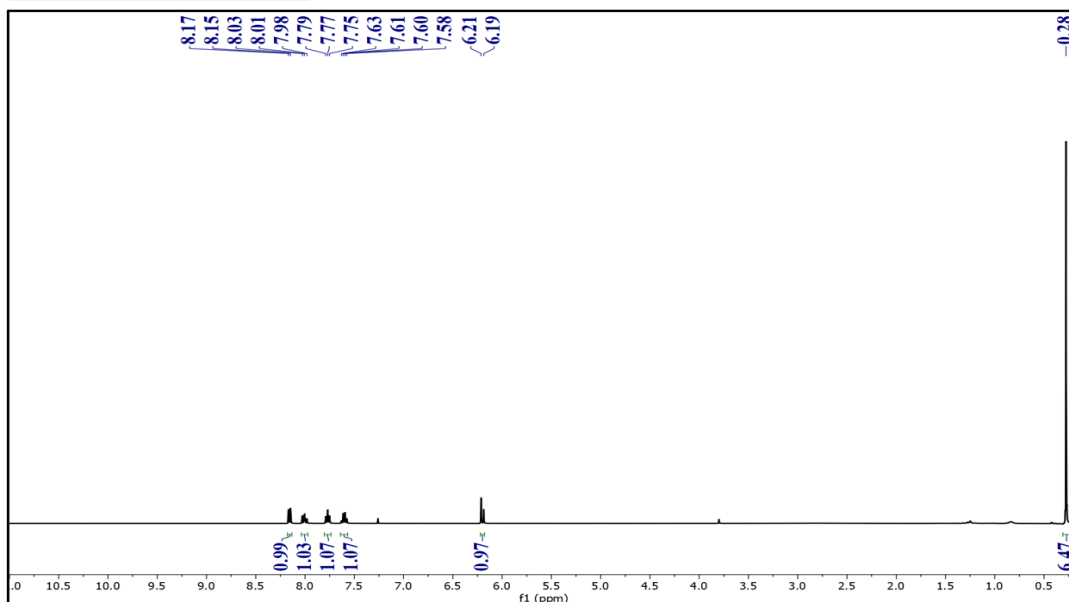

2-(3-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 8.34 (s, 1H, ArH), 8.25 (d, $J = 8$ Hz, 1H, ArH), 7.83 (d, $J = 8$ Hz, 1H, ArH), 7.63 (t, $J = 8$ Hz, 1H, ArH),
 5.61 (s, 1H, ArH), 0.28 (s, 9H, Alkyl H)

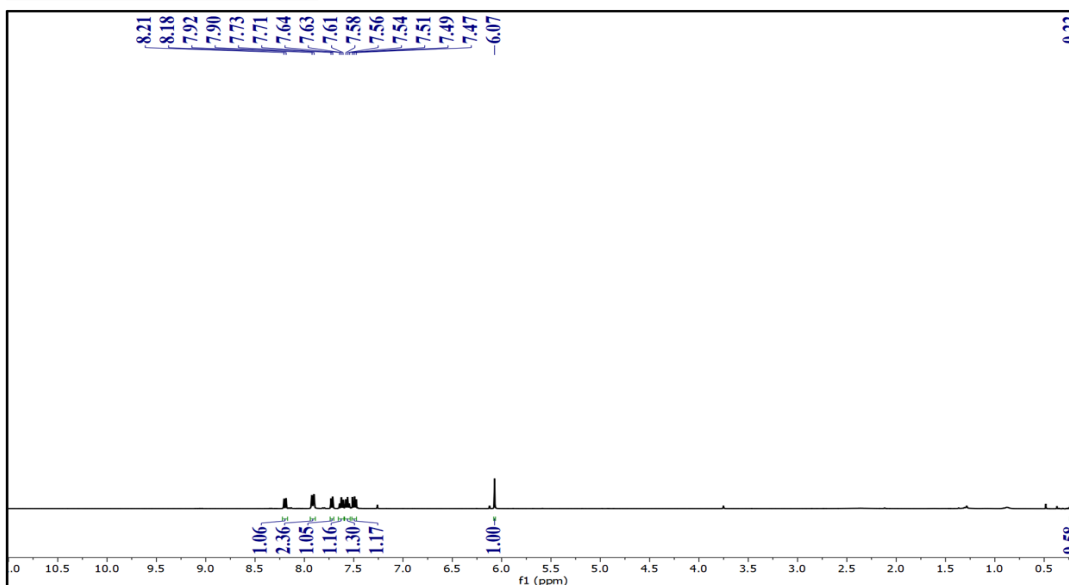


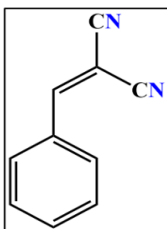

2-(2-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile :

^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 8.16 (d, 8 Hz, 1H, ArH), 8.01 (t, $J = 8$ Hz, 1H, ArH),
 7.77 (t, $J = 8$ Hz, 1H, ArH), 7.60 (m, $J = 8$ Hz, 1H, ArH),
 6.20 (d, 1H, ArH), 0.28 (s, 9H, Alkyl H)

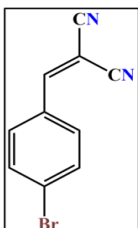
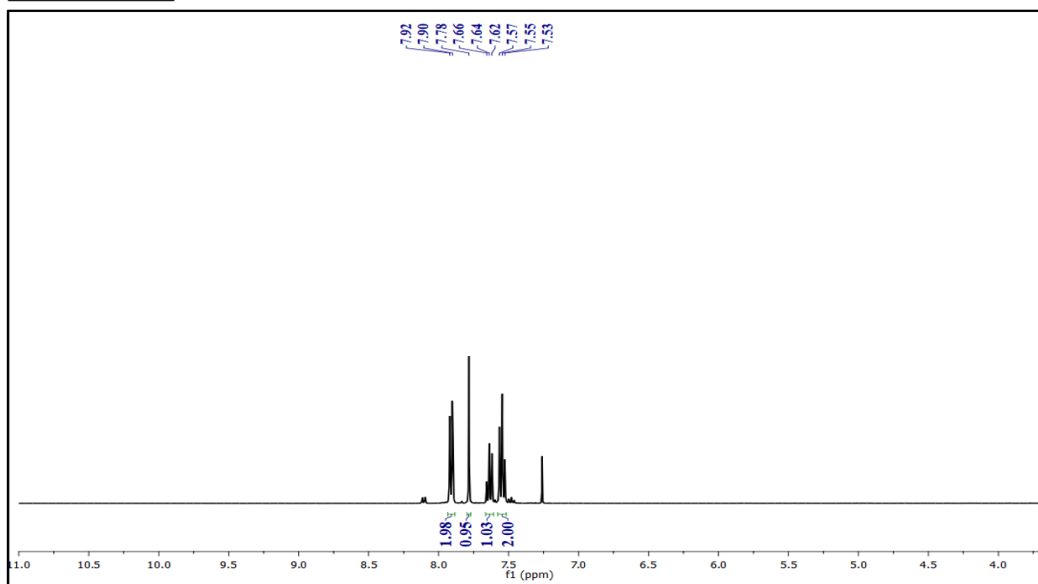

2-(naphthalen-1-yl)-2-((trimethylsilyl)oxy)acetonitrile :

^1H -NMR (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm):
 8.20 (d, 8 Hz, 1H, ArH), 7.91 (d, $J = 8$ Hz, 2H, ArH),
 7.72 (d, $J = 8$ Hz, 1H, ArH), 7.63 (t, $J = 8$ Hz, 1H, ArH),
 7.56 (t, $J = 8$ Hz, 1H, ArH), 7.49 (t, $J = 8$ Hz, 1H, ArH),
 6.07 (s, 1H, ArH), 0.22 (s, 9H, Alkyl H)

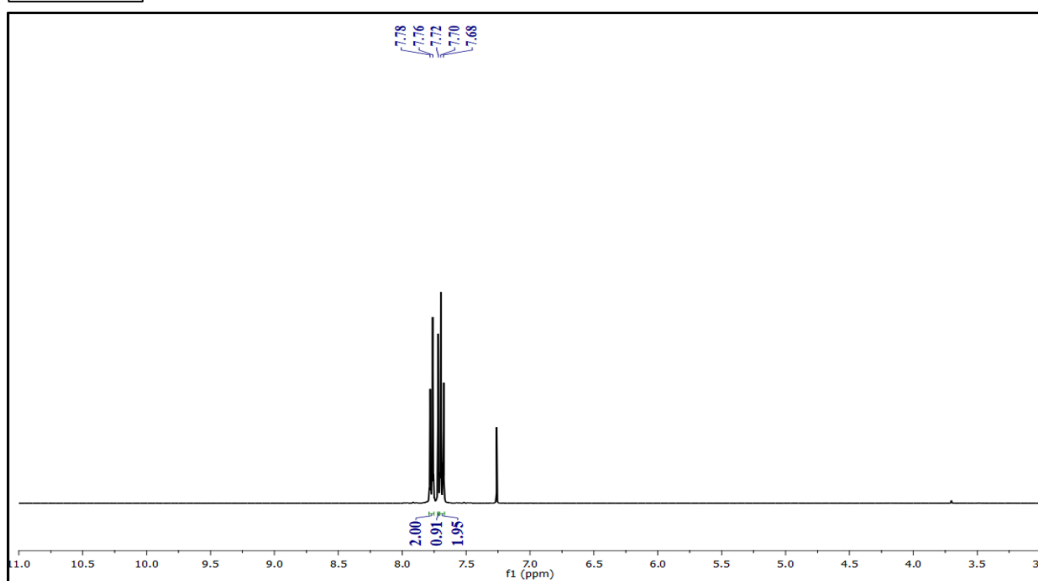


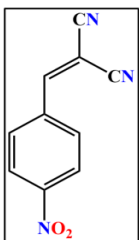

2-benzylidenemalononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.91 (d, $J=8$ Hz, 2H, ArH), 7.78 (s, 1H, ArH), 7.64 (t, $J=8$ Hz, 1H, ArH), 7.55 (t, 2H, $J=8$ Hz, ArH)

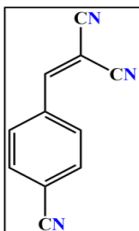
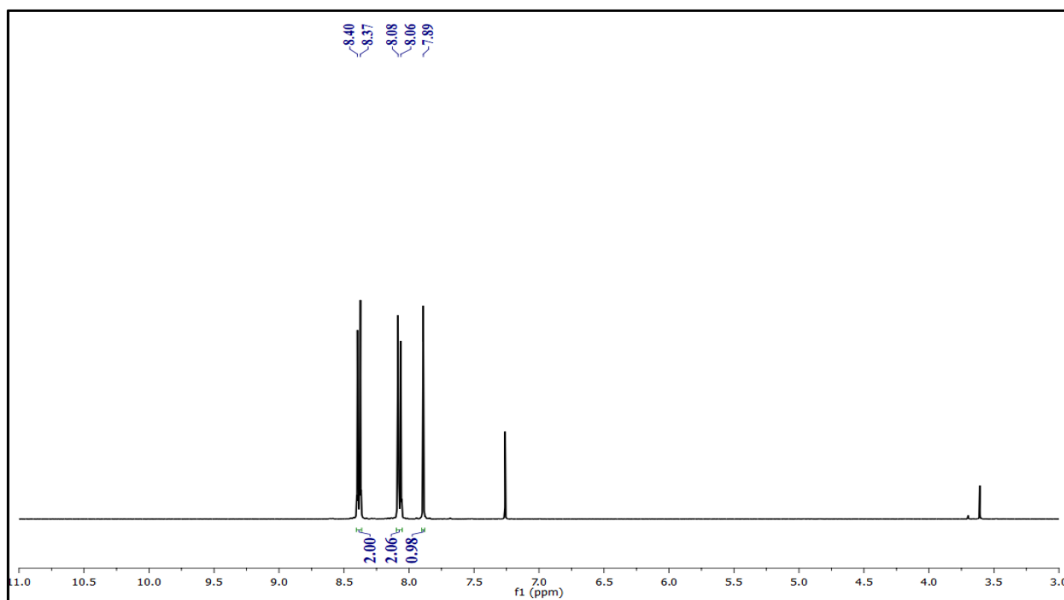

2-(4-bromobenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.77 (d, $J=8$ Hz, 2H, ArH), 7.72 (s, 1H, ArH), 7.69 (d, 2H, $J=8$ Hz, ArH)

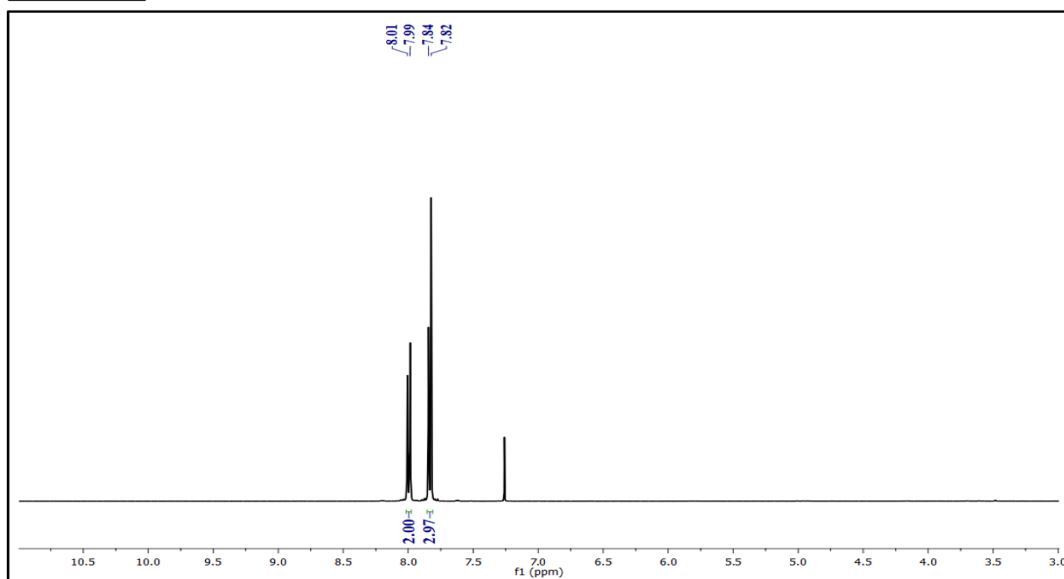


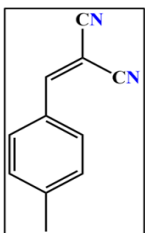

2-(4-nitrobenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.39 (d, $J=8$ Hz, 2H, ArH), 8.07 (d, 2H, $J=8$ Hz, ArH), 7.89 (s, 1H, ArH)

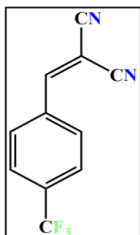
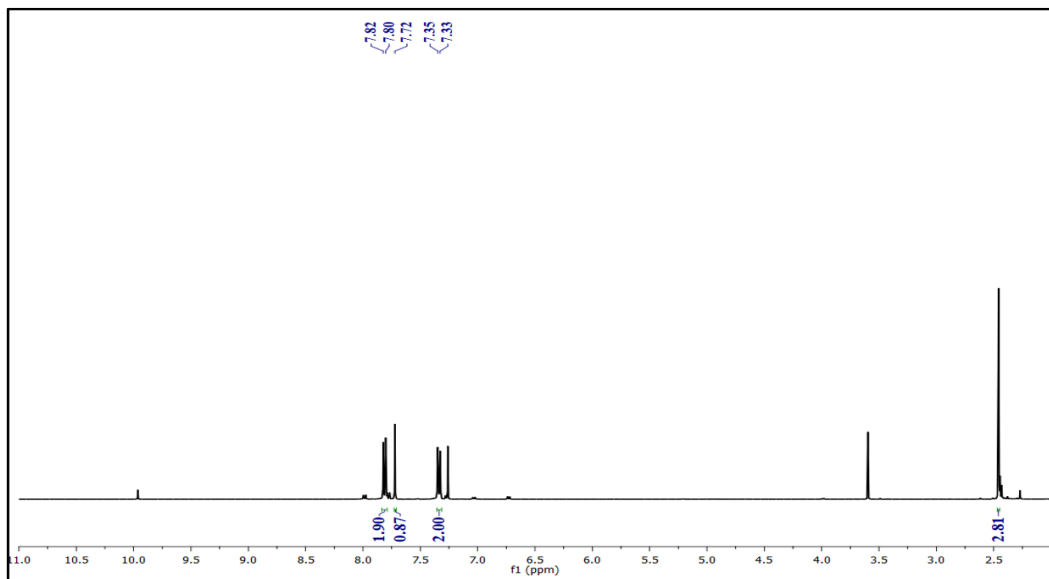

2-(4-cyanobenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.00 (d, $J=8$ Hz, 2H, ArH), 7.83 (d, 2H, $J=8$ Hz, ArH), 7.82 (s, 1H, ArH)

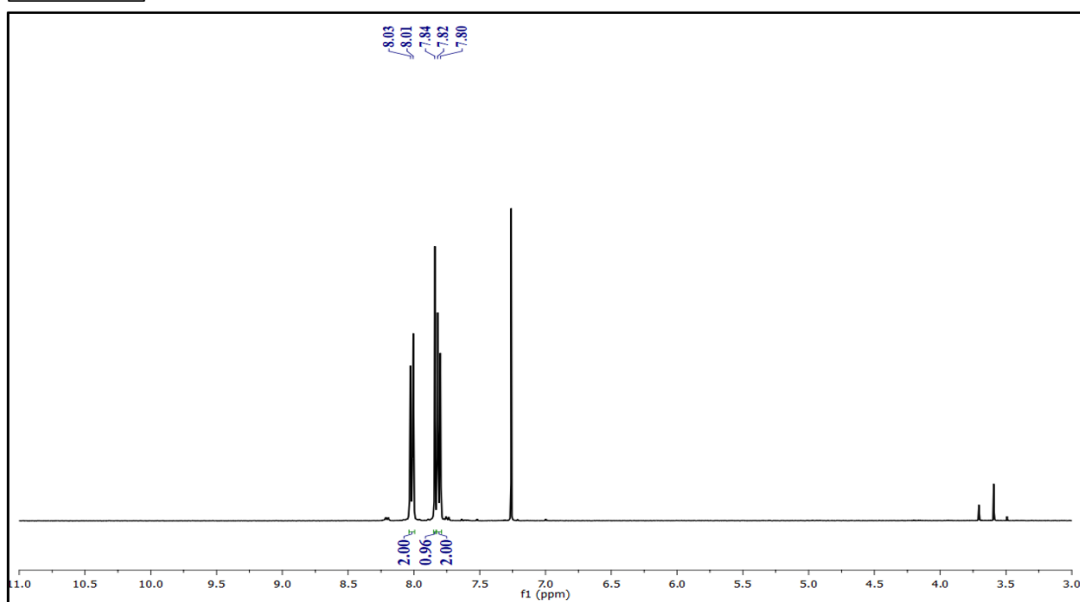


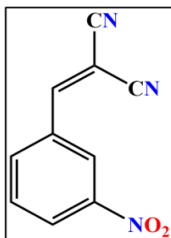

2-(4-methylbenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.81 (d, $J = 8$ Hz, 2H, ArH), 7.72 (s, 1H, ArH), 7.34 (d, 2H, $J = 8$ Hz, ArH), 2.49 (s, 3H, Alkyl H)

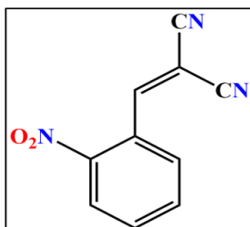
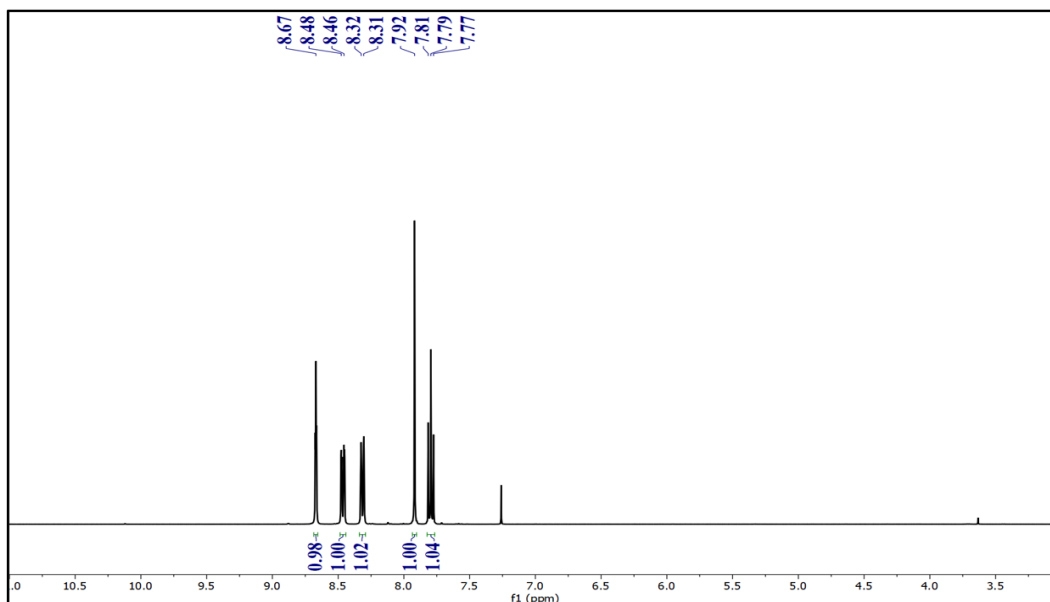

2-(4-(trifluoromethyl)benzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.02 (d, $J = 8$ Hz, 2H, ArH), 7.84 (s, 1H, ArH), 7.81 (d, 2H, $J = 8$ Hz, ArH)

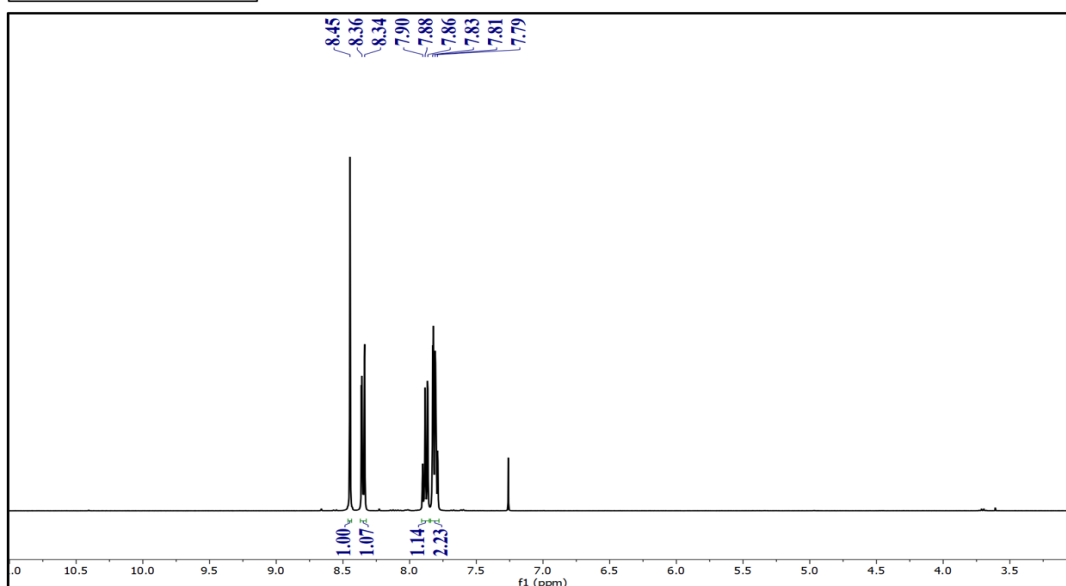


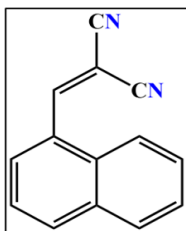

2-(3-nitrobenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.67 (s, 1H, ArH), 8.47 (d, 1H, $J = 8$ Hz ArH), 8.31 (d, 1H, $J = 8$ Hz, ArH), 7.92 (s, 1H, ArH), 7.79 (t, 1H, $J = 8$ Hz, ArH)

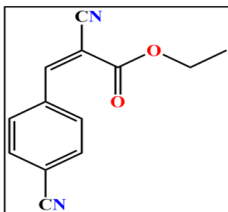
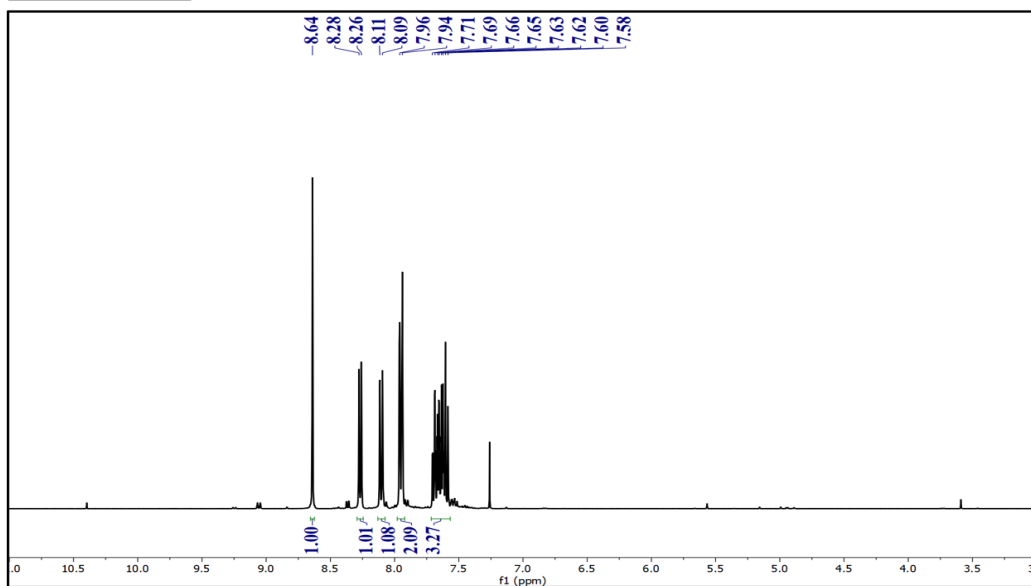

2-(2-nitrobenzylidene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.45 (s, 1H, ArH), 8.35 (d, 1H, $J = 8$ Hz ArH), 7.88 (t, 1H, $J = 8$ Hz, ArH), 7.81 (t, 2H, $J = 8$ Hz, ArH)

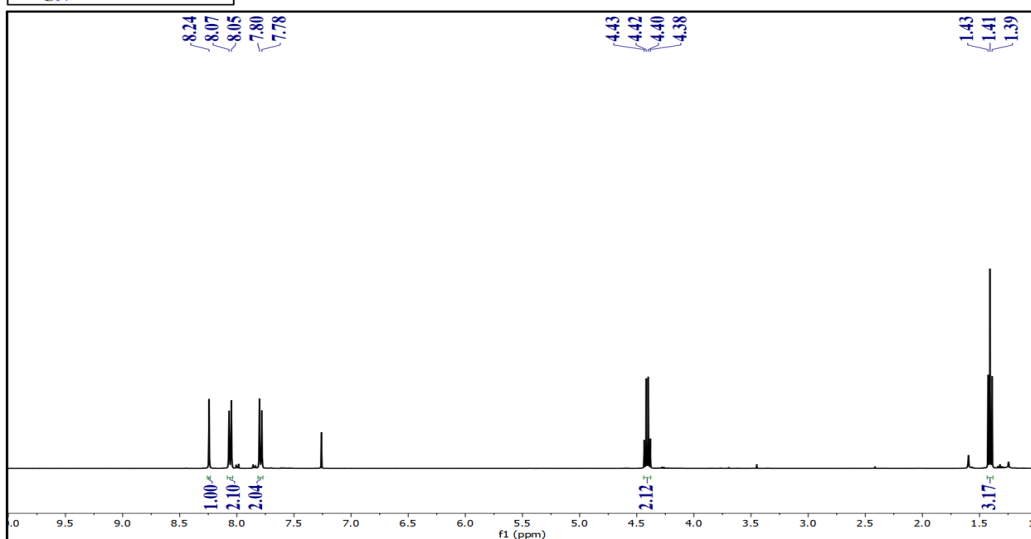


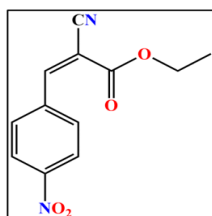

2-(naphthalen-1-ylmethylene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.64 (s, 1H, ArH), 8.27 (d, 1H, $J = 8$ Hz ArH), 8.10 (d, 1H, $J = 8$ Hz, ArH), 7.95 (d, 2H, $J = 8$ Hz, ArH), 7.64 (m, 3H, $J = 8$ Hz, ArH)

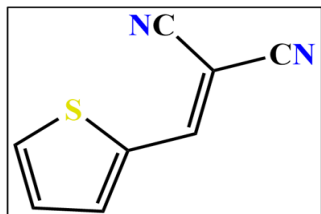
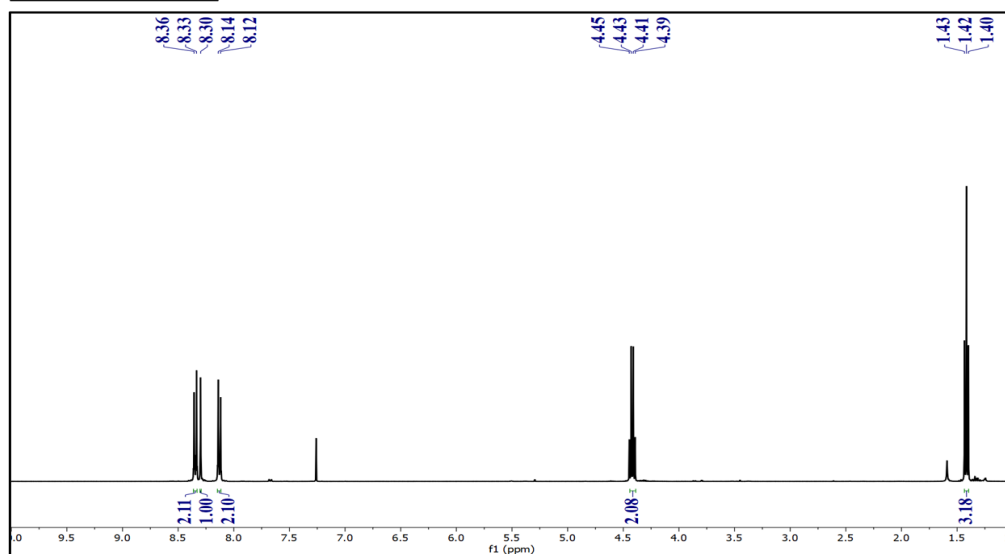

Ethyl-2-cyano-3-(4-cyanophenyl)acrylate:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.24 (s, 1H, ArH), 8.06 (d, $J = 8$ Hz, 2H, ArH), 7.79 (d, $J = 8$ Hz, 2H, ArH), 4.41 (m, $J = 8$ Hz, 2H), 1.41 (t, $J = 8$ Hz, 3H)

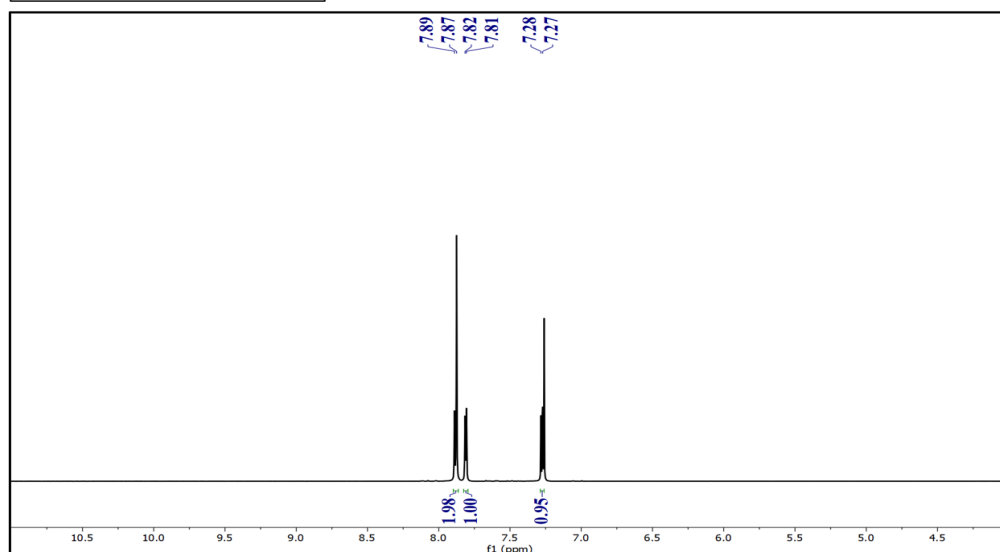


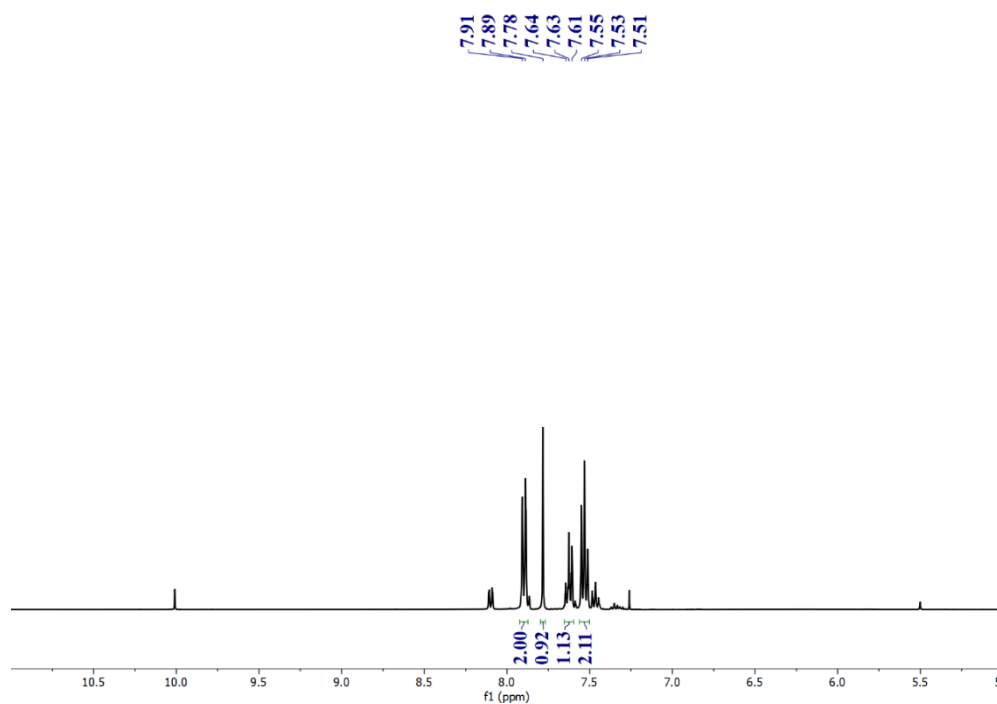

Ethyl-2-cyano-3-(4-nitrophenyl)acrylate:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 8.35 (d, $J = 8$ Hz, 2H, ArH), 8.30 (s, 1H, ArH), 8.13 (d, $J = 8$ Hz, 2H, ArH), 4.42 (m, $J = 8$ Hz, 2H), 1.42 (t, $J = 8$ Hz, 3H)

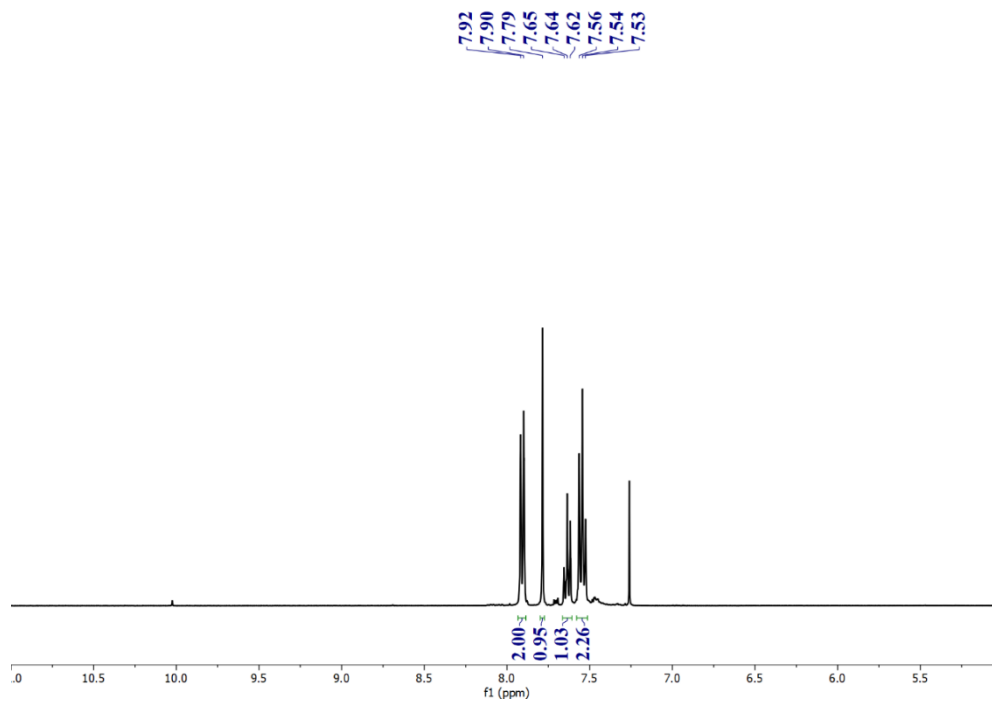

2-(thiophen-2-ylmethylene)malononitrile:

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C , TMS), δ (in ppm): 7.89 (s, 1H, ArH), 7.87 (s, 1H, ArH), 7.81 (d, $J = 8$ Hz, 1H, ArH), 7.26 (t, 1H, ArH)

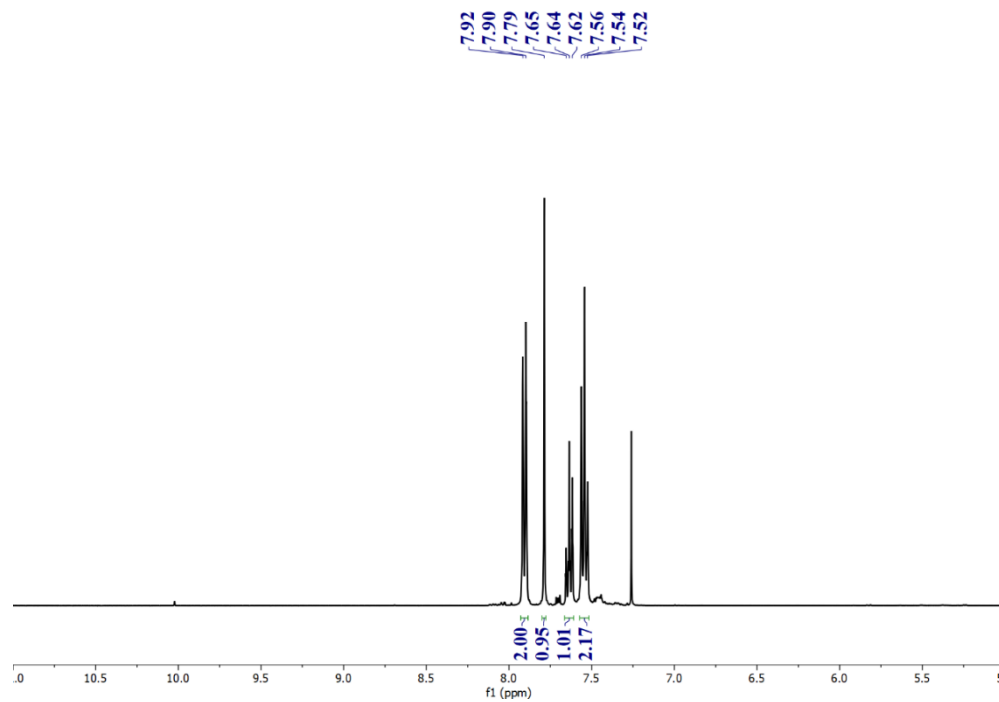




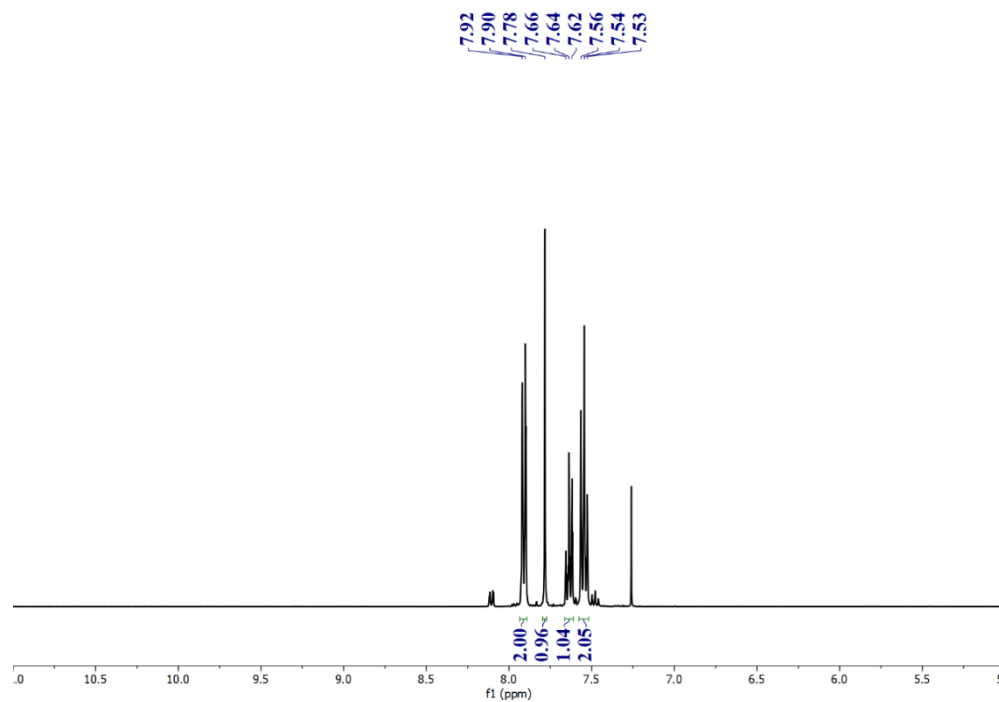
Appendix Figure 3.17. ¹H NMR spectra (CDCl₃) of the cascade catalysis under continuous flow (Run 1)



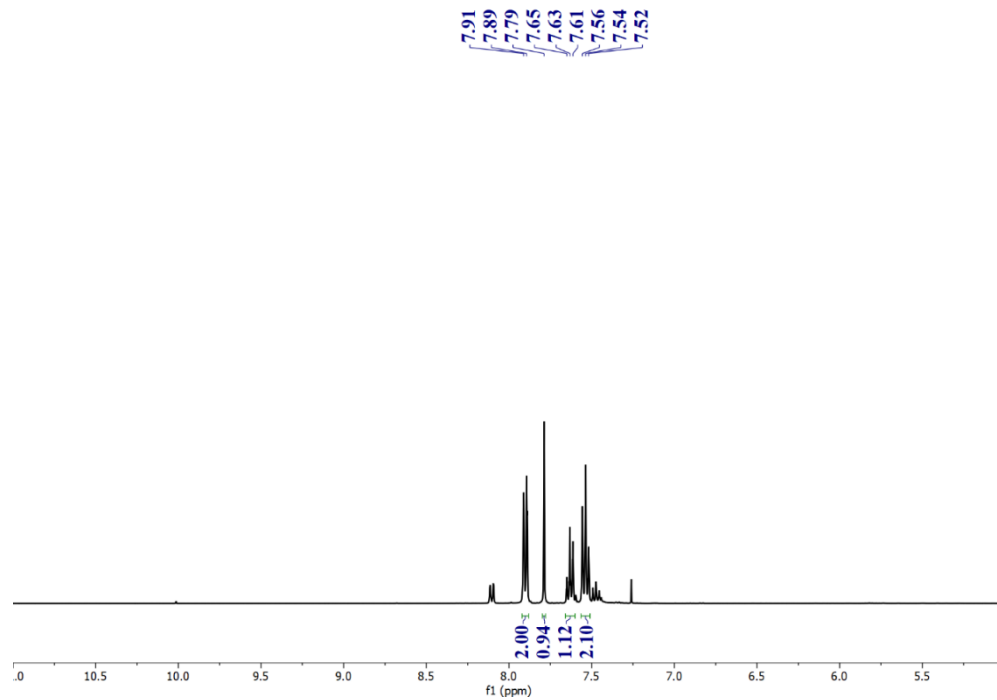
Appendix Figure 3.18. ¹H NMR spectra (CDCl₃) of the cascade catalysis under continuous flow (Run 2)



Appendix Figure 3.19. ¹H NMR spectra (CDCl₃) of the cascade catalysis under continuous flow (Run 3)



Appendix Figure 3.20. ¹H NMR spectra (CDCl₃) of the cascade catalysis under continuous flow (Run 4)



Appendix Figure 3.21. ¹H NMR spectra (CDCl₃) of the cascade catalysis under continuous flow (Run 5)

Appendix Table 3.1. Control experiments for 120-MI@OH catalyzed Knoevenagel condensation reaction

Entry	Catalyst	Solvent	Temp. (°C)	Time	Yield (%) ^b
1.	120-MI@OH (5 mg)	CH ₂ Cl ₂	RT	1 h	56
2.	120-MI@OH (5 mg)	MeOH	RT	1 h	65
3.	120-MI@OH (5 mg)	H ₂ O	RT	1 h	>99
4.	120-MI@OH (5 mg)	H ₂ O	RT	0.5 h	>99
5.	120-MI@Cl (5 mg)	H ₂ O	80	2h	51
6.	No Catalyst	H ₂ O	RT	1h	6.8
7.	Supernatant Liquid of the H ₂ O suspension of 120- MI@OH	H ₂ O	RT	1h	7.3

^a Reaction conditions (Unless otherwise mentioned): a solution of the carbonyl compound (0.8 mmol, 1 equiv.), H₂O (4 mL), malononitrile (0.8 mmol, 1 equiv.), and the heterogeneous catalyst HCP 120-MI@OH (5 mg) was stirred at the indicated temperature for noted time duration. ^b Yield determined from ¹H-NMR.

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Part-II

Fabrication of Task Specific Porous Polymer Nanotraps toward Segregation of Toxic Pollutants in Water

The escalating growth of global population combined with the surge in commodity and energy consumption has emerged as a threat to earth's sustainability of life. Consequently, this has led to immense growth of industries along with global urbanization. Compelling need for necessary goods of modernized societies has resulted in release of unprecedented toxic and hazardous wastes to water streams.^[1] As a result, there has been tremendous increase in water pollution driven by several toxic inorganic as well as organic contaminants.^[2] Having said that, the contemporary technologies to combat water pollution with excellent competency is still not at its best. The United Nations predicts around 10 billion global population while as much as 1 billion of them will not have access to clean water by 2025.^[3-4] Therefore, developing potent and novel materials and technologies to mitigate the pressing concern of water pollution has attracted attention of researchers worldwide. Along this line, Porous organic polymers (POPs) have emerged as efficient next generation materials as promising materials toward water remediation lately.^[5-6] POPs offer great leverage on account of their combined merits of traditional sorbent as well as advanced porous materials such as MOFs.^[7] Being crafted from purely organic functional moieties and propagated through multiple reactive sites via covalent bond formation, POPs are robust amorphous polymeric structures as discussed beforehand.^[8] Additionally, POPs can be both electrostatically neutral as well as charged. While neutral POPs are generally utilized to accommodate neutral guests the ionic POPs (iPOPs) serve as potential candidates for ion-exchange with the counter ions present in the framework.^[8-9] Neutral and ionic POPs (iPOPs) can be synthesized by judicious choice of various synthetic methodologies. In particular, cationic POPs can be constructed by doing quarternization reaction of multitopic aryl halide monomers and several aromatic heterocycles (e.g., imidazole, pyridine) giving free halides as anions.^[10] Also, post-synthetic modulation by alkylation of tertiary amines of the pristine POPs.^[11] On the other hand, anionic POPs can be constructed by deprotonation reaction of functional POPs bearing phenol, carboxylic acid, phosphonic acid, sulphonic acid etc.^[12] Owing to their synthetic versatility and functional tunability POPs have found utility in recognition and segregation of water pollutants toward ameliorating environmental pollution. POPs have two fundamental advantages that make them promising toward toxic pollutants segregation from water. The first being their high physiochemical stability provide by strong covalent bonds throughout the framework backbone which is a prerequisite in water remediation. And secondly, POPs are easily tuneable as the plethora of functional monomers can be used to render desired functionality decorated pore surfaces to fabricate task-specific materials.

Building on the design rationale discussed above this section comprises of two chapters i.e. chapter 4 and chapter 5. In the chapter 4, an ionic composite polymer is utilized to efficiently capture various class of organic micropollutants via magnetic separation. In chapter 5, Taking inspiration from nature, a charged

macroporous porous organic polymer (POP) was strategically designed for efficient simultaneous trapping of Hg^{2+} and Se (IV)/Se (VI) from water.

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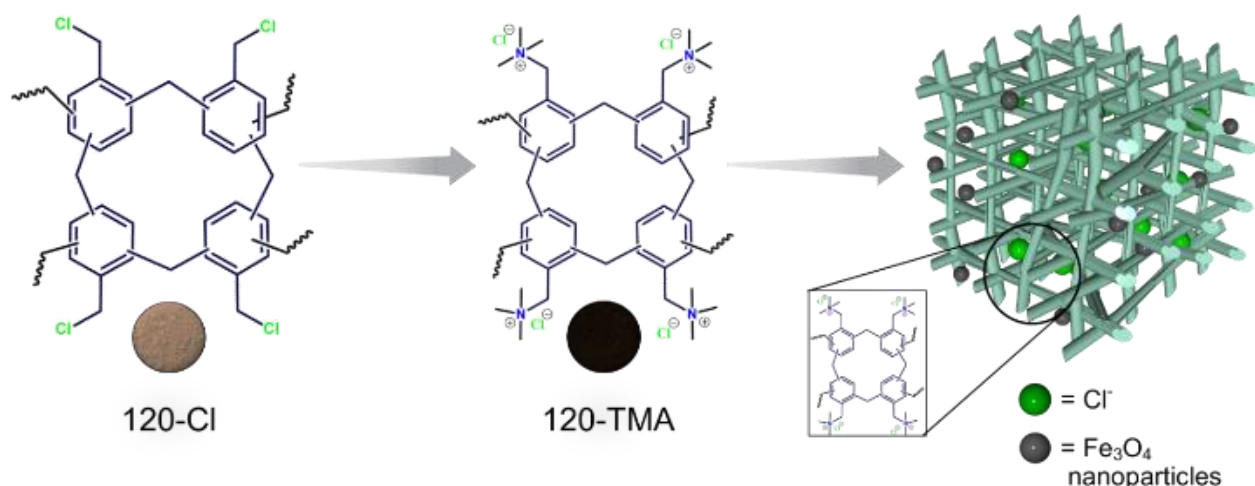
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Chapter 4

Magnetic Nanoparticle-Embedded Ionic Microporous Polymer Composite as an Efficient Scavenger of Organic Micropollutants

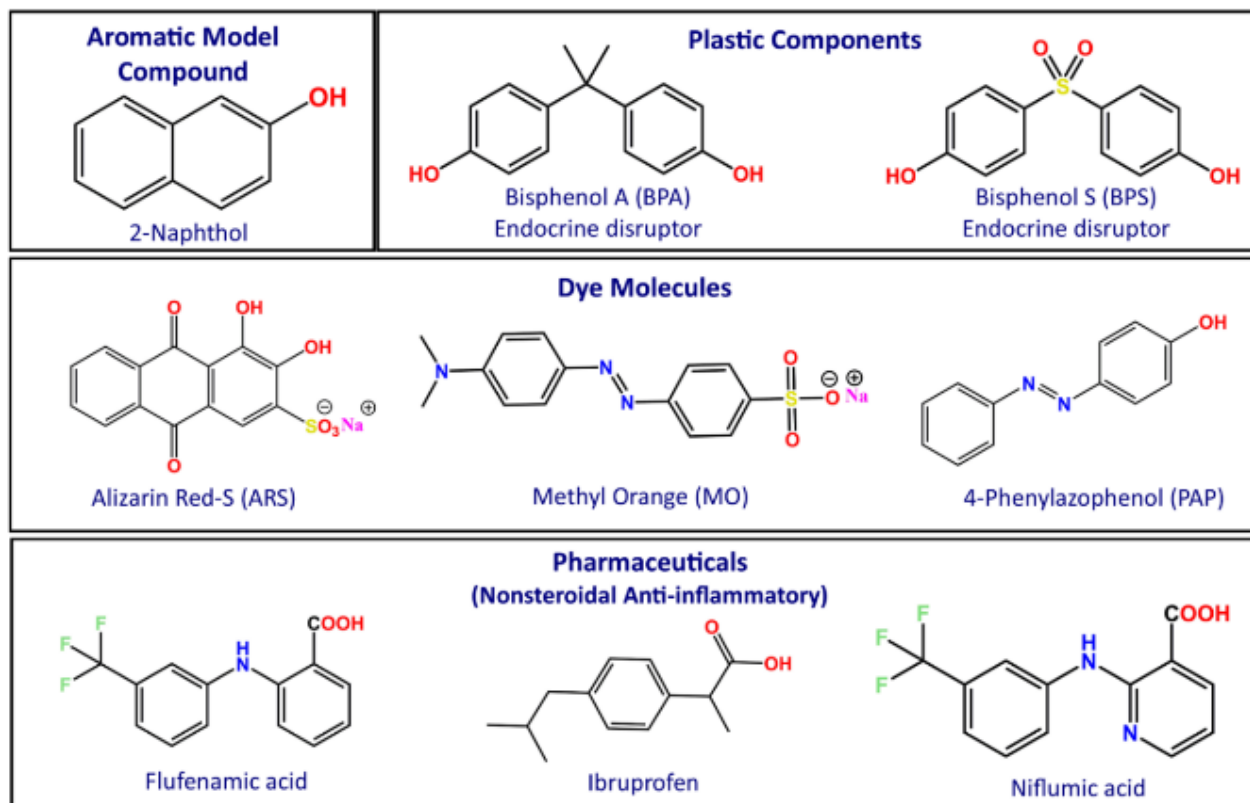
4.1 Introduction

Environmental pollution, by definition, is the accumulation of any contaminant, either in the form of a substance or energy, at a faster kinetics than its decomposition or dilution into nontoxic products.^[1] The gravity of environmental pollution and its after effects are so appalling that unrestricted access to clean freshwater along with good health and well-being features as the sustainable development goals of the United Nations.^[2] In particular, water pollution has grown into a genuine concern for the global population and has attracted consequential research interest worldwide.^[3–5] Recognizing this issue, the World Health Organization (WHO) reckons that 3 billion people around the globe lack access to safe drinking water.^[6] Organic micropollutants, a myriad array of molecules comprising organic dyes, pharmaceuticals, hormones, pesticides, and industrial chemicals, are dominant contributors toward water pollution.^[7,8] Of 100,000 commercially available dyes having a production rate over 7×10^5 tons annually, around 2% are discharged into various water bodies.^[9] Many, amongst these micropollutants, especially aromatic molecules, are biologically nondegradable and can have detrimental effects on the environment, aquatic ecosystem, and human health even when present at negligible concentrations owing to their mutagenic as well as carcinogenic nature.^[10,11] Additionally, there are organic micropollutants identified to be endocrine disruptors, while several others can cause severe aesthetic complications well as chronic toxicity when enriched in surplus amounts in humans and animals.^[12,13] On the other hand, categorically nonsteroidal anti-inflammatory drugs (NSAIDs) as anti-inflammatory and analgesic remain amongst the most prominently used pharmaceuticals. Statistically, a study implemented by the U.S. Department of Health and Human Services under The National Health Interview Survey disclosed that nearly 72 million adults (31.1% of U.S. population) conform to the regular usage of NSAIDs in 2010, accounting for a 40% increase after 2005.^[14] Furthermore, the large-scale and increasing production of NSAIDs with ever-increasing consumption intensifies the discharge of these pharmaceuticals, the aftermath being the continuous documentation of the emergence of these materials in various water bodies, for example, groundwater, surface water, and sewage water.^[15,16] As a result, the accumulation of these leaked NSAIDs known as “emerging pollutants” could prove poisonous toward the aquatic ecosystem or have adverse effects on human health via contamination of potable water.^[17] Therefore, it becomes apparent to develop fast, potent, and economic as well as environmentally benign wastewater remediation methods to ameliorate water pollution for the whole scientific and industrial community.^[18] The context-current technologies adopted or considered are inclusive of membrane filtration, coagulation, chemical oxidation, flocculation, photocatalytic degradation, and adsorption.^[19,20] As is known, adsorption driven entrapment offering



Scheme 4.1. Schematic Diagram of HCP 120-Cl and HCP 120-TMA and Schematic Illustration of HCP 120-TMA@Fe Composite.

ease of operation, versatility, and potency along with low energy economy and cost-effectiveness has come forth as a preferential option.^[21,22] Currently, activated carbons (ACs) and resins are amongst extensively utilized sorbent materials but remain suboptimal till date.^[23,24] Their major persisting impediments are sluggish kinetics, lesser efficiency, and extremely energy-intensive regeneration procedure, for example, 500–900 °C heating that often does not offer fully restorable capacity.^[25,26] Alternatively, functionalized mesoporous silica, zeolites, including metal–organic frameworks (MOFs), as well as layered double hydroxides (LDHs) and MXenes have also been explored in seeking potential sorbent materials toward removing toxic pollutants present in water.^[27–35] However, a narrow pore aperture of zeolites and inferior stability of MOFs prevent their applicability.^[36,37] To this end, it still remains challenging as well as a crucial research topic to rationally design and construct superior sorbent materials for fast and efficient trapping of toxic water pollutants. In comparison to ACs, porous organic solids have advanced as an emergent class of porous solids possessing superior chemical and thermal stability, high surface area, tunability of molecular architectures, not requiring heavy elements, and the feasibility of post-synthesis tailorability.^[38,39] Along the same line, porous organic polymers (POPs), crafted from simple inexpensive small molecules through self-condensation and also via the cross-linking strategy have gained considerable appreciation as sorbent materials in diverse applications that transcend beyond wastewater remediation.^[40,41] POPs offer a great leverage of molecular level control in order to realize tailor-made nanospace both in terms of porosity and desired chemical functionalities toward targeted applications.^[42,43] Built on strong covalent bonds, these nanomaterials are insoluble, potent, offer simple regeneration, and have exceptional stability under extreme conditions that make them desirable in practical water detoxification.^[44–46] Hyper-cross-linked polymers (HCPs) represent a relatively new subclass of porous organic polymers. A one-step Friedel–Crafts reaction serves as the cornerstone in constituting the network structure of aromatic molecules through extensive



Scheme 4.2. Chemical Structures of Organic Micropollutants Studied in This Work.

hyper-cross-linking polymerization with anhydrous FeCl_3 acting as the catalyst, while formaldehyde dimethyl acetal (FDA) behaves as an external cross-linker.^[47] The straightforward single-step synthetic protocol of HCPs in combination with their superior physiochemical stability, structural tunability through the variation of organic monomeric units, as well as mild and cost-effective synthesis have intrigued considerable research attention lately.^[48,49] These nanomaterials have displayed good potency in the areas of carbon capture,^[50] gas adsorption and separation,^[51] heterogeneous catalysis,^[52] sensing,^[53] drug delivery,^[54] and so forth. In fact, there are a few functionalized hyper-cross-linked polymers that have been investigated toward environmental remediation, illustrating faster kinetics and high uptake capacity along with good selectivity.^[55,56] Till date, HCPs have not been extensively utilized as an efficient scavenger to ameliorate water pollution and remain at a nascent stage. The design rationale in fabricating a polymer-based superior adsorbent material heavily relies on the structural aspect. Keeping this in mind, benzyl chloride was chosen as the monomer-building unit having a rigid aromatic skeleton as well as a flexible benzyl unit, allowing the desired modification via nucleophilic substitution. Following structural tuning, the polymer can be converted to a cationic framework backbone having free exchangeable chloride ions that can enhance the adsorption capacity on account of ion exchange. Additionally, the presence of aromatic

rings plays a vital role in increasing the affinity of polymer networks toward pollutant substrates through π - π interactions.^[57] The existence of flexible methylene ($-\text{CH}_2-$) linkages throughout the polymer architecture not only benefits in realizing a high specific surface area but also enhances the adsorption rate toward pollutant trapping of the polymer. Lastly, a simple method of synthesis, viz., facile Friedel–Crafts alkylation reaction catalyzed by inexpensive anhydrous FeCl_3 , rather than utilizing expensive precious metal-based catalysts, was performed, making the process economically feasible. Alternatively, easy and rapid extraction of adsorbent materials out of the sample matrix, following the adsorption process, serves felicitous as opposed to time-consuming filtration or tedious centrifugation, which is energetically taxing. As a result, developing efficient and suitable methods for retrieving the sorbent post-adsorption is of great importance. Encapsulating magnetic nanoparticles within the porous matrix of an organic polymer can lead to the benefit of overcoming this issue conveniently. Based on these points of consideration, herein, we report a facile synthesis of a cationic composite polymer 120-TMA@Fe, illustrating exceptional adsorption proficiency and swift kinetics toward a wide variety of organic micropollutants. In fact, 120-TMA@Fe outperformed commercial standard AC and was found to be easily recyclable with an intact efficiency several times, exemplifying sustainability. Additionally, the pollutant adsorption capability exhibited by 120-TMA@Fe upon harsh chemical treatments as well as in real-world samples established its competence toward practical applicability.

4.2 Experimental

4.2.1 Materials and measurements.

Unless otherwise specified, all reagents and solvents were available commercially and were used without any further purification. Aqueous stock solutions of pollutants were prepared using deionized water at neutral pH.

4.2.2 Synthesis

Synthesis of HCP-120: HCP-120 was synthesized from cross-coupling of benzyl chloride (Scheme-1) by following our previous report. To a flame dried round bottom flask benzyl chloride (300 mg, 1.7625 mmol) was taken and to that 20 ml of anhydrous 1, 2- dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) was added. To this reaction mixture, formaldehyde dimethyl acetal (470 μl , 5.288 mmol) and anhydrous FeCl_3 (860 mg, 5.288 mmol) were added respectively. Following this, the reaction mixture was heated at 50 $^\circ\text{C}$ for 5 h and then was allowed to reflux at 80 $^\circ\text{C}$ for 18 h (Scheme-1). On completion of the reaction a dark brown coloured precipitate was obtained which was then filtered off and extensively washed with DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained brown coloured solid material was further purified via Soxhlet extraction with chloroform for 24 h and then with tetrahydrofuran

for 24 h to remove any unreacted monomers along with any metal catalyst residues. Then the polymer was heated at 120 °C under vacuum for 24 h to obtain the guest free activated HCP-120 with which further works have been carried out. Yield: 335 mg.

Synthesis of HCP120-TMA: Desolvated HCP-120 (200 mg) was taken in a round bottom flask and to that 20 ml of acetonitrile (MeCN) was added (Scheme-2). Then to the reaction mixture 5 mL of Trimethyl amine (TMA) was added dropwise allowed stir for 48 h at reflux temperature. On completion of the reaction dark brown colored precipitate was filtered off and washed with water for several times to remove excess TMA. Then the precipitate was again washed with DMF, methanol, water, chloroform, dichloromethane and THF repeatedly. Thus obtained dark brown coloured solid material (HCP@TMA) was then kept in MeOH (25 ml) for 3 days and MeOH was changed two times in a day to remove the high boiling solvents from the porous network of HCP@TMA. Then the solvent exchanged phase of HCP@TMA was heated at 140 °C under vacuum to obtain the guest free activated material and with this phase further works have been carried out. Yield: 226 mg.

Synthesis of HCP120-TMA@Fe: A beaker was charged with 200 mg of activated HCPTMA (Scheme-4). To this solid mixture, 1.08 g (4 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 397.5 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added and dissolved in 36 mL DI water. A volume of 4 mL of NH_4OH (30%) was then added rapidly. After 2 min, 1.26 g (6 mmol) of citric acid monohydrate was added. The solution was sonicated for 1 h. Once the reaction was complete, the Fe_3O_4 nanoparticles were sedimented using a magnet for 30 min. The supernatant was discarded followed by the addition of 20 mL acetone. After sonicating briefly, the NPs were again sedimented using a magnet. This procedure was repeated three more times. The brown precipitate was then dispersed in 10 mL water and filtered under vacuum. The product was washed with copious amount of water until colourless filtrate was obtained. Yield: 220 mg.

4.2.3 Physical Measurements

High resolution solid-state NMR spectrums were recorded at ambient pressure on a 500 MHz Bruker AVANCE III spectrometer. UV-Vis spectra were recorded using the Shimadzu UV 2600 Spectrophotometer. The morphology was investigated by scanning electron microscopy using FEI Quanta 3D dual beam FESEM at 30KV. HRTEM images were recorded on JEOL USA JEM-2200 FS Transmission Electron Microscope. Fourier transform infrared spectroscopy (FTIR) spectra were measured on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets in 400- 4000 cm^{-1} range. Solid state UV-Vis studies have been performed on Shimadzu UV 3600 plus UV-VIS-NIR Spectrophotometer. The powder X-ray diffraction patterns were obtained from a Bruker D8 Advance X-ray diffractometer at room temperature (rt) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). Thermogravimetric Analyses (TGA) were performed in the

temperature range of 30–800 °C on a PerkinElmer STA 6000 analyzer under a N₂ atmosphere at a heating rate of 10°C min. The surface area and pore size distribution analyses of polymers were performed on a BelSorp-max instrument from Bel Japan, using N₂ adsorption and desorption at 77 K. Prior to adsorption measurements, the samples were activated at 120 °C under vacuum for 12 hours using BelPrepvacII.

4.2.4 Micropollutant Adsorption Studies

4.2.4.1. Water Regain Analysis:

The polymer subject to water regain study was first dried and then dispersed in deionized water for 1 hour. Thus obtained wet polymer was then collected via filtration and weighed. This procedure was repeated three times in order to find out the average water regain of the polymer compound. The water regain of the polymer, which is expressed as the weight percent, was determined from the average of three measurements by using the following equation:

$$\text{Water regain} = \frac{W_w - W_d}{W_d} \times 100\%$$

Where W_w (mg) and W_d (mg) are the mass of the wet and dry polymers, respectively.

4.2.4.2. Pollutant Capture Experiments:

The pollutant concentration was calculated by using UV-vis spectroscopy after establishing a standard curve at room temperature. The pollutant removal efficiency (%) by the adsorbent polymer under investigation was determined utilizing the following equation:

$$\text{Pollutant removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where C_0 (mM) and C_t (mM) represents the concentrations of pollutant solutions before and after adsorption, respectively.

The amount of pollutant adsorbed by the polymer was calculated from the following equation:

$$q_t = \frac{(C_0 - C_t)Mw}{m}$$

Where q_t (mg g⁻¹) is the amount of pollutant adsorbed per g of adsorbent material at time t (min). C_0 (mmol L⁻¹) and C_t (mmol L⁻¹) represent the initial and residual concentration of pollutant in the stock solution and

filtrate, respectively; m (g) is the mass of adsorbent used for the study. M_w (g mol^{-1}) is the molar mass of the micropollutant under consideration

4.2.4.3. Adsorption Kinetics Study:

Initially 2 mL 0.1 mM and 0.5 mM aqueous stock solution of the respective surrogate micropollutants were taken in a UV cuvette and subsequently their initial absorbance was measured. 1 mg of activated polymer was added to the cuvette and the absorbance spectra of the supernatant solutions were recorded accordingly at different time intervals. The concentration of the pollutants in the filtrate was determined by UV-Vis spectroscopy subsequently.

The adsorption kinetics were further quantified utilizing Ho and McKay's pseudo-second-order model from which the apparent rate constant k_{obs} can be obtained [1]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{\text{obs}} q_e^2}$$

where q_t and q_e are the adsorbate uptakes (mg adsorbate per g polymer) at time t (min) and at equilibrium, respectively, and k_{obs} is an apparent second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The rate constant k_{obs} can be calculated from the intercept and slope of the plot of t/q_t against t .

Weber's intra-particle diffusion model was used to identify the diffusion mechanism during the adsorption process. It can be expressed by the following equation [2]:

$$q_t = k_{id} t^{\frac{1}{2}} + A$$

Where k_{id} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{1/2}$), A is the intercept representing the boundary layer thickness (mg g^{-1}).

4.2.4.4. Adsorption Capacity Studies:

The polymer under investigation (2 mg) was washed with H_2O (5 mL) for 5 min and then filtered. The polymer was then added to a solution of the surrogate micropollutant (4 mL) at initial concentrations of 0.1 mM, 0.25 mM, 0.5 mM, 0.8 mM, and 1.0 mM, respectively. The suspensions were stirred to reach equilibrium and were then filtered off. The absorption intensity of the filtrate was finally calculated from UV-Vis spectroscopy.

A Langmuir adsorption isotherms were generated by plotting $1/q_e$ versus $1/C$ using the following equation [3]:

$$\frac{1}{q_e} = \frac{1}{q_{max,e}} + \frac{1}{q_{max,e} \cdot K \cdot C}$$

Where q_e (mg g^{-1}) is the amount of pollutant adsorbed at equilibrium, $q_{max,e}$ (mg g^{-1}) is the maximum adsorption capacity of adsorbent at equilibrium, C (mol L^{-1}) is the residual pollutant concentration at equilibrium, and K (mol^{-1}) is the equilibrium constant..

4.2.4.5. Regeneration Experiments:

120-TMA@Fe (10 mg) was added into a solution of methyl orange (0.1 mM, 10 mL) and stirred at room temperature. After equilibrium was judged to have been reached, the solid was separated by centrifugation, treated with 10 mL tetrabutylammonium chloride solution (40% V/V) for about 12 h to release the methyl orange (monitored by color changes). Then, the solid was separated off, washed with copious amount of deionized water. The resulting material was used for the subsequent adsorption experiments.

4.2.5.6. Selectivity Studies:

In this study, 2 mg each of 120-TMA@Fe were taken in a glass vial separately with a mixed binary stock solution having 1 mL of target pollutant solution (0.2 mM) and 1 mL of interfering anion solution (Cl^- , NO_3^- , CO_3^{2-} and SO_4^{2-}) (0.2 mM) for ~12 h under constant stirring. After 12 h, the suspensions were filtered, and the absorption intensity of the filtrate was analysed using UV-Vis spectroscopy from the protocol described above. The capture proficiency in the presence of interfering anions was monitored with respect to a blank reference of the competing anion and target pollutant solution.

4.3 Results and Discussion

As shown in Appendix Scheme 4.1, HCP 120-Cl was synthesized via a simple one step FeCl_3 -catalyzed Friedel–Crafts reaction of monomer benzyl chloride in the presence of an external cross-linker formaldehyde dimethyl acetal (FDA) in 1,2-dichloroethane at 80 °C for 24 h. Typically, the reaction mixture containing the monomer, external cross-linker along with the catalyst in 1,2- dichloroethane was heated for 5 h at 50 °C to facilitate the formation of the initial network and further heated at 80 °C for the completion of the condensation reaction. During the course of the reaction, a dark brown precipitate was observed, indicating the formation of microporous polymeric networks through cross-linking polymerization. After the reaction was completed, the obtained precipitate was extensively washed with water, N, N'-dimethylformamide (DMF), methanol (MeOH), tetrahydrofuran (THF), and chloroform (CHCl_3) and collected via filtration. The resulting polymer was then subjected to further purification through Soxhlet extraction with CHCl_3 and THF for 24 h respectively to get rid of any unreacted monomers as well as oligomers. Desolvation of 120-Cl was carried out by heating the polymer at 120 °C for 12 h under a vacuum. Subsequently, activated 120-Cl was treated with trimethyl amine $[\text{N}(\text{CH}_3)_3]$ in acetonitrile under reflux conditions for 48 h to result in a cationic network 120-TMA (Appendix Scheme 4.2). The HCPs were found to be insoluble in various solvents tested, including dimethyl sulfoxide (DMSO), DMF, CHCl_3 , THF, MeOH, and water. The insolubility of these materials provides initial evidence of covalent cross-linking to generate porous polymeric networks. Additionally, to facilitate simple and fast separation, the cationic polymer was combined with Fe_3O_4 nanoparticles (NPs) via in situ reduction of FeCl_3 to construct magnetically retrievable composite polymer, viz., 120-TMA@Fe (Appendix Scheme 4.3).

The synthesized HCPs were further validated of their proposed structures via thorough characterization with Fourier transform infrared (FT-IR) and solid-state ^{13}C NMR spectroscopy. The FT-IR spectra of the resulting HCPs showed consistent peaks corresponding to the expected networks (Figure 4.1a). Both 120-Cl and 120-TMA displayed characteristic aromatic C=C bands at ca. 1600–1660 cm^{-1} . The peaks attributed to C–H vibrations at ca. 2931 cm^{-1} (stretching) and 1450 cm^{-1} (bending) were correlated to the $-\text{CH}_2-$ bond of the polymers. Additionally, the FT-IR spectra of HCP 120-TMA@Fe showed the simultaneous presence of all the above mentioned characteristic bands along with the emergence of a new peak at ca. 580 cm^{-1} ascribed to Fe_3O_4 nanoparticles.^[58] The peak assigned at 580 cm^{-1} indicates the successful loading of Fe_3O_4 nanoparticles (NPs) onto the HCP matrix. ^{13}C CP/MAS NMR spectroscopy was utilized to further substantiate the chemical composition of the resulting polymeric networks (Figure 4.1d). Three main peaks at around 36, 130, and 136 ppm were observed for both the polymers. The signal at 36 ppm attributed to the methylene linkage confirmed the $-\text{CH}_2-$ bond formation. Peaks at 130 and 136 ppm were corroborated with nonsubstituted (i.e., hydrogenbearing) and substituted aromatic carbon atoms, respectively,

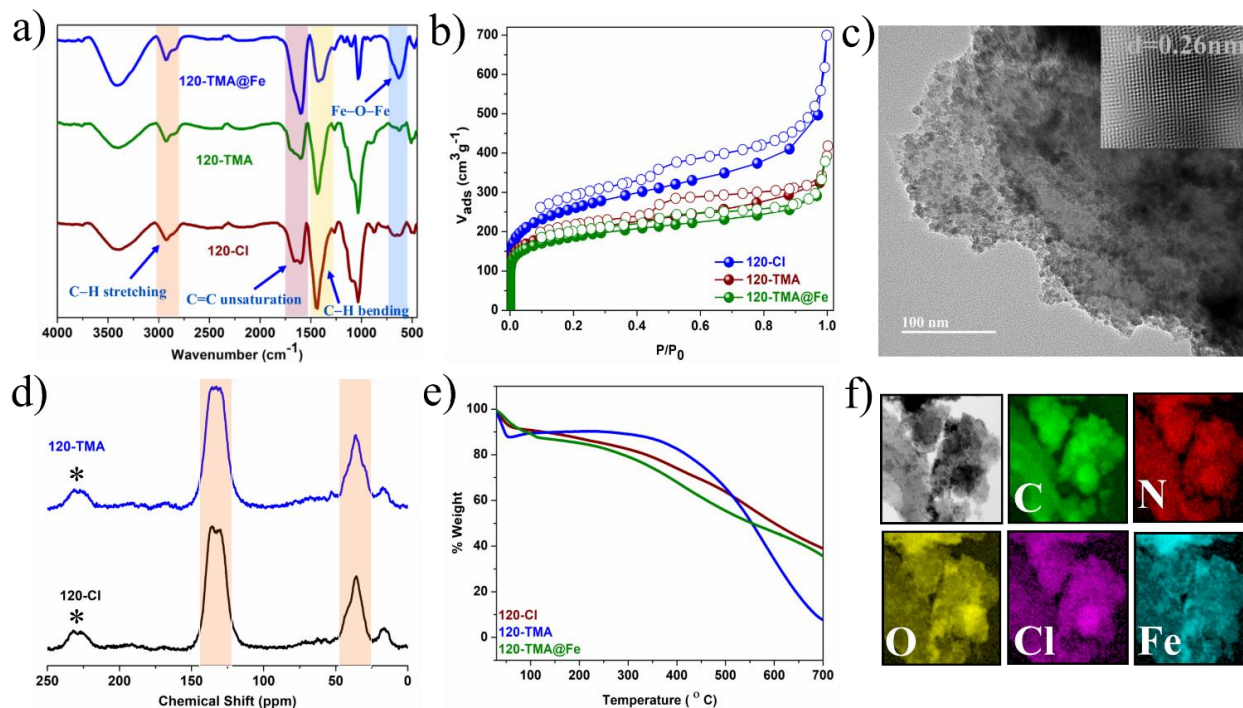


Figure 4.1. (a) FT-IR spectra of 120-Cl (brown), 120-TMA (green) and 120-TMA@Fe (blue). (b) N₂ adsorption curves of 120-Cl (blue), 120-TMA (brown) and 120-TMA@Fe (green). (c) HRTEM image of 120-TMA@Fe. (d) Solid-state ¹³C NMR spectra of polymer 120-Cl (black) and 120-TMA (blue). (e) TGA curves (Under N₂ atmosphere) of 120-Cl (brown), 120-TMA (blue) and 120-TMA@Fe (green). (f) STEM-EDS mapping profile of 120-TMA@Fe.

by comparing with the literature values.^[59] Thermal stability assessment of the HCPs was done by performing the thermogravimetric analysis (TGA).

All the HCPs displayed an initial weight loss below 100 °C in their pristine phases that can be correlated with the loss of residual organic solvents within the polymers. After the initial loss, no loss was observed till 400 °C, accounting for their excellent thermal stability (Figures 4.1e, and Appendix 4.2–4.4). Beyond 400 °C, all the HCPs showed rapid weight loss up to 700 °C, indicating gradual decomposition of the polymers. After performing their thermal analysis, the HCPs were tested for their porosity. Taking a cue from the TGA study, all the polymers were activated through degassing at 120 °C under a vacuum for 12 h prior to N₂ adsorption/desorption measurements at 77 K. The N₂ sorption profile of these polymers can be classified as type II, rational with the abundance of micropores and mesopores (Figure 4.1b, Appendix 4.5–4.7 and 4.9–4.11). All the HCPs exhibited a distinct steep N₂ gas uptake at very low relative pressures ($P/P_0 < 0.1$) that correspond to gas adsorption in micropores. However, at high pressure regions, all the

polymers displayed slight hysteresis loops along with pronounced pore filling, implying the abundance of mesopores and macropores allowing unrestricted multilayer adsorption in all the polymers.^[60] To our delight, all the polymers displayed high specific surface areas. The Brunauer–Emmett–Teller (BET) surface areas from the N₂ adsorption profiles of the HCPs were calculated to be 998, 734, and 640 m²g⁻¹ for HCP 120-Cl, 120-TMA, and 120-TMA@Fe, respectively. The gradual decrease in the surface area for both 120-TMA and the magnetic composite 120-TMA@Fe can be attributed to the successive post-synthetic modification and nanoparticle loading, leading to a partial pore filling of the polymers.

The recorded powder X-ray diffraction (PXRD) profile of HCP 120-Cl illustrated a typical broad peak pattern, consistent with the POPs reported in the literature (Appendix 4.12). This observation indicates the amorphous nature of the polymer. For 120-TMA@Fe, the composite formation was once again validated from its PXRD pattern. The XRD pattern of 120-TMA@Fe revealed the presence of five broad peaks at $2\theta = 30.16^\circ$, 35.65° , 43.27° , 57.20° , and 63.04° that corresponds to (220), (311), (400), (333), and (440) of crystalline Fe₃O₄ (JCPDS no. 82-1533) (Appendix 4.13). The obtained diffraction pattern was also found to be consistent with literature values,^[61] hence confirming the successful loading of the magnetic NPs. The amount of iron loading was calculated to be 16.8 wt % for 120-TMA@Fe by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

The microstructure and bulk morphology of the polymers were investigated using field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) analyses. FE-SEM images of the pristine polymers reveal an irregular-shaped dense amorphous morphology (Appendix 4.14). Additionally, the energy-dispersive X-ray spectroscopy (EDX) spectra and elemental mapping corroborated well with the homogeneous distribution of all the elements (Appendix 4.15–4.17). HR-TEM images of the prepared composite 120-TMA@Fe show uniform dispersion of Fe₃O₄ NPs within the polymer without any agglomeration, which proves beneficial for adsorption (Figure 4.1c and Appendix 4.18). The presence of all the elements in a homogeneous manner was further illustrated from the scanning TEM-EDX (STEM-EDX) mapping profile (Figure 4.1f).

In particular, for water-purification applications, water regain comes forth as an important property. To access the hydrophilicity of the polymers under investigation, “water regain” analysis was carried out. An increased hydrophilicity was observed for 120-TMA compared to 120-Cl as it was found to retain up to 78.66% of its original weight upon dispersion in H₂O. For the pristine 120-Cl, the value was determined to be 38.53% (Appendix Table 4.2). The increased hydrophilic nature of 120@TMA further aids in the adsorption process. Chemical robustness of a material under different conditions serves as one of the fundamental prerequisites toward water purification. To determine the stability of the polymer in question,

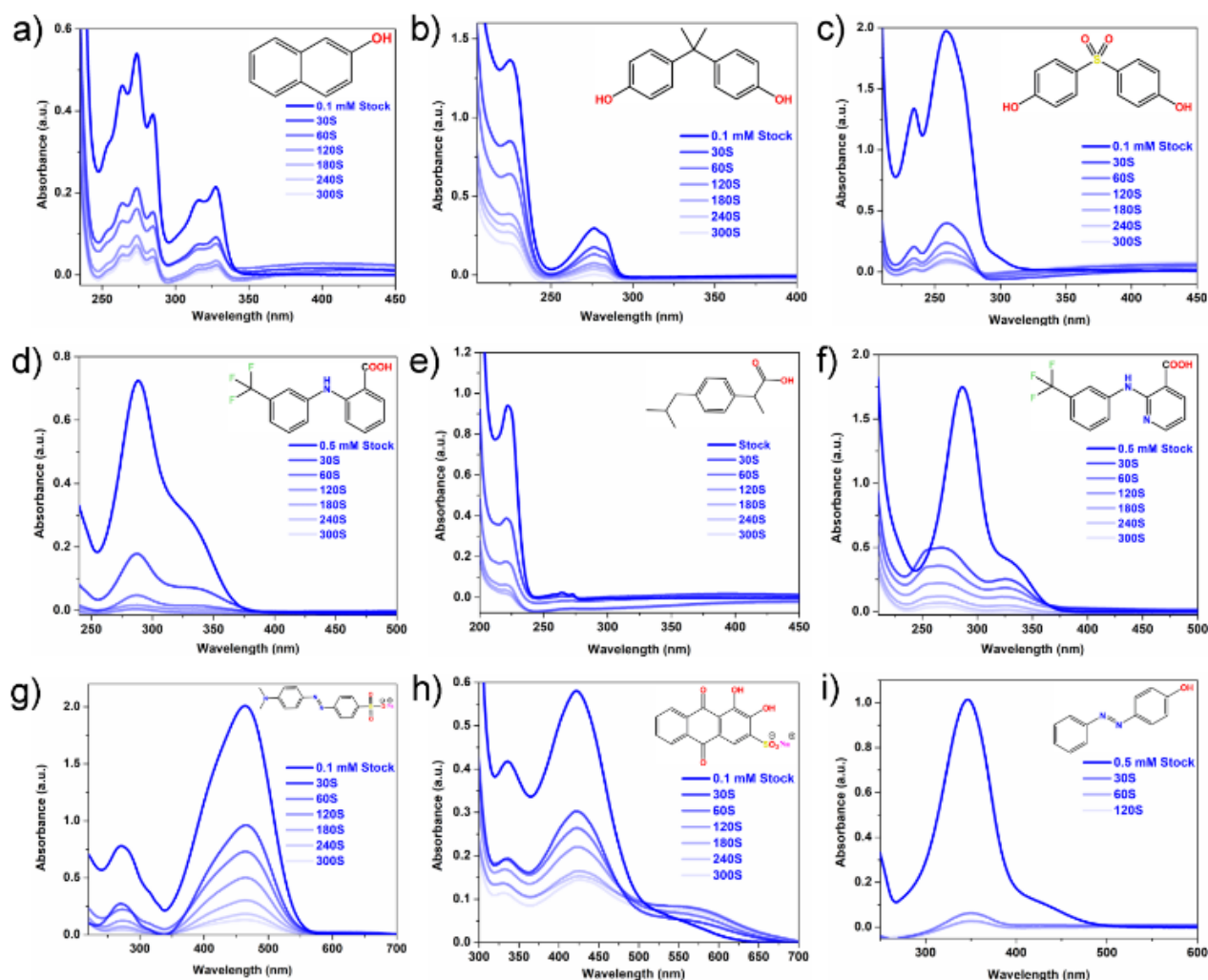


Figure 4.2. UV-Vis absorption spectra recorded as a function of increasing adsorption times for aqueous solutions of (a) 2-Naphthol, (b) Bisphenol A, (c) Bisphenol S, (d) Flufenamic acid, (e) Ibuprofen, (f) Niflumic acid, (g) Methyl Orange, (h) Alizarin Red S and (i) 4-Phenylazophenol in the presence of 120-TMA@Fe (1.0 mg), respectively.

it was subjected to various harsh chemical treatments. The exceptional stability of 120-TMA@Fe was demonstrated by less than 10% weight loss when treated under different chemical environments like acidic and basic media, various solvents, as well as oxidizing and reducing agents (Appendix 4.19). Additionally, the chemically treated phases were characterized thoroughly with FE-SEM, FT-IR, TGA, and so forth. The FE-SEM images of the polymer upon the treatment of harsh acidic (1 N HCl) and basic (1 N NaOH) media showed no significant deviation accounting for its durability (Appendix 4.20). The FT-IR spectra revealed no obvious change in the spectra with retention of all the characteristic peaks (Appendix 4.1), while the TGA profiles were found to be similar for the post-treated samples compared to the pristine phase

(Appendix 4.21). These experiments in combination substantiate its superior physiochemical stability, making it an ideal sorbent material toward detoxification of water.

Motivated by the chemical stability and cationic nature of the polymer, we zeroed our interest in evaluating its potential in the adsorptive removal of organic micropollutants from the water medium. A wide range of toxic surrogate pollutants was chosen with varying functionality, electronic configuration, as well as hydrophilicity and size. As depicted in Scheme 4.2, we have tested a series of pollutant molecules, including anionic dyes (MO, alizarin red s, and phenyl azo phenol), plasticizers (bisphenol A and bisphenol S), anionic pharmaceuticals^[62] (ibuprofen, niflumic acid, and flufenamic acid), and aromatic model compound 2-naphthol. In each case, 1 mg of the polymer (120-TMA@Fe) was dispersed in an aqueous micropollutant stock solution (0.1 mM, 2 mL) for the adsorption studies. A stock solution of 2 mL 0.5 mM was used for phenyl azo phenol (PAP), niflumic acid (Niflu), and flufenamic acid (Flu) because of low intense absorption peaks. After establishing the standard calibration curves, the pollutant removal efficiency along with the uptake of micropollutants was calculated through monitoring the differences in UV–vis absorbance intensity in the water medium (Appendix 4.22–4.30).

To evaluate the competence of 120-TMA@Fe toward micropollutant trapping, the kinetics experiment was performed. Typically, an in situ kinetic titration of the organic pollutants was conducted by taking 2 mL of the stock solutions with 1 mg of the sorbent polymer and monitoring the pollutant concentration at different time intervals at their corresponding absorption maxima by UV–vis spectroscopy. A declining trend in the UV–vis absorption intensity was observed for all the toxic pollutants tested with the passing of time. As depicted in Figure 4.2, 120-TMA@Fe illustrated excellent potency in the effective removal of all these micropollutants. Interestingly, very rapid kinetics of capture was observed in all the cases with the equilibrium reaching within only 5 min (Figures 4.3b and Appendix 4.32–4.34).

Under the abovementioned assay conditions, 120-TMA@Fe could almost completely remove most of the pollutants subject to investigation. In particular, an exceptional removal of 99.7% for both ibuprofen (Ibu) and flufenamic acid (Flu) along with 97.5% removal efficiency toward niflumic acid (Niflu). A similar performance was observed in the case of bisphenol A (BPA), bisphenol S (BPS), and 2-naphthol (2-NO) with 98.6, 96.4, and 90.3%, removal, respectively. Amongst anionic dyes, the % removal was found to be 97.8 and 93.5 for PAP and MO, while a relatively inferior 75.1% removal was observed for alizarin red S (ARS) (Figure 4.3a). The pollutant adsorption was also associated with a distinct color change of the analyte solutions visible to the naked eye (Appendix 4.31). The superior adsorptive performance of 120-TMA@Fe for these organic micropollutants can be correlated with its structural features. Generally, the sorption of any toxic pollutant by a sorbent dwells upon both the affinity toward target analytes by the virtue of its

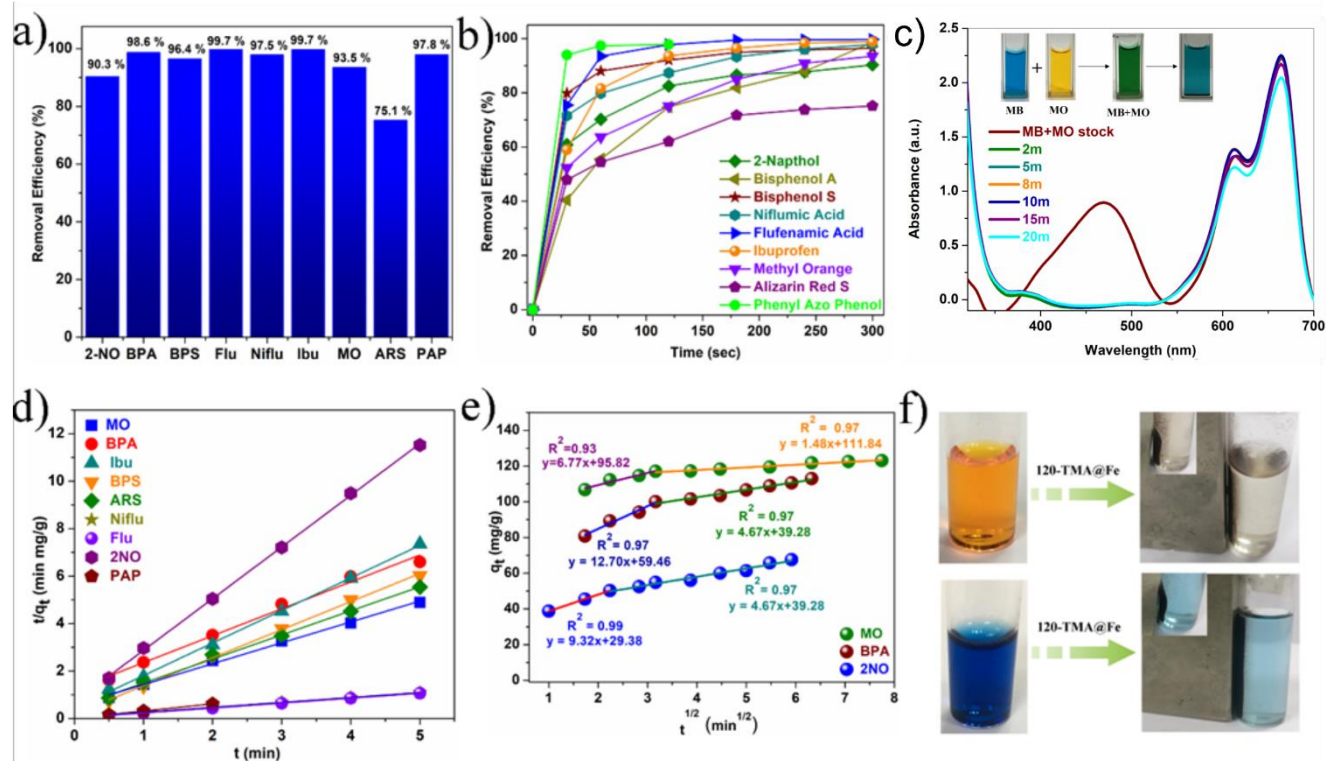


Figure 4.3. (a) Removal efficiency of each organic micropollutant by 120-TMA@Fe. (b) Time dependent adsorption process of each organic micropollutant (0.1 mM) by 120-TMA@Fe. (c) UV-Vis absorption spectra of binary aqueous solutions consisting of Methyl Orange and Methylene Blue (0.1 mM in each). (d) Fits to a pseudo-second-order model for each organic micropollutant. (e) Fits to intra-particle diffusion model for Methyl Orange (MO), Bisphenol A (BPA) and 2-Naphthol (2NO). (f) Decolorisation and magnetic separation of dye molecules post adsorption by 120-TMA@Fe.

molecular construction along with physical attributes in the bulk scale of the material like the pore size, pore volume, surface area, effective residual charge, and flexibility. In the case of 120-TMA@Fe, the adsorbent adsorbate attraction can be governed by a few putative aspects, including (1) electrostatic interactions (both dipole–dipole and monopole-dipole interactions); (2) van der Waals forces and H-bonding interactions; (3) cation– π interactions; (4) π – π electron donor–acceptor (EDA) interactions, and so forth. The strong adsorption of anionic dyes, pharmaceuticals, as well as phenolic derivatives emphasize the fact that electrostatic interactions are the significant prevailing factor in trapping these molecules. Additionally, the abovementioned effects in synergy with Coulombic attractions render ultrafast sorption kinetics in 120-TMA@Fe toward the micropollutants.

Generally, the contact times required for the maximum amount of adsorption to take place reflect their

capture efficiencies. The trend observed for 120-TMA@Fe reveals that very less contact time was needed for the entrapment of all the pollutants tested. In fact, within only 5 min, maximum efficiencies were reached, achieving apparent equilibrium adsorption. To disseminate in depth information of the prevailing adsorption kinetics, Ho and McKay's pseudo-second-order kinetic model was adopted.^[63] The obtained kinetics fitting for all the analytes were found to be in good agreement with the pseudo-second order model validated by excellent correlation coefficients ($R^2 = 0.99$) (Figures 4.3d and Appendix 4.35). Additionally, the good consistency observed for experimental data with the model-predicted data indicates the nature of the sorption process to be chemisorption-driven by electrostatic interactions.^[64,65] The calculated apparent rate constant (k_{obs}) values for the adsorptive removal process are listed in Appendix Table 4.3. The obtained rate constants (K_{obs}) for all the organic micropollutants enable 120-TMA@Fe as a promising sorbent material toward rapid wastewater remediation. In order to seek further insight into the rate-determining step in the adsorption process of these pollutant substrates, three micropollutants, MO, 2-naphthol, and bisphenol A were chosen. The uptake data of these substrates were then examined according to Weber's intraparticle diffusion model (Figure 4.3e).^[66] In general, the transportation of an adsorbate micropollutant from its solution to the adsorbent can be composed of many steps, inclusive of (1) external diffusion, (2) surface diffusion, (3) pore diffusion (intra-particle diffusion), and (4) adsorption onto the pore surface.^[67,68] For 120-TMA@Fe, a similar double linear pattern was observed for each pollutant substrate. It is worth mentioning that the two straight lines, however, do not proceed through the origin. This observation points out that intraparticle diffusion does not prevail as the exclusive rate-determining step, while the overall adsorption procedure may be governed by multiple diffusion mechanisms.^[69] The first fitting line in Weber's diffusion model can be ascribed to the mass transfer of the pollutant adsorbate molecules from the bulk solution to the adsorbent surface, while the second fitting line is likely to mirror the intraparticle diffusion taking place within 120-TMA@Fe (Figure 4.3e). Furthermore, to study the impact of micropollutant concentrations upon the adsorption process of 120-TMA@Fe, a series of pollutant stock solutions with varying concentrations were subject to adsorption studies. The adsorption studies revealed that the higher the initial pollutant concentration, the higher is the adsorption. This observation can be rationalized in connection with higher driving force toward mass transfer. Appendix 4.36–4.44 illustrates equilibrium pollutant uptake plotted against the residual micropollutant concentration postadsorption process consistent with the Langmuir adsorption model evident from very good correlation coefficient values, indicating 120-TMA@Fe to be a system where adsorption sites are similar.^[70] We also calculated the maximum uptake capacity ($q_{\text{max,e}}$) using the Langmuir adsorption isotherm equation for all the micropollutants. For 120-TMA@Fe, the uptake capacity ($q_{\text{max,e}}$) was determined to be 357 mg g⁻¹ for MO ($R^2 = 0.99$), 555 mg g⁻¹ for bisphenol A ($R^2 = 0.99$), and 285 mg g⁻¹ for ibuprofen ($R^2 = 0.96$) (Appendix 4.37, 4.39, and 4.44). The maximum uptake capacity for all the pollutant substrates is listed in

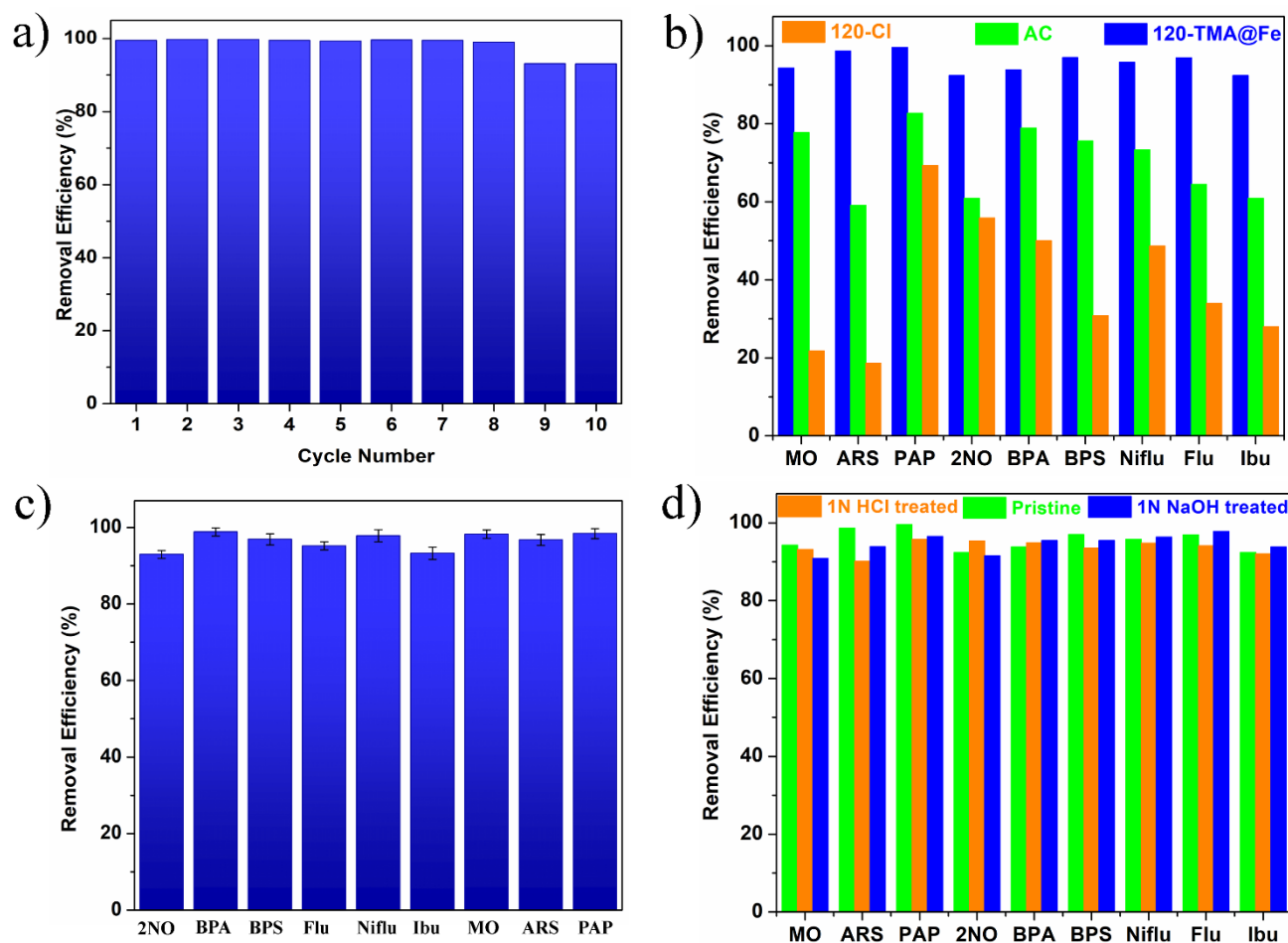


Figure 4.4. (a) The regeneration cycles of 120-TMA@Fe after the adsorption of Methyl Orange. (b) Removal efficiency comparison of each organic micropollutant with 120-Cl, 120-TMA and 120-TMA@Fe. (c) Removal efficiency of each organic micropollutant by 120-TMA@Fe at 0.1 mM in river water. (d) Removal efficiency of each organic micropollutant by 120-TMA@Fe after acid (1 N HCl) and base (1 N NaOH) along with pristine phase.

Appendix Table 4.4. The capacity values obtained for 120-TMA@Fe validate its potency as a superior sorbent material amongst the reported materials. To specify, the adsorption capacities of 120-TMA@Fe for bisphenol A, ibuprofen, and MO stand tall amongst the highest values reported so far in the literature (Appendix Table 4.5-4.7). To verify if adsorption occurred on the surface as opposed to inside the pores, we have performed low-temperature N₂ adsorption of MO-loaded polymer composites. A distinct decrease in the uptake amount was observed indicating that the adsorption process is taking place inside the pores (Appendix 4.8). Furthermore, the pollutant-loaded phase of 120-TMA@Fe was thoroughly characterized

by FT-IR (Appendix 4.52), solidstate UV-vis spectroscopy (Appendix 4.53), as well as FE-SEM (Appendix 4.54), confirming the structural stability of 120-TMA@Fe upon adsorption with no significant changes being observed in comparison with pristine 120-TMA@Fe.

The competent performance of 120-TMA@Fe to successfully adsorb anionic micropollutants in an efficient manner propelled us to explore its selectivity based on charge specificity. To confirm this, a binary dye mixture-based adsorption study of dye molecules was carried out. An equimolar mixture consisting of anionic MO and cationic methylene blue (2 mL) was exposed to 1 mg of 120-TMA@Fe to monitor the adsorption behavior through UV-vis measurement. As was observed, under similar experimental conditions, only 4% of cationic methylene blue removal was achieved, while for the anionic MO ~93% removal was attained within 5 min (Figure 4.3c). Additionally, adsorption equilibrium was reached at 20 min with the relative removal of 9.21% methylene blue and 94.1% MO. These results verify the selective nature of 120-TMA@Fe and substantiate the dominance of electrostatic interactions at play in defining the adsorption efficiency toward organic micropollutants. The selective adsorption behavior was also evident from the color change observed during the course of the experiment. The color of the mixed binary dye solution gradually changed from green to blue with the progress of time, indicating the dominant abundance of nonadsorbed methylene blue in the residual stock solution after reaching equilibrium. It is noteworthy to mention that 120-TMA@Fe shows an almost identical removal of MO both in a single-component (~93.5%) as well as in binary mixture (~94.1%) study to illustrate its unaltered efficiency. Furthermore, the micropollutant removal efficiency of 120-TMA@Fe was also compared with that of the pristine polymer HCP 120-Cl and commercially available AC (Appendix 4.45). As shown in Figure 4.4b, 120-TMA@Fe outperforms both AC and its pristine neutral polymer in terms of the removal efficiency toward all the pollutants. Upon keeping the respective sorbent materials in pollutant stock solution for a certain amount of time to enable adsorption equilibrium, it was observed that ~21.79, ~77.12, and ~94.31% removal of MO could be achieved with neutral polymer 120-Cl, AC, and 120-TMA@Fe, respectively. Overall, a similar trend was observed for the rest of the pollutant substrates, where 120-Cl displayed inferior adsorption performance presumably due to the lack of electrostatic interactions within the polymer network. On the other hand, AC illustrated moderate removal performance that proved suboptimal in comparison with 120-TMA@Fe, establishing its superiority over AC.

The reusability of a material serves as a priori in wastewater treatment. To test the regeneration capability of 120-TMA@Fe, we performed recyclability experiments taking 0.1 mM MO as the model pollutant. After each adsorption cycle, polymer regeneration was carried out using tetrabutylammonium chloride solution (40% V/V) under ambient conditions. 120-TMA@Fe displayed an almost intact removal performance of MO over 10 cycling experiments, which firmly confirm the reusability of this material along with

sustainability (Figure 4.4a). A similar intact performance efficacy was observed for all the other pollutants up to 3 cycles (Appendix 4.48). Furthermore, 120-TMA@Fe showed unaltered capture potency in the presence of coexisting ions like NO_3^- , Cl^- , SO_4^{2-} , and CO_3^{2-} , advocating its superior adsorptive nature (Appendix 4.46 and 4.50).

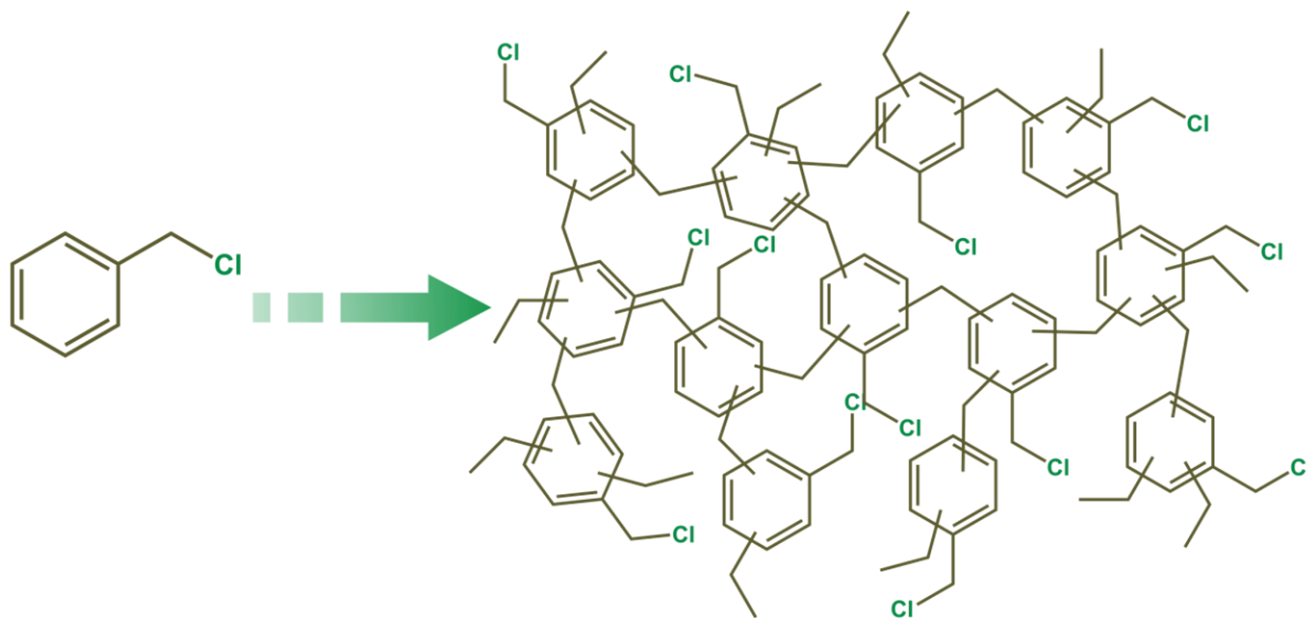
The conceptual feasibility of 120-TMA@Fe composite polymer toward wastewater remediation in terms of real-time applications was also investigated. To implement this, we have designed a fixed-bed stationary-phase column-based experimental set up (Appendix 4.55). Stock solutions of all the pollutants were run through a bed of 120-TMA@Fe, and the column eluent solution was subjected to UV–vis analysis. An exceptional capture efficiency was observed in all the cases, while distinct colorless eluents were observed for dyes (Appendix 4.47 and 4.51). To verify its adsorption efficiency under harsh chemical conditions, 120-TMA@Fe was treated with both 1 N HCl and 1 N NaOH prior to adsorption experiments. To our delight, 120-TMA@Fe showed remarkable performance with acid-treated as well as base-treated phases of the material and no significant drop in the pollutant removal efficiency (Figure 4.4d). Motivated by this, we turned our focus toward testing the competence of 120-TMA@Fe in real-world water samples collected from Mutha River (Pune, India). After exposing the 0.1 mM pollutant-spiked Mutha River water to 120-TMA@Fe for 12 h, their respective removal amount was calculated from UV–vis spectroscopy. Satisfyingly, exceptional pollutant removal efficiency amounting to ~92–98% was observed in this case also (Figure 4.4c). The outstanding capability of 120-TMA@Fe to perform in such a complex solution matrix can be regarded as further evidence for a potent sorbent material toward entrapping these organic micropollutants. Keeping in mind the feasibility of recovery or separation of the polymer adsorbent, Fe_3O_4 nanoparticles were integrated within the polymer matrix in 120-TMA@Fe that enables easy recovery (Figure 4.3f). Post the pollutant capture process, 120-TMA@Fe can be easily separated from the solution using a magnet by the virtue of its magnetic nature without requiring neither centrifugation associated with energy footprints nor the filtration technique that is time-consuming.

4.4 Conclusions

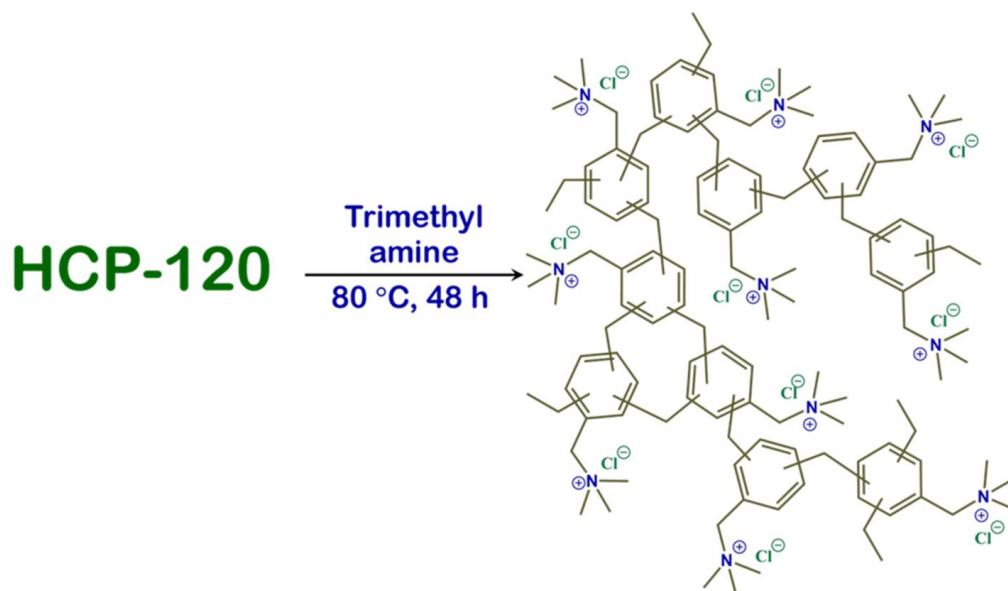
In this work, we have synthesized a cationic composite polymer 120-TMA@Fe through post-synthetic modifications and explored its potential toward wastewater remediation. The pristine polymer built from simple and easily available monomers was conveniently modified to construct a cationic framework backbone for the desired electrostatic interactions. Additionally, Fe_3O_4 NPs were incorporated to allow the easy magnetic separation of the composite polymer. 120-TMA@Fe displayed an exceptional efficiency highlighted by its rapid kinetics in removing all the pollutants from the water medium. Cationic polymer composite 120-TMA@Fe also illustrated superior adsorption behavior by outperforming its neutral

precursor polymer 120-Cl as well as industrial standard adsorbent AC against all the tested pollutants. Notably, 120-TMA@Fe was also found to be very convenient in pollutant removal after exposure to harsh chemical treatments (1 N HCl and 1 N NaOH) as well as complex solution matrices such as river water samples. Furthermore, the polymer could be recovered effortlessly by using a magnet, while the sustainability of 120-TMA@Fe in the long run was established through unaltered regeneration performance over 10 cycles. The excellent sorption efficiency of 120-TMA@Fe, which is reflected directly in its uptake capacity and rapid adsorption kinetics, was attributed to be mainly electrostatic-driven while other interactions were also at play in a synergistic manner. The results obtained in this work may help in the rational design and potential utilization of polymers offering structural tunability as well as cost-effectiveness toward target-specific water-purification applications.

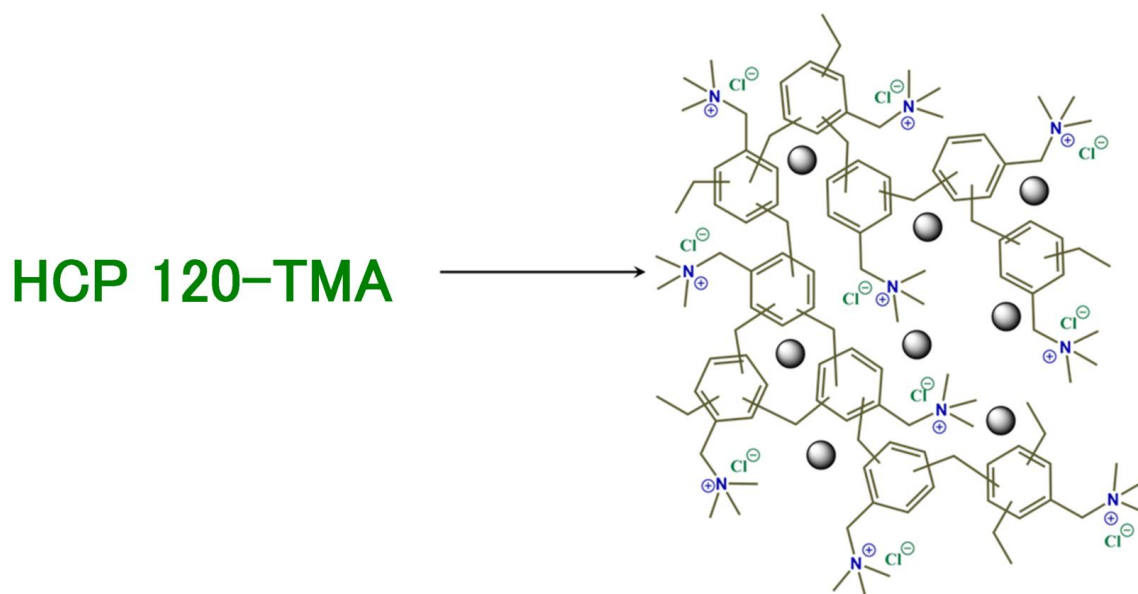
4.5 Appendix section



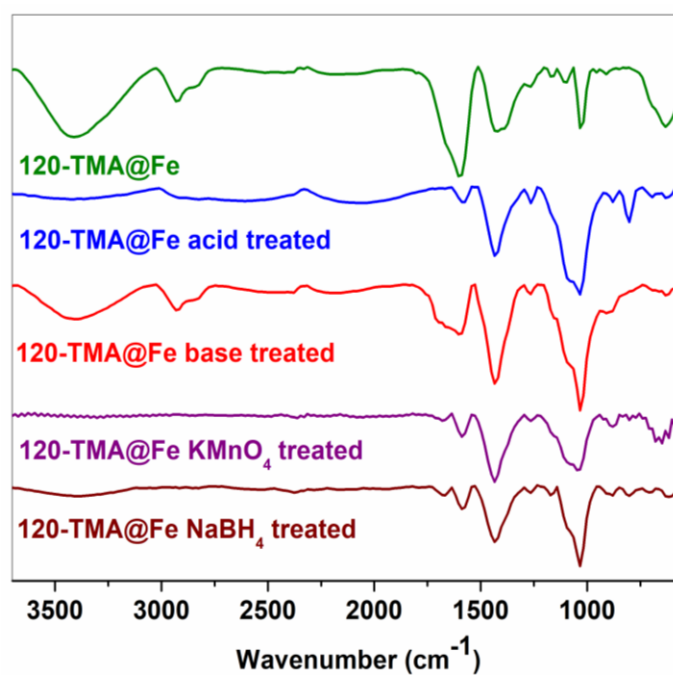
Appendix scheme 4.1. Schematic representation showing synthesis of HCP-120.



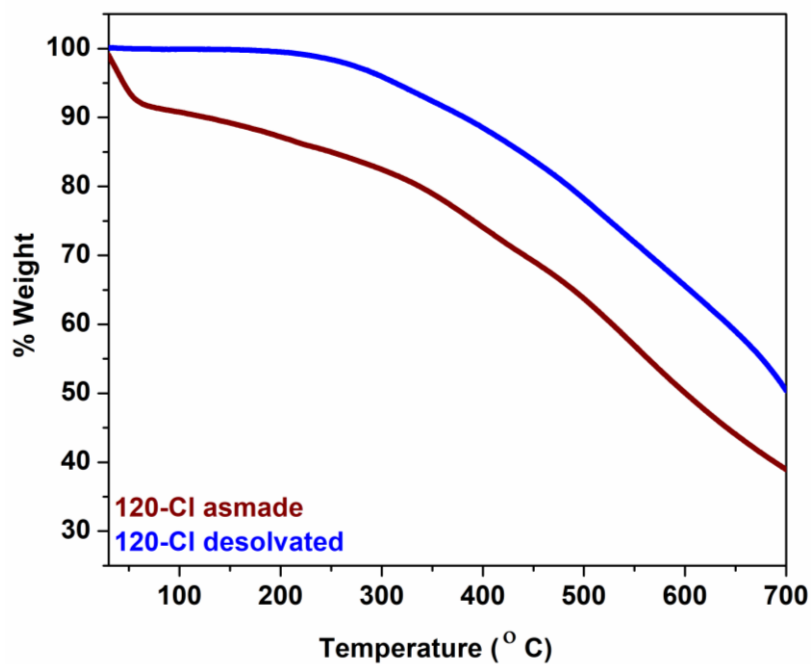
Appendix Scheme 4.2. Schematic representation showing synthesis of HCP 120-TMA.



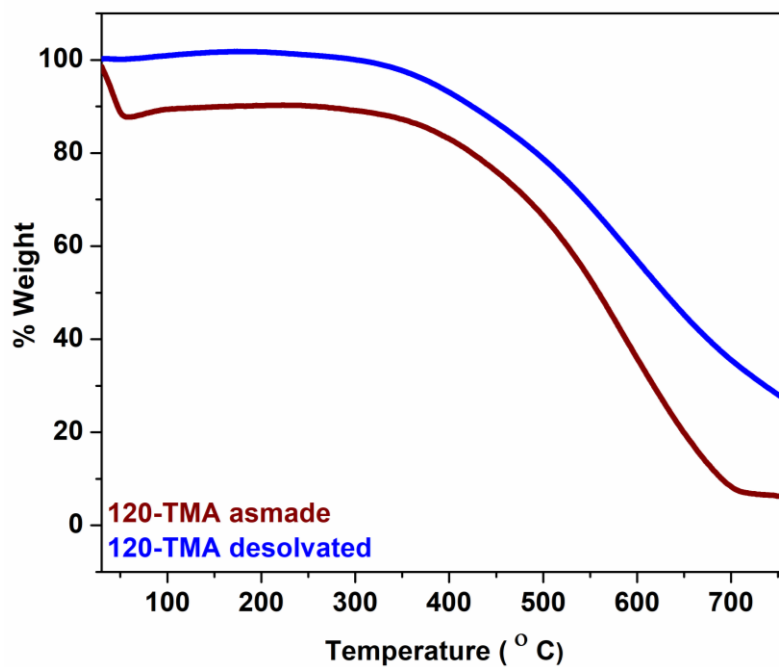
Appendix Scheme 4.3. Schematic representation showing synthesis of HCP 120-TMA@Fe.



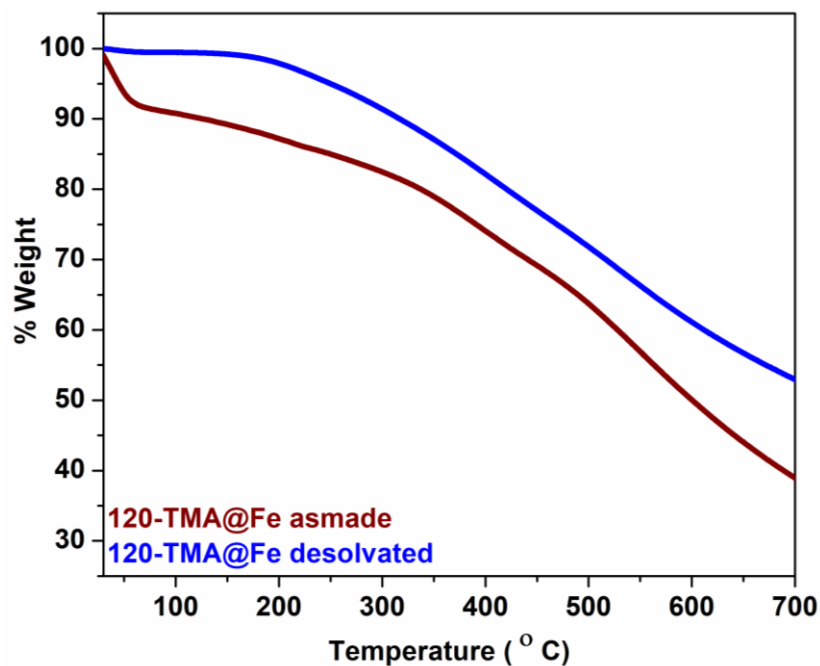
Appendix Figure 4.1. Infra-red (IR) spectra of 120-TMA@Fe (olive green), 120-TMA@Fe acid treated (blue), 120-TMA@Fe base treated (red), 120-TMA@Fe KMnO_4 treated (purple) and 120-TMA@Fe NaBH_4 treated (brown)



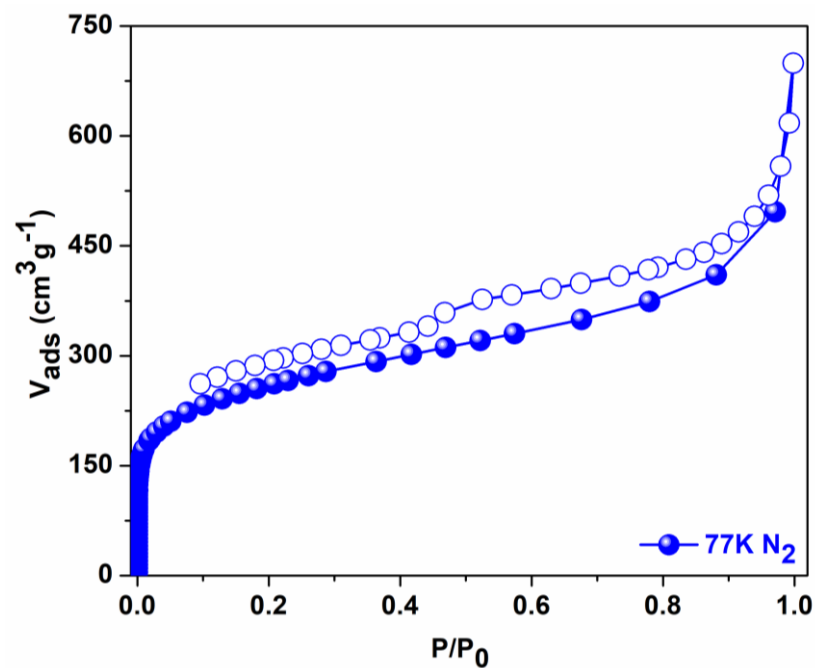
Appendix Figure 4.2. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-Cl (brown) and activated 120-Cl (blue).



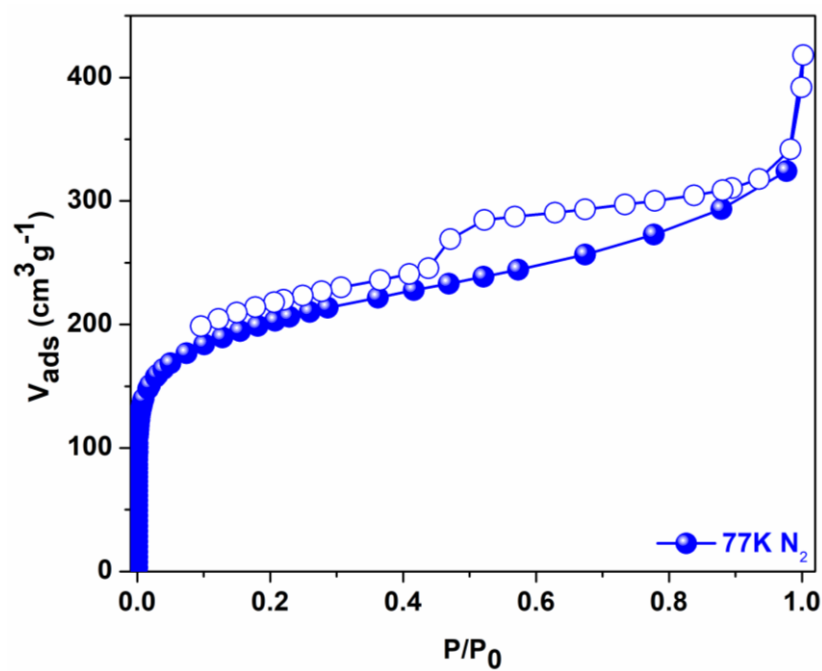
Appendix Figure 4.3. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-TMA (brown) and activated 120-TMA (blue).



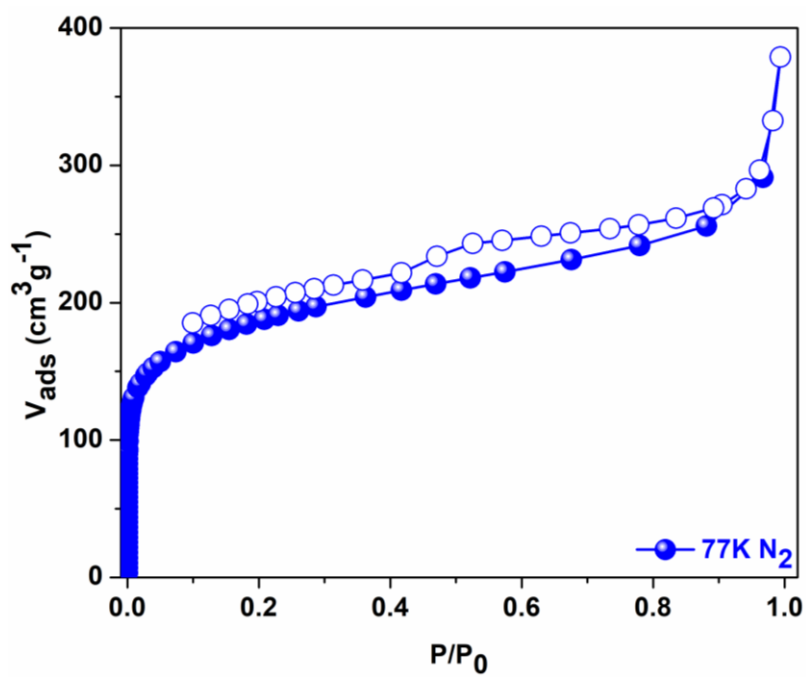
Appendix Figure 4.4. Thermogravimetric profile (Under N₂ atmosphere) for pristine 120-TMA@Fe (brown) and activated 120 TMA@Fe (blue).



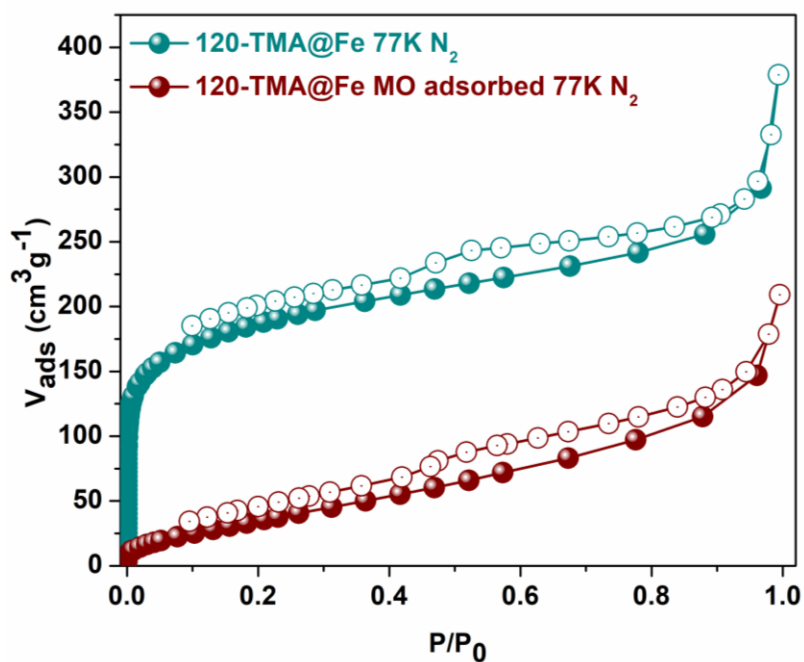
Appendix Figure 4.5. N₂ adsorption profile at 77 K for 120-Cl.



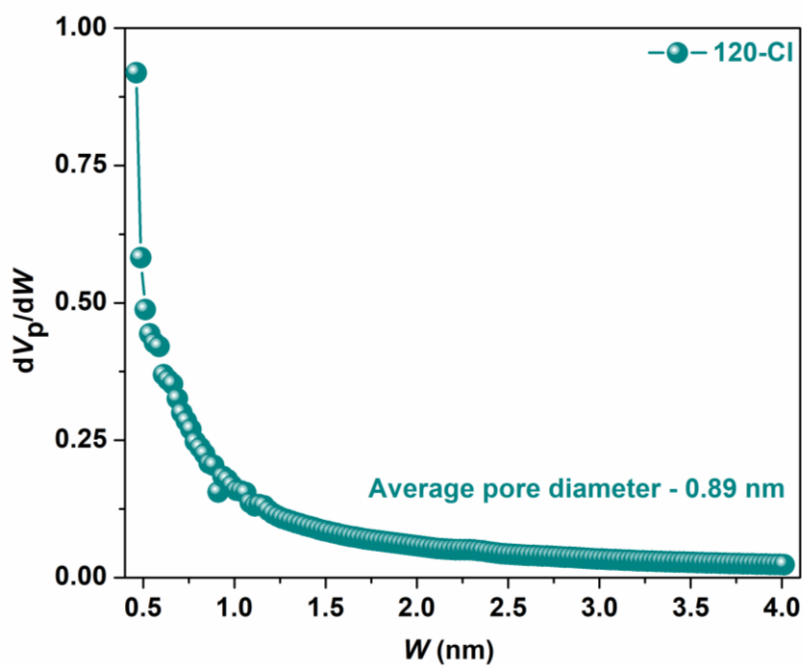
Appendix Figure 4.6. N_2 adsorption profile at 77 K for 120-TMA.



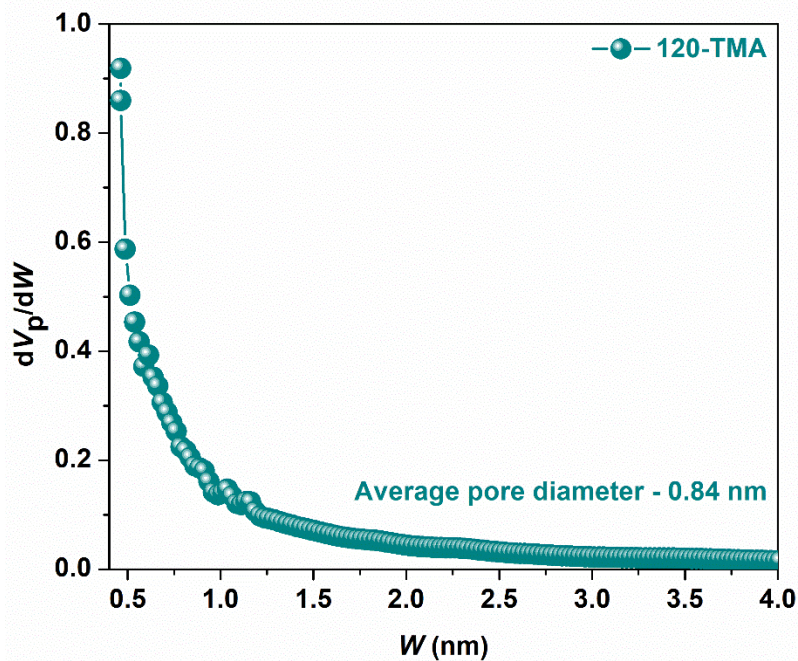
Appendix Figure 4.7. N_2 adsorption profile at 77 K for 120-TMA@Fe.



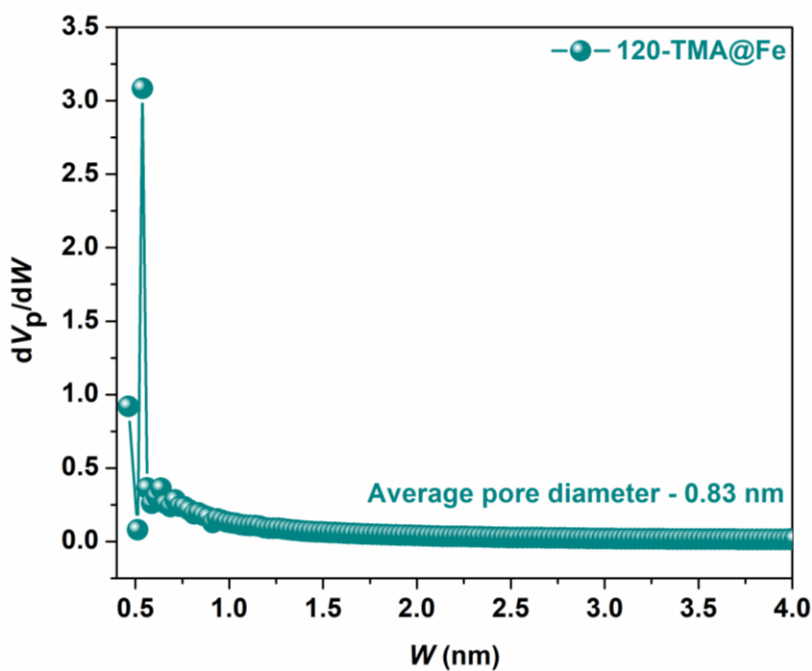
Appendix Figure 4.8. N_2 adsorption profile at 77 K for 120-TMA@Fe (cyan) and MO loaded 120-TMA@Fe (brown).



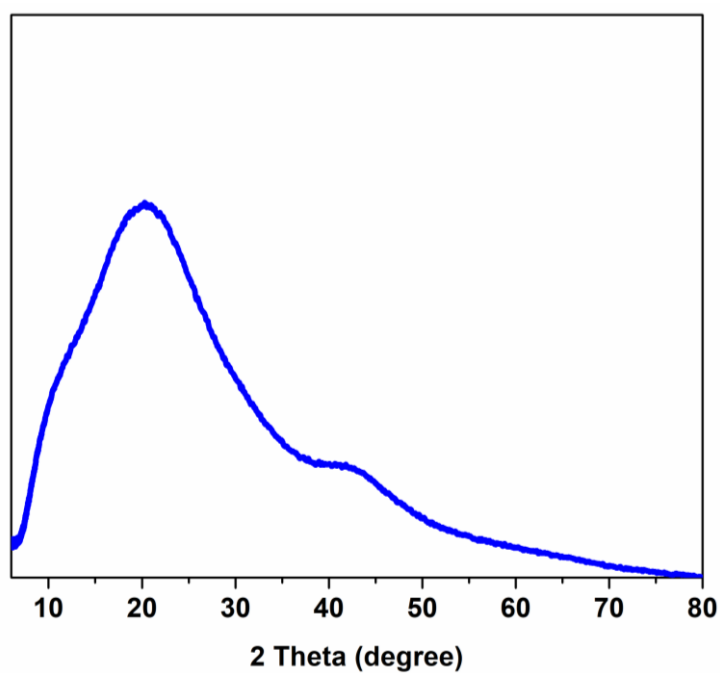
Appendix Figure 4.9. HK plot for 120-Cl from N_2 adsorption (at 77 K) at low pressure region.



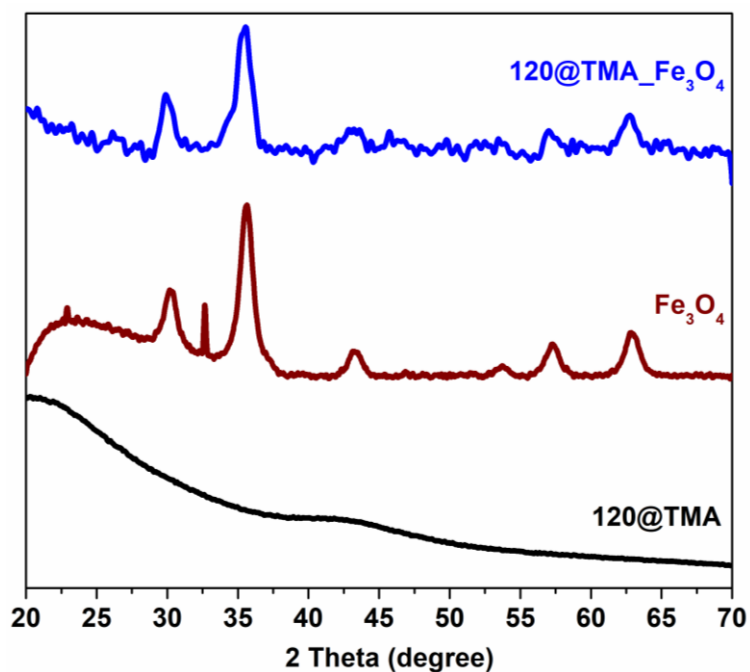
Appendix Figure 4.10. HK plot for 120-TMA from N₂ adsorption (at 77 K) at low pressure region.



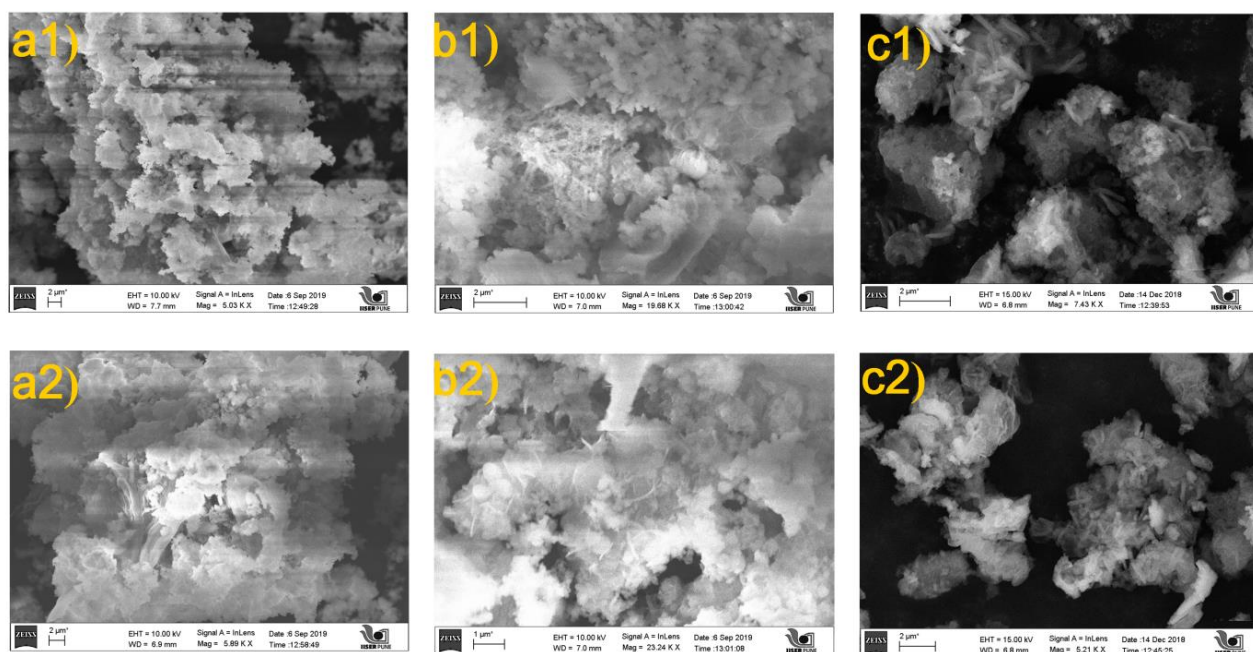
Appendix Figure 4.11. HK plot for 120-TMA@Fe from N₂ adsorption (at 77 K) at low pressure region.



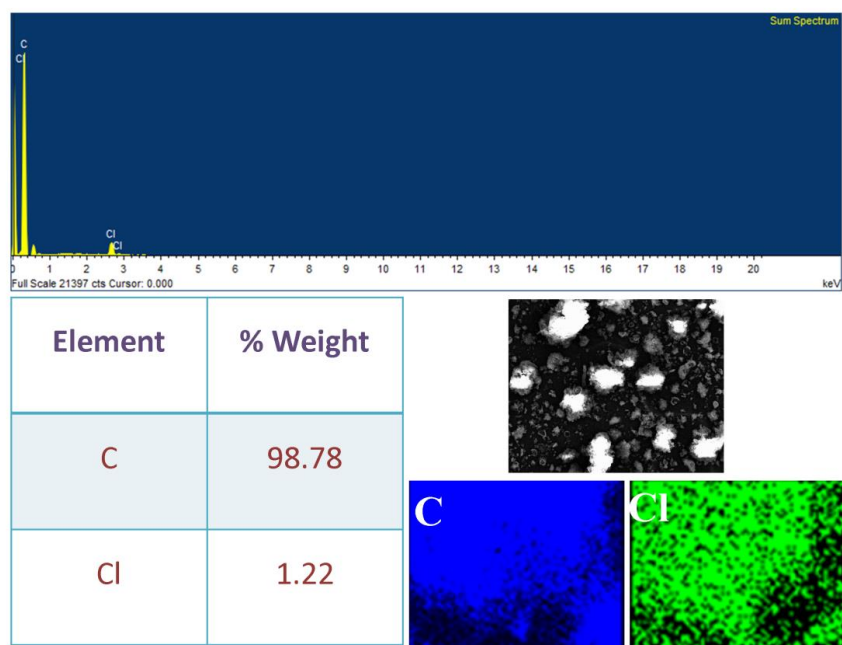
Appendix Figure 4.12. PXRD pattern of polymer 120-Cl.



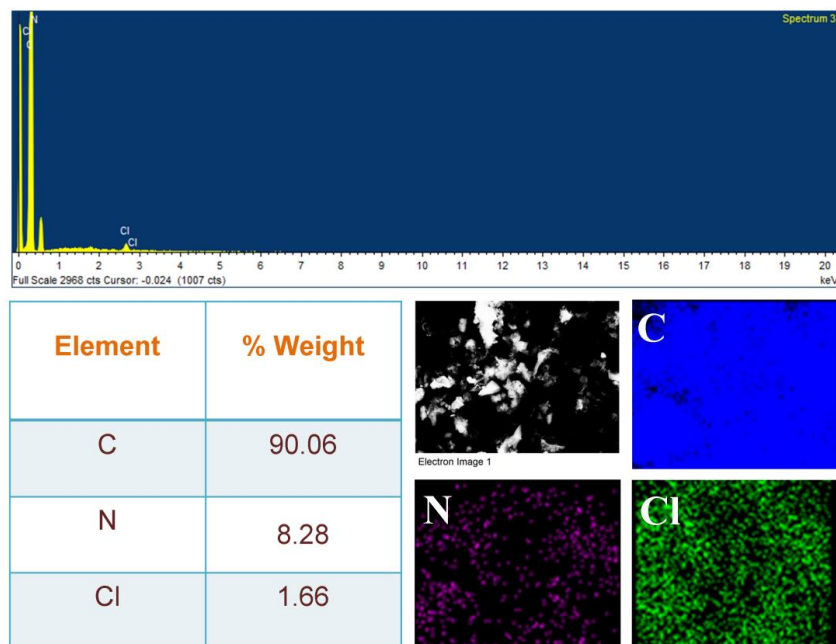
Appendix Figure 4.13. PXRD patterns of polymer 120-Cl (black), bare Fe₃O₄ NPs (brown) and 120-TMA@Fe (blue).



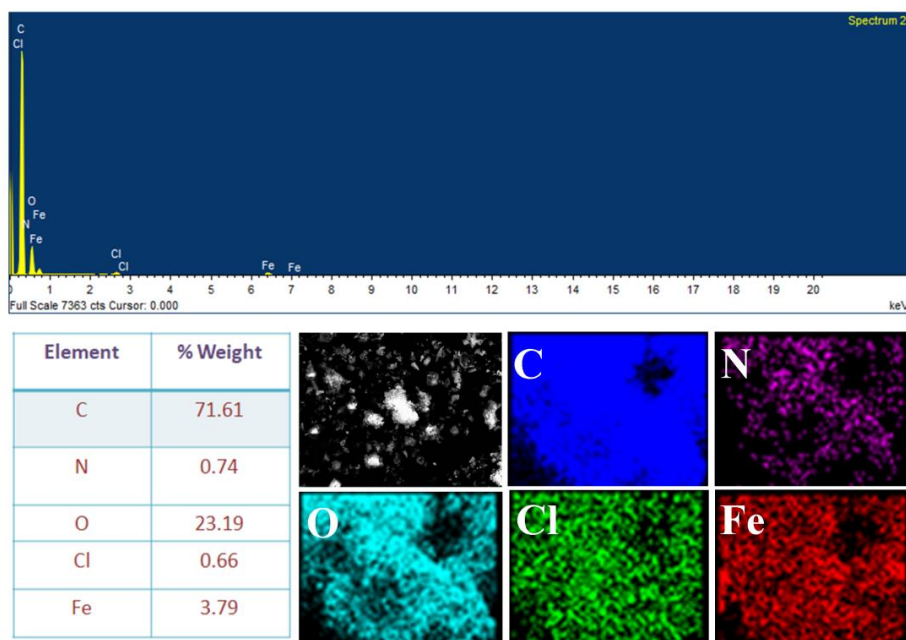
Appendix Figure 4.14. Magnified FESEM images of (a1-a2) 120-Cl, (b1-b2) 120-TMA and (c1-c2) 120-TMA@Fe, scale bar = 1-2 μM .



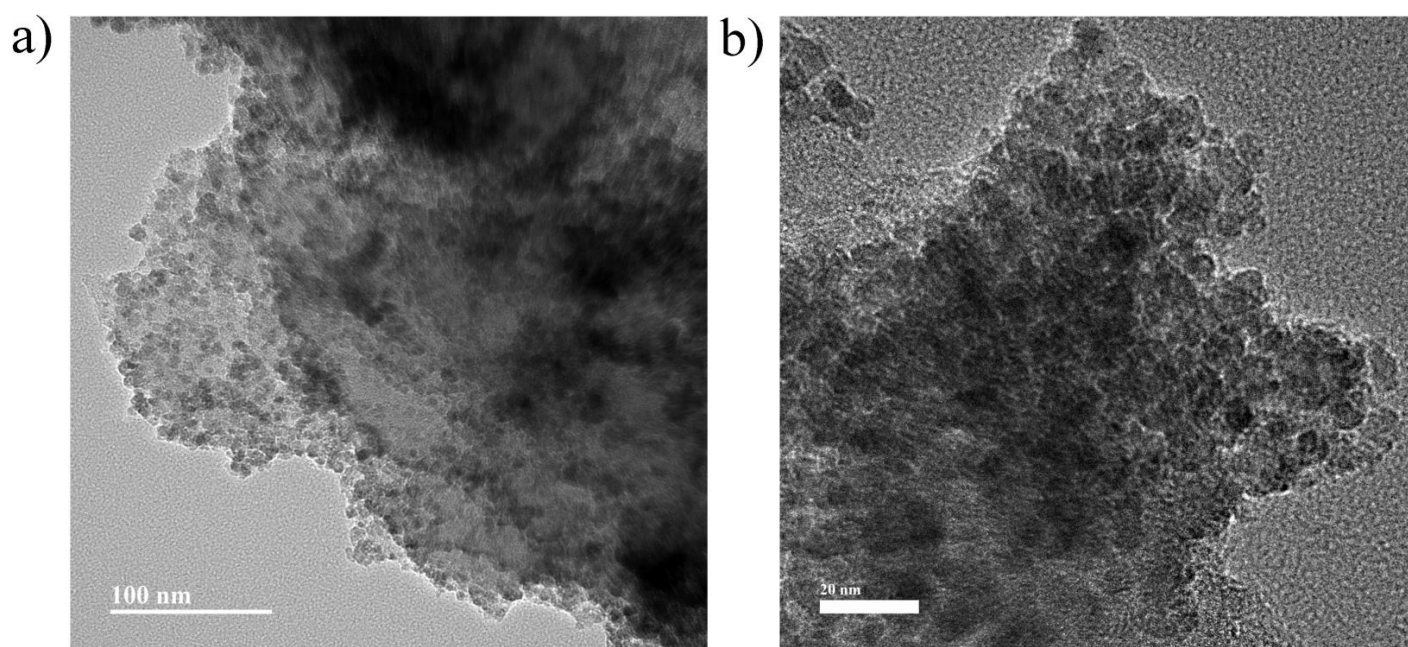
Appendix Figure 4.15. EDX analysis and elemental mapping of 120-Cl.



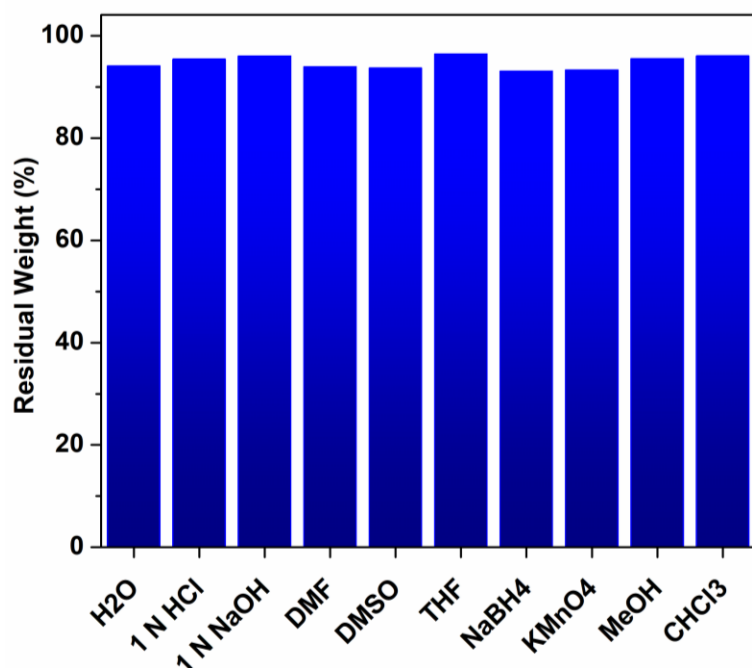
Appendix Figure 4.16. EDX analysis and elemental mapping of 120-Cl.



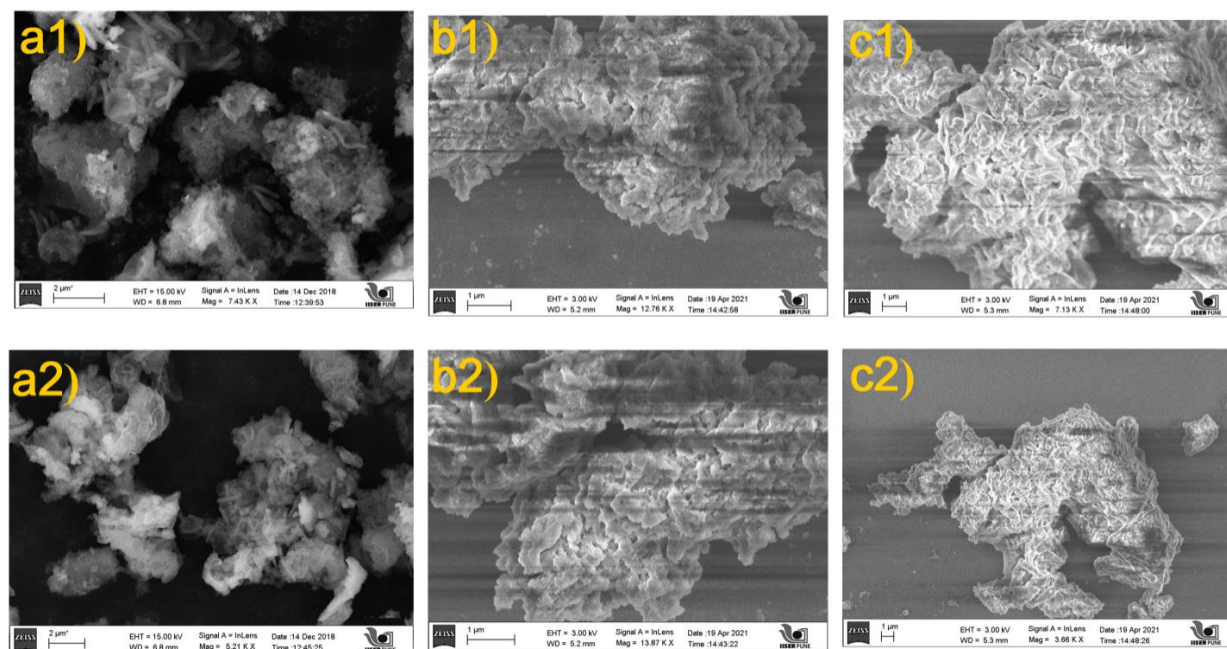
Appendix Figure 4.17. EDX analysis and elemental mapping of 120-TMA@Fe.



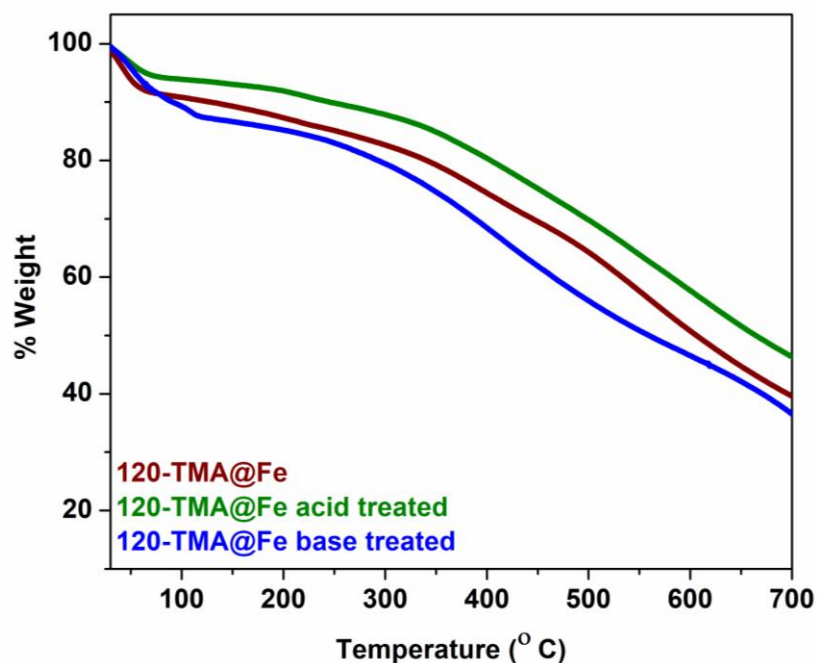
Appendix Figure 4.18. HRTEM images of 120-TMA@Fe.



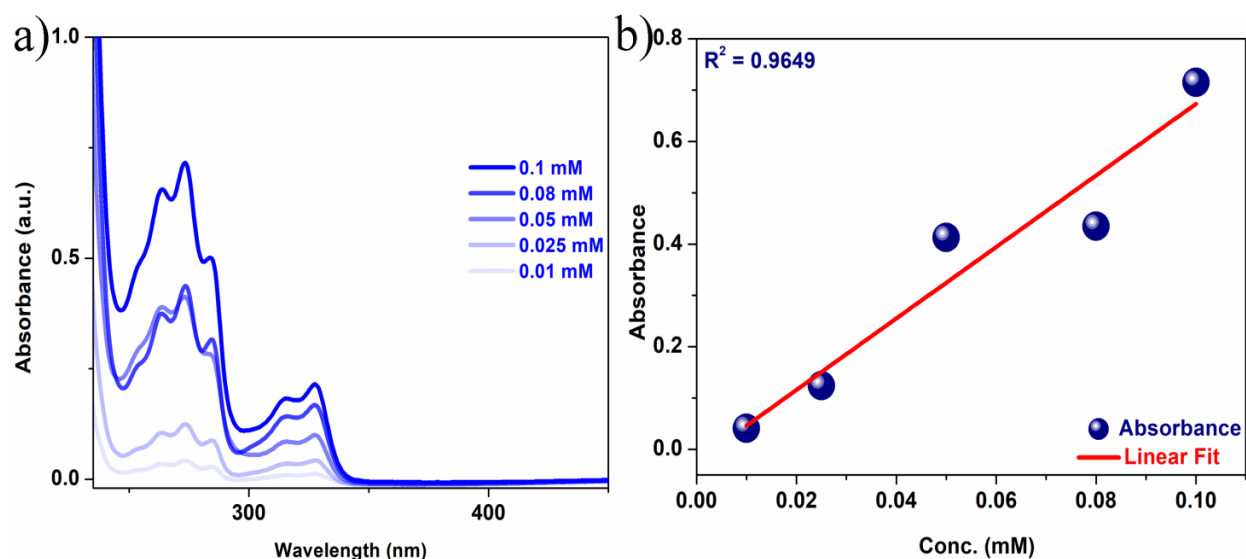
Appendix Figure 4.19. Residual weight of 120-TMA@Fe after treating with various solutions.



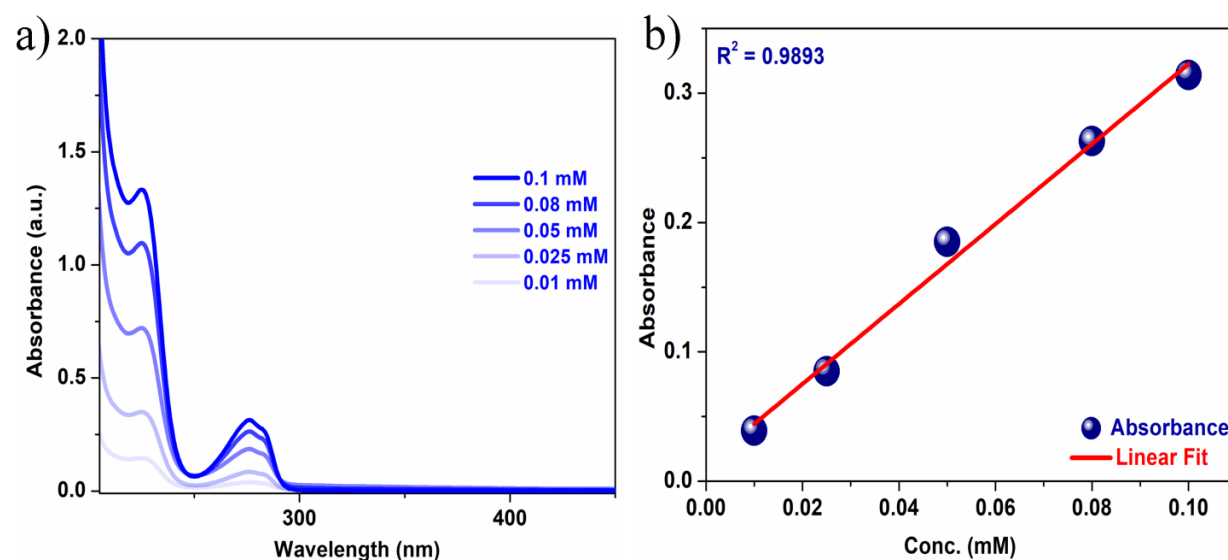
Appendix Figure 4.20. Magnified FESEM images of (a1-a2) pristine 120-TMA@Fe, (b1-b2) 120-TMA@Fe acid treated and (c1-c2) 120-TMA@Fe base treated, scale bar = 1-2 μm .



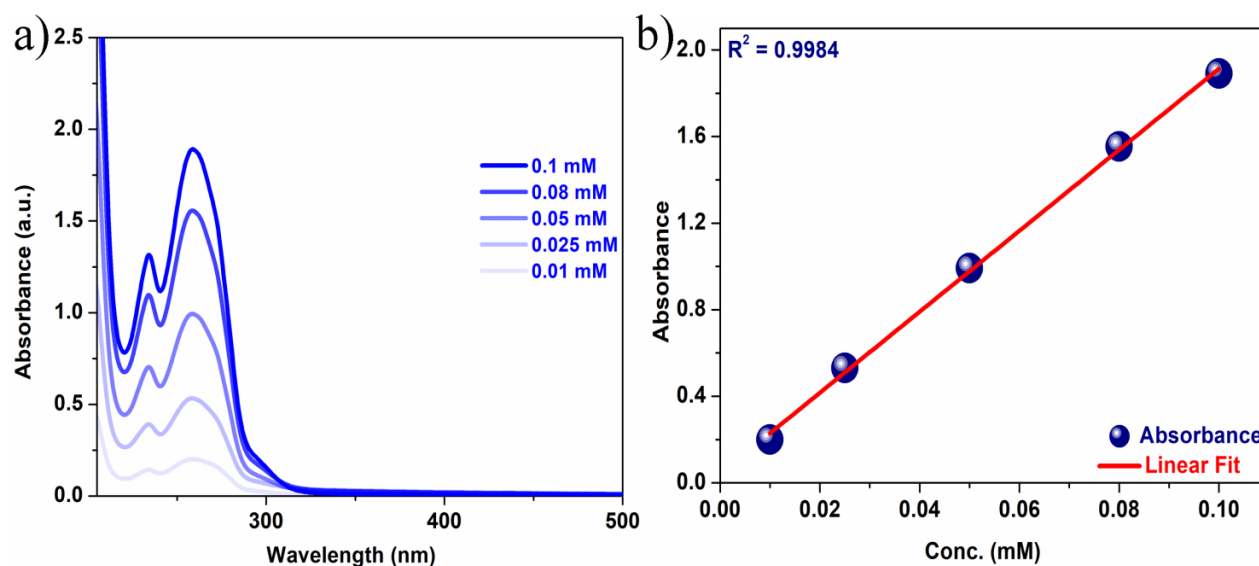
Appendix Figure 4.21. Thermogravimetric profile for pristine 120-TMA@Fe (brown), 120-TMA@Fe acid treated (olive green) and 120-TMA@Fe base treated (blue).



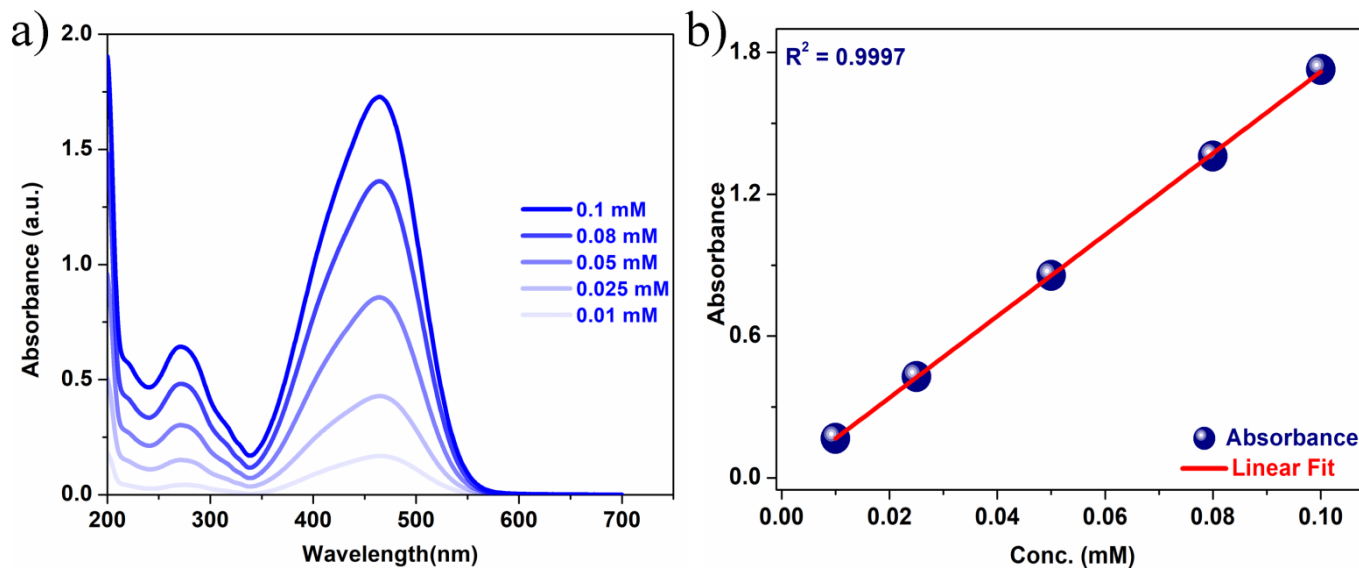
Appendix Figure 4.22. UV-Vis spectra of 2-Naphthol at different concentrations (left). Standard curve plotted based on the absorbance at 273 nm (right).



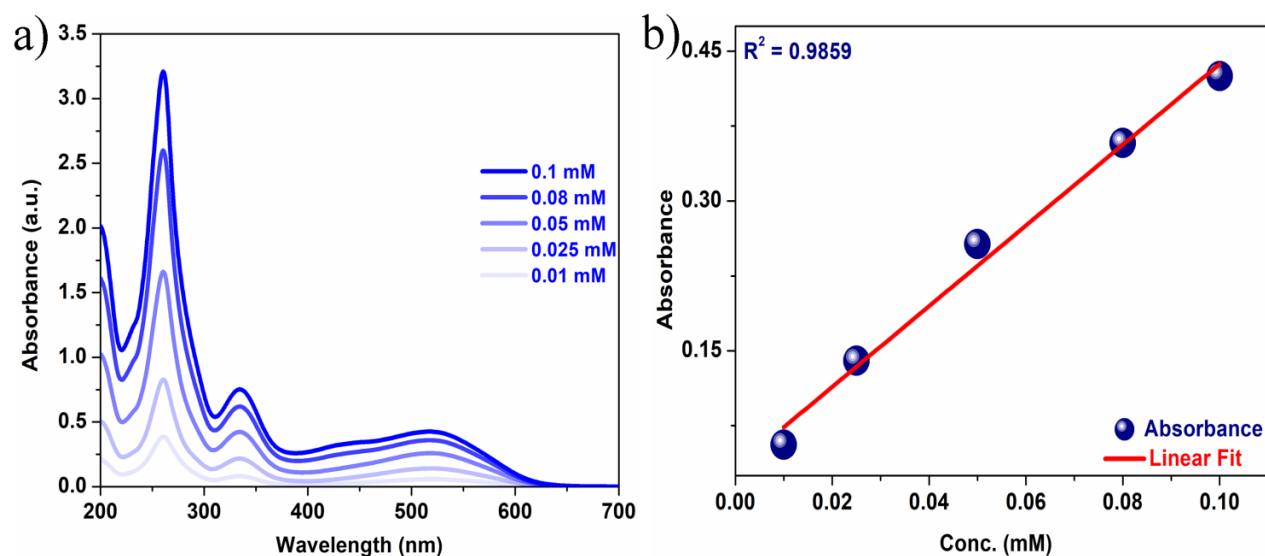
Appendix Figure 4.23. UV-Vis spectra of Bisphenol-A at different concentrations (left). Standard curve plotted based on the absorbance at 276 nm (right).



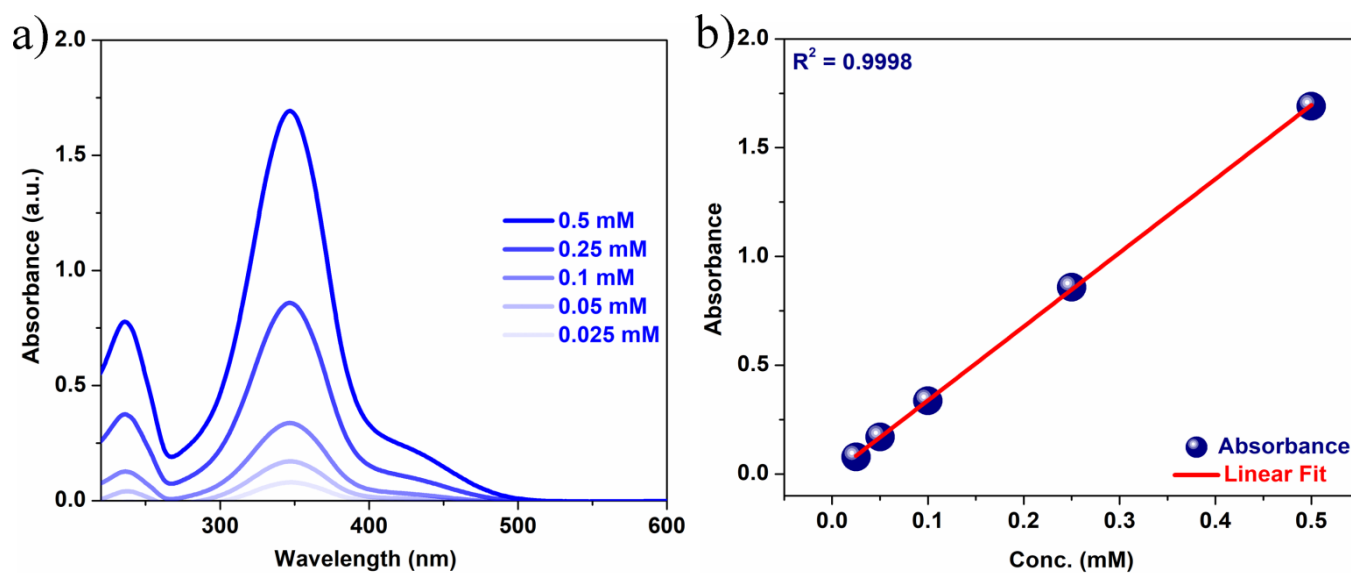
Appendix Figure 4.24: UV-Vis spectra of Bisphenol-S at different concentrations (left). Standard curve plotted based on the absorbance at 259 nm (right).



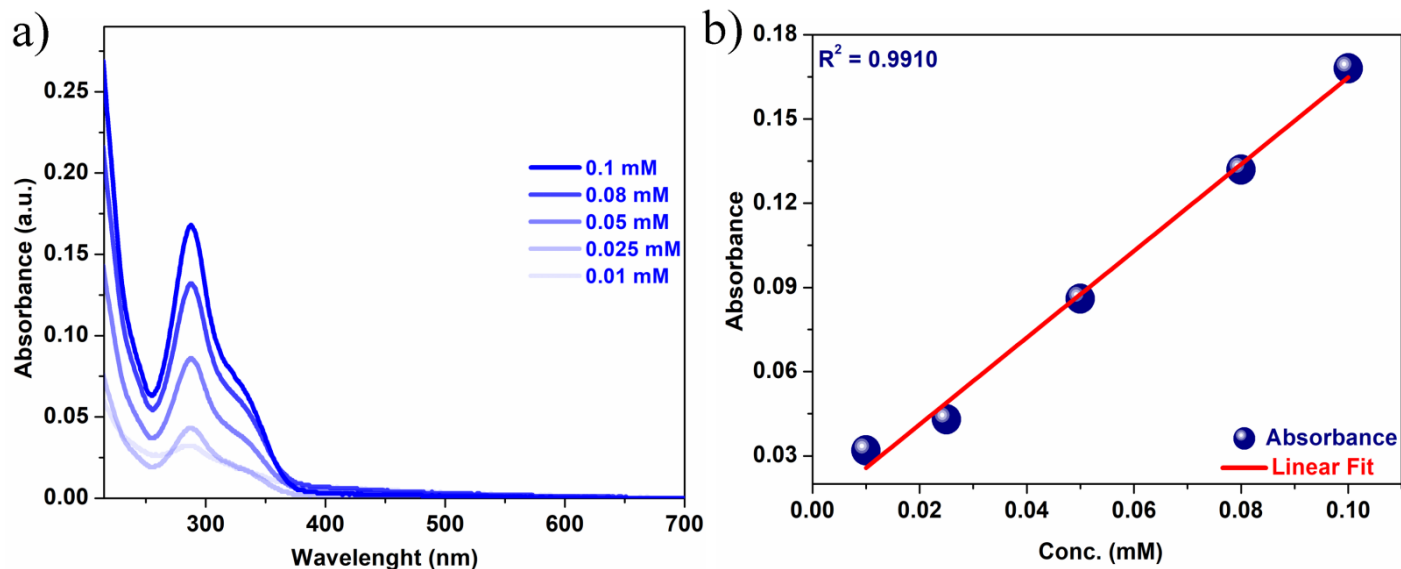
Appendix Figure 4.25: UV-Vis spectra of Methyl Orange at different concentrations (left). Standard curve plotted based on the absorbance at 462 nm (right).



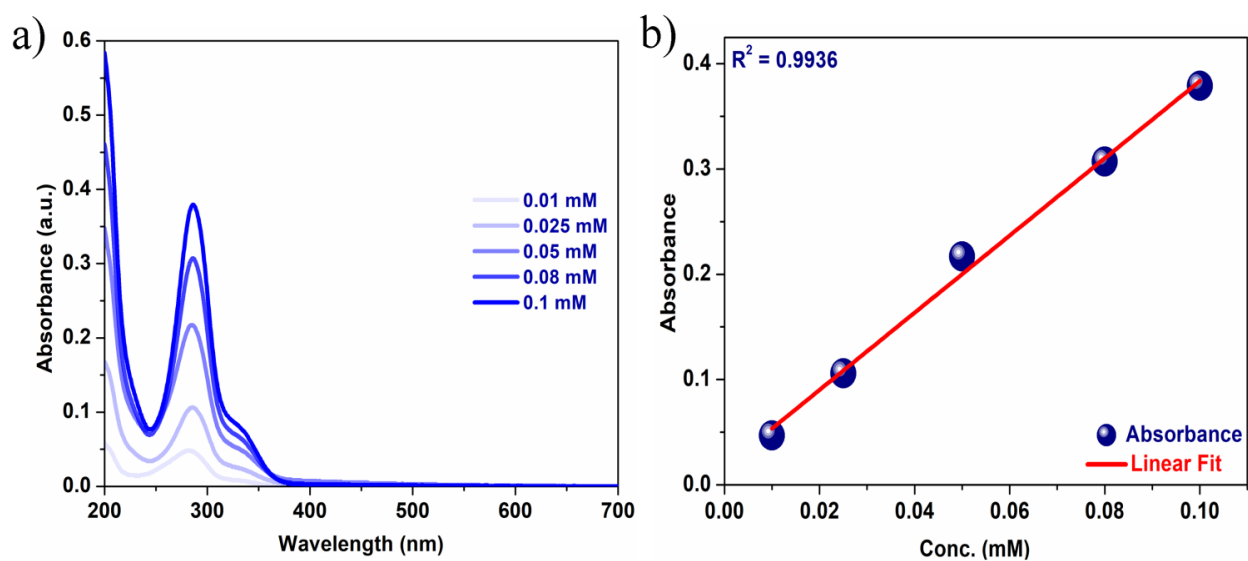
Appendix Figure 4.26. UV-Vis spectra of Alizarin Red S at different concentrations (left). Standard curve plotted based on the absorbance at 522 nm (right).



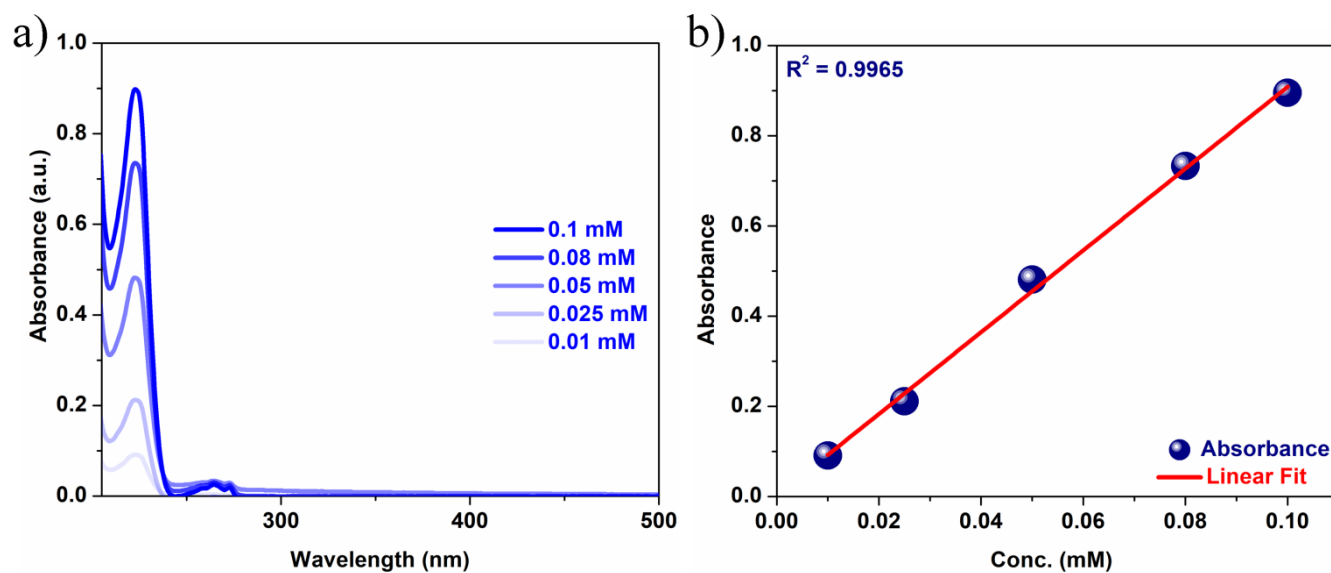
Appendix Figure 4.27. UV-Vis spectra of 4-Phenylazophenol at different concentrations (left). Standard curve plotted based on the absorbance at 346 nm (right).



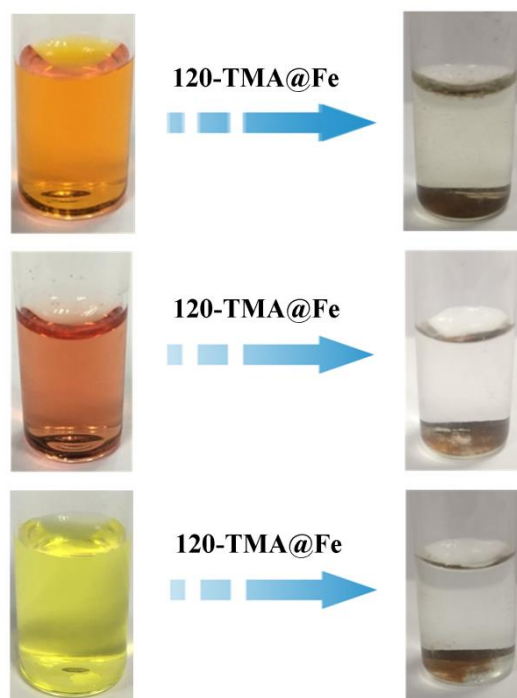
Appendix Figure 4.28. UV-Vis spectra of Flufenamic acid at different concentrations (left). Standard curve plotted based on the absorbance at 288 nm (right).



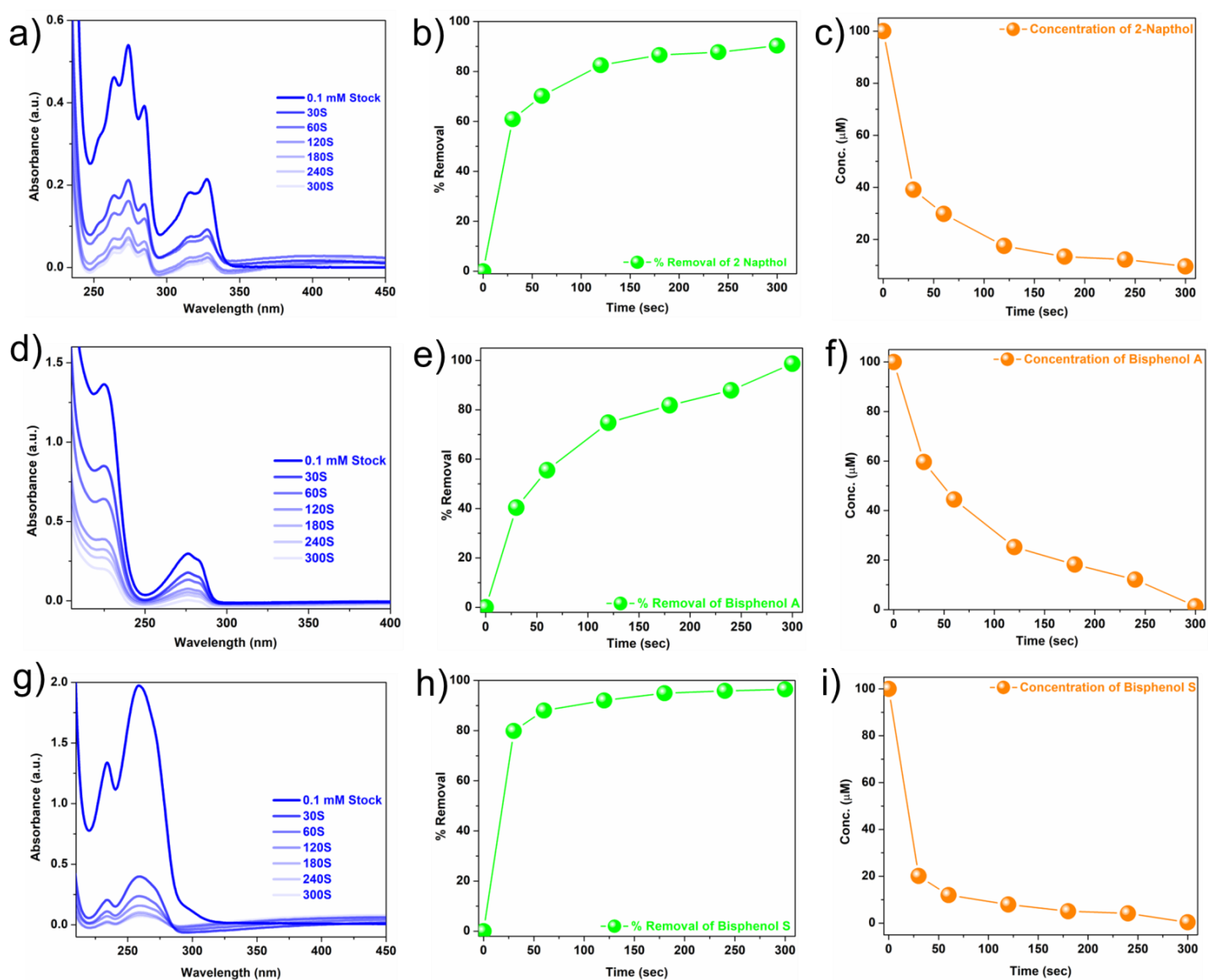
Appendix Figure 4.29. UV-Vis spectra of Niflumic acid at different concentrations (left). Standard curve plotted based on the absorbance at 386 nm (right).



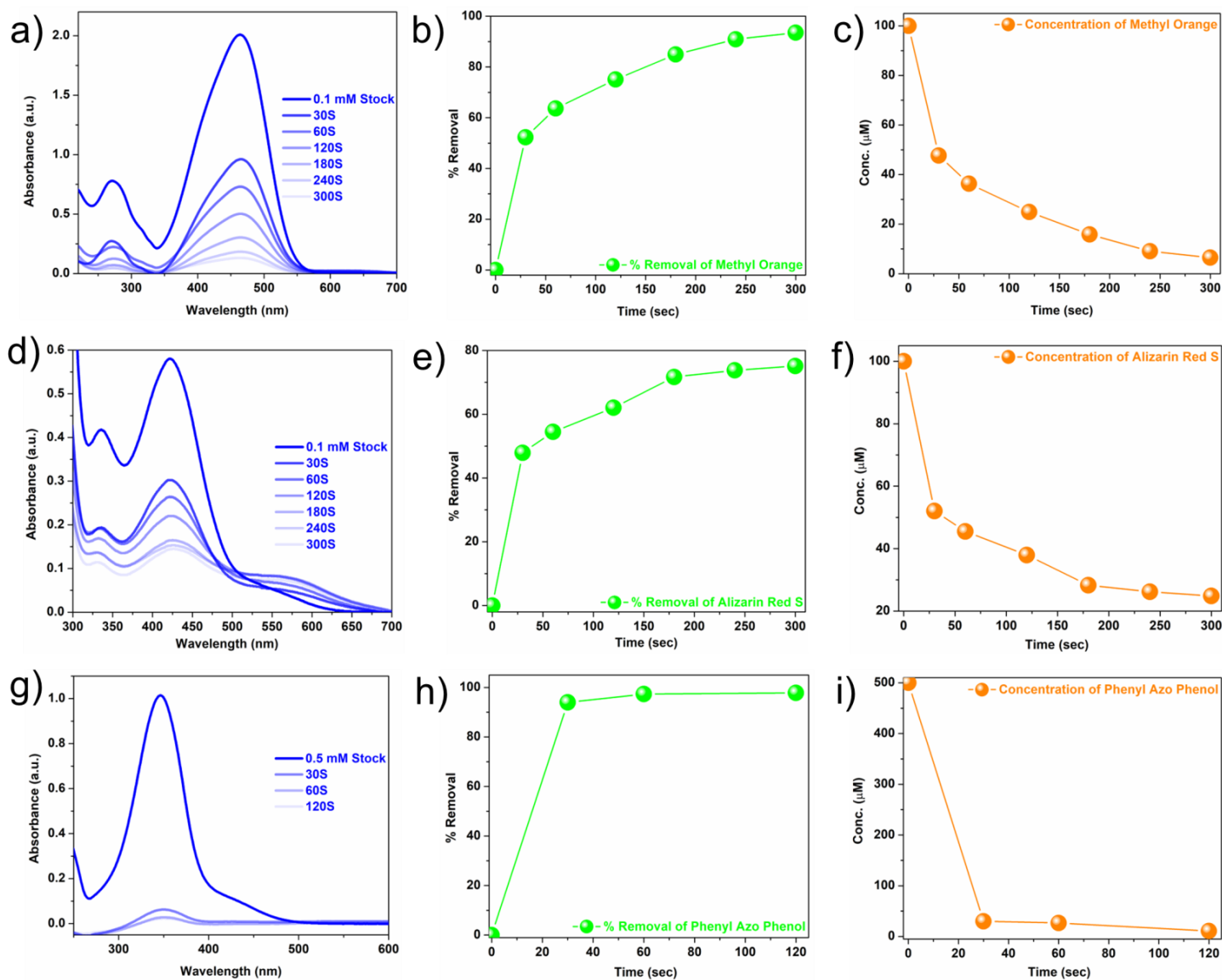
Appendix Figure 4.30. UV-Vis spectra of Ibuprofen at different concentrations (left). Standard curve plotted based on the absorbance at 222 nm (right).



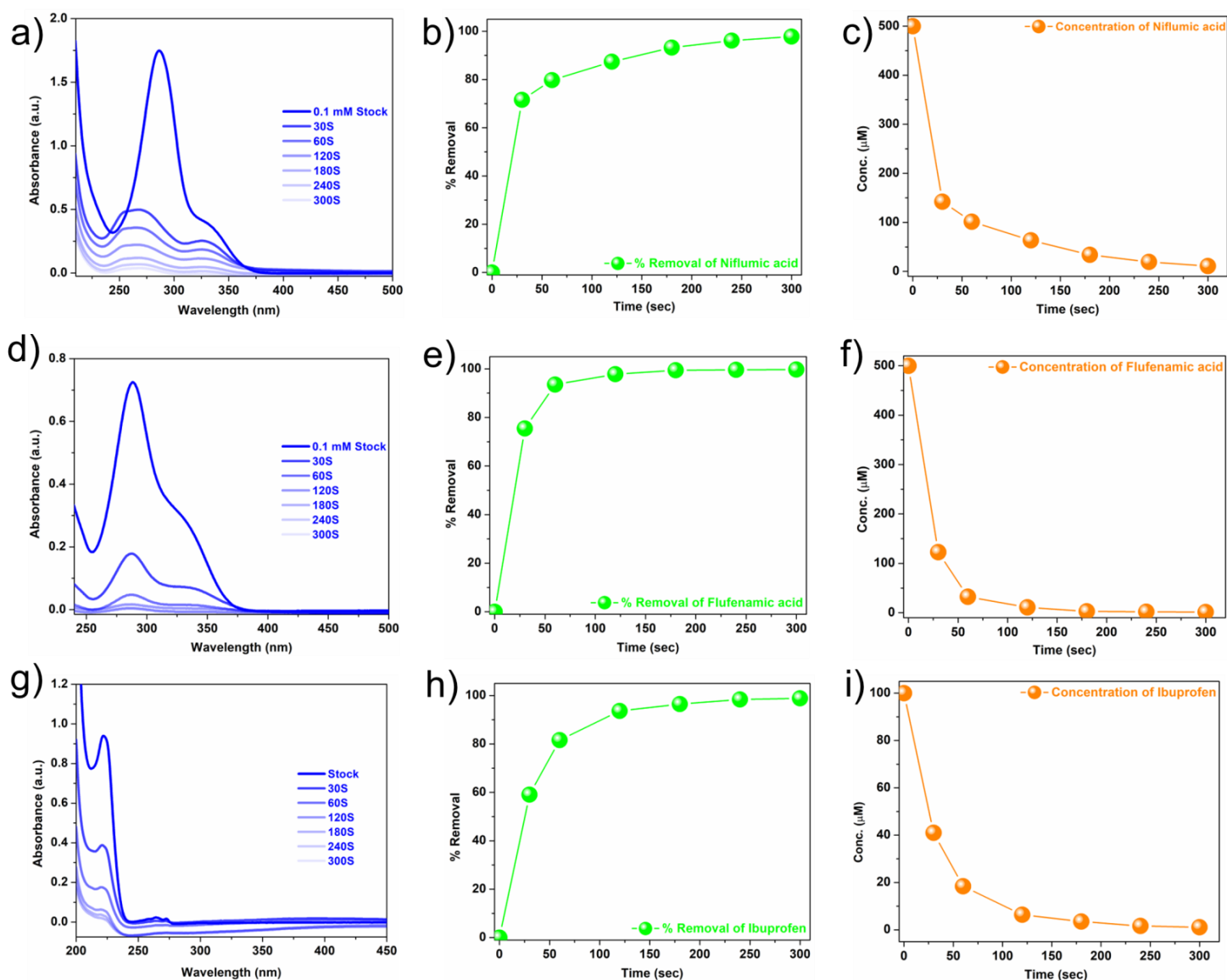
Appendix Figure 4.31. Visual color changes after dye adsorption by 120-TMA@Fe.



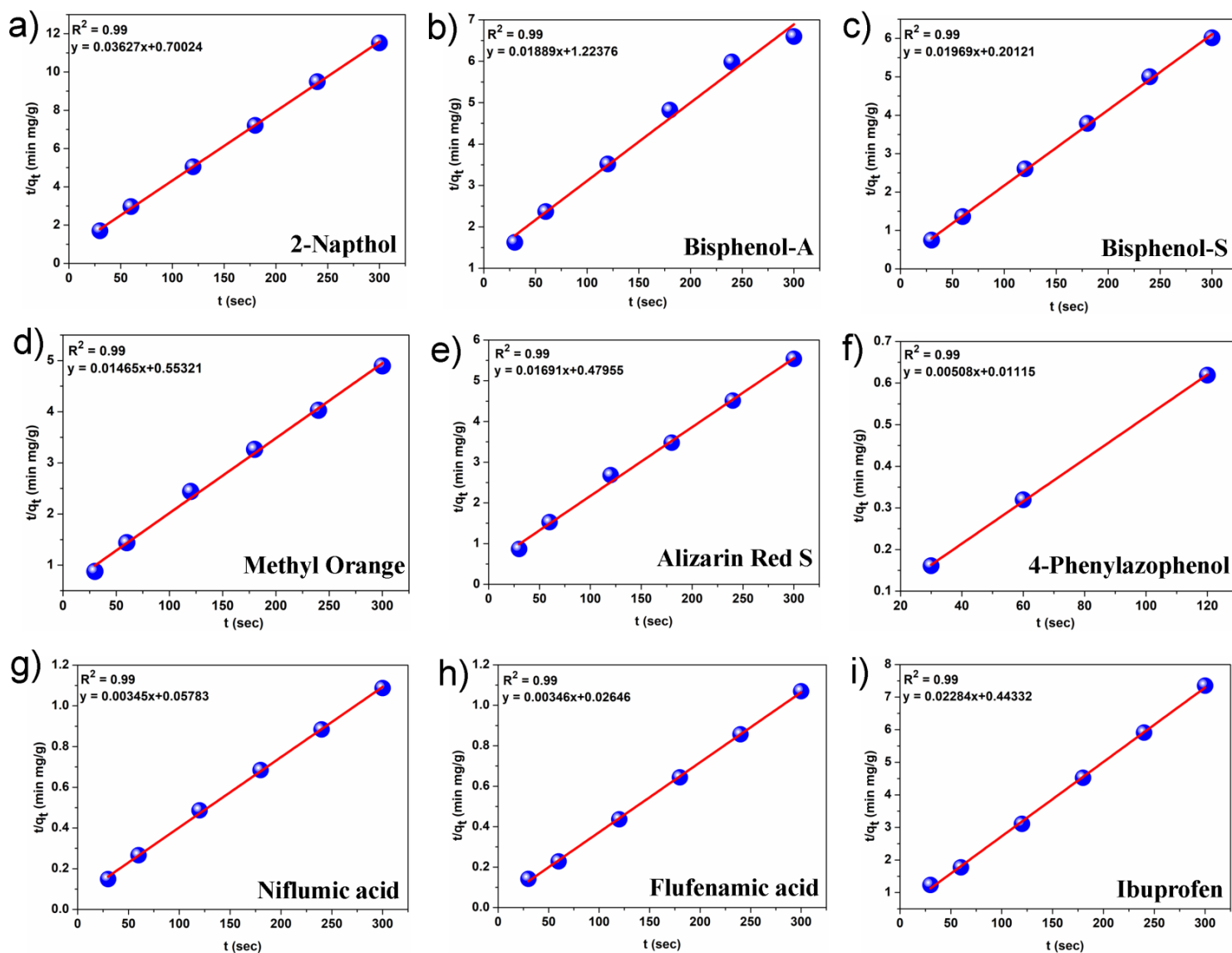
Appendix Figure 4.32. UV-Vis spectra of 2-Naphthol, Bisphenol-A and Bisphenol-S solution (a,d,g), their % removal (b,e,h) and change in concentrations (c,f,i) in presence of 120-TMA@Fe at different time.



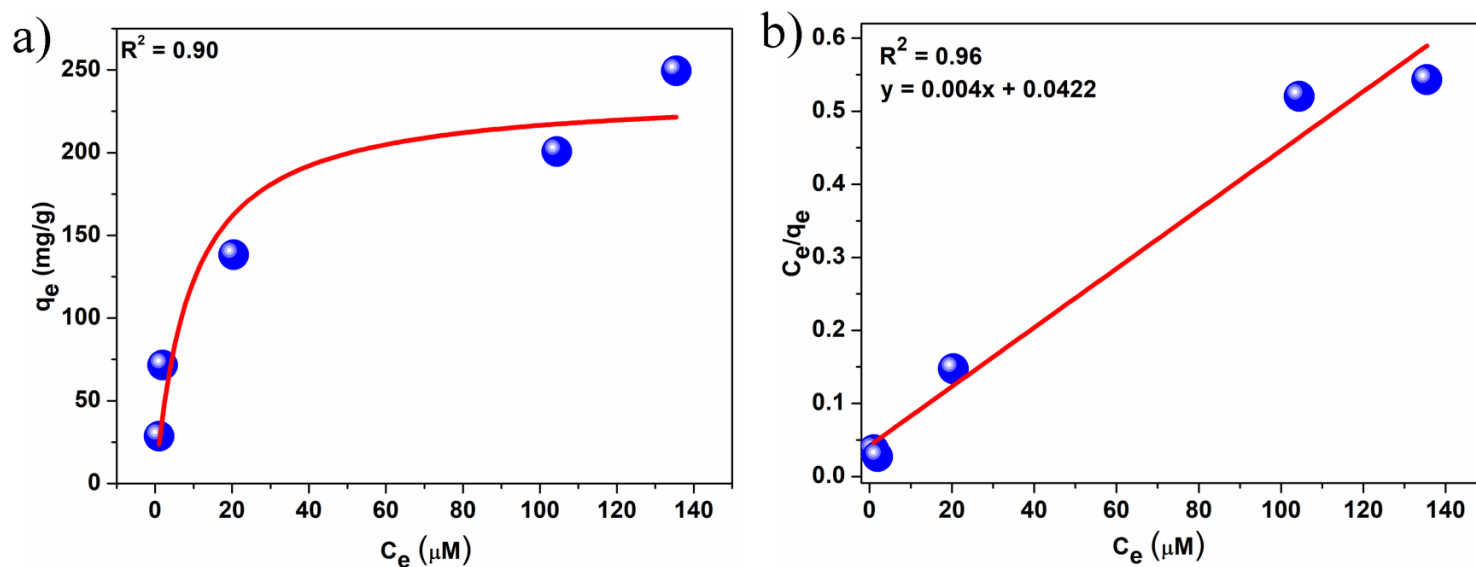
Appendix Figure 4.33. UV-Vis spectra of Methyl Orange, Alizarin Red S and 4-Phenylazophenol solution (a, d, g), their % removal (b, e, h) and change in concentrations (c, f, i) in presence of 120-TMA@Fe at different time.



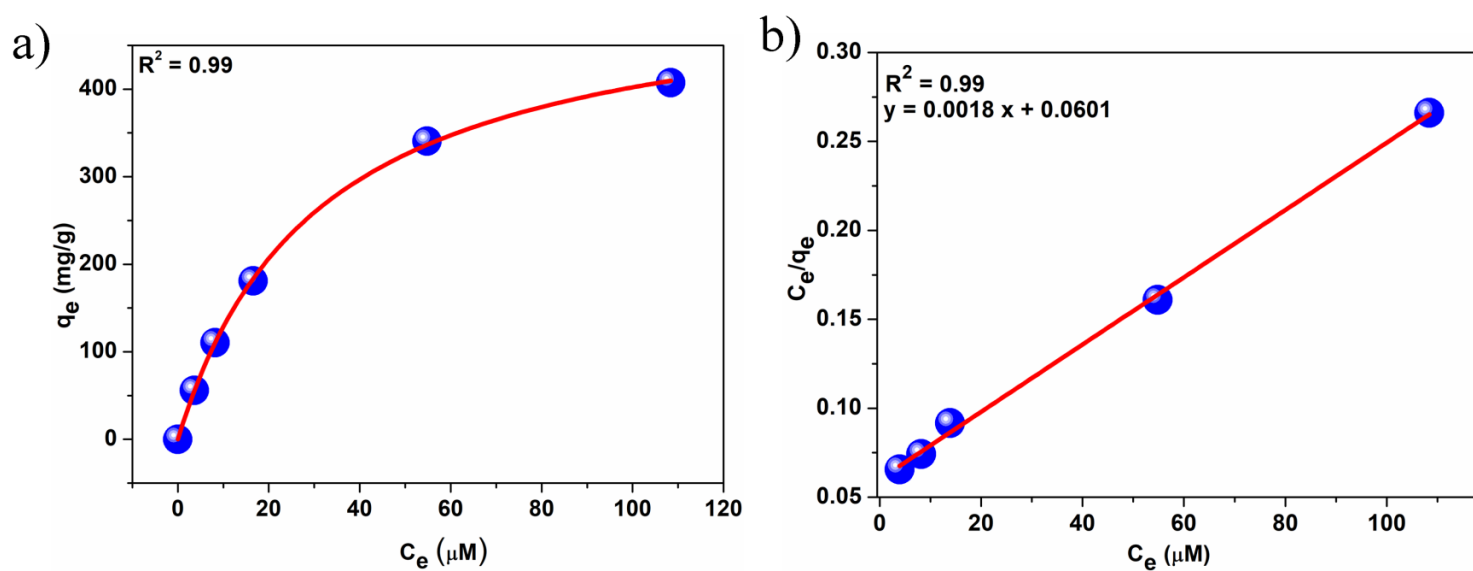
Appendix Figure 4.34. UV-Vis spectra of Niflumic acid, Flufenamic acid and Ibuprofen solution (a, d, g), their % removal (b, e, h) and change in concentrations (c, f, i) in presence of 120-TMA@Fe at different time.



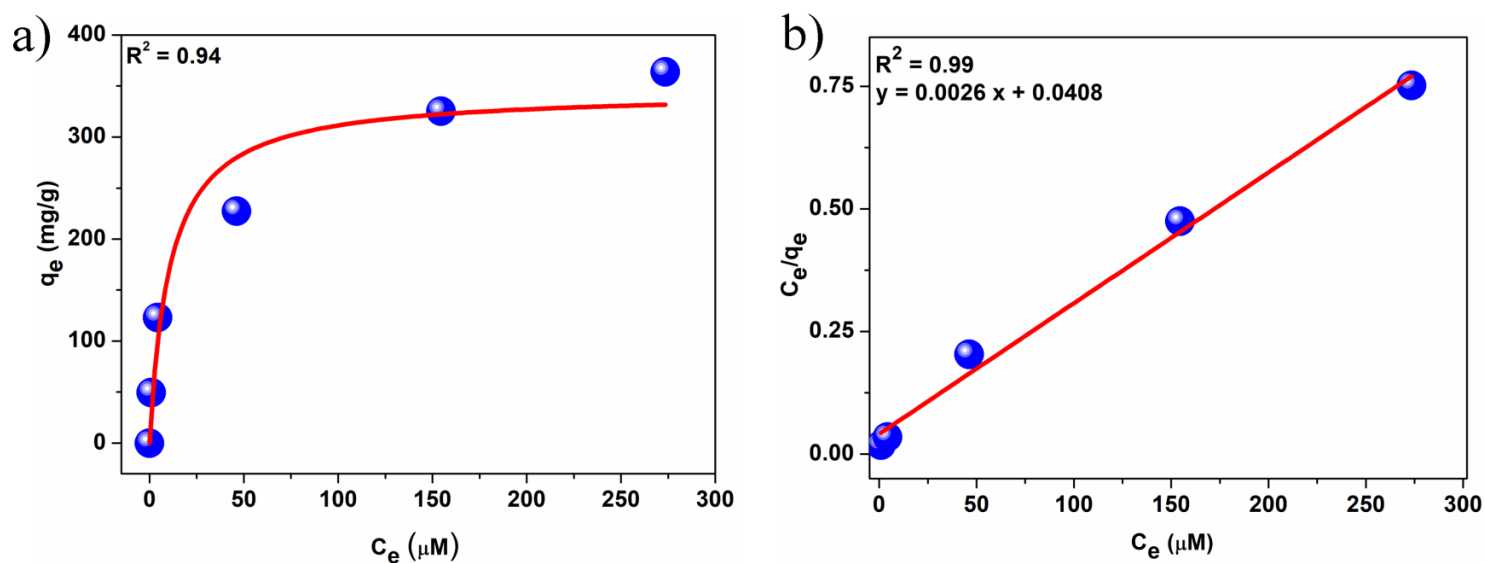
Appendix Figure 4.35. Pseudo-second order plots of adsorption kinetics for 120-TMA@Fe. Where, t (in min) is the contact time for each pollutant solution with 120-TMA@Fe and q_t (in mg g^{-1}) is the quantity of each pollutant adsorbed per gram of 120-TMA@Fe.



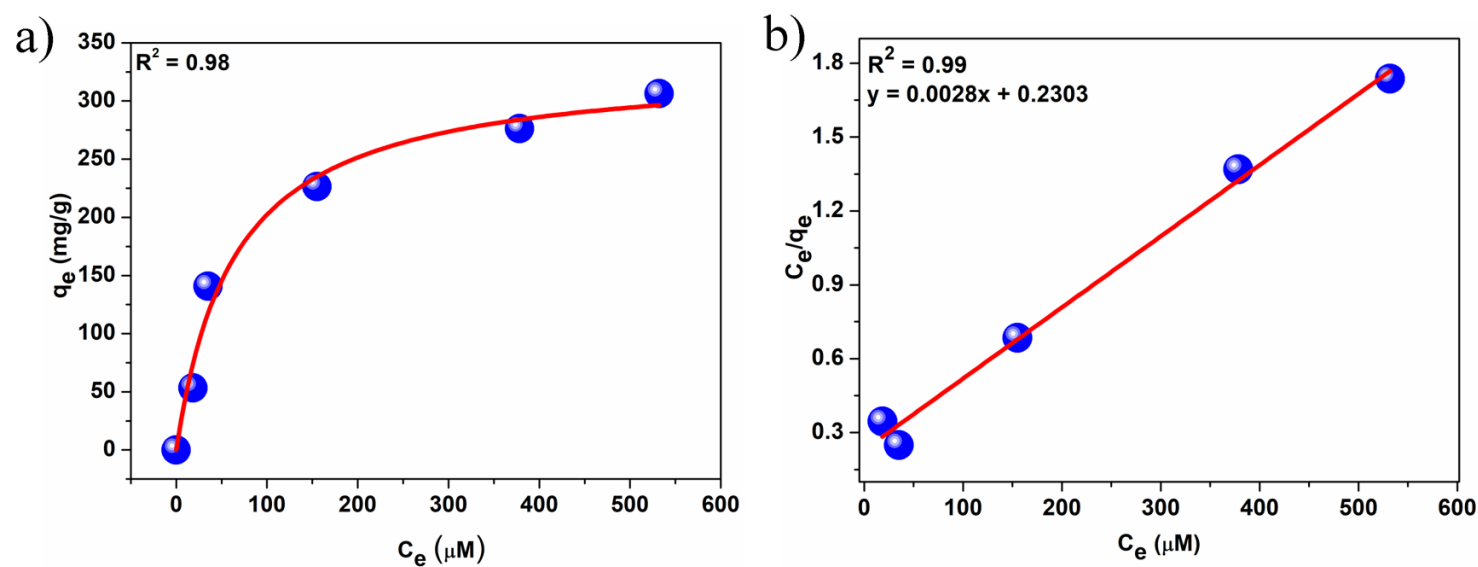
Appendix Figure 4.36. Concentration dependent adsorption profile of 120-TMA@Fe towards 2-Naphthol and its corresponding Langmuir linear fitting model.



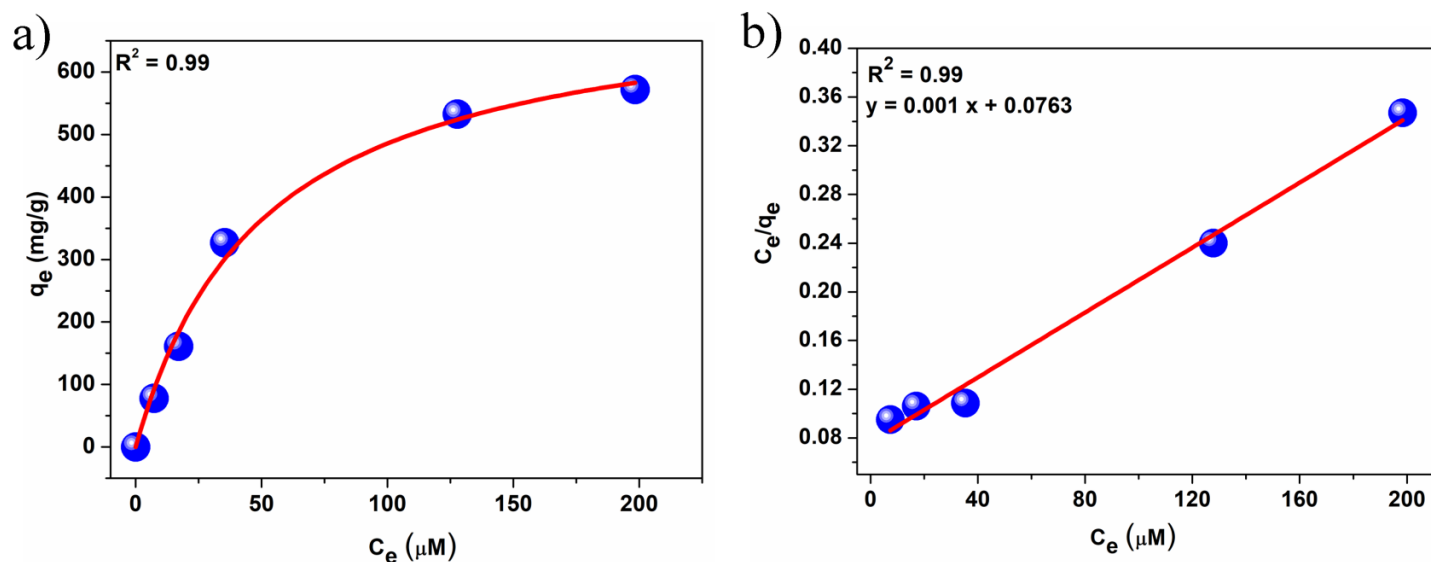
Appendix Figure 4.37. Concentration dependent adsorption profile of 120-TMA@Fe towards Bisphenol-A and its corresponding Langmuir linear fitting model.



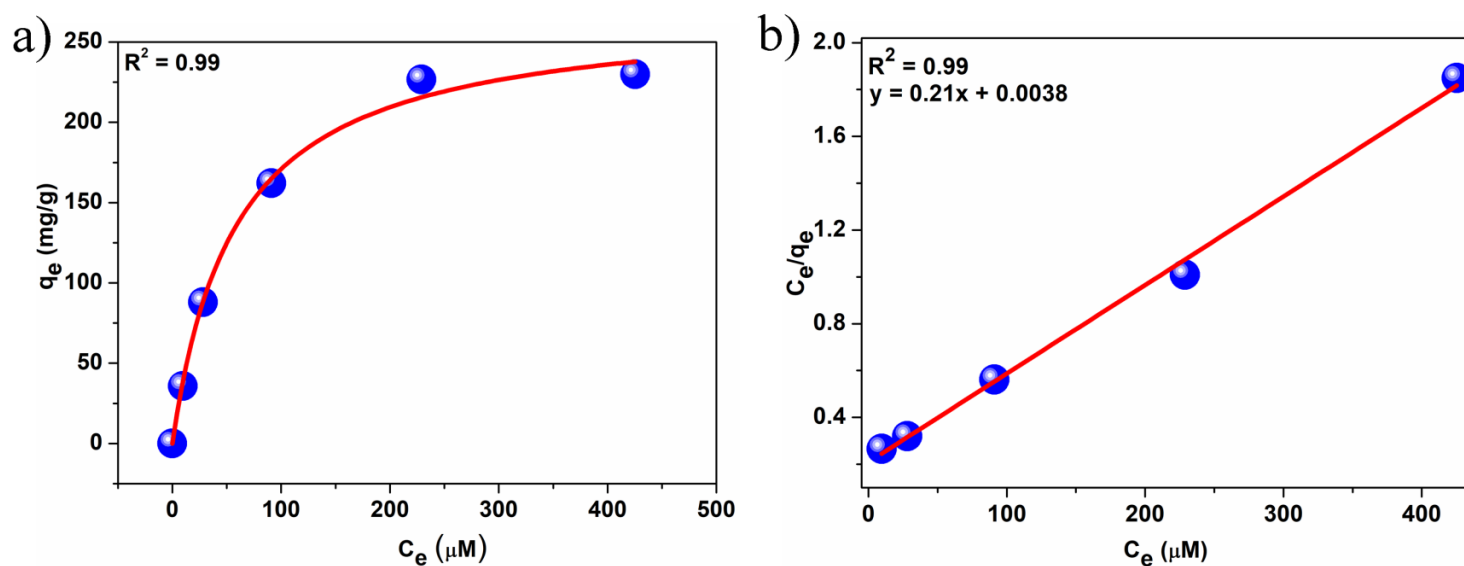
Appendix Figure 4.38. Concentration dependent adsorption profile of 120-TMA@Fe towards Bisphenol-S and its corresponding Langmuir linear fitting model.



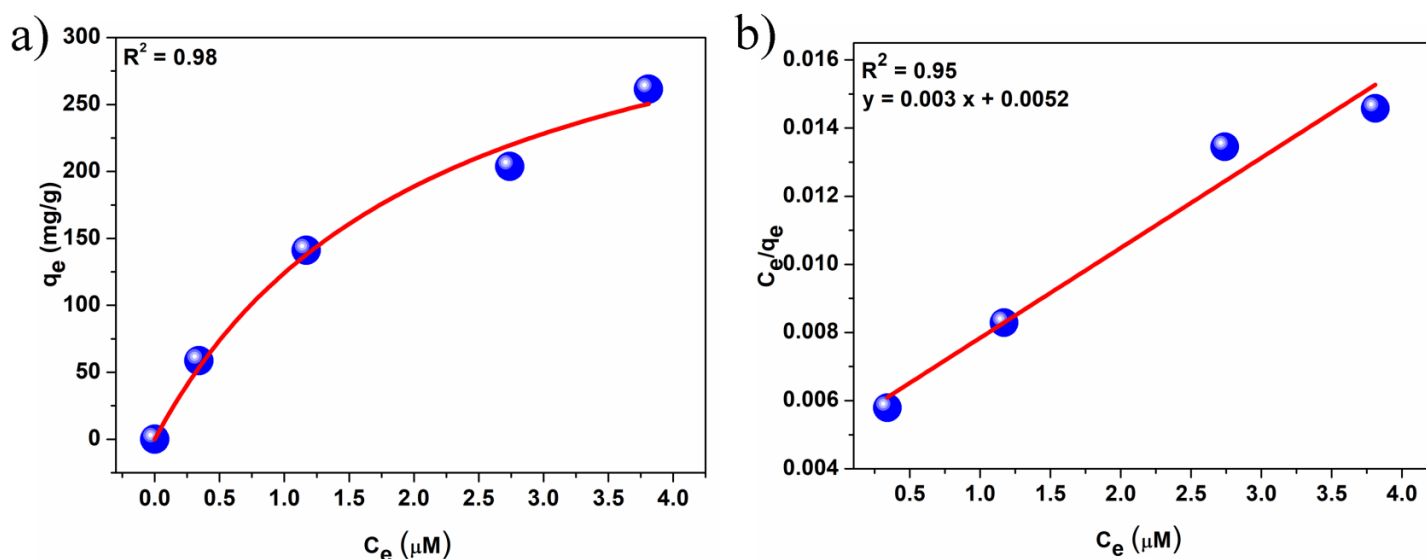
Appendix Figure 4.39. Concentration dependent adsorption profile of 120-TMA@Fe towards Methyl Orange and its corresponding Langmuir linear fitting model.



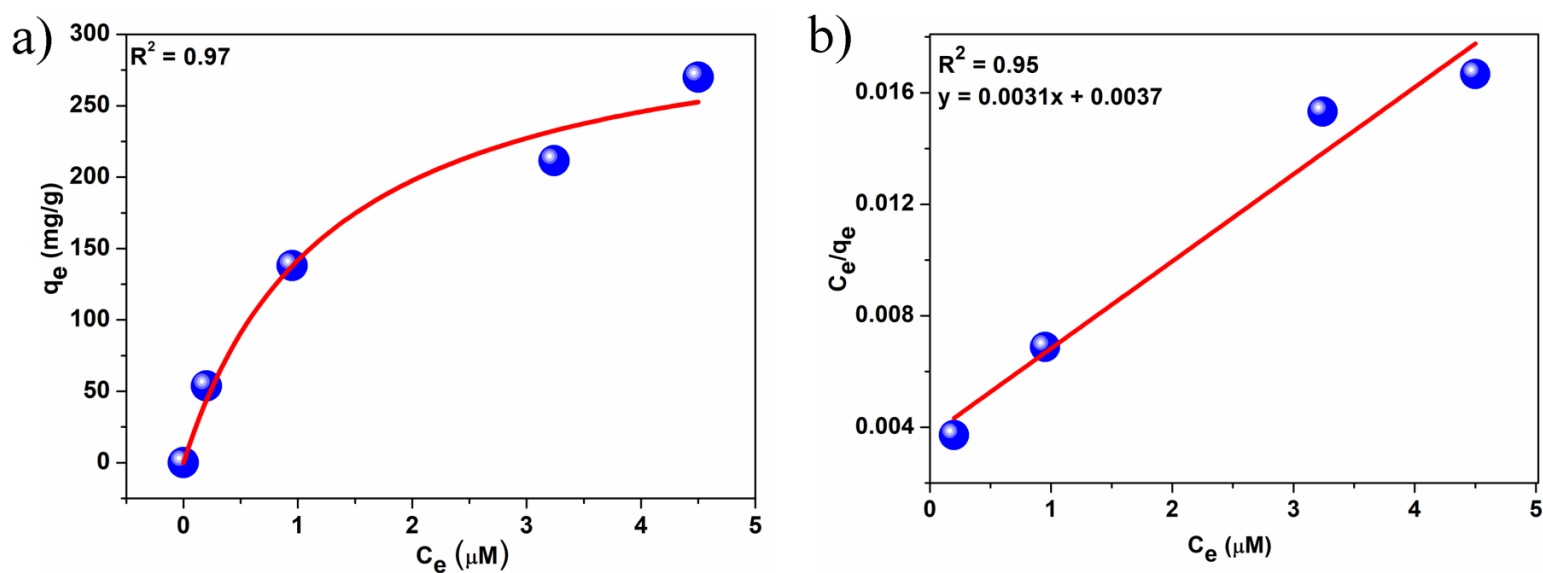
Appendix Figure 4.40. Concentration dependent adsorption profile of 120-TMA@Fe towards Alizarin Red S and its corresponding Langmuir linear fitting model.



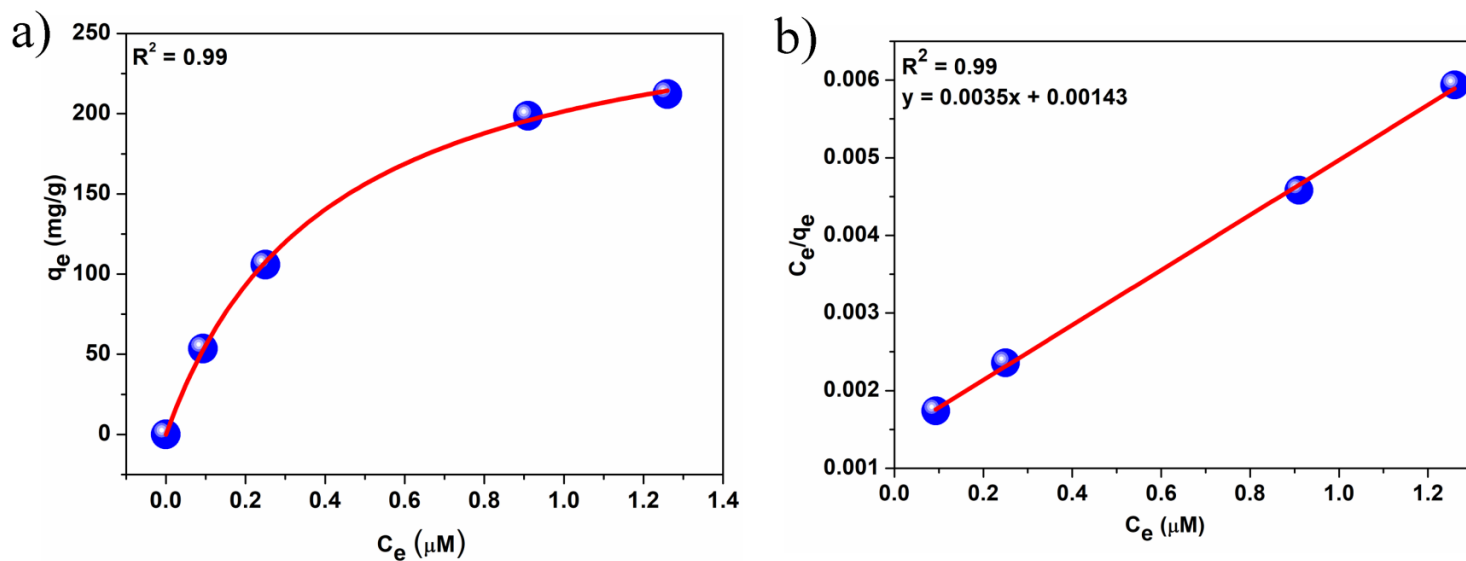
Appendix Figure Table 4.41. Concentration dependent adsorption profile of 120-TMA@Fe towards 4-Phenylazophenol and its corresponding Langmuir linear fitting model.



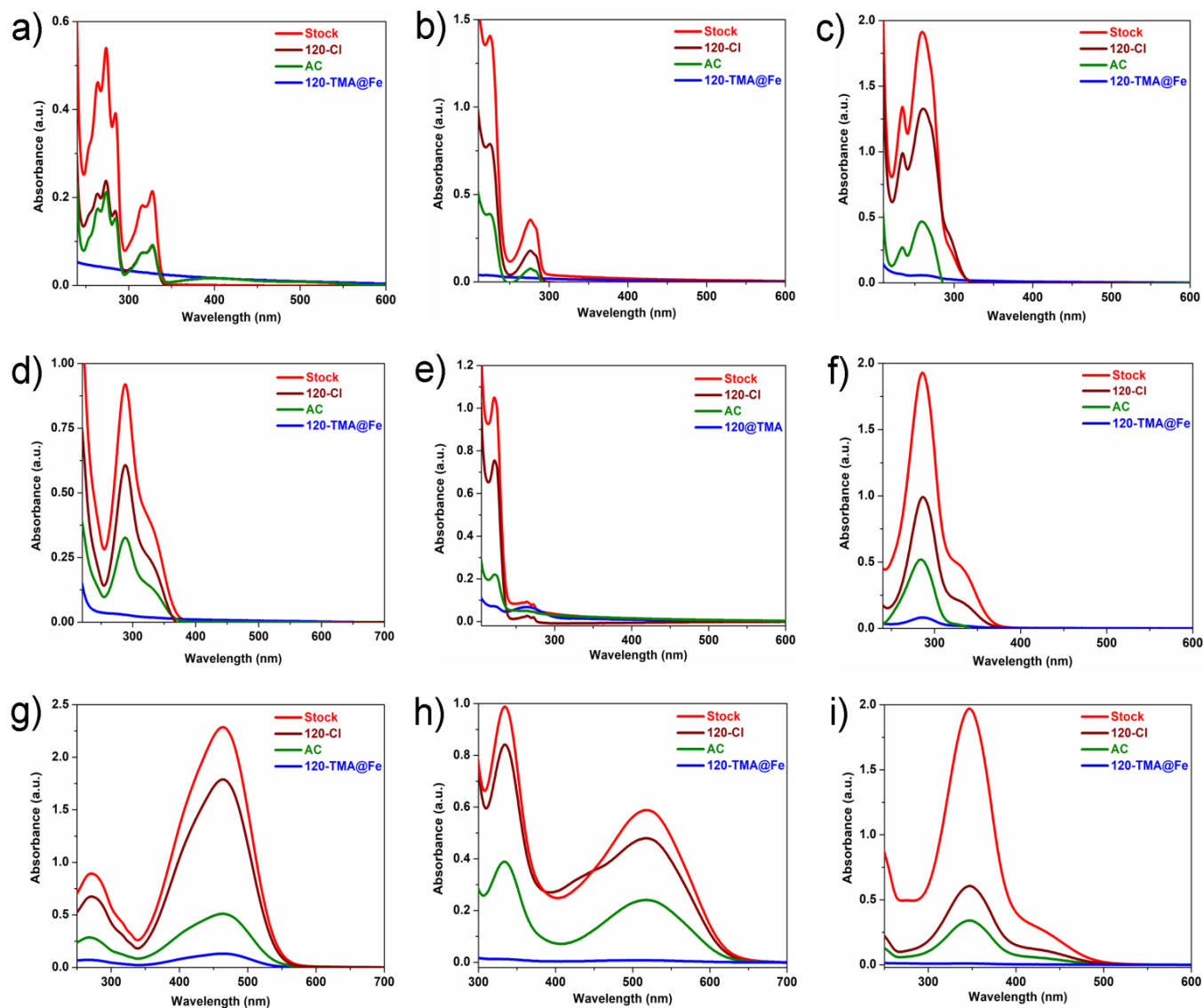
Appendix Figure 4.42. Concentration dependent adsorption profile of 120-TMA@Fe towards Niflumic acid and its corresponding Langmuir linear fitting model.



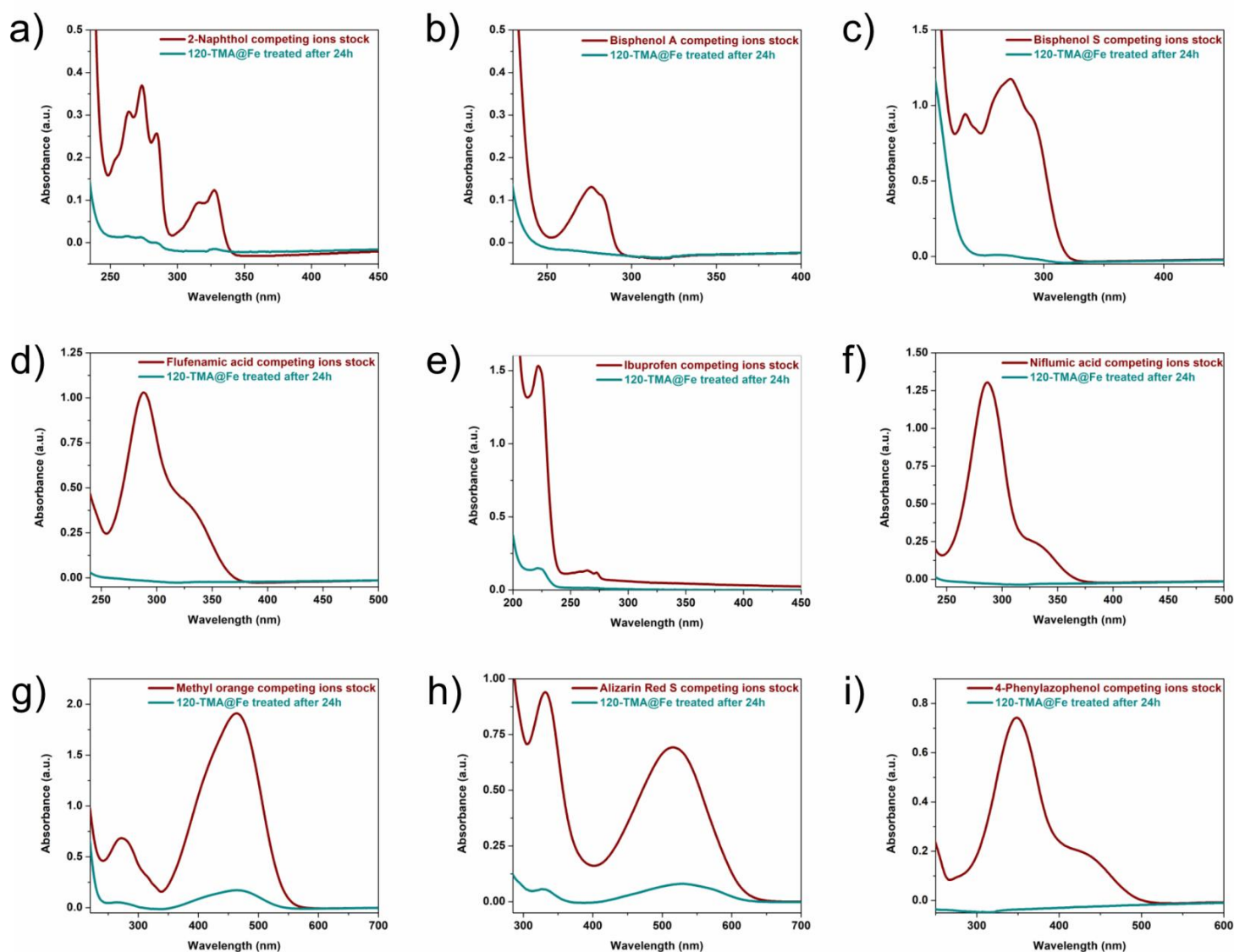
Appendix Figure 4.43. Concentration dependent adsorption profile of 120-TMA@Fe towards Flufenamic acid and its corresponding Langmuir linear fitting model.



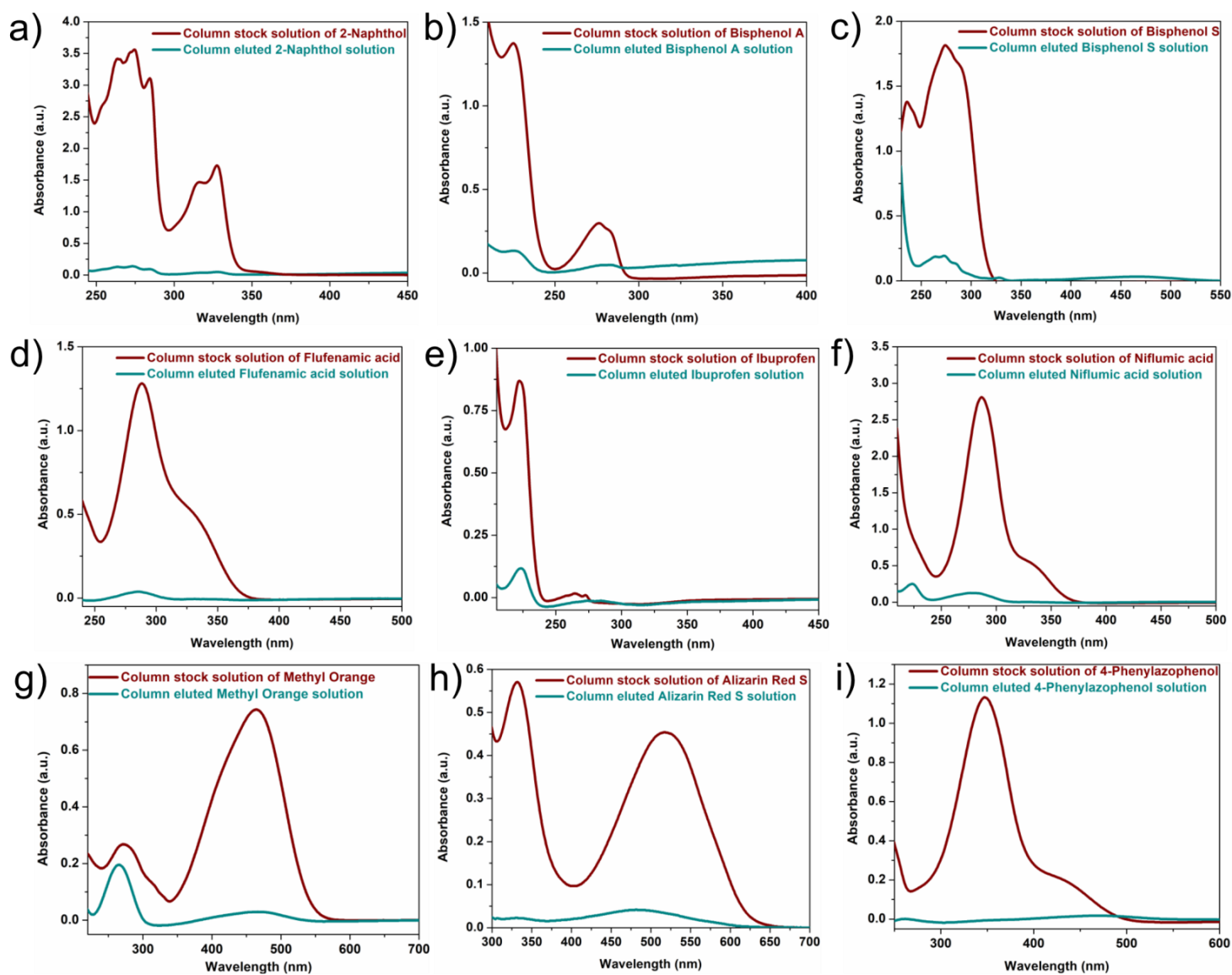
Appendix Figure 4.44. Concentration dependent adsorption profile of 120-TMA@Fe towards Ibuprofen and its corresponding Langmuir linear fitting model.



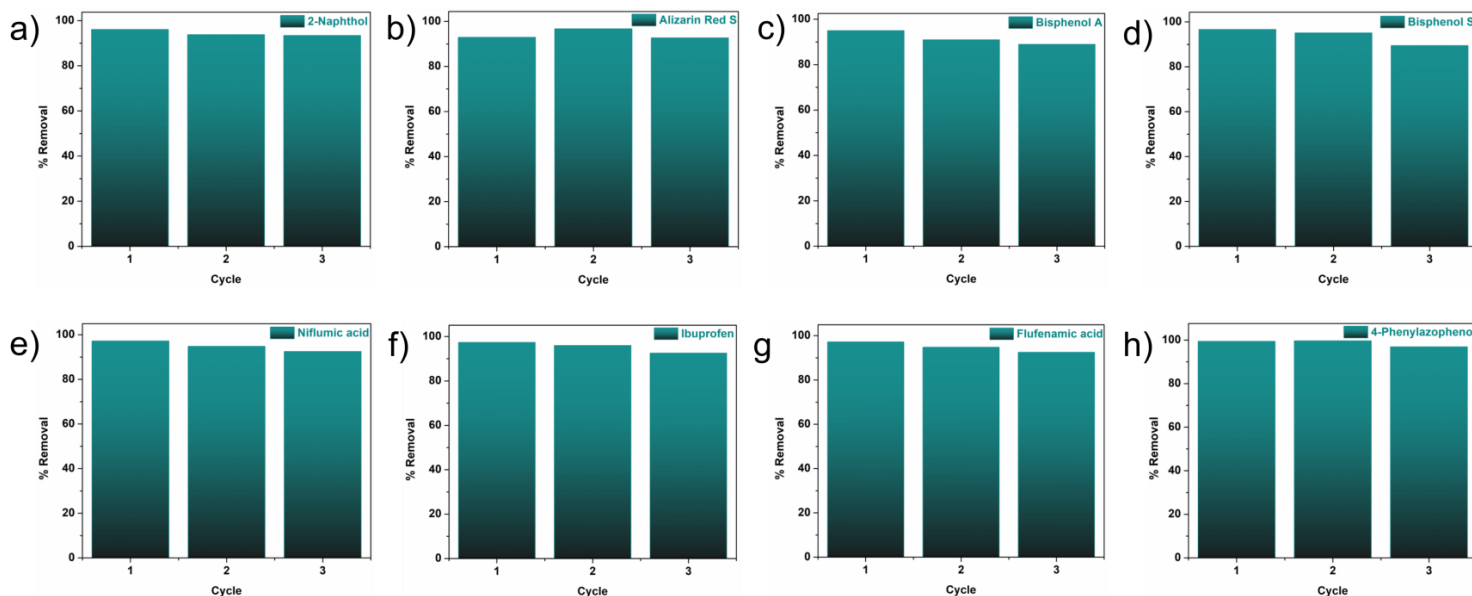
Appendix Figure 4.45. UV-Vis spectra of 2-Naphthol (a) , Bisphenol-A (b), Bisphenol-S (c), Flufenamic acid (d), Ibuprofen (e), Niflumic acid (f), Methyl Orange (g), Alizarin Red S (h) and 4-Phenylazophenol (i) solution in presence of 120-Cl (brown), Activated Carbon (olive green) and 120-TMA@Fe (blue).



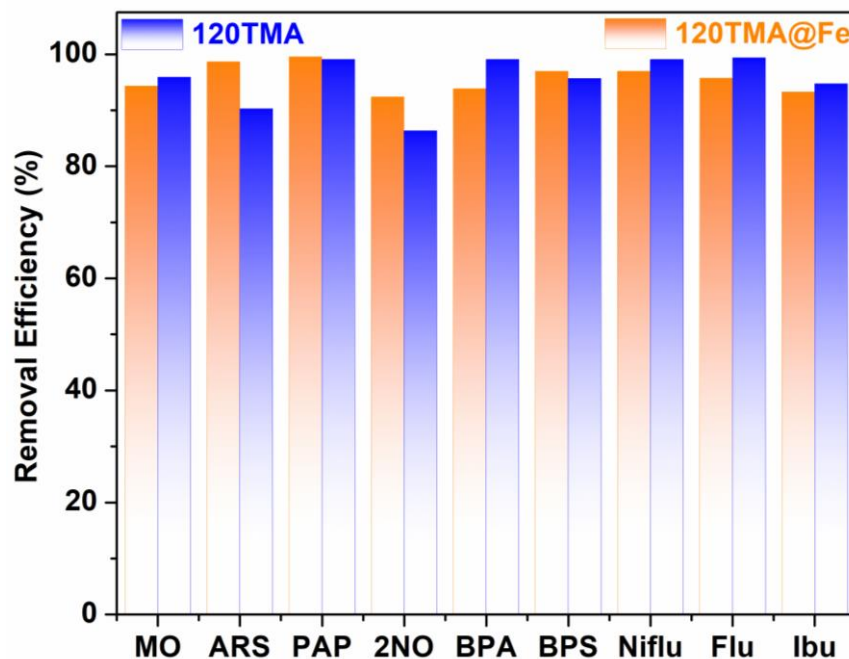
Appendix Figure 4.46. UV-Vis spectra of 120-TMA@Fe when treated with the mixture of competing ions solution containing each organic micropollutant - 2-Naphthol (a) , Bisphenol-A (b), Bisphenol-S (c), Flufenamic acid (d), Ibuprofen (e), Niflumic acid (f), Methyl Orange (g), Alizarin Red S (h) and 4-Phenylazophenol (i).



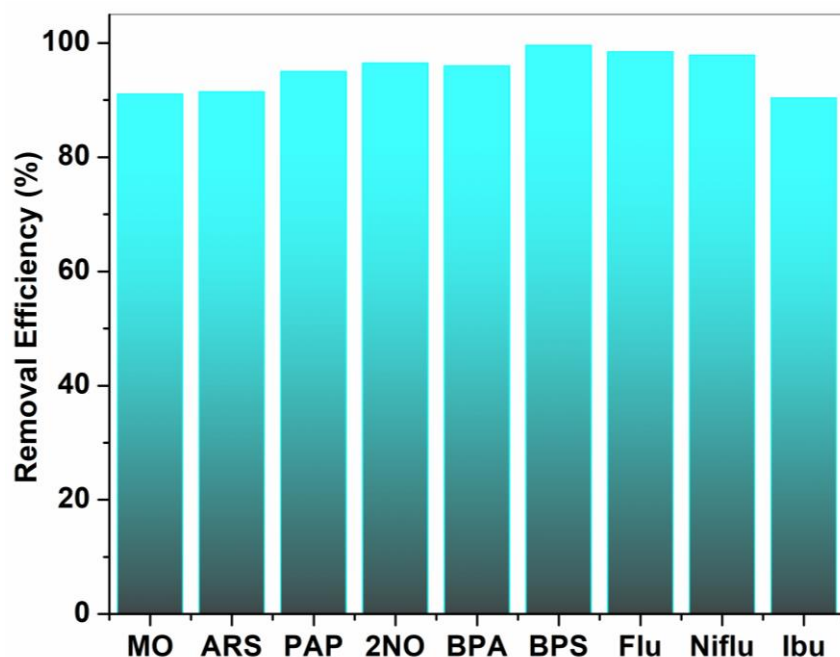
Appendix Figure 4.47. UV-Vis spectra of organic pollutant solution before (wine red) and after (dark cyan) passing through the 120-TMA@Fe loaded column - 2-Naphthol (a) , Bisphenol-A (b), Bisphenol-S (c), Flufenamic acid (d), Ibuprofen (e), Niflumic acid (f), Methyl Orange (g), Alizarin Red S (h) and 4-Phenylazophenol (i).



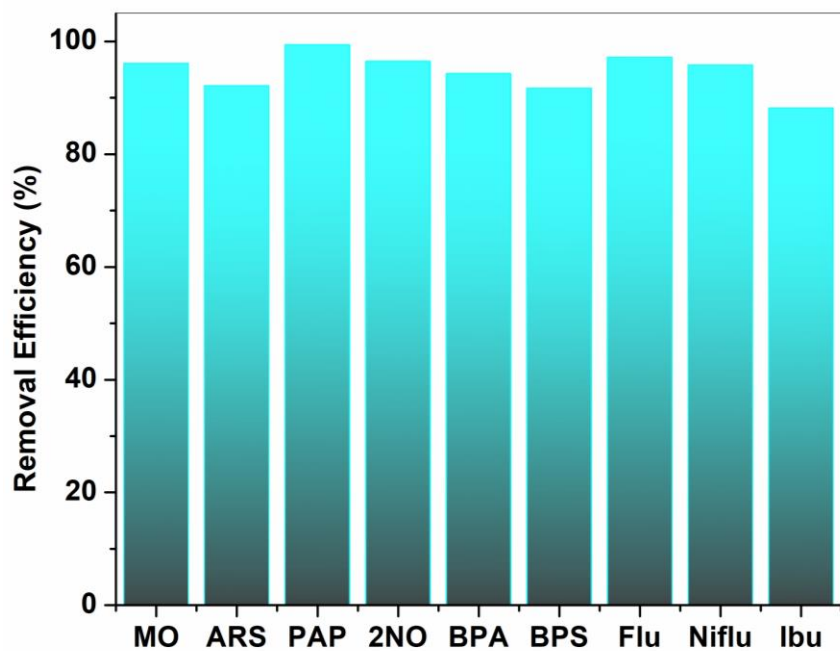
Appendix Figure 4.48. The regeneration cycles of 120-TMA@Fe after the adsorption of 2-Naphthol (a), Alizarin Red-S (b), Bisphenol A (c), Bisphenol S (d), Niflumic acid (e), Ibuprofen (f), Flufenamic acid (g) and 4-Phenylazophenol (h).



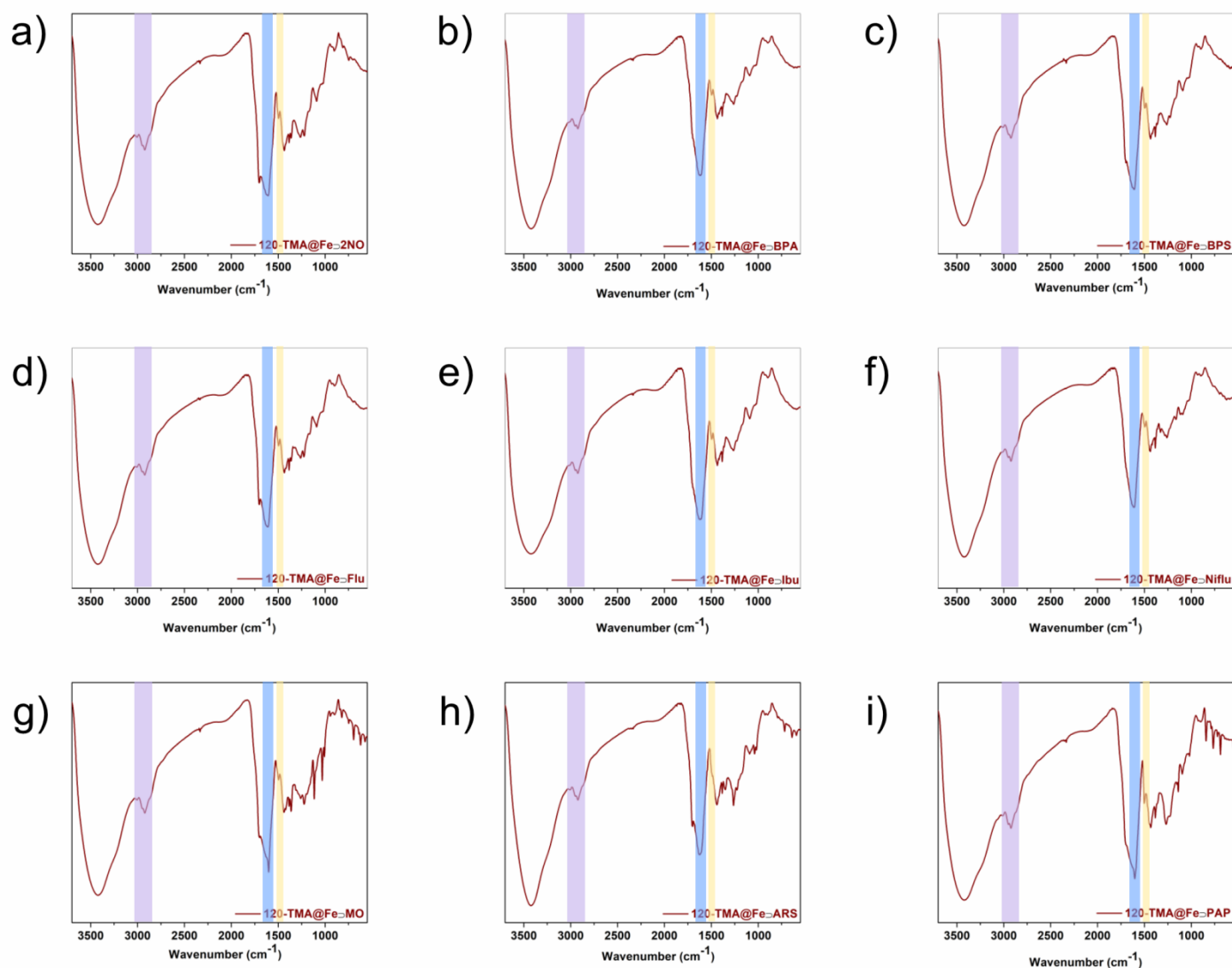
Appendix Figure 4.49. Removal efficiency comparison of each organic micropollutant with 120-TMA and 120-TMA@Fe.



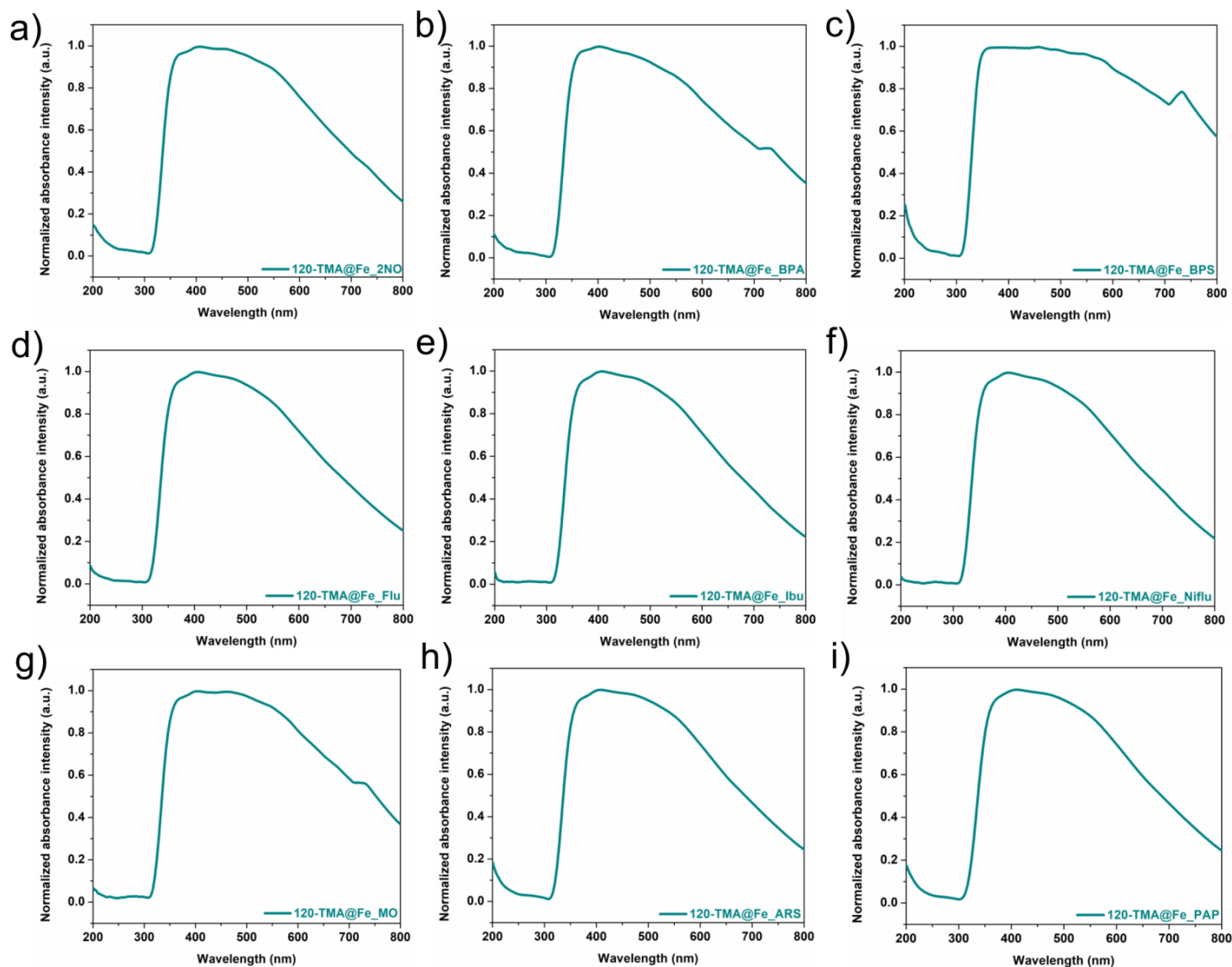
Appendix Figure 4.50. Removal efficiency comparison of each organic micropollutant with 120-TMA@Fe in presence of competing ions mixture containing NaNO_3 , Na_2SO_4 , NaCl and K_2CO_3 .



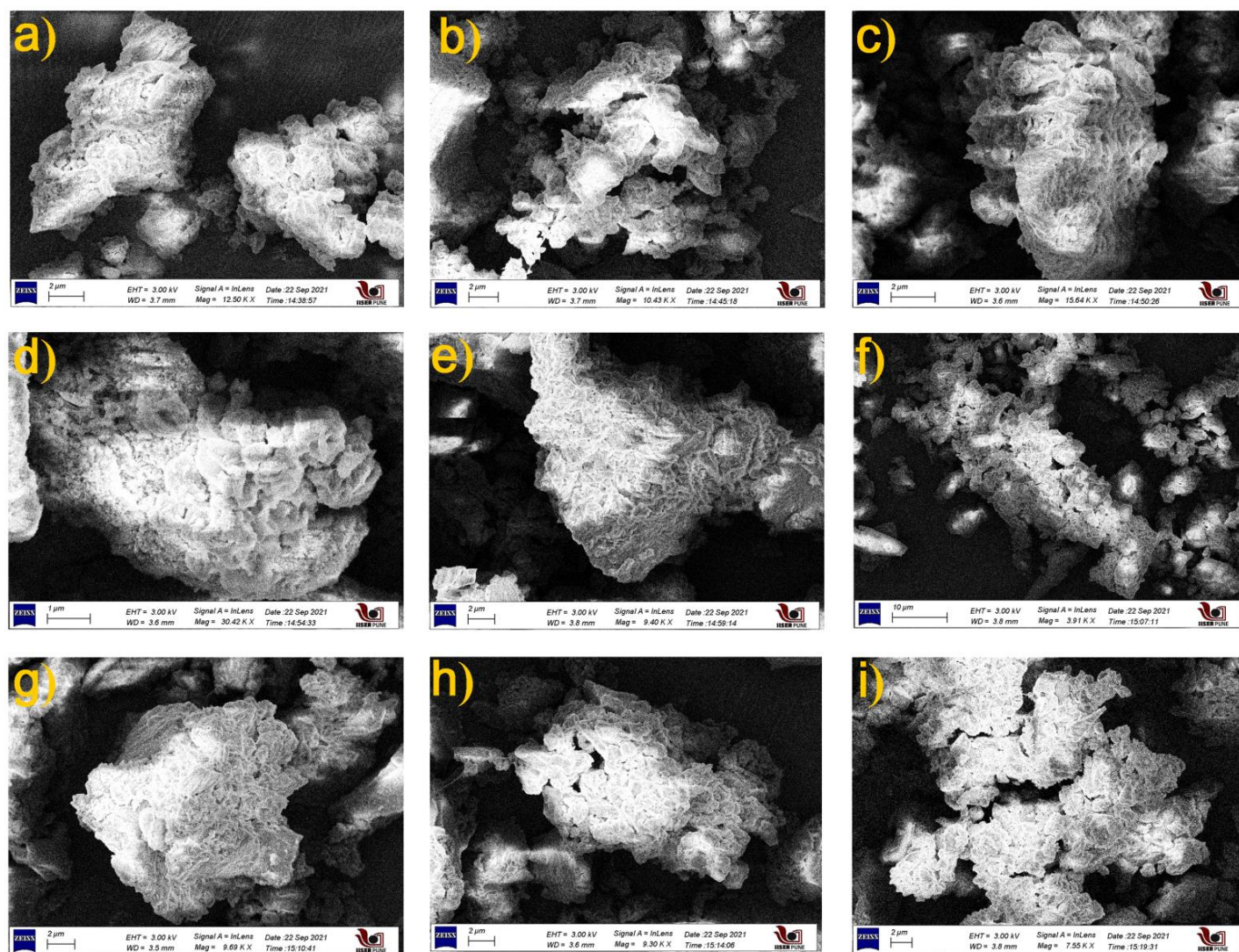
Appendix Figure 4.51. Removal efficiency comparison of each organic micropollutant by 120-TMA@Fe bed in column.



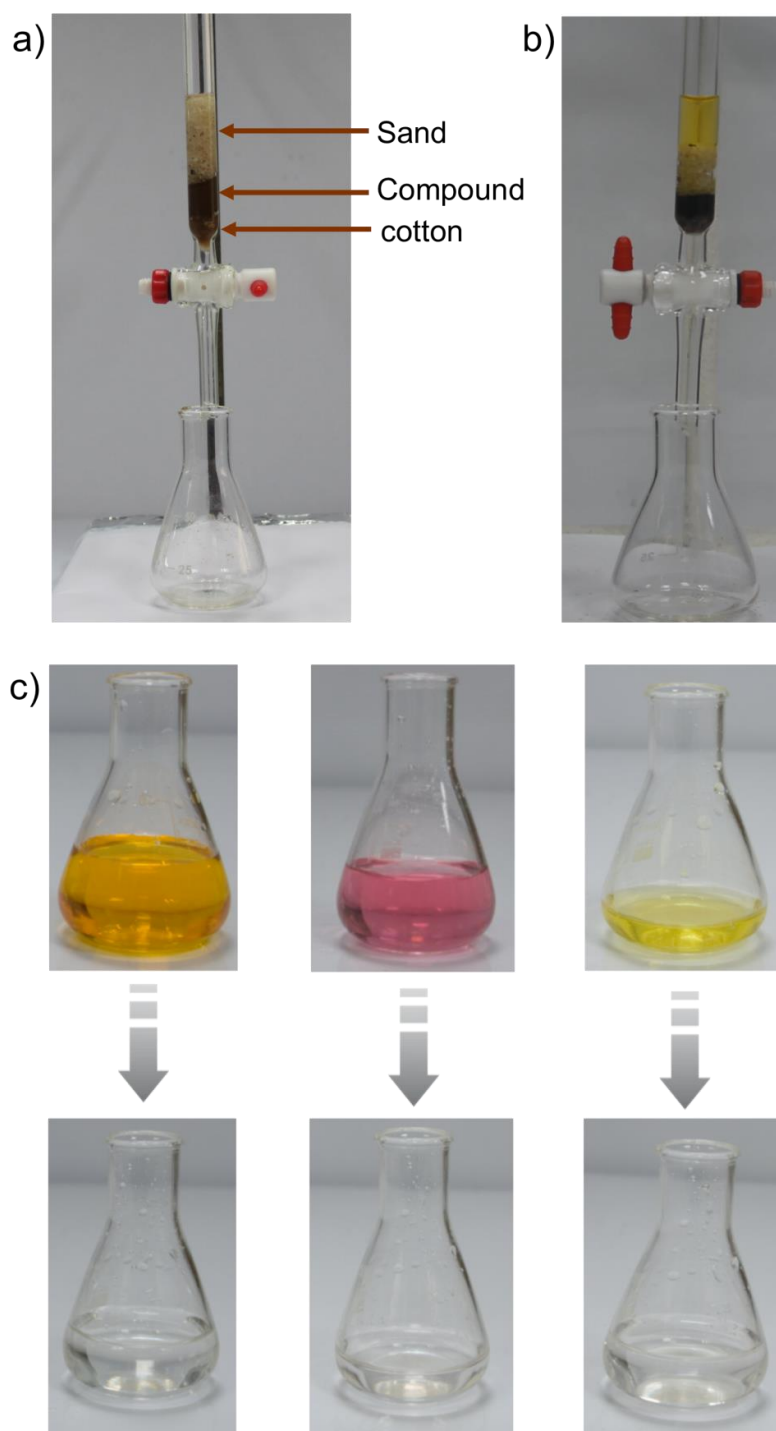
Appendix Figure 4.52. FT-IR spectra of 120-TMA@Fe upon pollutant adsorption- 120-TMA@Fe $\supset$ 2NO (a) , 120-TMA@Fe $\supset$ BPA (b), 120-TMA@Fe $\supset$ BPS (c), 120-TMA@Fe $\supset$ Flu (d), 120-TMA@Fe $\supset$ Ibu (e), 120-TMA@Fe $\supset$ Niflu (f), TMA@Fe $\supset$ MO (g), TMA@Fe $\supset$ ARS (h) and 120-TMA@Fe $\supset$ PAP (i).



Appendix Figure 4.53. Solid state UV-Vis spectra of 120-TMA@Fe upon pollutant adsorption - 120-TMA@Fe $\supset$ 2NO (a) , 120-TMA@Fe $\supset$ BPA (b), 120-TMA@Fe $\supset$ BPS (c), 120-TMA@Fe $\supset$ Flu (d), 120-TMA@Fe $\supset$ Ibu (e), 120-TMA@Fe $\supset$ Niflu (f), TMA@Fe $\supset$ MO (g), TMA@Fe $\supset$ ARS (h) and 120-TMA@Fe $\supset$ PAP (i).



Appendix Figure 4.54. Magnified FESEM images of 120-TMA@Fe upon pollutant adsorption - 120-TMA@Fe $\supset$ MO (a), 120-TMA@Fe $\supset$ ARS (b), 120-TMA@Fe $\supset$ PAP (c), 120-TMA@Fe $\supset$ 2NO (d), 120-TMA@Fe $\supset$ BPA (e), 120-TMA@Fe $\supset$ BPS (f), TMA@Fe $\supset$ Flu (g), TMA@Fe $\supset$ Niflu (h) and 120-TMA@Fe $\supset$ Ibu (i).



Appendix Figure 4.55. Representation of 120-TMA@Fe loaded column used for column chromatographic separation of organic micropollutants from water (a), Capture of Methyl orange by 120-TMA@Fe bed in column (b), Column stock solution (above) and column eluted solution (below) of Methyl Orange, Alizarin Red S and 4-Phenylazophenol respectively.

Appendix Table 4.1. Porosity parameters of the polymer **120-Cl**, **120-TMA** and **120-TMA@Fe**.

	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore width (nm)
120-Cl	998	0.61	0.89
120-TMA	734	0.56	0.84
120-TMA@Fe	640	0.56	0.83

Appendix table 4.2. Water regain analysis of the polymer **120-Cl** and **120-TMA**.

	W_d (mg)	W_w (mg)	Water regain
120-Cl	5.15	7.42	36.9 %
	5.11	7.65	41.5 %
	5.28	7.62	37.2 %
120@TMA	5.07	9.12	79.8 %
	5.32	9.45	77.6 %
	5.05	9.02	78.6%

Appendix Table 4.3. Equilibrium uptake percentages, amount of adsorbed surrogate micropollutant and uptake rates for 120-TMA@Fe

Pollutants	% Uptake	Uptake q_e (mg/g)	K_{obs} ($g\ mg^{-1}\ min^{-1}$)
2-Naphthol	90.3 %	26.04	0.00187
Bisphenol A	98.6 %	45.47	0.00029
Bisphenol S	96.4 %	49.87	0.00192
Methyl Orange	93.5 %	61.28	0.00038
Alizarin Red S	75.1 %	54.19	0.00059
4-Phenylazophenol	97.8 %	193.86	0.00231
Ibuprofen	99.7 %	40.8	0.00117
Flufenamic Acid	99.7 %	280.1	0.00045
Niflumic Acid	97.5 %	276.01	0.00020

Appendix Table 4.4. Maximum adsorption capacities toward various organic micropollutants for 120-TMA@Fe

Pollutants	$Q_{max,e}$ (mg/g)
2-Naphthol	250
Bisphenol A	555.55
Bisphenol S	374.53
Methyl Orange	357.14
Alizarin Red S	599.5
4-Phenylazophenol	263.15
Ibuprofen	285.71
Flufenamic Acid	322.58
Niflumic Acid	333.33

Appendix Table 4.5. Maximum Methyl Orange (MO) adsorption capacities comparison of 120-TMA@Fe with reported state-of-the art materials.

Type	Adsorbent	$q_{\max}$ (mgg ⁻¹)	Reference
Polymer	120-TMA@Fe	357.14	This work
Layered Double Hydroxide (LDH)	Calcined MgNiAl	375.4	<i>Chem. Eng. J.</i> , 2012 , 187, 142–149
	Zn/Al-LDO	181.9	<i>J. Colloid Interface Sci.</i> , 2007 , 316 284–291
Clay and mineral	Na-MMT	24.0	<i>Chem. Eng. J.</i> , 2011 , 171, 1150–1158
	CTMAB-MMT	128.2	<i>Chem. Eng. J.</i> , 2011 , 171, 1150–1158
	Lapindo volcanic mud	333.3	<i>J. Hazard. Mater.</i> , 2010 , 755–762
Carbon nanotubes	multiwalled carbon nanotubes (MWCNTs)	51.7	<i>Chem. Eng. J.</i> , 2011 170, 82–89
	activated carbon nanotubes (CNTs-A)	149	<i>ACS Appl. Mater. Interfaces</i> , 2012 , 4, 11, 5749–5760
	CNTs	51.7	<i>Chem. Eng. J.</i> , 2011 , 170, 82–89
MOF	MOF-235	477	<i>J. Hazard. Mater.</i> , 2011 , 185, 507–511
	SCNU-Z1-Cl	285	<i>Inorg. Chem.</i> , 2019 , 58, 2899–2909
	MIL-53(Cr)	57.9	<i>J. Hazard. Mater.</i> , 2010 , 181, 535–542
	MIL-101	114	<i>J. Hazard. Mater.</i> , 2010 , 181, 535–542
	ED-MIL-101	160	<i>J. Hazard. Mater.</i> , 2010 , 181, 535–542
	PED-MIL-101	194	<i>J. Hazard. Mater.</i> , 2010 , 181, 535–542

	UPC-102-Zr	112	<i>J. Mater. Chem. A</i> , 2018 , 6, 24486–24495
Composite	PCEC-C composite	189.39	<i>ACS Sustainable Chem. Eng.</i> , 2017 , 5, 1871–1880
	magnetic cellulose beads-activated carbon (MCB-AC)	2.12	<i>J. Hazard. Mater.</i> , 2009 , 171, 340–347
	cellulose hydrogel assisted by Fe ₂ O ₃ nanoparticles	15.38	<i>Cellulose</i> , 2017 , 24, 903–914
	chitosan/alumina composite	30.33 ± 6	<i>J. Chem. Eng. Data</i> , 2012 , 57, 412–419
	chitosan based semi IPN composite hydrogel	180.24	<i>Composites, Part B</i> , 2012 , 43, 1570–1578
	CANEX300	160.2	<i>ACS Appl. Mater. Interfaces</i> , 2018 , 10, 20499–20511
	CANEX1000	180.2	<i>ACS Appl. Mater. Interfaces</i> , 2018 , 10, 20499–20511
	core-shell structured graphene oxide-chitosan beads	353	<i>ACS Appl. Mater. Interfaces</i> , 2015 , 7, 14439–14445
Polymer	Carboxymethyl cellulose (CMC)	100	<i>Colloids Surf., A</i> , 2011 , 380, 143–151
	hyper-cross-linked polymeric adsorbent	70	<i>Colloids Surf., A</i> , 2008 , 330, 55–61
	AHCP-1	103.74	<i>Polym. Chem.</i> , 2018 , 9, 4724–4732
	TPP-NH ₂	213.2	<i>RSC Adv.</i> , 2017 , 7, 30500–30505
	C-NSANaph-HCP@Br	1009.73	<i>J. Mater. Chem. A</i> , 2018 , 6, 20653–20658
Gel	F-PANI2 xerogel	148	<i>ACS Sustainable Chem. Eng.</i> , 2017 , 5, 9325–9337

Appendix Table 4.6. Maximum Bisphenol A (BPA) adsorption capacities comparison of 120-TMA@Fe with reported state-of-the art materials.

Type	Adsorbent	$q_{\max}$ (mgg ⁻¹)	Reference
Polymer	120-TMA@Fe	555.55	This work
Carbon	CMK-3	178.57	<i>Chem. Eng. J.</i> , 2012 , 187, 142–149
	MCMK-3	238.01	<i>J. Colloid Interface Sci.</i> , 2007 , 316, 284–291
	EFB-activated carbon	41.98	<i>Air, Soil Pollut.</i> , 2014 , 225, 2148
Nanomaterials	Graphene	181.6	<i>Langmuir</i> , 2012 , 28, 8418–8425
	sulfur-doped titanium dioxide hollow spheres (MICST)	191	<i>J. Clean. Prod.</i> , 2020 , 274, 122929
	CTAB-modified graphite	125.01	<i>Applied Surface Science</i> , 2018 , 428, 165–170
	rGO	94.01	<i>Chem. Eng. Res. Des.</i> , 2016 , 109, 573–585
	MAP-GBM	324	<i>Chem. Eng. J.</i> , 2017 , 334, 948–956
Composite	Al-MOF/SA-CS composite beads	136.9	<i>Chemosphere</i> , 2019 , 237, 124493–12511.
	CPAB/EGIS/B	119.88	<i>Microporous and Mesoporous Materials</i> , 2020 , 308, 110450
MOF	PCN-222	487.69±8.37	<i>Sci. Rep.</i> , 2017 , 7, 6297
	Al-MOF	326	<i>Inorg. Chem.</i> , 2020 , 59, 5538–5545
	MIL-101(Cr)	252.5	<i>Desalin. Water Treat.</i> , 2015 , 54, 93–102

	MIL-53(Al)	325	<i>J. Colloid Interface Sci.</i> , 2013 , 405, 157–163
	MIL-53(Al)-F127	465	<i>J. Colloid Interface Sci.</i> , 2013 , 405, 157–163
Polymer	EPI-CDP	84	<i>Journal of Inclusion Phenomena</i> , 2002 , 44, 429–431
	P-CDP	88	<i>Nature</i> , 2016 , 529, 190–194
	CaIP4	403	<i>ACS Appl. Mater. Interfaces</i> , 2018 , 10, 2976–2981
	NHCP-3	562	<i>RSC Adv.</i> , 2018 , 8, 36812–36818
	HCP(BnCD-DCX)	278	<i>Sep. Purif. Technol.</i> , 2017 , 195, 130–137
	PPOP	653	<i>Chemosphere</i> , 2021 , 265, 129161
	β -CD NFs	120	<i>Nano Res.</i> , 2020 , 13, 1933–1942

Appendix Table 4.7. Maximum Ibuprofen (Ibu) adsorption capacities comparison of 120-TMA@Fe with reported state-of-the art materials.

Type	Adsorbent	$q_{\max}$ (mgg ⁻¹)	Reference
Polymer	120-TMA@Fe	285.71	This work
Carbon	MPC	206.5	<i>R. Soc. Open Sci.</i> , 2019 , 6, 190058
	Modified AC(H ₂ O ₂)	190.7	<i>Carbon.</i> , 2013 , 54, 432–443
	Commercial AC	160	<i>Carbon.</i> , 2013 , 54, 432–443
	PCDM-1000	320	<i>Chem. Eng. J.</i> , 2017 , 314, 50-58

Clay and mineral	IBP- Zeo-Sep	22.17	<i>Chem. Eng. J.</i> , 2019 , 371, 868-875
	IBP- O-Sep	64.25	<i>Chem. Eng. J.</i> , 2019 , 371, 868-875
MOF	Fe-BTC	76.3	<i>Materials</i> , 2021 , 14, 2293
	Fe ₃ O ₄ -FeBTC	142.9	<i>Materials</i> , 2021 , 14, 2293
	ZIF-8	29	<i>Chem. Eng. J.</i> , 2017 , 314, 50-58
	[Zn(1,3-bdc) _{0.5} (bzim)]	163.9	<i>New J. Chem.</i> , 2019 , 43, 5518-5524
COF	TpBD-(CF ₃) ₂	119	<i>Chem. Eur. J.</i> , 2018 , 24, 10601 – 10605
Resin	Magnetic ion-exchange resins	23.55	<i>J. Environ. Sci.</i> , 2015 , 31, 226 – 234

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Chapter 5

Harnessing Bio-inspired Antagonism in a Charged Macroporous Organic Polymer toward Enhanced Pollutant Segregation from Water

5.1 Introduction

Water contamination has emerged as a direct threat to sustainable life on this earth, lending pivotal significance to seeking efficient wastewater remediation technologies. ^[1-2] Consequently, several technologies such as precipitation, ^[3-4] adsorption, ^[5-6] degradation ^[7-8] etc have been tested toward containment of water contaminants. Amongst them, adsorption, in particular ion-exchange based sorption, has come forth as a promising technique featuring high efficiency and selectivity toward segregating ionic water contaminants. ^[9-11] Along this line, various ionic sorbent materials that include ion-exchange resins, ^[12-15] layered double hydroxides (LDHs), ^[16-18] porous hydrogels, ^[19-22] ionic metal-organic frameworks (iMOFs) ^[23-31] have been employed as adsorbents. Having said that, suboptimal stability of iMOFs in harsh conditions have thwarted their applicability while resins and LDHs are curbed by sluggish kinetics and poor capacity. Although, porous hydrogels offer low-cost synthesis, high surface area and good mechanical strength, they do not display appreciable uptake capacity and kinetics toward pollutant sequestration. Hence, it is topical to design and fabricate potent adsorbents showcasing enhanced stability, ease of synthesis and superior performance.

Selenium, when present in trace amounts serve as a necessary nutrient element for both humans & animals. ^[32-34] However, problems related to Se toxicity as well as deficiency is existing worldwide ^[35-36] as dietary deficiency of Se (<40 µg/day) and toxicity (>400 µg/day) dwells in the narrowest of ranges. ^[37] Also, radioactive selenium (⁷⁹Se) has prolonged half-life (3.27×10^5 years) and its acute exposure can induce severe respiratory issues, various defects and neurological disorders causing tremendous health and environmental hazards. ^[38-41] Remediation of selenium-contamination is an arduous task as its toxicity and mobility is strongly redox state dependant. ^[42-43] Typically, in water (oxic conditions), Se exists as oxyanions, i.e., selenate (Se(VI), (SeO_4^{2-}), hydroselenite (HSeO_3^-) and selenite (Se(IV) (SeO_3^{2-}) at various pH. ^[44-45] Similarly, heavy metal cations such as Hg^{2+} can cause severe harm to living beings and has come forth as a pressing concern toward environmental remediation. Mercury (Hg), being extremely toxic in nature, is very persisting and causes severe environmental hazard through bioaccumulation. ^[46-48] It should be mentioned that both mercury and selenium has been listed as priority pollutants by the United States Environmental Protection Agency (US EPA) owing to their toxicity and hazardous nature. Thus, to effect their containment, efficient removal of both Hg^{2+} as well as selenium from wastewater is of immediate necessity in order to combat water pollution.

Ionic porous organic polymers (iPOPs), as a new class of functionalized porous organic material have emerged with great potential towards pollutant scavenging from water. ^[49-52] iPOPs, crafted from robust covalent linkages present superior stability under harsh chemical environments along with their facile structural design and convenience of structural modulation. In addition, charged framework and easily

exchangeable residual ions significantly aid in amplifying the sorption of target analytes. The *modus operandi* in iPOPs toward sequestration of water contaminants mainly rely on diffusion of analytes coupled with accessible ion-exchangeable-sites inside its pores.^[53-54] Hitherto, variety of synthetic methodologies have been document in the literature to ameliorate water pollution, however, most of them are restricted by uniform pores.^[55-56] Hence, the performance toward pollutant segregation, especially with regard to sorption kinetics have been curbed profoundly owing to poor mass-transfer between smaller pores along with limited active site accessibility by virtue of pore blocking by the residing counter ions in the charged skeleton.^[57] As a result, ionic POPs have often struggled with sluggish kinetics as well as suboptimal efficiency in removing targeted noxious pollutants pertaining to water detoxification.

Imparting hierarchical porosity (meso and macro range) onto porous structures can prove to be a boon in eclipsing these fundamental pitfalls. Accordingly, materials bearing higher pore size and volume together with enhanced accessibility to active sites, shortened diffusion-path and swift mass transfer have surfaced.^[58-59] Notwithstanding that efforts have been put forward in fabricating architectures showcasing simultaneously coexisting micro and mesopores, sporadic growth has been observed.^[60-64] Along this line, crafting hierarchically porous structures that bridges micro to macroporous terrain offering superior accessibility, assorted pore-size and increased pore volume to expedite mass transport can be promising.^[65-69] On the flip side, integrating multiporosity, in particular macropores, within a microporous skeleton, more often than not is plagued by disruption of the structure as well as entanglement or interpenetration.^[70-72] Additionally, amalgamation of electrostatics (ionicity) and hierarchical macroporosity in a singular material can prevail to be effectual for trapping specific toxic pollutants in a more selective and efficient manner. Although innovative contribution has been made toward organic micropollutants remediation through induction of disordered hierarchical macroporosity in a neutral porous structure^[73], rational construction of charged hierarchically macroporous framework is highly sought after.

Keeping these points in perspective and taking inspiration from nature, herein, we have zeroed in harnessing bioinspired synergistic detoxification by exploiting Hg-Se antagonism, long prevailing in biota that is extensively studied by biologists over the last 70 years.^[74-79] Reports have disclosed that selenium (Se) can safeguard animals from toxic mercury (Hg) species, however, Se can prove to be extremely toxic in surplus amount to most animals. A 1:1 ratio between Hg and Se is considered biologically inert as uncovered from researches into Hg-se antagonism. Taking leverage of Hg-Se antagonism understanding at molecular-level, we have strategically designed a modified macroporous polymer (mPOP@MoS₄²⁻) featuring sulfur motifs as functional sites that can mimic cysteine-based enzymes to effect improved simultaneous Hg-Se coadsorption.

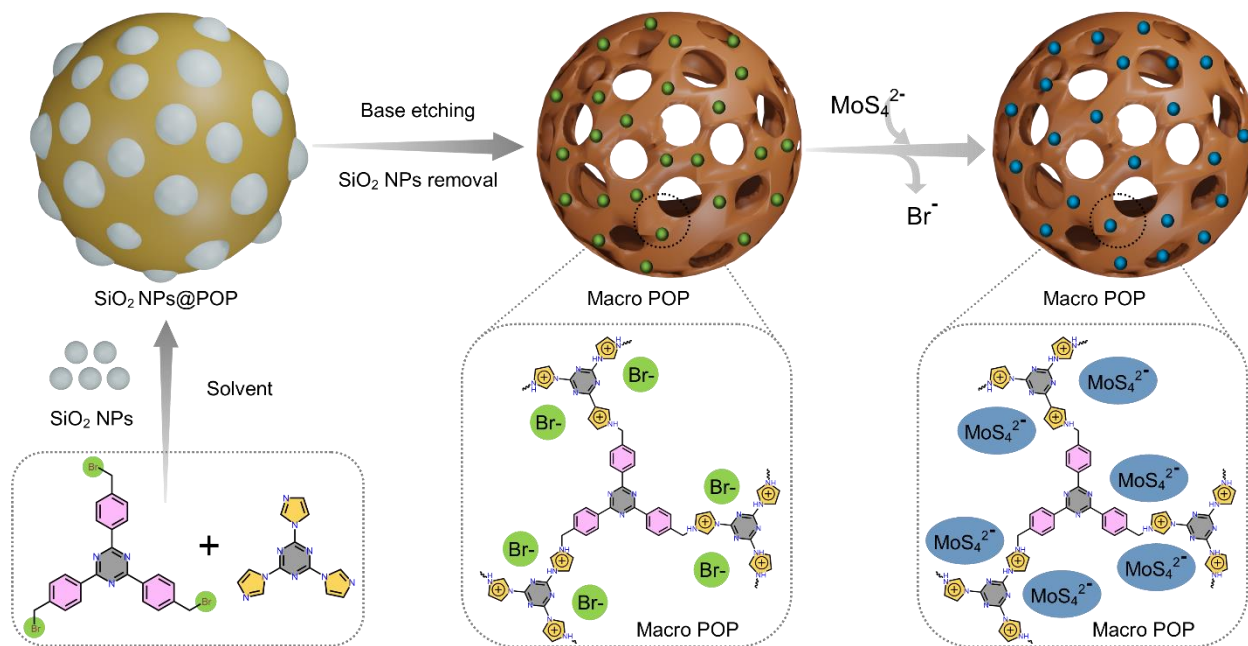


Figure 5.1. Schematic illustration and diagrams of stepwise synthetic protocol of mPOP@MoS₄²⁻.

5.2 Experimental

5.2.1. Materials and Methods

All materials were obtained commercially unless noted otherwise.

5.2.2. Synthesis

Synthesis of Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine: This precursor compound was prepared by following a reported protocol with little modifications (Appendix scheme 5.1).^[86]

Synthesis of 2,4,6-tri(1H-imidazol-1-yl)-1,3,5-triazine: This precursor molecule was also synthesized by following a reported protocol (Appendix scheme 5.2).^[87]

Synthesis of mPOP: Cationic macroporous organic polymer (mPOP) was synthesized according to the following protocol. In a clean oven dried 100 mL round-bottom flask, 2,4,6-tri(1H-imidazol-1-yl)-1,3,5-triazine (0.80 mmol, 223.41 mg) was dissolved in 20 mL DMF. To this, 300 mg of synthesized

monodispersed silica nanoparticles (as template) were added and the mixture was subjected to sonication for 30 min. Following this, a DMF solution (20 mL) of Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine (0.80 mmol, 470.51 mg) was added. After that, the reaction mixture was allowed to react under stirring at 110 °C over the course of 24 h. After 24 h, the reaction set up was cooled down to room temperature and 1 mL benzyl bromide was added to it. The mixture was further reacted at 80 °C for additional 7 h. After that, the reaction was cooled down to room temperature and the precipitate was collected via centrifugation to give SiO₂@POP. The obtained polymer was thoroughly washed with DMF, H₂O, MeCN, EtOH and acetone at least thrice to remove any unreacted monomers. To obtain the macroporous polymer (mPOP), the silica templates were etched by treating the SiO₂@POP with 20 ml of 4 M aqueous ammonium bifluoride (NH₄HF₂) solution at room temperature. The resulting product were washed with copious amount of deionized water, ethanol, THF, acetone, respectively, until the supernatant appeared colourless. Finally, the product was dried at 80 °C under vacuum to obtain the desolvated mPOP for further use.

5.2.3. Pollutants Capture Study:

The aqueous stock solution of all the pollutants was prepared by dissolving a certain amount of sodium or nitrate salts of different pollutants in ultrapure deionized water and the different concentration solutions were prepared by diluting the stock solution with the required amount of distilled water unless otherwise mentioned. The concentrations of water pollutants in the current study for all the experiments were determined by ICP-AES and ICP-MS (**for ultra-low concentrations, ~1 ppm**) analysis respectively. All the adsorption experiments were carried out under ambient conditions. All the data points were collected in triplicate through ICP analysis to plot the final adsorption results.

5.2.3.1. Time Dependent Pollutant Adsorption Study:

The benchmark protocol that we adopted for the adsorption kinetics experiments is as follows. The capture study of various pollutants (Se(IV)/Se(VI)/Hg²⁺) was performed in 15 mL glass vial equipped with magnetic stir bars with a constant stirring rate of 350 r.p.m. Typically, 5 mg of the adsorbent material was taken in 5 mL of 10 ppm stock solution of Se(IV)/Se(VI), (20 ppm for Hg²⁺) different pollutants, individually. After continuous stirring for different time intervals at room temperature the solution was collected through a syringe with having 0.22 µm nylon membrane filter. The concentration of this filtrate was measured through ICP-AES 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 pollutants with time by using the following equations:

$$D_t = \frac{C_0 - C_f}{C_0} \times 100\%$$

Where, D_t is the pollutant removal efficiency, C_0 is the initial concentration of the pollutants, C_f = final concentration of the pollutants at specific times.

5.2.3.2. Adsorption Isotherm Experiment:

5 mg of material was dispersed in 10 mL aqueous stock solutions of pollutants having different initial concentrations. After ~12 hours the filtrates were collected through syringe filter (0.22 μm) and the concentrations were measured through ICP-AES and further fitted according to the following equations,

Langmuir model, $Q_e = Q_m \cdot C_e / (K_d + C_e)$; Where, C_e (ppm) and Q_e (mg g^{-1}) are the pollutant concentration at equilibrium and amount of pollutant adsorbed at equilibrium respectively. Q_m (mg g^{-1}) is the maximum amount of pollutant 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.

5.2.3.3. Distribution Coefficient (K_d) Value Calculation:

The distribution coefficient (K_d) value as used for the determination of the affinity and selectivity of sorbents for pollutants, is given by the equation:

$$K_d = [V \{ (C_0 - C_e) / C_e \}] / m;$$

Where, V is the volume of the analyte solution (mL), m is the amount of solid adsorbent (g), C_0 is the initial concentration of pollutant, and C_e is the equilibrium concentration of pollutant.

5.2.3.4. Pollutants Uptake Capacity:

The amount of pollutants adsorbed per gram of the material was determined by treating 5 mg of material to 10 mL of ~500 ppm (~2000 ppm for Hg^{2+}) solution of respective pollutants for ~12 hours under stirring condition at room temperature. After 24 hours, the sorbent material was filtered off and the filtrate was characterized through ICP-AES by diluting the solution with 2% HNO_3 . The adsorption capacity per gm was calculated using following equation:

$$Q_t = (C_0 - C_f) \cdot V / m;$$

Where, Q_t , C_o , C_t , V and m are the capacity of adsorbent, initial concentration of the pollutant solution, final concentration of the pollutants at equilibrium, volume of the test solution and mass of the material used for the adsorption study respectively.

5.2.3.5. Pollutant Capture Study in Presence of Competing Ions:

For testing the materials performance under the influence of competing ions, large excess (~10 fold, ~100-fold) of competing salts such as, NaCl, NaNO₃, Na₂SO₄ were added to the different pollutant stock solutions and capture studies were carried out by following the previously described method. The capture efficiency was monitored through ICP-AES measurement.

5.2.3.6. Trace Amount Capture Study:

Trace amount (1 ppm) of Se (IV)/ Se (VI) capture study were performed following the similar kinetics adsorption experiment described previously. The kinetics of adsorption study was measured at different time intervals, taking ~1000 ppb stock solution of Se (IV)/ Se (VI) in water. The concentration of the analytes at different times were monitored by ICP-MS experiments.

5.2.3.7 Dynamic Column Exchange-based Flow-through Se (IV) Capture Study:

To check the continuous Se (IV) oxyanion removal efficiency by the ionic macroporous polymer (mPOP@MoS₄²⁻), a column exchange-based flow-through experiment was performed by packing the adsorbent material inside a column as bed for dynamic Se (IV) capture. After that, a stock solution of ~50 ppm of Se (IV) aqueous solution was allowed to pass through the column bed with a fixed flow rate of 0.5 mL/min, controlled by a water-flow-regulator, and the drops per minute was recorded with the help of a stopwatch. A bed-volume of ~5 mL of the column eluted solution was collected in different containers. The concentration of Se (IV) in these solutions were then analyzed through ICP-MS analysis.

5.2.4 Physical Measurements:

All infra-red (IR) spectra were recorded using a NICOLET 6700 FT-IR spectrophotometer, using KBr pellets in the range of 450–4000 cm⁻¹. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer STA 6000 TGA analyser under an N₂ atmosphere with a heating rate of 10°C min⁻¹. FESEM was performed using a FEI Quanta 3D dual beam FESEM at 30 kV. For high-resolution TEM analysis, all the samples were dispersed in isopropanol (0.5 mg/mL) and sonicated for 20 min. Then, the samples were left as is for 2 min, and the top part of the dispersed solution was taken for preparing TEM samples on a lacey carbon-coated copper grid (Electron Microscopy Science). TEM images were recorded on the HRTEM (JEM-2200FS, JEOL) operating at acceleration voltage of 200 kV. Solid-state ¹³C cross polarization- magic angle spinning (CP-MAS) spectra were conducted on a Bruker 500 MHz NMR spectrometer with a CP-MAS

probe. Carbon chemical shifts are expressed in parts per million (δ scale). N₂ gas adsorption-desorption measurements were carried out using BelSorp-Max instrument (Bel Japan). Before performing adsorption measurements, the activated samples were heated at 110 °C under vacuum for 12 hours using BelPrepvacII. To perform XPS analysis, as-obtained powder samples were stuck to conductive paste and then measured by X-ray photoelectron spectroscopy using K-Alpha+ model (Thermo Fischer Scientific, UK) with Al K α source. Zeta potential measurements were conducted on a Anton Paar Litesizer 500 series instrument. Measurement cell: Omega cuvette Mat. No. 155765, Target temperature 25.0 °C, Equilibration time – (Series parameter), Henry factor 1.1 (Other), Adjusted voltage (Automatic Mode), Number of runs 20, Solvent – water. Raman spectra were acquired with an BRUKER RFS 27 MultiRAM FT Raman Spectrometer (633 nm laser). The ITC experiments were done on a Malvern MicroCal PEAQ-ITC micro calorimeter equipped with 20 (19+1) injection cycle method capacity, a sample volume of 280 μ L with a sample cell size of 200 μ L and injection syringe volume of 40 μ L for each set of experiments.

5.3 Results and Discussion

Hierarchically porous ionic polymer (mPOP@MoS₄²⁻) was crafted by introducing silica (SiO₂ NPs) templated quaternization reaction followed by strategic post-synthesis modulation via ion-exchange strategy. Firstly, mono-dispersed (~ 200 nm) silica-nanoparticles were synthesized, which were then used as hard template to construct the hierarchical macroporous polymeric network. Briefly, DMF solution of 2,4,6-tri(1H-imidazol-1-yl)-1,3,5-triazine was homogeneously mixed with SiO₂ NPs via sonication followed by the addition of another precursor (Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine) and heating to initiate the polymerization reaction. Consequently, SiO₂@POP was obtained as a pale yellow precipitate which after selective removal of SiO₂ NPs under mild condition resulted in the macroporous organic polymer (mPOP). The desired final compound (mPOP@MoS₄²⁻) was achieved by performing ion-exchange of the pristine mPOP with aqueous solution of (NH₄)₂MoS₄ to replace the bromide anions (Br⁻) with sulfide-containing MoS₄²⁻. Strategic incorporation of MoS₄²⁻ anions was executed to harness the Hg-Se antagonism prevailing in nature to mimic bioinspired synergistic detoxification. Additionally, judicious introduction of MoS₄²⁻ can boost the stability of sulfur-functionalized polymers and can easily bypass the difficulty of traditional sulfur-functionalized compounds such as -SH & S_x²⁻ groups that are prone to oxidation which in turn decreases their efficiency.^[84]

Typically, insolubility of the porous polymers in common organic solvents marked the indication of extended framework formation. Additionally, the polymers were corroborated of their proposed composition and structures with the help of following thorough characterization techniques. Fourier transform infrared (FT-IR) spectra of SiO₂@POP displayed characteristic Si-O-Si stretching frequency at 1070 cm⁻¹ along with the presence of all the peaks corresponding to the imidazolium polymer network (Appendix 5.2). The post-modified macroporous polymer mPOP@MoS₄²⁻ exhibited bands at 1512 cm⁻¹ attributed to the C=N stretching while the successful imidazolium unit formation throughout the framework was validated from the signal at 1140 cm⁻¹ (Figure 5.2a). Additionally the peak at 1359 cm⁻¹ was ascribed to the C-N stretching frequency of the triazine ring. To understand the composition of the polymer at molecular level, solid state ¹³C NMR spectroscopy (¹³C SS NMR) was utilized. The ¹³C SSNMR spectrum of parent mPOP showed broad signals around 115 to 140 ppm that were attributed to the aromatic and imidazolium carbon atoms (Appendix 5.1, Figure 5.2b). In particular, the 135 ppm peak was ascribed to the C2 carbon of the imidazolium ring while the presence of triazine ring was confirmed from the sp² carbon peak at 168 ppm. Additionally, a peak at 52 ppm assured the presence of aliphatic methylene carbon (-CH₂-) in the network. These observations aligns well with the reported literature of imidazolium based POPs.^[80-81] Thermogravimetric analysis (TGA) under nitrogen atmosphere advocated good thermal robustness of the macroporous polymer up to ~380 °C indicating excellent structural robustness (Figure 5.2c,

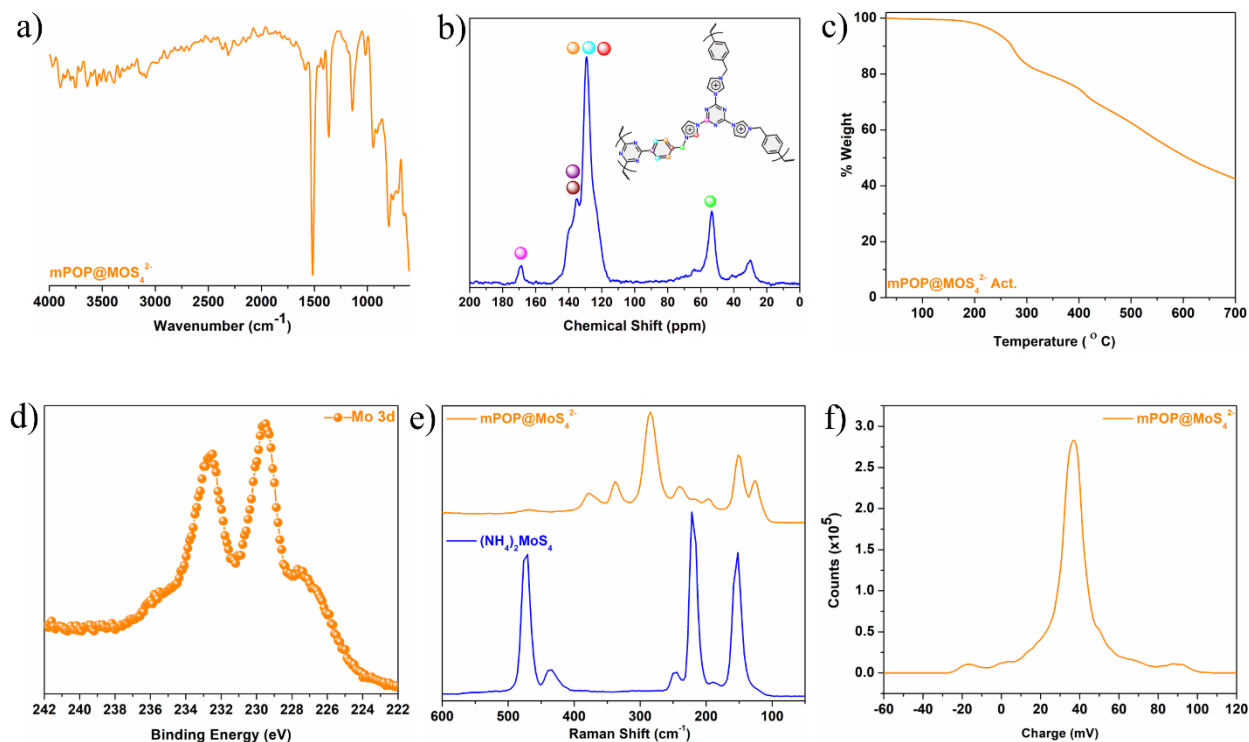


Figure 5.2. (a) FT-IR spectrum of mPOP@MoS₄²⁻. (b) Solid-state ¹³C CP/MAS NMR spectrum of pristine mPOP. (c) TGA profile of activated mPOP@MoS₄²⁻. (d) Mo (3d) XPS spectrum of mPOP@MoS₄²⁻. (e) Raman spectra of mPOP@MoS₄²⁻ (orange) and (NH₄)₂MoS₄ (blue). (f) ζ-potential profile of mPOP@MoS₄²⁻.

Appendix 5.3). Low temperature (77K) nitrogen sorption of the pristine mPOP was carried out to investigate its porosity. As illustrated in Appendix 5.4, a type IV isotherm profile was observed with almost no N₂ uptake at low pressure region along with the presence of H3 hysteresis loop indicating the abundance of interconnected mesopores within the polymer. In addition, the uptake amount of nitrogen at high relative pressure strongly suggests the abundance of macropores throughout the network of mPOP. Overall, the N₂ sorption analysis indicates hierarchical macro/microporosity of the polymer which is further supported by the pore size distribution analysis from the N₂ sorption profile of the polymer (Appendix 5.5).

Morphological investigation of the macroscopic structure of mPOP was performed through microscopic analysis such as transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) etc. FESEM images of the template i.e., silica-nanoparticles (SiO₂ NPs) revealed successful synthesis of monodispersed SiO₂-NPs with consistent average size of ~200 nm (Appendix 5.6). The homogeneous dispersion of SiO₂-NPs within the porous polymer during its synthesis aids in the formation

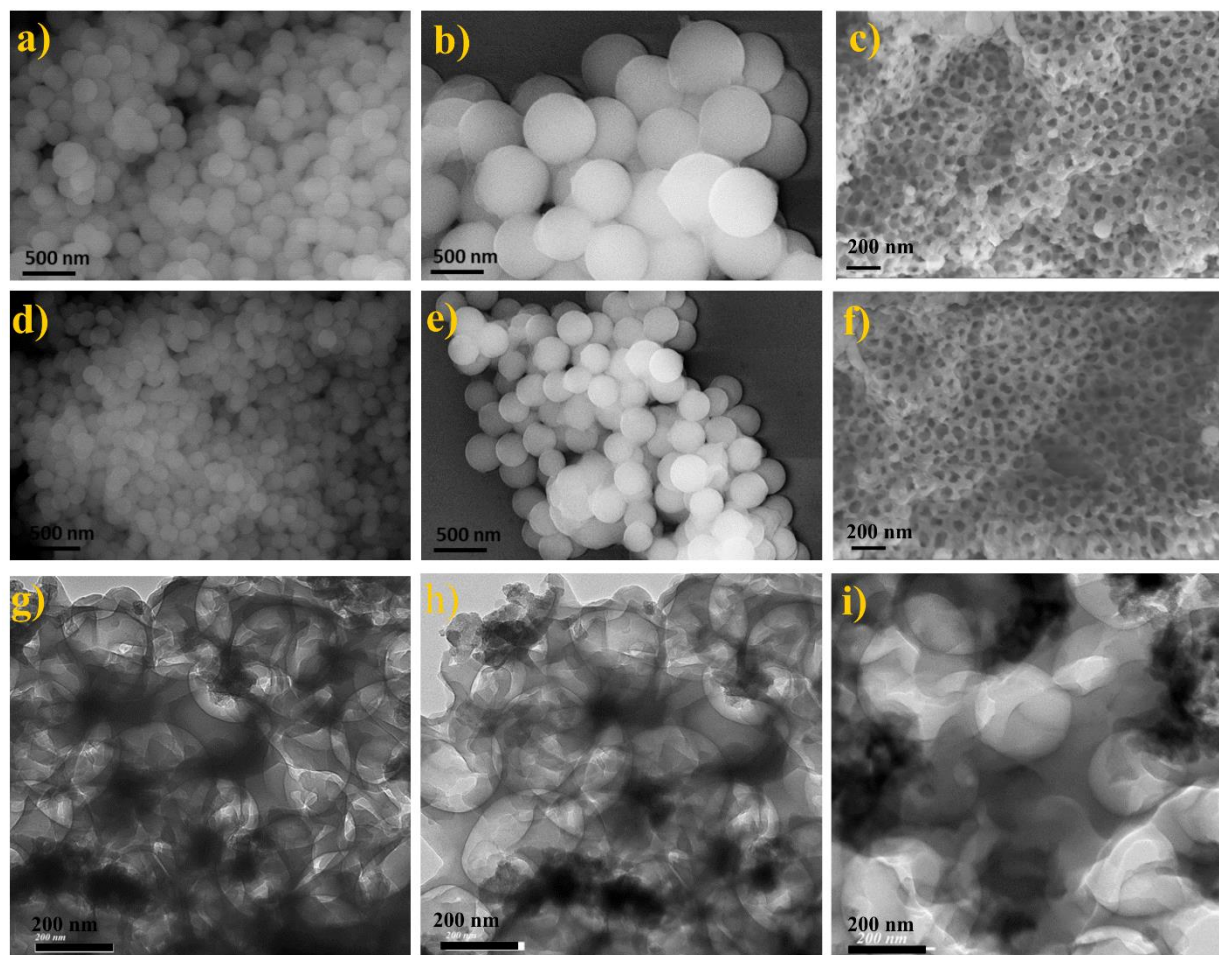


Figure 5.3. (a) & (d) FESEM images of SiO₂-nanoparticles. (b) & (e) FESEM images of SiO₂@POP. (c) & (f) FESEM images of mPOP@MoS₄²⁻. (g) , (h) & (i) TEM images of mPOP@MoS₄²⁻ showing interconnected macropores inside.

of spherical homogeneous SiO₂@POP composite which is evident from the SEM images (Figures 5.3b, 5.3e). The successful etching of template silica-nanoparticles and formation of uniform hierarchical macropores throughout the polymer was clearly observed from the FESEM images (Figures 5.3c, 5.3f). It is worth mentioning that the macropore formation was found to be consistent which is reflected from their homogeneity over large areas as depicted from FESEM images at different magnification (Appendix 5.8, Figures 5.3c, 5.3f). Satisfyingly, the average diameter of the macropores were found to be matching with the template size (~200 nm) (Appendix 5.7). Additional, SEM images support robust nature of the macroscopic structure of the polymer without any apparent collapse of the framework after removal of the template (Appendix 5.7, 5.8). Furthermore, interconnected macroscopic skeleton was validated from the TEM images, which showed interconnected hierarchical pores (Figures 5.3g, 5.3h, 5.3i). The elemental

composition of pristine and modified macroscopic polymers were established from the energy dispersive spectroscopy (EDS) analysis. All the concerned elements were found to be present in a homogeneous manner in all the cases (Appendix 5.9, 5.10).

Moreover, the successful incorporation of MoS_4^{2-} anions in the modified macroporous polymer was confirmed from X-ray photoelectron spectroscopy (XPS). Survey-scan analysis as illustrated in Appendix 5.11, shows presence of all the elements confirming its composition. The state of S and Mo upon ion-exchange was verified from the Mo (3d) XPS spectra which indicated stable presence of MoS_4^{2-} after intercalation (Figure 5.2d). To get further insights into the Mo-S stretching bands, Raman spectra were recorded. Based on reference values reported (ranging from 400-510 cm^{-1}),^[82] we observed two distinct peaks at 473 cm^{-1} and 440 cm^{-1} (assigned to Mo-S stretching) for $(\text{NH}_4)_2\text{MoS}_4$ which was used as a reference for comparison. However, the modified polymer mPOP@MoS_4^{2-} displayed Mo-S stretching bands were seen at 378 cm^{-1} , 338 cm^{-1} and 284 cm^{-1} respectively (Figure 5.2e). We attribute this shift to the interaction of MoS_4^{2-} with framework backbone which matches well with the reported literature.^[83] Zeta-potential measurement of mPOP@MoS_4^{2-} revealed positive charge on the surface (ζ - potential= +37.5 mV), confirming its cationic nature (Figure 5.2f).

Pollutant Capture Study:

Structurally robust ionic porous materials have been employed as potential sorbent materials to capture several toxic contaminants from water. Building on this perspective, inducing macroporosity within a framework material can facilitate swift mass diffusion through the interconnected hierarchical pores with free transport of the target analytes resulting in enhanced proficiency. Hence, in this study mPOP@MoS_4^{2-} was employed toward segregation of toxic metal cations (Hg^{2+}) and hazardous oxyanions of selenium (selenate & selenite) from water medium.

Toxic Metal Ion Removal by mPOP@MoS_4^{2-} :

Owing to the presence of thiophilic sulfur motifs in the form of counter anions in mPOP@MoS_4^{2-} , its capture performance toward Hg^{2+} was initially put to test. The kinetics of Hg^{2+} sorption was carried out with ~20 ppm stock solution. Delightfully, mPOP@MoS_4^{2-} displayed high competence toward the removal of Hg^{2+} from water with >99% removal capability within only 5 minutes while rapid equilibrium was attained in the kinetics study (Figure 5.4a). This swift kinetic removal can be assigned to the combined merits of abundant hierarchical macropores along with high thiophilicity of MoS_4^{2-} anions inside the framework that is selective to soft acid metal cations on account of its soft basic nature. In addition, the Hg^{2+} sorption kinetics was further disseminated by adopting Ho and McKay's pseudo-second-order model. The observed kinetics was found to be in good agreement with the pseudo-second-order kinetic model

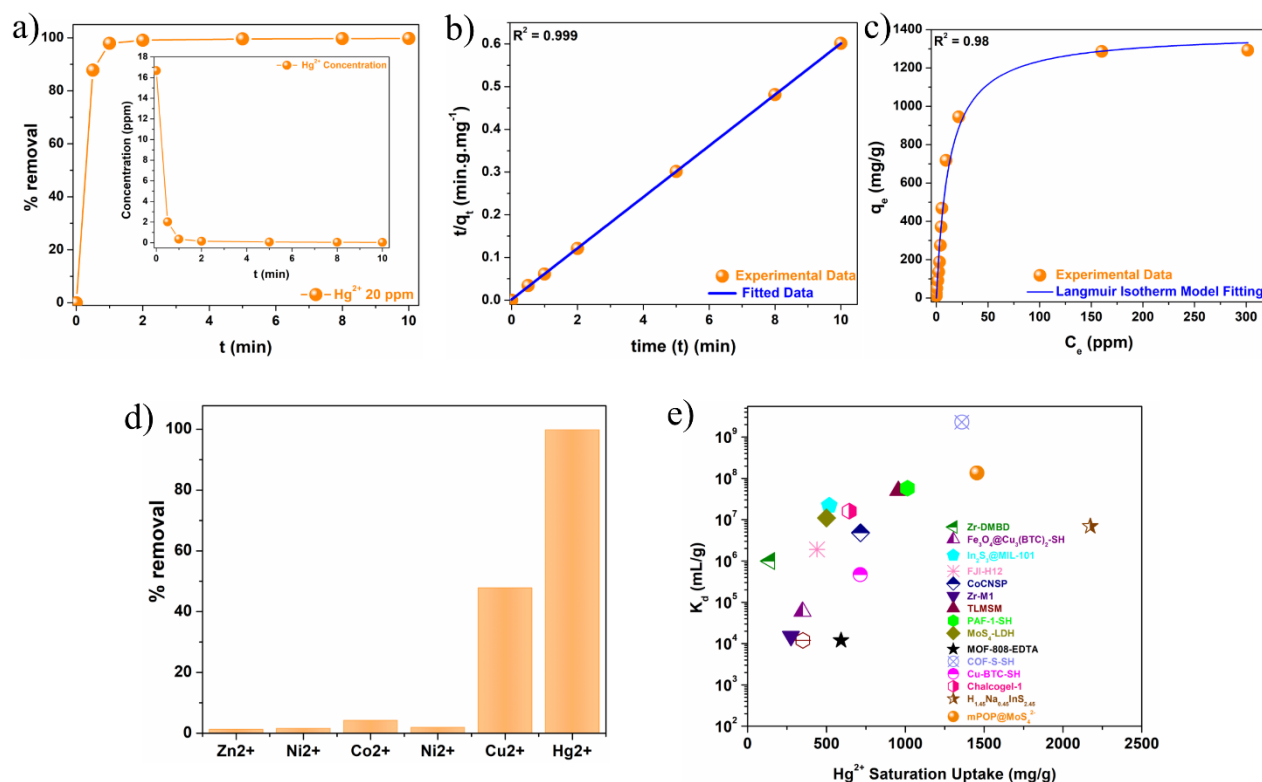


Figure 5.4. (a) Time-dependent adsorption of Hg^{2+} , Conc. Vs time plot for Hg^{2+} (inset). (b) Pseudo-second-order fitting plot of Hg^{2+} . (c) Langmuir isotherm model for Hg^{2+} . (d) Removal efficiency of five mixed metal ion systems (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Hg^{2+}) by mPOP@MoS_4^{2-} . (e) Comparison of the maximum retention capacity of $\text{Hg}(\text{II})$ and K_d of some benchmark materials under similar conditions (ref 18, 88-100).

(Figure 5.4b). Inspired by such rapid capture efficiency, we further investigated the uptake capacity by preparing a series of Hg^{2+} stock solution with varying concentrations from 10-2000 ppm. 5 mg of mPOP@MoS_4^{2-} material was taken in 5 mL of each stock solutions and was stirred at RT for ~ 12 h to establish adsorption equilibrium. Subsequently, the residual concentration was determined by ICP-AES analysis to calculate the uptake capacity. Figure 5.4c, shows the equilibrium Hg^{2+} uptake as a function of residual Hg^{2+} concentration. The adsorption isotherm of Hg^{2+} was found to follow the Langmuir isotherm model as evident from the excellent fit with correlation coefficient value (Figure 5.4c). The calculated maximum uptake capacity (Q_{max}) toward Hg^{2+} by mPOP@MoS_4^{2-} was found to be 1.45 g/g which stands tall amongst the best reported values in the literature so far (Figure 5.4e). To further verify the selective trapping of Hg^{2+} , various competing metal cations (Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+}) with differing thiophilicities were mixed with the Hg^{2+} stock solution and capture performance was monitored. As shown in Figure 5.4d, mPOP@MoS_4^{2-} displayed exceptional specificity toward selective removal of Hg^{2+} from these solutions. This confirms the high degree of affinity of mPOP@MoS_4^{2-} toward Hg^{2+} which is also advocated by its

excellent distribution coefficient (k_d) value obtained in the order of 10^8 (1.35×10^8 mL/g) (Figure 5.4e). Thus, mPOP@MoS₄²⁻ shows tremendous potency toward selective Hg²⁺ removal from water even in presence of competing ions with superior uptake capacity, rapid kinetics and exceptional binding affinity.

Simultaneous Capture of Toxic Metal and Oxyanions by mPOP@MoS₄²⁻:

Motivated by the cationic framework backbone of mPOP@MoS₄²⁻ that facilitates anion scavenging as well as abundance of hierarchical macroporous structure we zeroed our interest toward the adsorption of selenium oxyanions (Se (IV)/Se (VI)) that are extremely toxic and is often difficult to remove owing to their characteristic weaker binding affinity. The kinetics of Se (IV)/Se (VI) were carried out using 10 ppm initial stock solutions of the respective analytes. As opposed to Hg²⁺ sorption kinetics, we observed only moderate to good removal of both Se (IV) and Se (VI) oxyanions. After 10 minutes of adsorption ~82% and ~65% removal was observed for Se (IV) and Se (VI) respectively (Appendix 5.17, 5.18, 5.21 & 5.22). The competence of mPOP@MoS₄²⁻ toward uptake of these toxic anions were evaluated by taking 5-500 ppm stock solutions of the respective analytes and performing equilibrium adsorption at RT for 12 h. The maximum uptake capacities of these oxyanions were calculated to be 144.6 mg/g (Se (IV)) and 131.2 mg/g (Se (VI)) respectively (Appendix 5.19, 5.20, 5.23 & 5.24) which is at par with the reported literature.

Inspired from the Hg-Se antagonism prevailing for so long in nature, we envisioned that the segregation of Se oxyanions could be amplified both in terms of kinetics and uptake amount in presence of Hg²⁺ ions. Interestingly, a marked difference in the sorption performance of mPOP@MoS₄²⁻ towards both Se (IV) and Se (VI) was observed with the coexistence of Hg²⁺ ions. A cooperative effect at play was seen that led to efficacious trapping of Se oxyanions as well as Hg²⁺ ions. This simultaneous adsorption was prevailing for both Se (IV) and Se (VI) when using mPOP@MoS₄²⁻ as the sorbent material. In particular, when 20 ppm Hg²⁺ was present, exceptional co-adsorption of selenium oxyanions and Hg²⁺ was observed. The kinetic studies revealed that within 10 minutes simultaneous removal of Se (IV) and Hg²⁺ was achieved with >97% of Se (IV) was captured along with >99% Hg²⁺ removal (Figure 5.5a, Appendix 5.27 & 5.29). Similarly, >98% Se (VI) & >99% Hg²⁺ was removed in 10 minutes when tested for Se (VI) + Hg²⁺ mixture solution (Figure 5.5d, Appendix 5.28 & 5.30). Pseudo-second-order kinetic model was found as the best fit in both the cases (Figures 5.5c & 5.5f). Enthused by these results, we went ahead to investigate the uptake capacity of Se oxyanions in presence of 20 ppm Hg²⁺ solution. Remarkably, almost 2 fold increase in the uptake capacity of both the oxyanions were accomplished with values reaching up to 286.8 mg/g for Se (IV) (Figure 5.5b, Appendix 5.25) and 268.1 mg/g for Se (VI) (Figure 5.5e, Appendix 5.26). These capacity values make mPOP@MoS₄²⁻ rank as one of the best materials toward Se oxyanion removal reported so

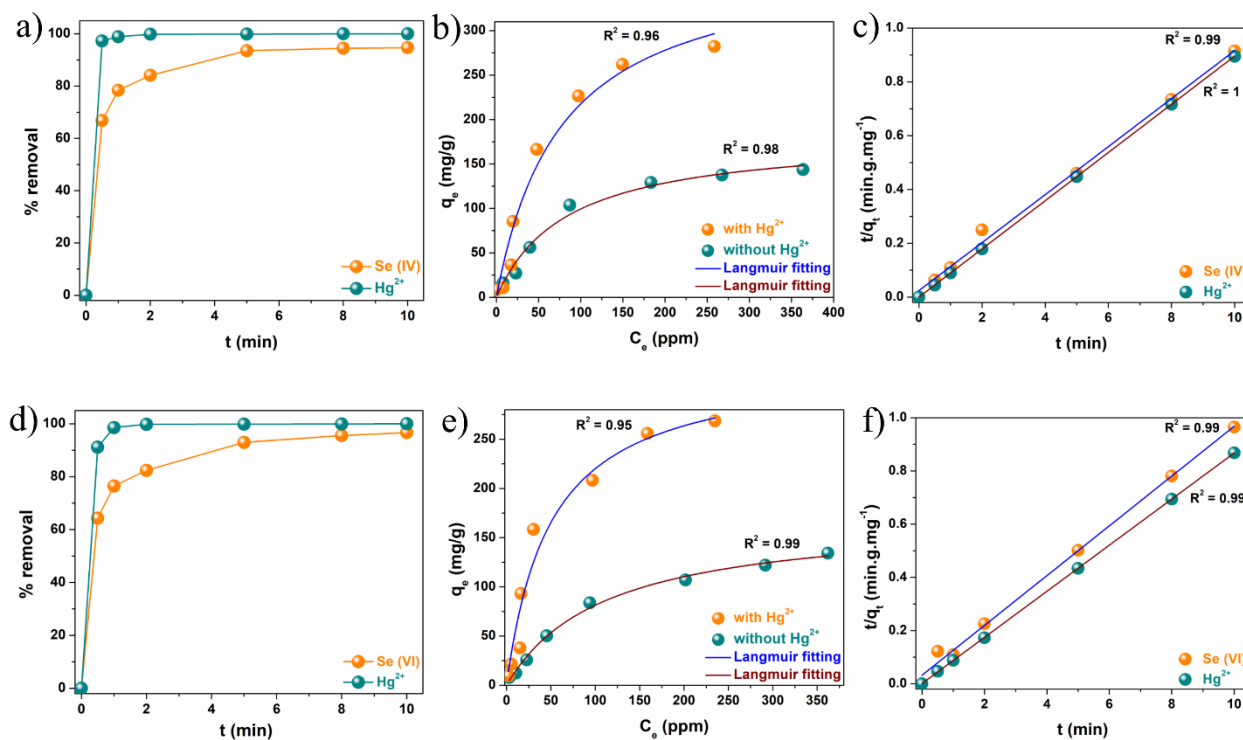


Figure 5.5. (a) Sorption kinetics curves for Hg^{2+} (10 ppm) and SeO_3^{2-} (10 ppm) during Hg/Se coadsorption. (b) Sorption isotherms for SeO_3^{2-} with and without 20 ppm of Hg^{2+} by mPOP@MoS_4^{2-} . (c) Pseudo-second-order fitting plot of Hg^{2+} and SeO_3^{2-} during Hg/Se coadsorption. (d) Sorption kinetics curves for Hg^{2+} (10 ppm) and SeO_4^{2-} (10 ppm) during Hg/Se coadsorption. (e) Sorption isotherms for SeO_4^{2-} with and without 20 ppm of Hg^{2+} by mPOP@MoS_4^{2-} . (f) Pseudo-second-order fitting plot of Hg^{2+} and SeO_4^{2-} during Hg/Se coadsorption.

far (Appendix Table 1, Appendix Table 2). Additionally, the adsorption isotherms of the analytes were found to obey Langmuir model in both the cases (Figures 5.5b, 5.5e) with excellent fitting values. It should be pointed out that fixed concentration of Hg^{2+} at 20 ppm the relative Se (IV)/Se (VI) concentration had great effect in the simultaneous removal proficiency where excellent removal was observed for 5–20 ppm concentration beyond which the performance declined. This observation aligns well with Hg-Se antagonism, whereby a 1:1 molar ratio is optimal to attain biological inertness.^[85] To further establish the exclusiveness of the Hg-Se antagonism, we checked the sorption performance of both Se (IV)/Se (VI) in presence of Cu^{2+} , known for its moderate thiophilicity. As illustrated in Appendix 5.37, the presence of 20 ppm Cu^{2+} did not have any significant effect in the adsorption of Se (IV)/Se (VI) in terms of sorption kinetics as no marked improvement in the kinetic behaviour was observed where ~71% Se (VI) (~66% removal without Cu^{2+}) and ~45% Cu^{2+} was removed in 10 minutes. The uptake capacity of Se (VI) reached

151 mg/g with a mere 20 mg increase as opposed to the capacity value 131.2 mg/g for individual Se (VI) (Appendix 5.36). This control experiment shows that Cu^{2+} / Se (VI) pair do not show any superior removal efficiency both in kinetics and uptake amount and highlights the importance of Hg-Se antagonism towards synergistic detoxification of Se oxyanions (Appendix 5.35-5.38). Furthermore, pertaining to practical applicability of mPOP@MoS_4^{2-} , dynamic breakthrough sorption was performed under continuous flow. With a feed solution of 50 ppm Se (IV) and fixed flow rate of 0.5 mL/min the compound showed excellent proficiency in continual removal of Se (IV) at room temperature where almost 99% Se removal was achieved upon passing ~ 180 mL of the oxyanion solution (Figure 5.6c). Selectivity of mPOP@MoS_4^{2-} toward Se (IV)/ Se (VI) was also tested in presence of interfering anions (Cl^- , NO_3^- , SO_4^{2-}) by taking ~ 10 fold & ~ 100 fold excess of them to mimic real world scenario. Satisfyingly, mPOP@MoS_4^{2-} displayed uncompromised capture efficiency of both Se (IV) & Se (VI) amongst large excess of competing anions advocating its potency toward selective removal of Se oxyanions from water (Appendix 5.31 & 5.32). Additionally, the competence of mPOP@MoS_4^{2-} was also put to test under real world samples such as river water, bottled water and lake water where intact performance was observed punctuating the efficiency of mPOP@MoS_4^{2-} to perform under such complex sample matrix (Figure 5.6b, Appendix 5.31 & 5.32).

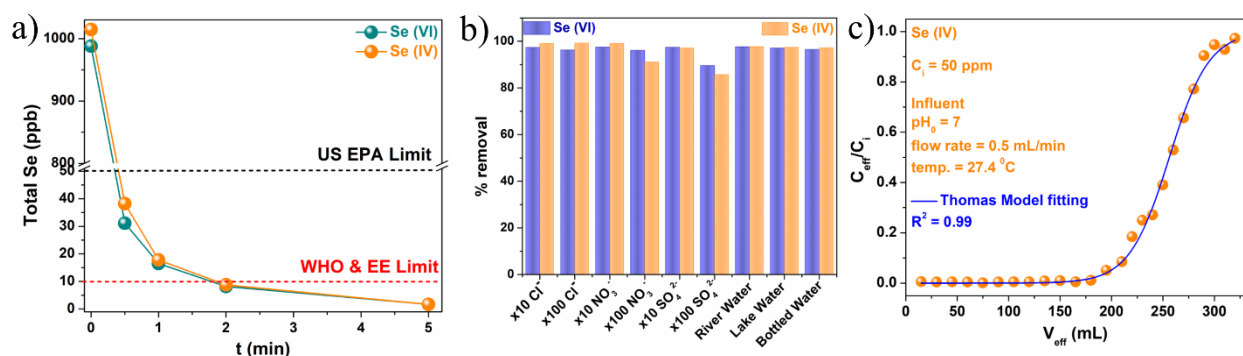


Figure 5.6. (a) Trace amount (1 ppm) capture study of Se (IV)/ Se (VI) by mPOP@MoS_4^{2-} . (b) Selectivity study of Se (IV)/ Se (VI) in presence of excess competing anions by mPOP@MoS_4^{2-} . (c) Breakthrough sorption curve for Se (IV) capture by mPOP@MoS_4^{2-} (initial conc. 50 ppm).

Another important aspect of a potent sorbent is the ability to trap pollutants in trace concentration. To put this to test, we performed low concentration capture studies of Se (IV) and Se (VI) with ~ 1 ppm (~ 1000 ppb) stock solution. The kinetics experiment with mPOP@MoS_4^{2-} revealed that within only 30 seconds the concentration of Se (IV)/ Se (VI) were reduced to < 50 ppb (US EPA limit 50 ppb) while it took only 2 minutes to bring down the concentration below 10 ppb (WHO & EE limit) further highlighting the competency of mPOP@MoS_4^{2-} in ultrafast trace amount Se oxyanion capture from water (Figure 5.6a,

Appendix 5.33, 5.34). Thus $\text{mPOP}@MoS_4^{2-}$ could serve as an ideal sorbent to effectively remove selenium oxyanions with significantly improved efficiency in presence of Hg^{2+} by harnessing the Hg-Se antagonism.

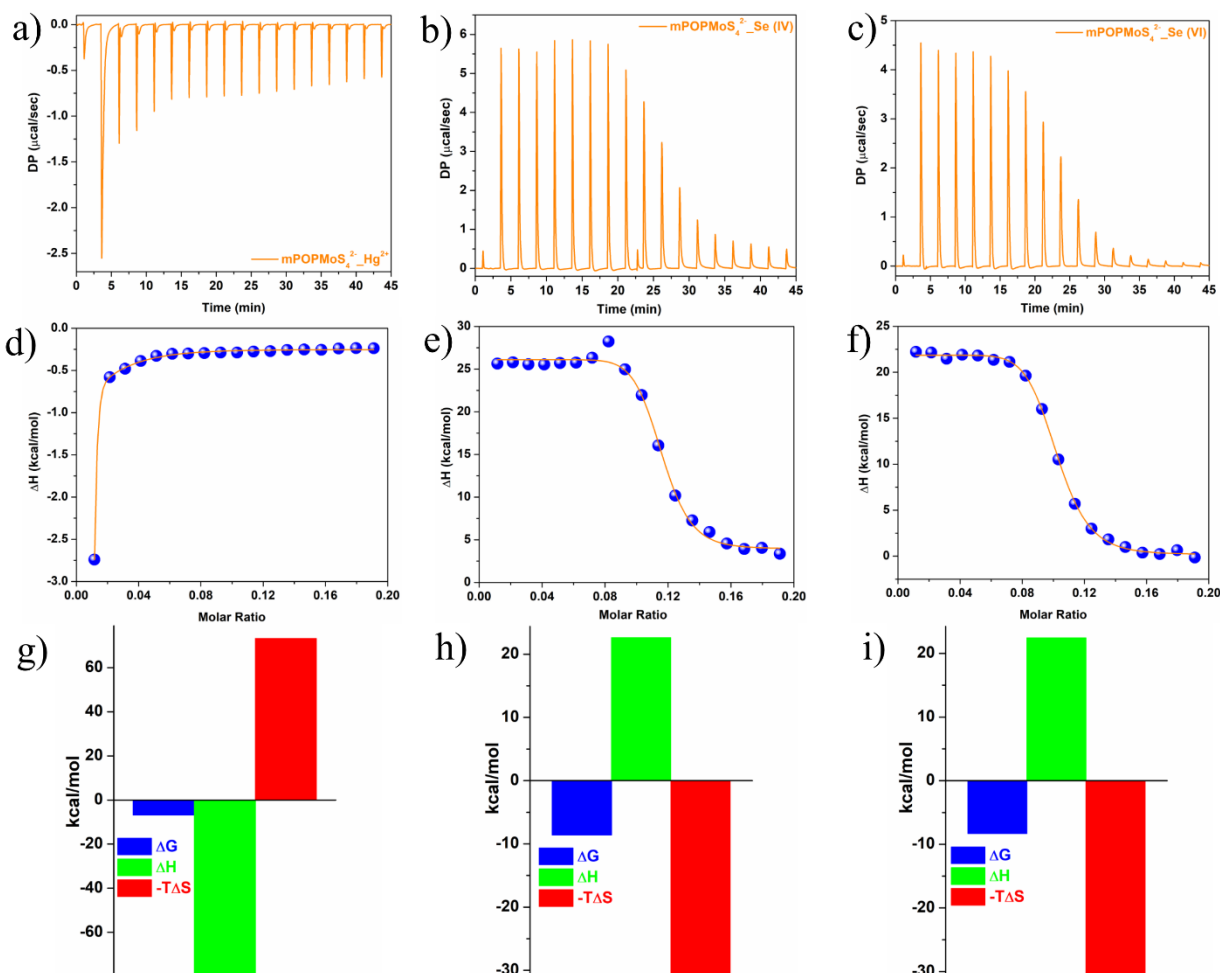


Figure 5.7. (a) ITC thermogram of Hg^{2+} . (b) ITC thermogram of Se (IV). (c) ITC thermogram of Se (VI). (d) Heat of injection profile for Hg^{2+} sorption. (e) Heat of injection profile for Se (IV) sorption. (f) Heat of injection profile for Se (VI) sorption. (g) Signature curve for Hg^{2+} adsorption. (h) Signature curve for Se (IV) adsorption. (i) Signature curve for Se (VI) adsorption.

Post Capture Characterization:

After performing the capture experiments $\text{mPOP}@MoS_4^{2-}$ was thoroughly analysed by XPS, FT-IR spectroscopy, SEM-EDS elemental mapping etc. Additionally, isothermal titration calorimetry (ITC) was utilized to get thermodynamic insights into the sorption procedure. The FT-IR spectra of $\text{mPOP}@MoS_4^{2-}$ after adsorption of Hg^{2+} , Se (IV) & Se (VI) were recorded that confirmed the post-adsorption stability of $\text{mPOP}@MoS_4^{2-}$ with no drastic change in the characteristic peaks of the polymer indicating framework

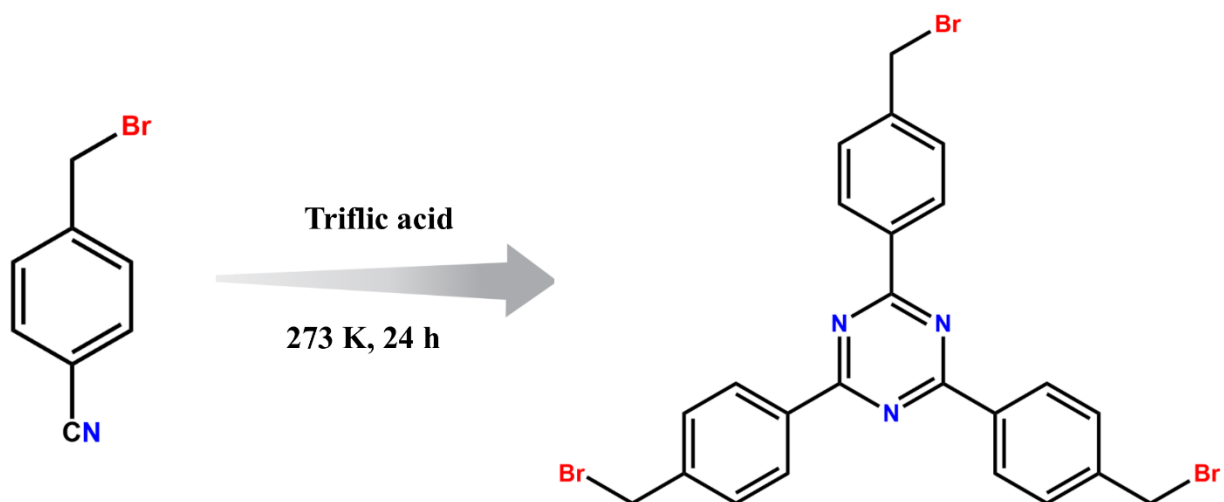
retention (Appendix 5.39). SEM-EDS mapping profile shows successful capture of all the toxic pollutants and their homogeneous distribution throughout mPOP@MoS₄²⁻ (Appendix 5.46 & 5.47). Hg₂⁺ adsorbed sample showed the presence of Hg (4f) signals along with other structural constituents (Appendix 5.40-5.41). XPS analysis of Se (IV) and Se (VI) adsorbed mPOP@MoS₄²⁻ shed some interesting insights to the capture of Se oxyanions (Appendix 5.42-5.45). From literature values, the Se 3d_{5/2} energy for Se (IV) appears at around 58.0 eV,^[84] however, Se (IV) adsorbed mPOP@MoS₄²⁻ sample displayed Se 3d_{5/2} energy at 55.2 eV which in turn indicate that during the sorption process Se (IV) is reduced to Se (0) (Appendix 5.43). This observed redox-chemistry is also seen in biological systems^[85] and is also in line with the reported literature where similar results were noted.^[84-85] On the contrary, Se (VI) adsorbed sample showed Se 3d_{5/2} peak at 58.4 eV which is in line with reported SeO₄²⁻ compounds, confirming that the valence state of Se (VI) do not vary upon sorption by mPOP@MoS₄²⁻ (Appendix 5.45).

Additionally, the ITC experiment gave critical information regarding the thermodynamic parameters of the sorption process. The ITC thermogram of Se (IV) & Se (VI) confirmed the adsorption of these oxyanions onto mPOP@MoS₄²⁻ as an endothermic process with negative value of Gibbs free energy suggesting strong binding affinity of these anions toward the sorbent while the sorption was found to be thermodynamically favourable (Figure 5.7b, 5.7e, 5.7h & 5.7c, 5.7f, 5.7i). However, the Hg₂⁺ sorption appeared to be exothermic in nature while the Gibbs free energy was calculated as negative to make the adsorption thermodynamically feasible (Figure 5.7a, 5.7d, 5.7g).

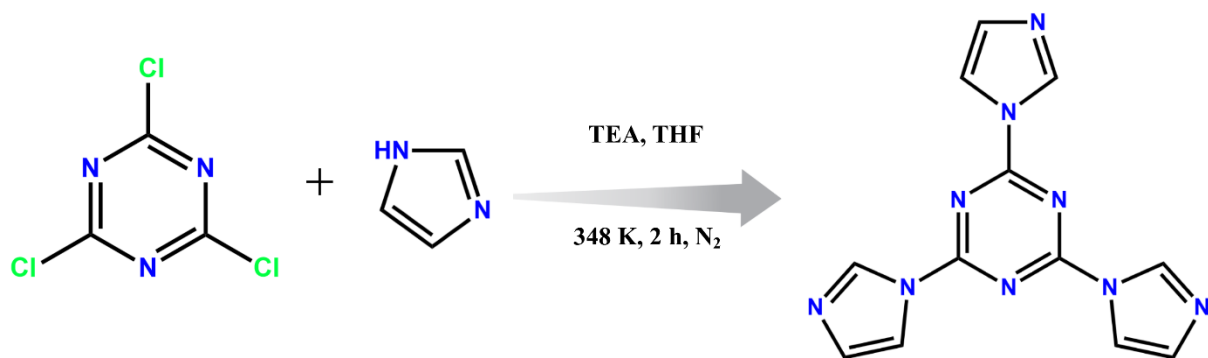
5.4 Conclusions

In summary, this work present an innovative amalgamation bioinspired design rationale, iconicity and interconnected hierarchical porosity in a single material toward targeted removal selective toxic contaminants from water. Tapping on to the potential of Hg-Se antagonism, synergistic water detoxification of Hg and Se oxyanions was accomplished with excellent efficiencies (>99% removal in minutes). Also, exceptional uptake of Hg₂⁺ coupled with swift kinetics could be attributed to the interconnected hierarchical pores that promotes mass diffusion and active site accessibility. The overall enhanced pollutant capture performance comes as a combination of functional MoS₄²⁻ anion as well as macroscopic structure of the polymer which is beneficial toward their sequestration from water. Interestingly, this study fosters one of the few instances where cationic as well as anionic water pollutants were segregated with equal competency by a cationic sorbent. More importantly, this study fresh insights toward task-specific efficient adsorbent design and may trigger more research into bridging two or more properties in a single material in order to realize improved performance.

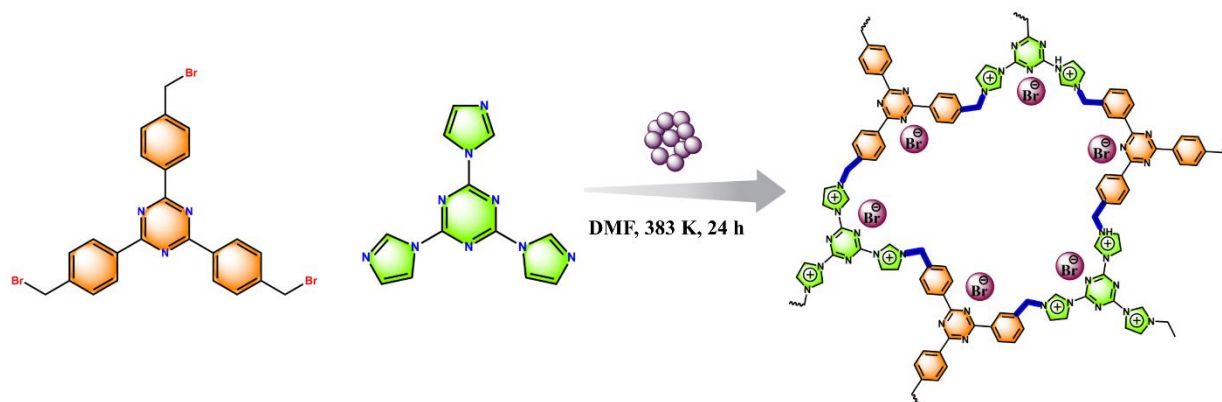
5.5 Appendix section



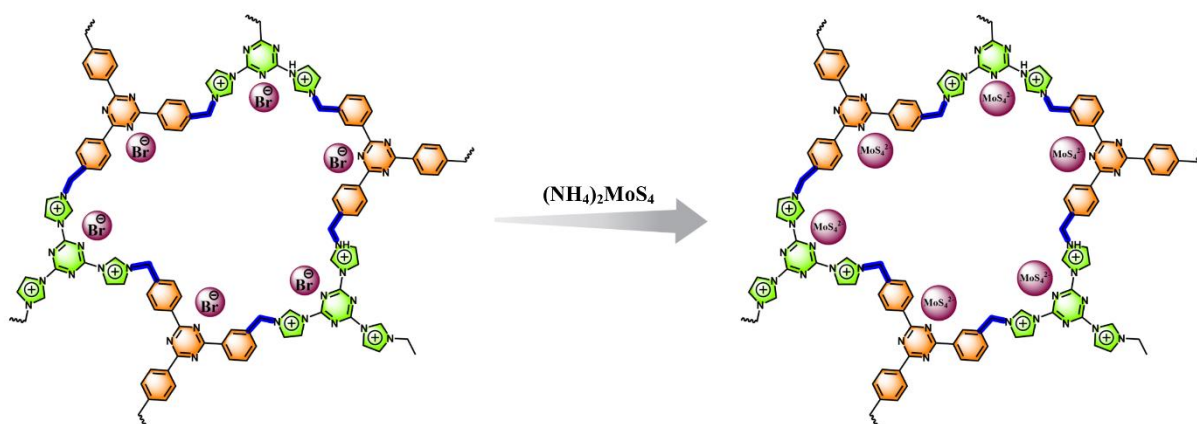
Appendix scheme 1. Representation of the protocol employed for the synthesis of Tris-(4-bromomethyl-phenyl)-[1,3,5] triazine.



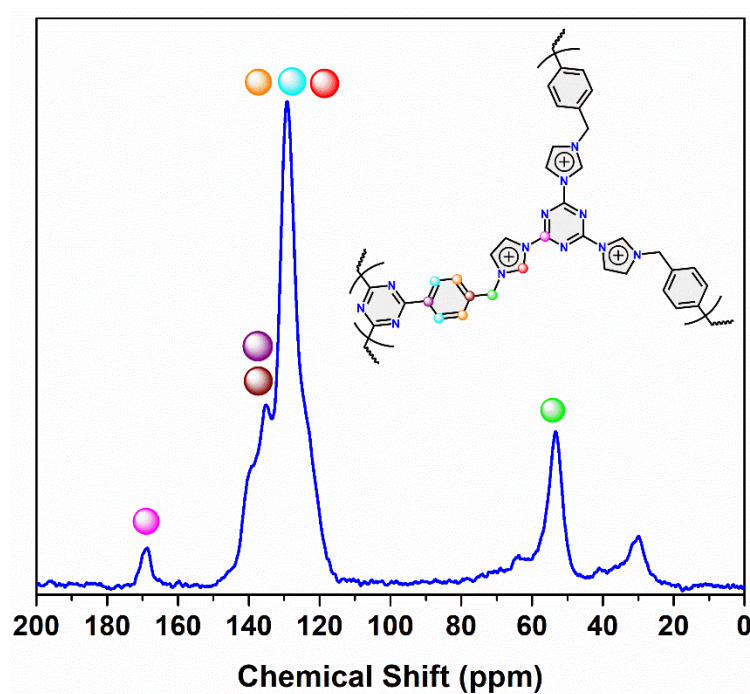
Appendix scheme 2. Representation of the protocol employed for the synthesis of 2,4,6-tri(1H-imidazol-1-yl)-1,3,5-triazine.



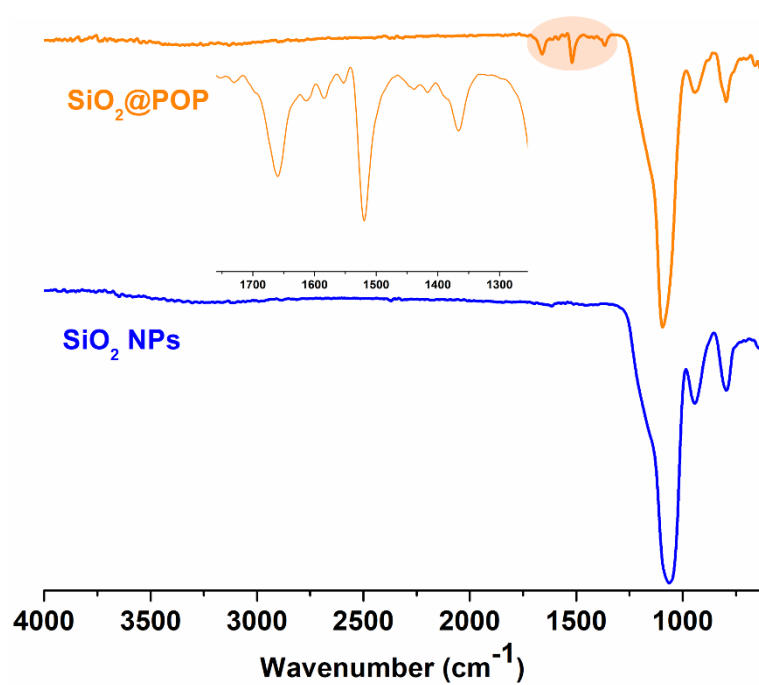
Appendix scheme 3. Representation of the protocol employed for the synthesis of **SiO₂@POP** (SiO₂ NPs omitted for clarity).



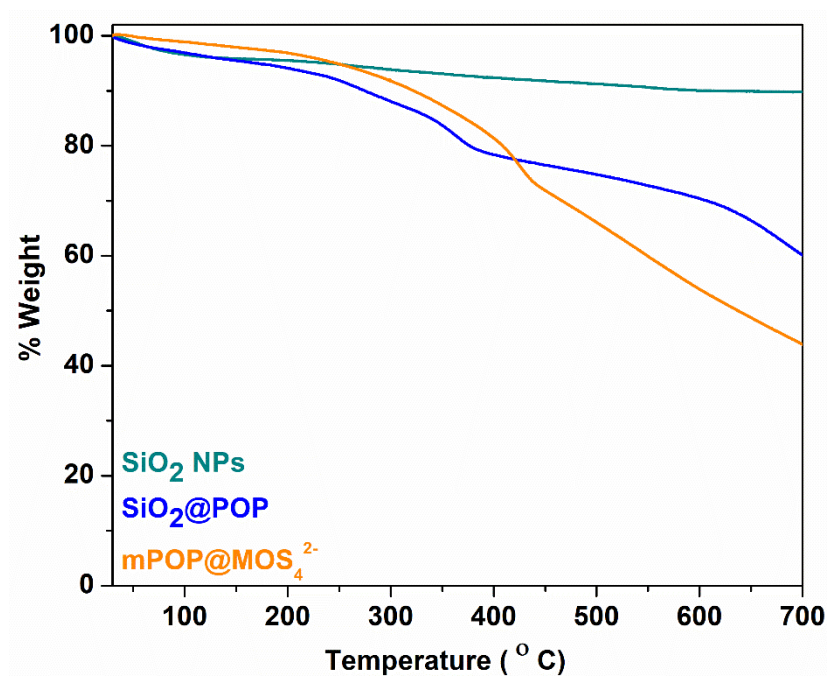
Appendix scheme 4. Representation of the protocol employed for the synthesis of **mPOP@MoS₄²⁻**.



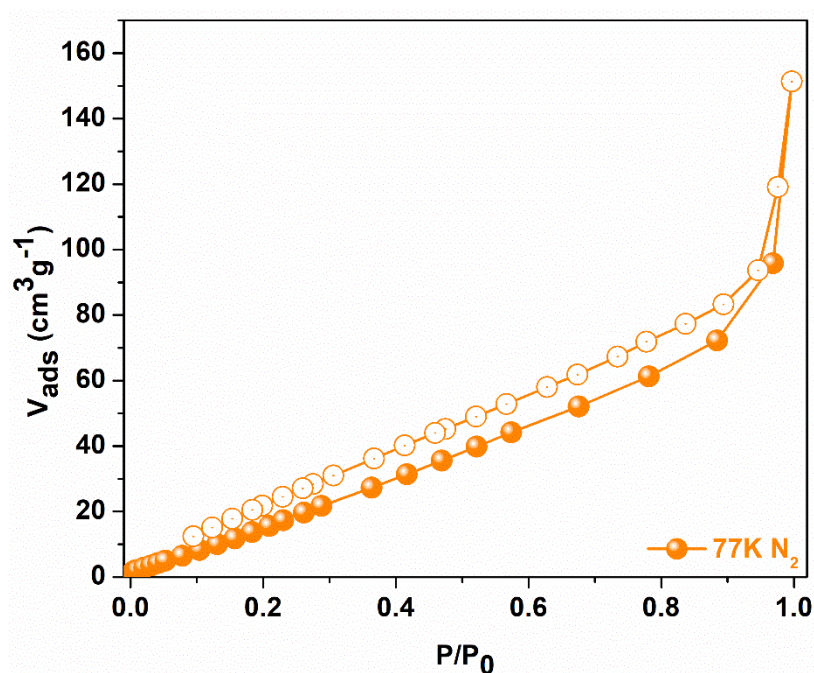
Appendix Figure 5.1. ^{13}C SSNMR spectrum of pristine mPOP.



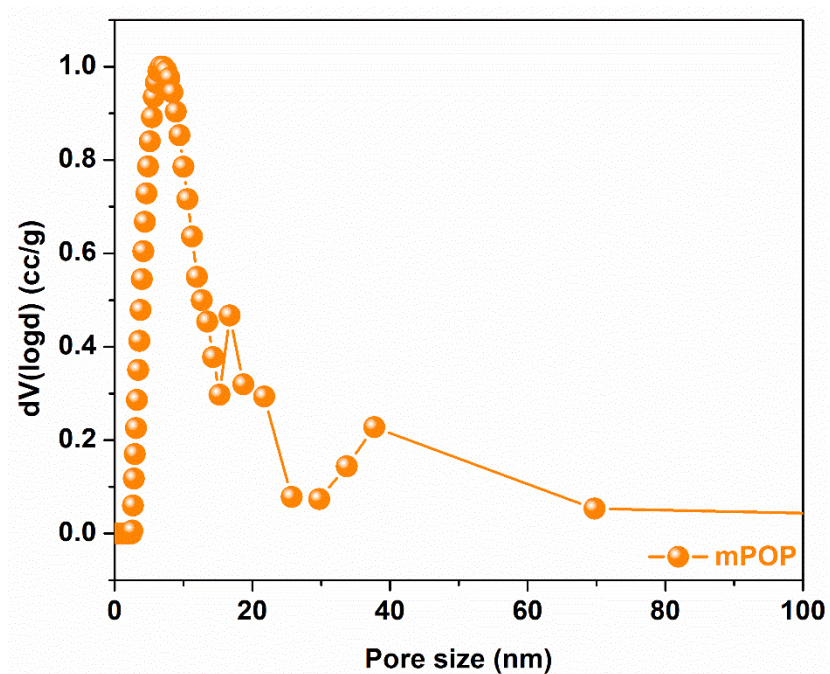
Appendix Figure 5.2. FT-IR spectra of SiO_2 NPs (blue) & $\text{SiO}_2@$ POP (orange).



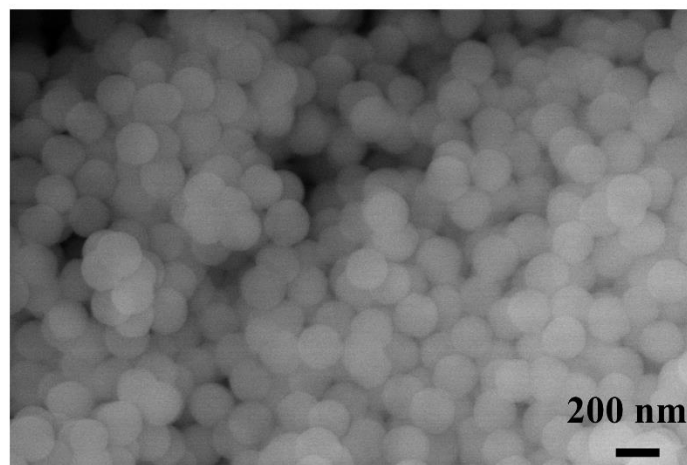
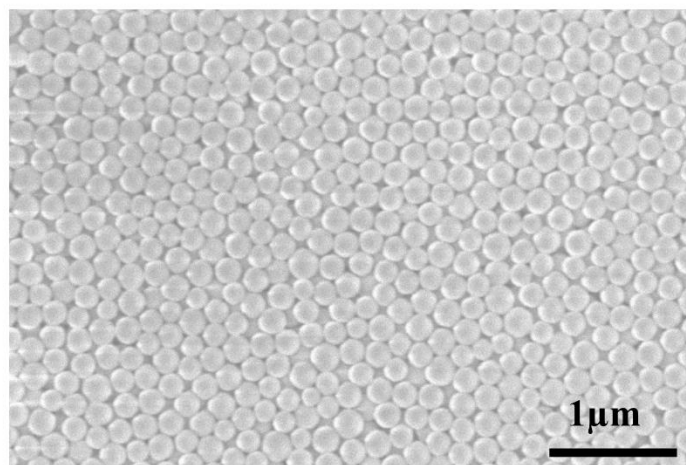
Appendix Figure 5.3. TGA profiles (Under N₂ atmosphere) for SiO₂ NPs (cyan), SiO₂@POP (blue) & mPOP@MoS₄²⁻ (orange).



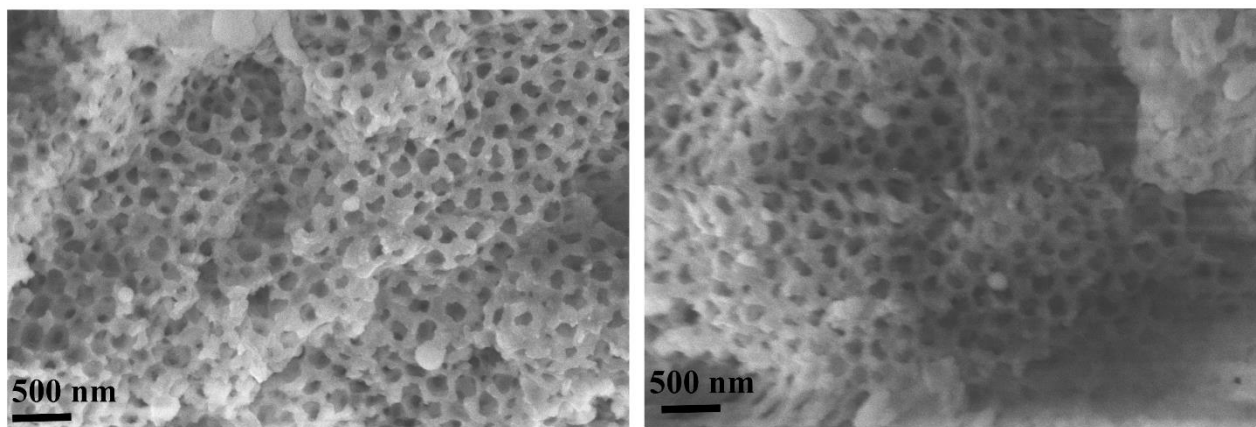
Appendix Figure 5.4. Low temperature N₂ sorption profile of mPOP@MoS₄²⁻.



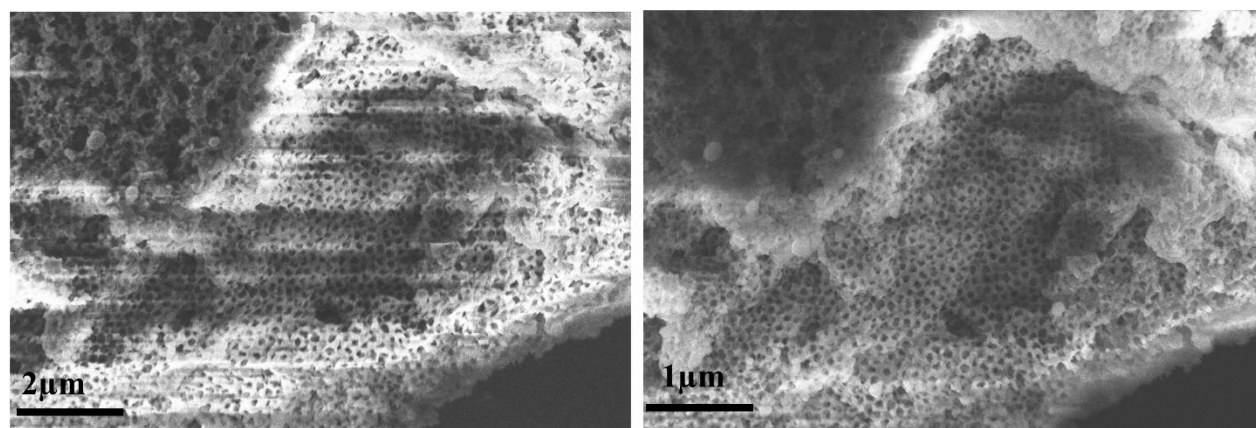
Appendix Figure 5.5. BJH pore size distribution obtained from N₂ sorption of mPOP@MoS₄²⁻.



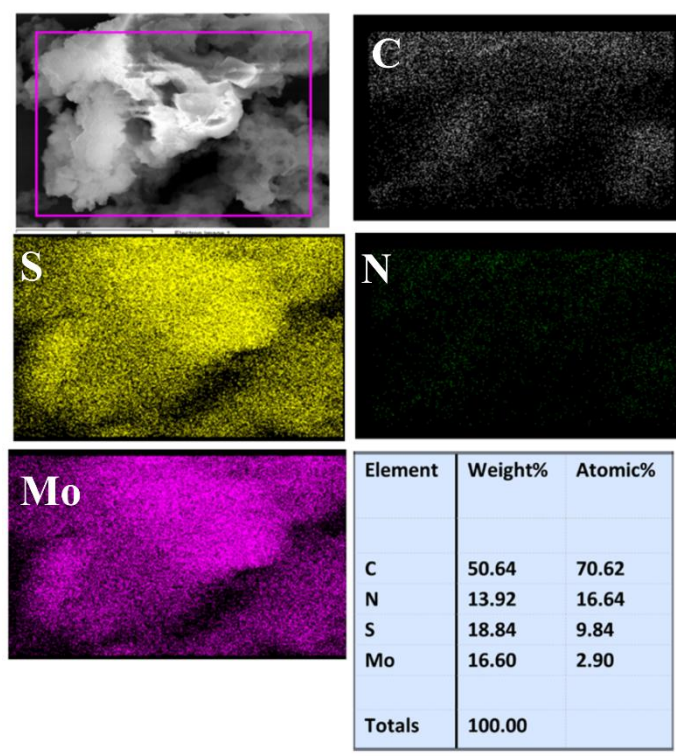
Appendix Figure 5.6. FESEM images of SiO₂ NPs at different magnification.



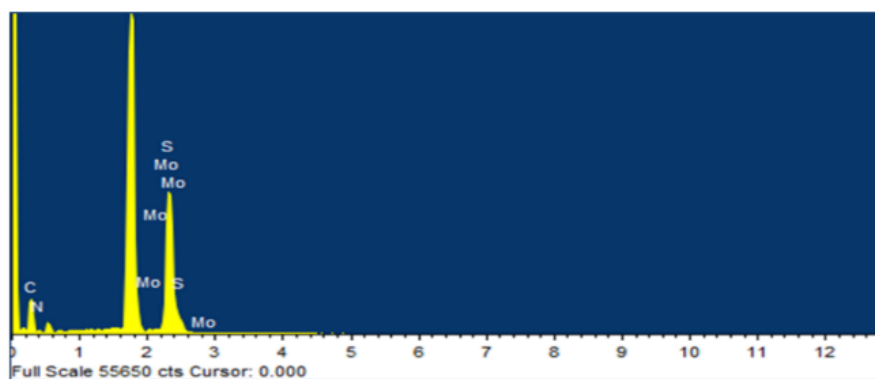
Appendix Figure 5.7. FESEM images of mPOP@MoS₄²⁻ showing uniform interconnected hierarchical pores.



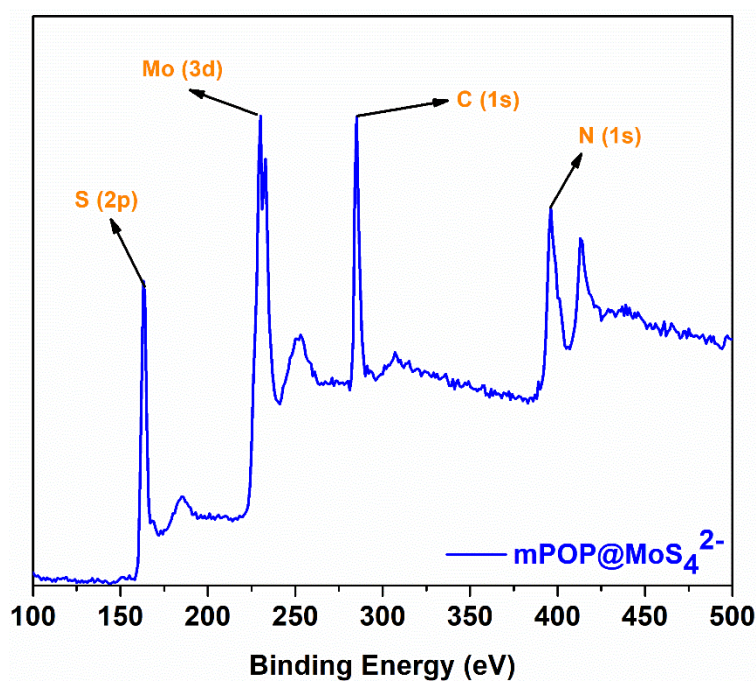
Appendix Figure 5.8. FESEM images of mPOP@MoS₄²⁻ over large area over low magnification.



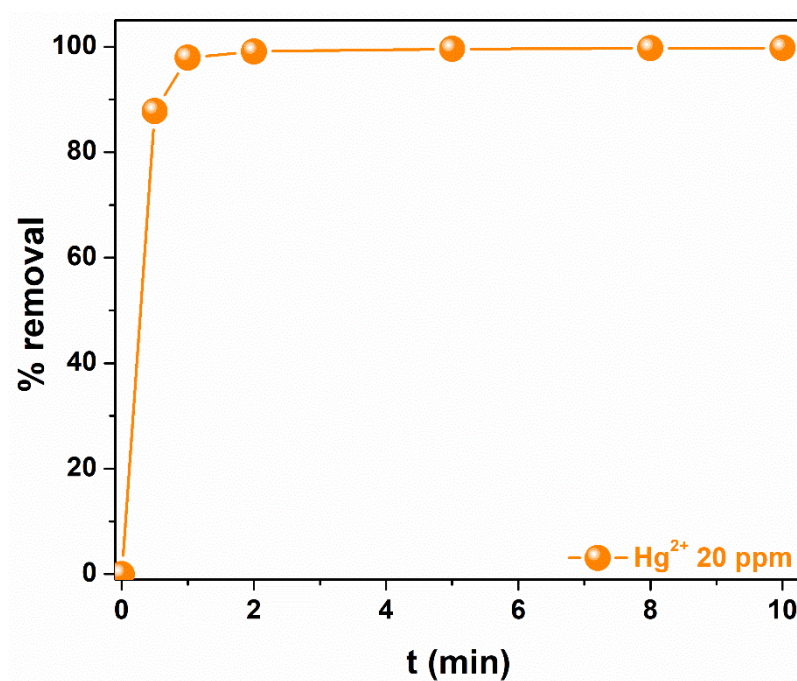
Appendix Figure 5.9. Elemental mapping of mPOP@MoS₄²⁻.



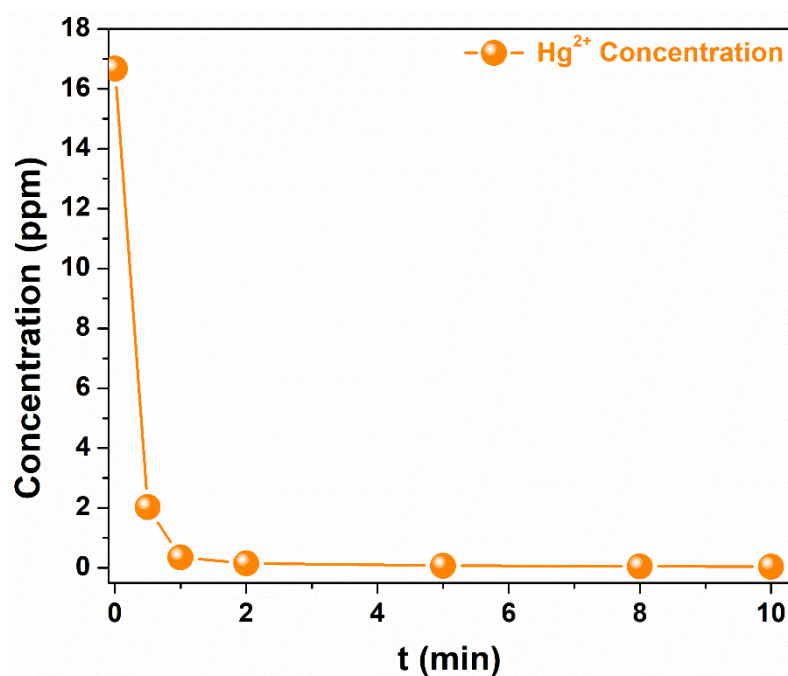
Appendix Figure 5.10. SEM-EDS spectra of mPOP@MoS₄²⁻.



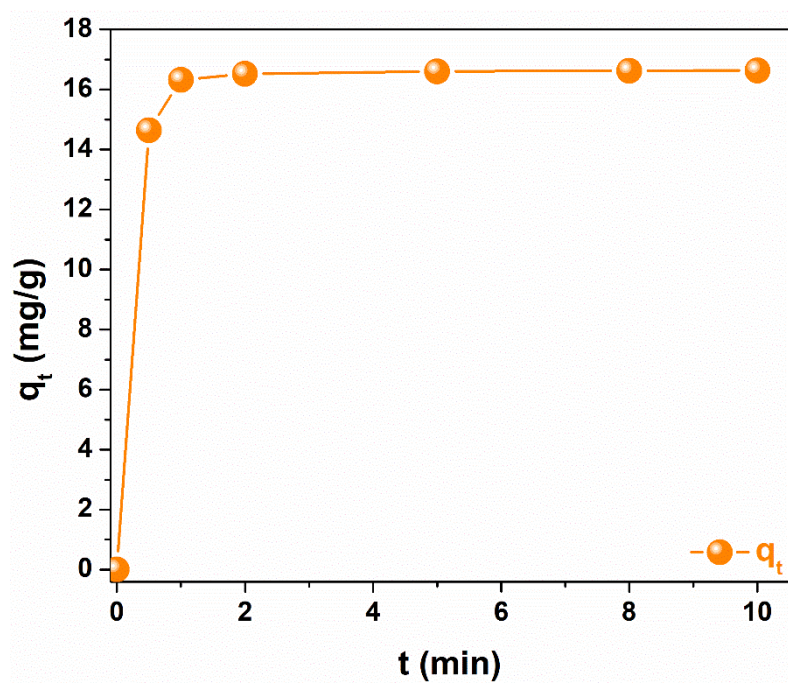
Appendix Figure 5.11. XPS survey scan of mPOP@MoS₄²⁻.



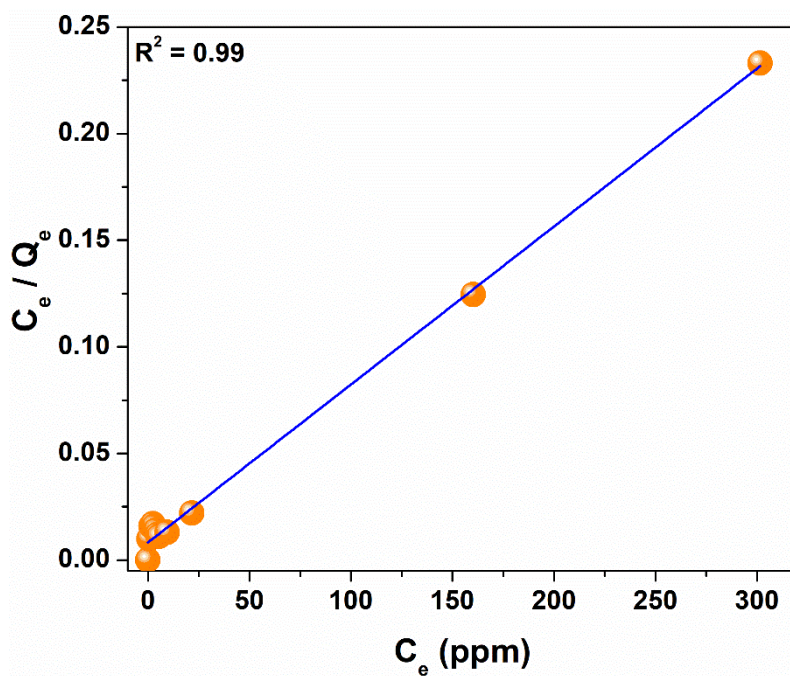
Appendix Figure 5.12. Removal kinetics of Hg²⁺ by mPOP@MoS₄²⁻.



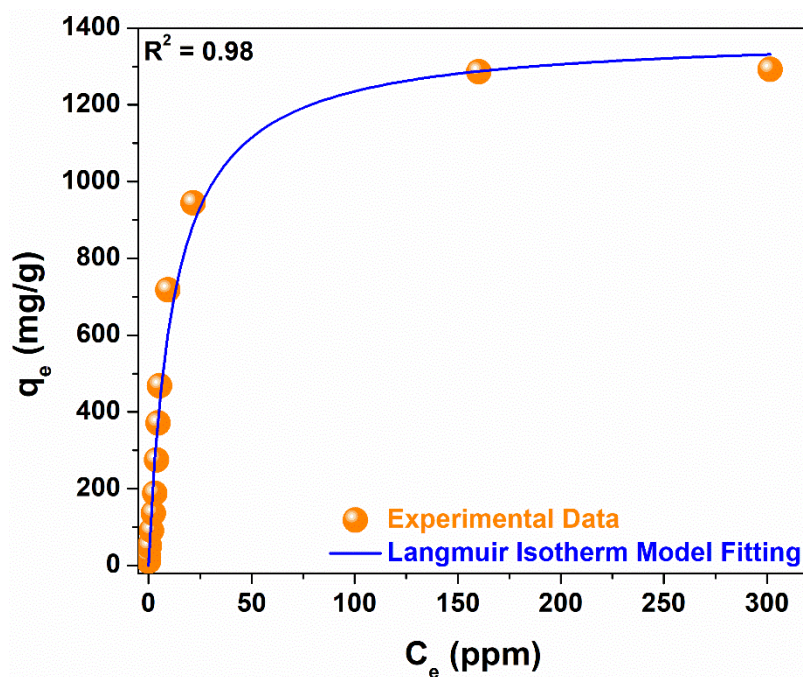
Appendix Figure 5.13. Change in concentration Of Hg^{2+} with time.



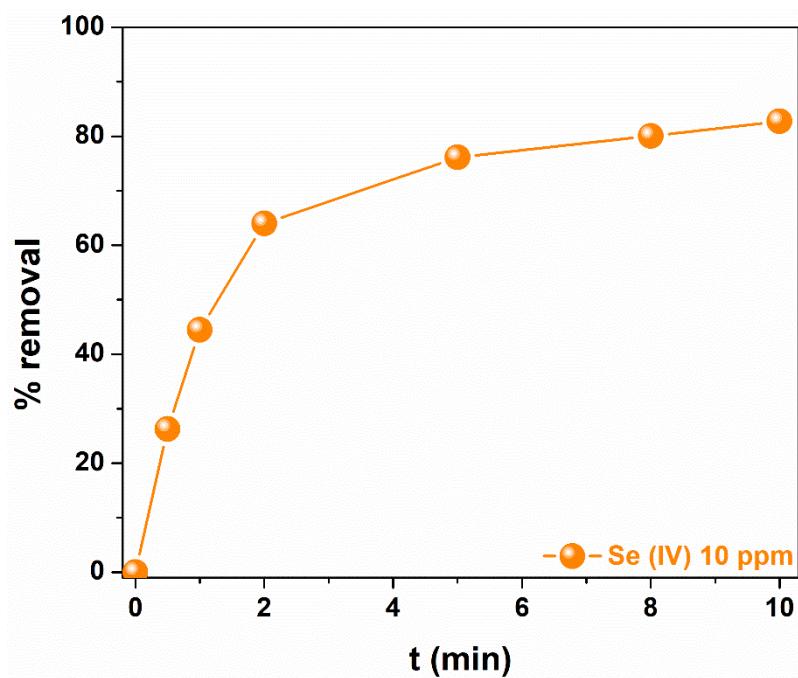
Appendix Figure 5.14. q_t vs t curve for Hg^+ kinetics.



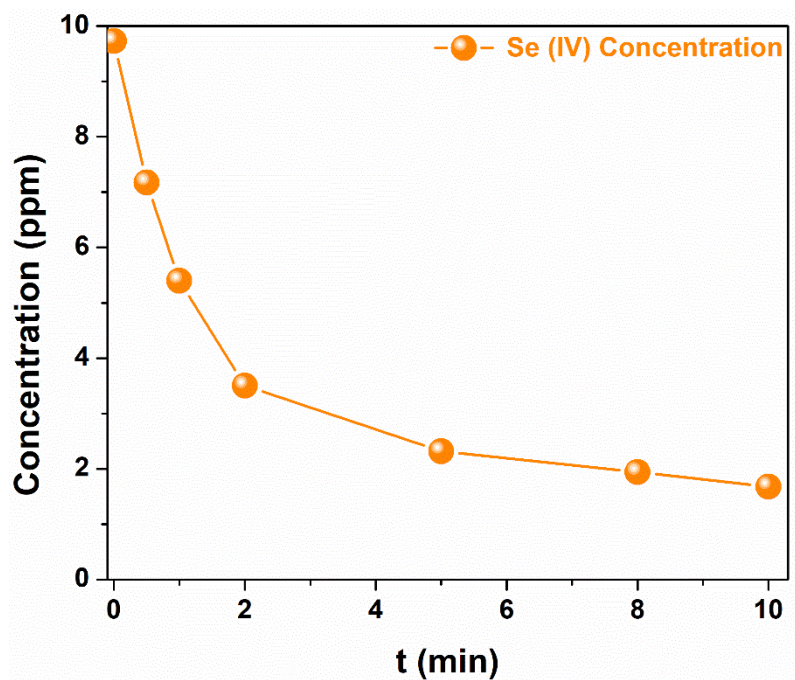
Appendix Figure 5.15. Langmuir linear fitting model for Hg^{2+} .



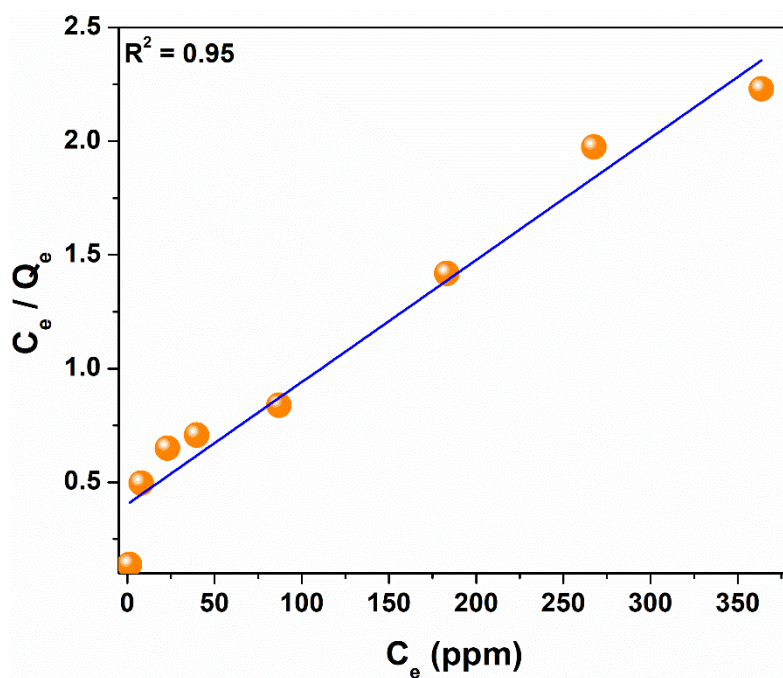
Appendix Figure 5.16. Langmuir isotherm model for Hg^{2+} sorption.



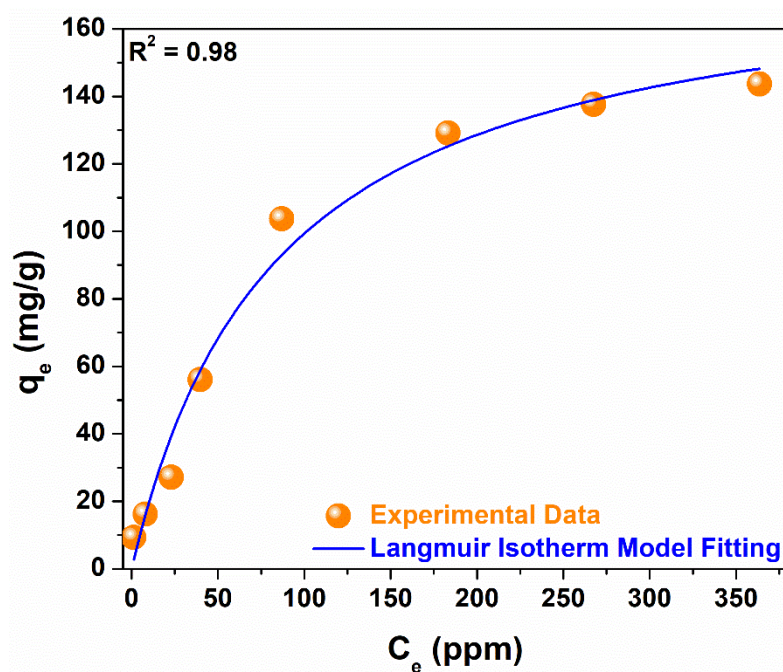
Appendix Figure 5.17. Removal kinetics of Se (IV) by mPOP@MoS₄²⁻.



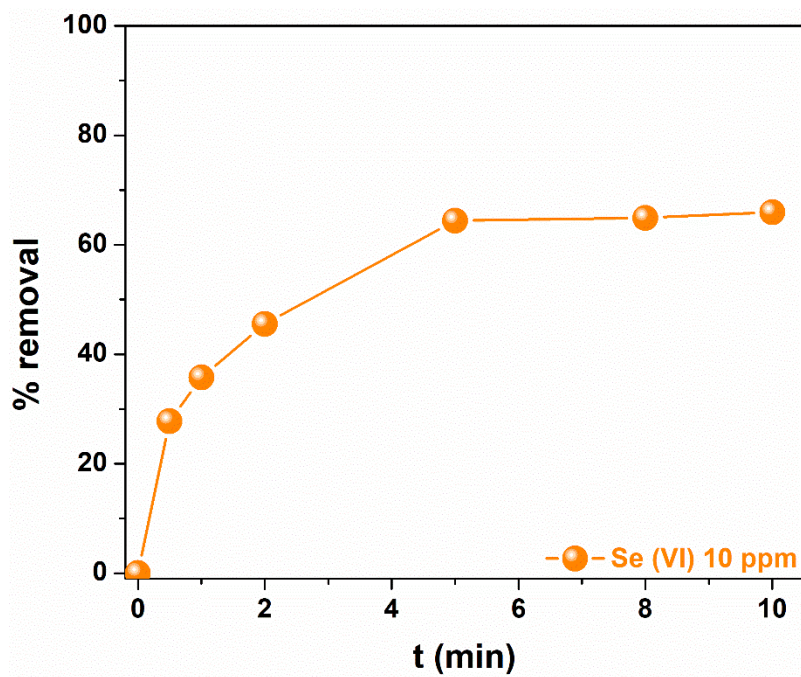
Appendix Figure 5.18. Change in concentration Of Se (IV) with time.



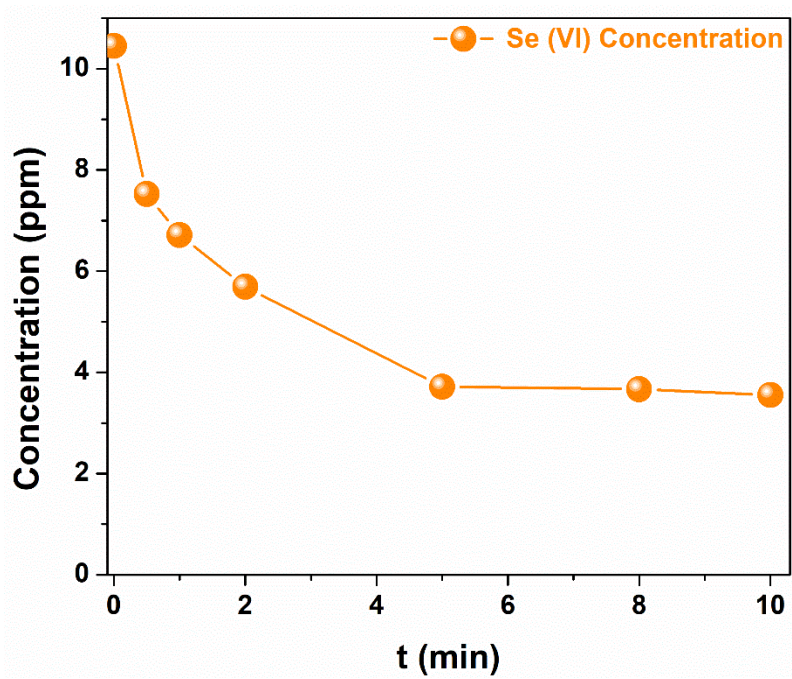
Appendix Figure 5.19. Langmuir linear fitting model for Se (IV) sorption.



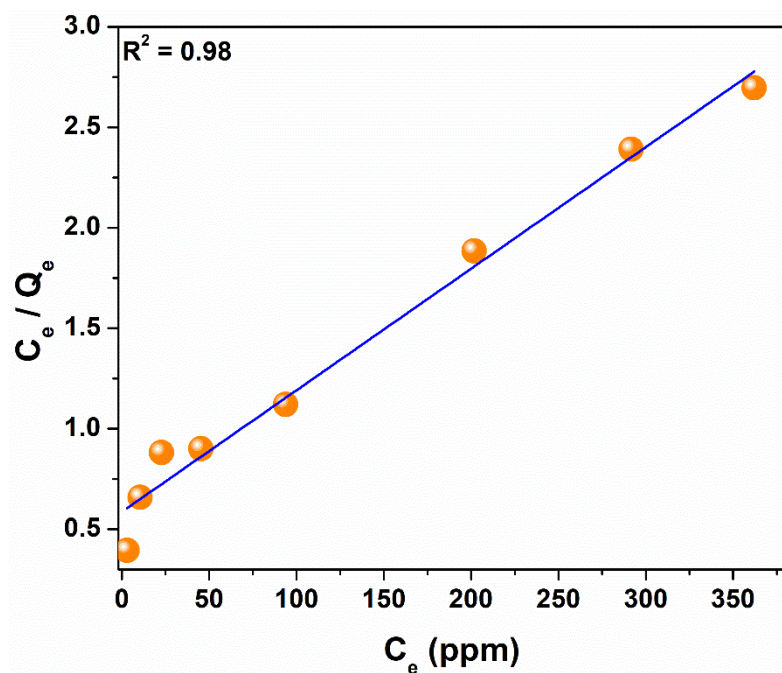
Appendix Figure 5.20. Langmuir isotherm model for Se (IV).



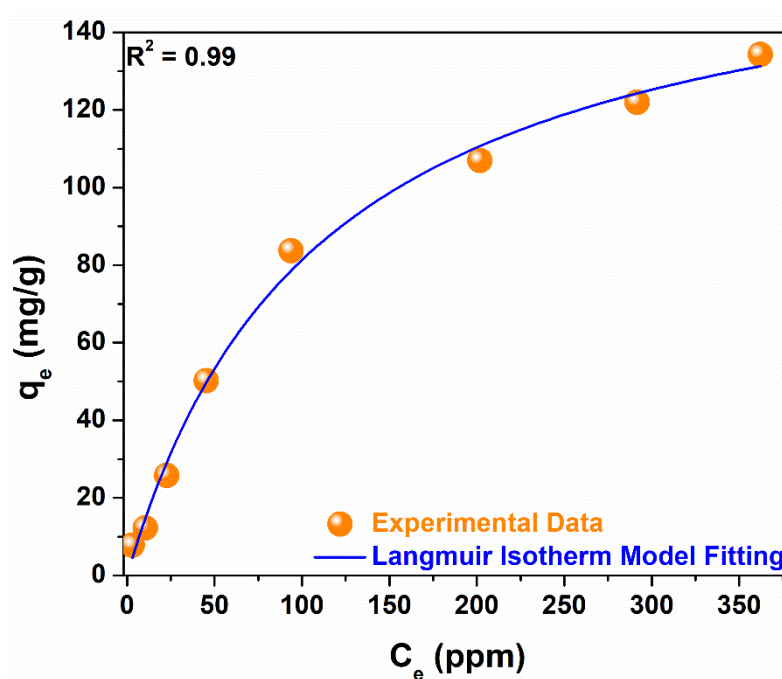
Appendix Figure 5.21. Removal kinetics of Se (VI) by mPOP@MoS₄²⁻.



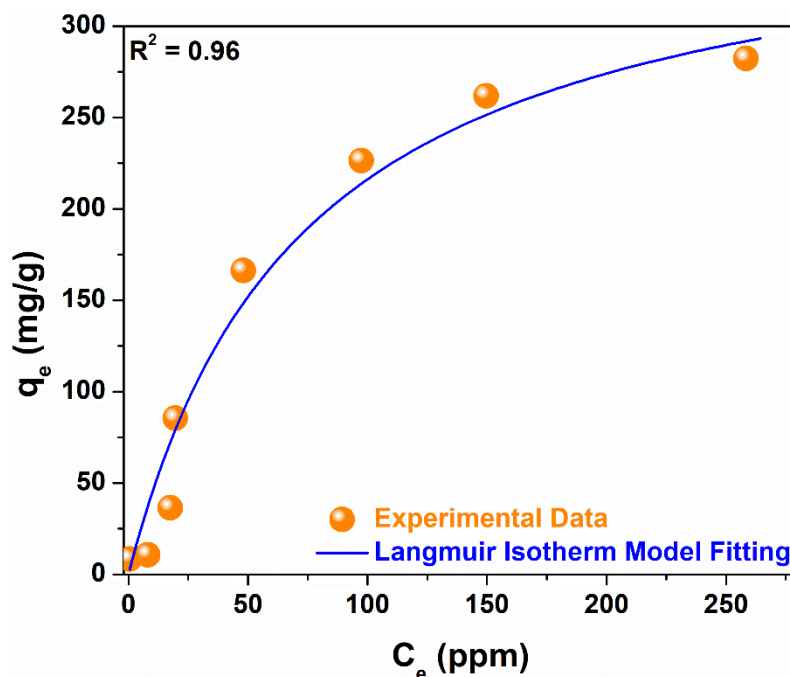
Appendix Figure 5.22. Change in concentration Of Se (VI) with time.



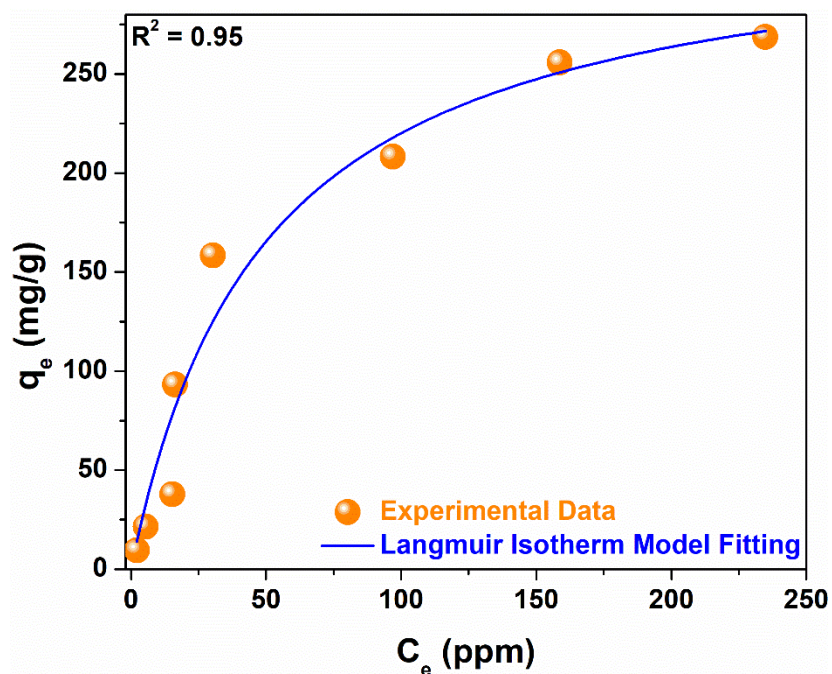
Appendix Figure 5.23. Langmuir linear fitting model for Se (VI) sorption.



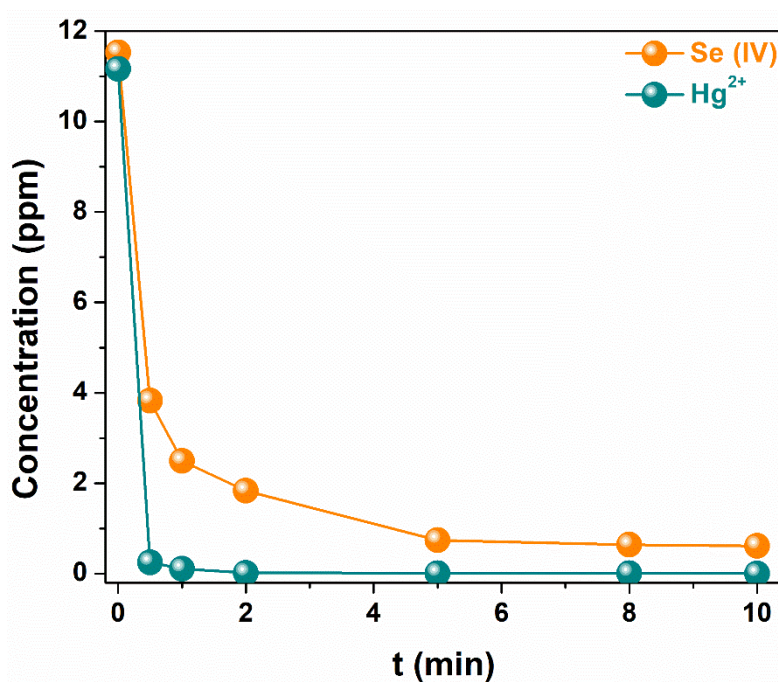
Appendix Figure 5.24. Langmuir isotherm model for Se (VI).



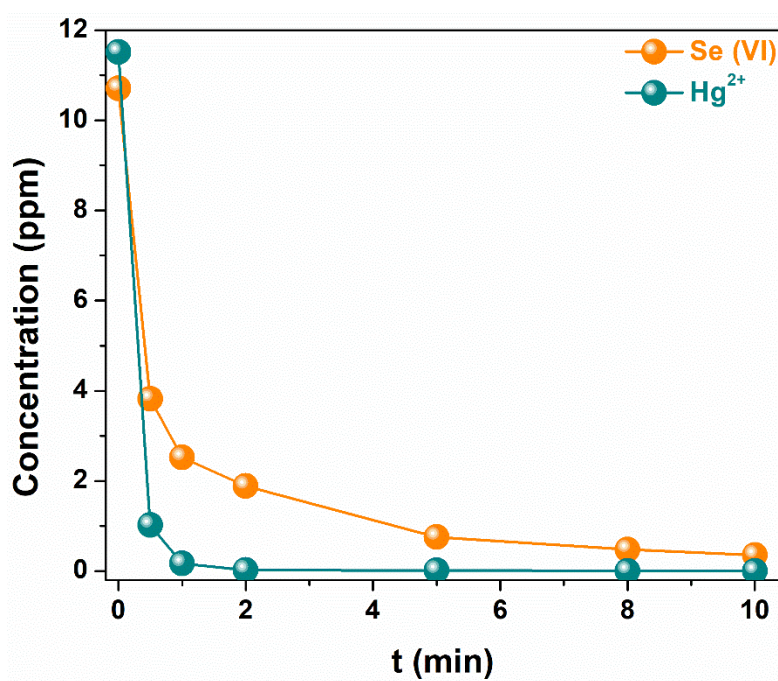
Appendix Figure 5.25. Langmuir isotherm model for Se (IV) with 200 ppm Hg^{2+} .



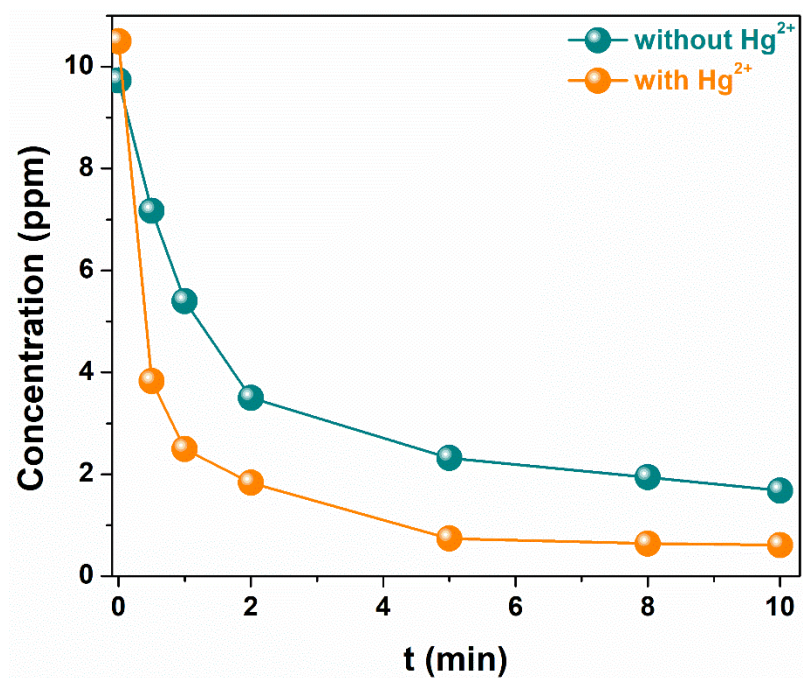
Appendix Figure 5.26. Langmuir isotherm model for Se (VI) with 20 ppm Hg^{2+} .



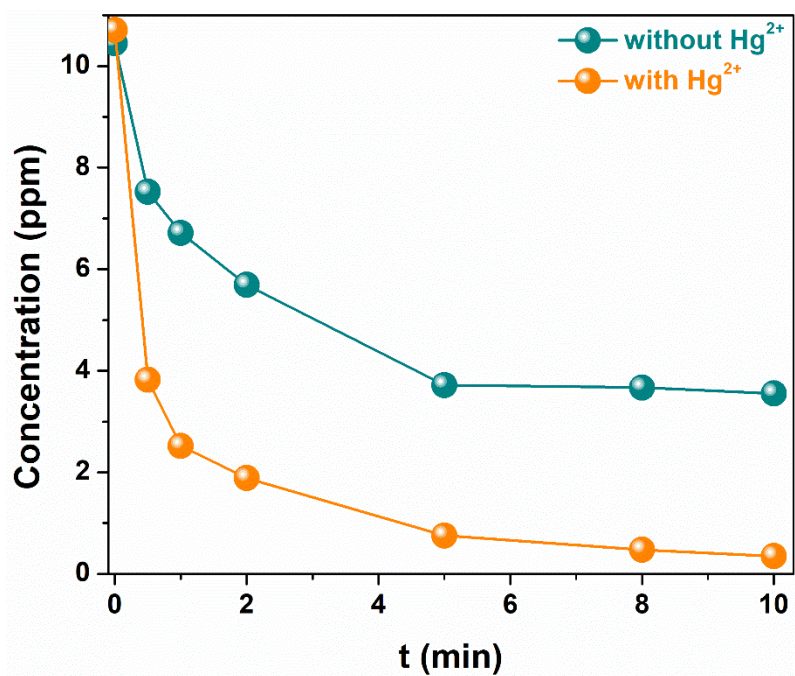
Appendix Figure 5.27. Simultaneous change in concentration Of Se (IV) & Hg²⁺ with time.



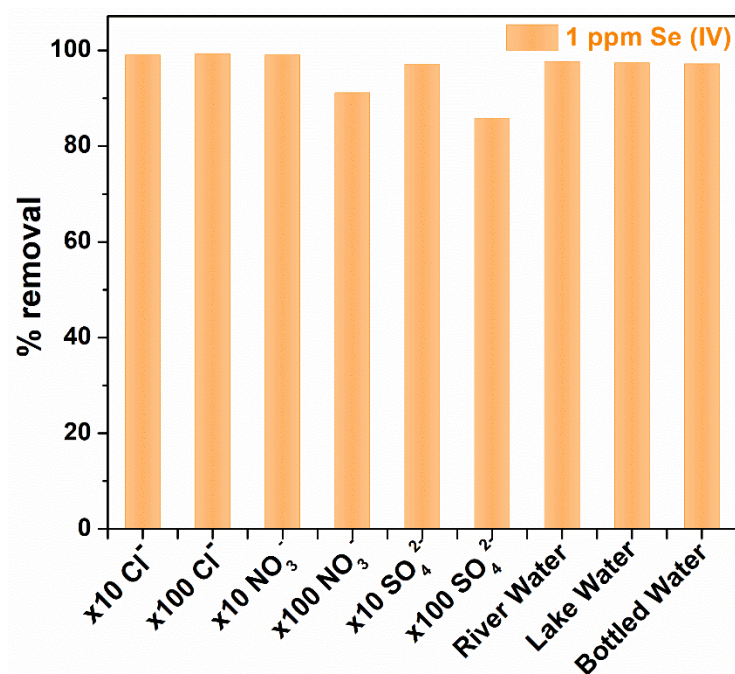
Appendix Figure 5.28. Simultaneous change in concentration Of Se (VI) & Hg²⁺ with time.



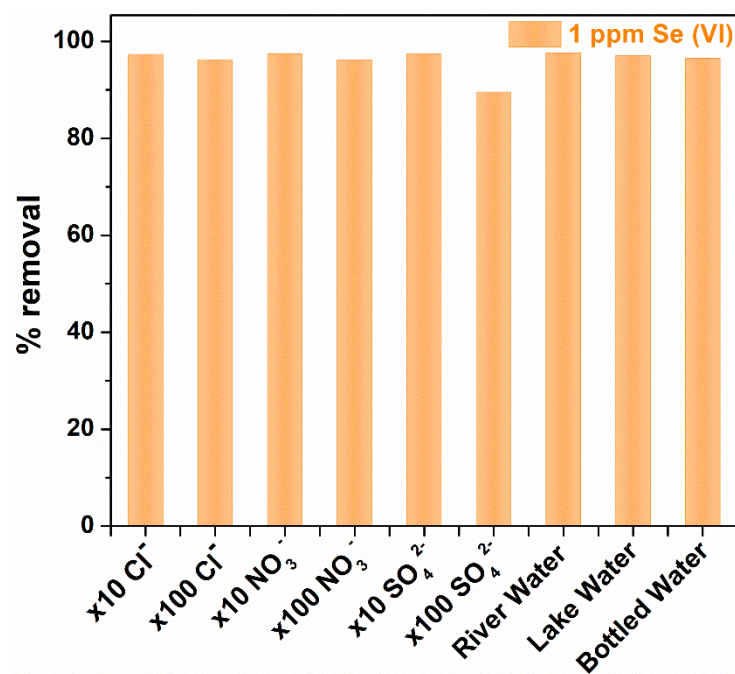
Appendix Figure 5.29. Change in concentration Of Se (IV) with & without Hg²⁺ with time.



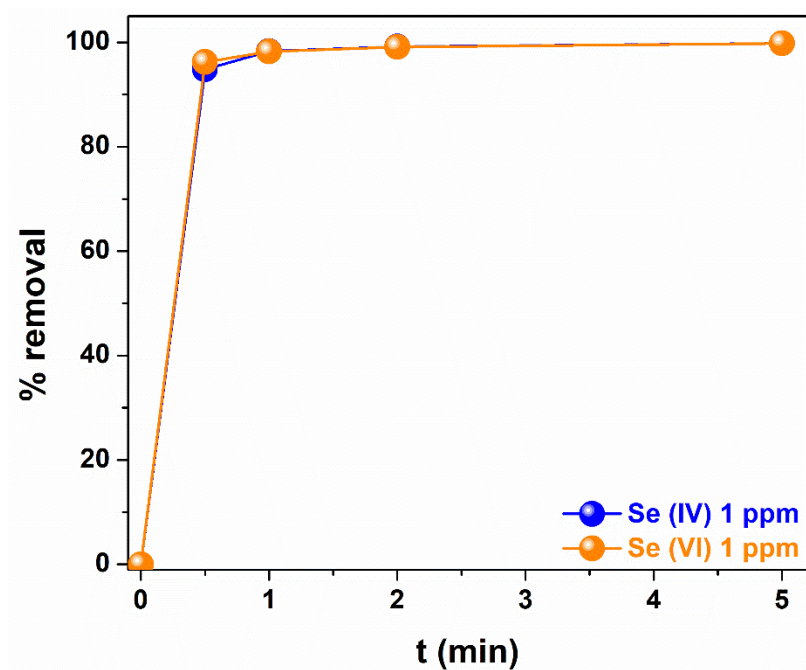
Appendix Figure 5.30. Change in concentration Of Se (VI) with & without Hg²⁺ with time.



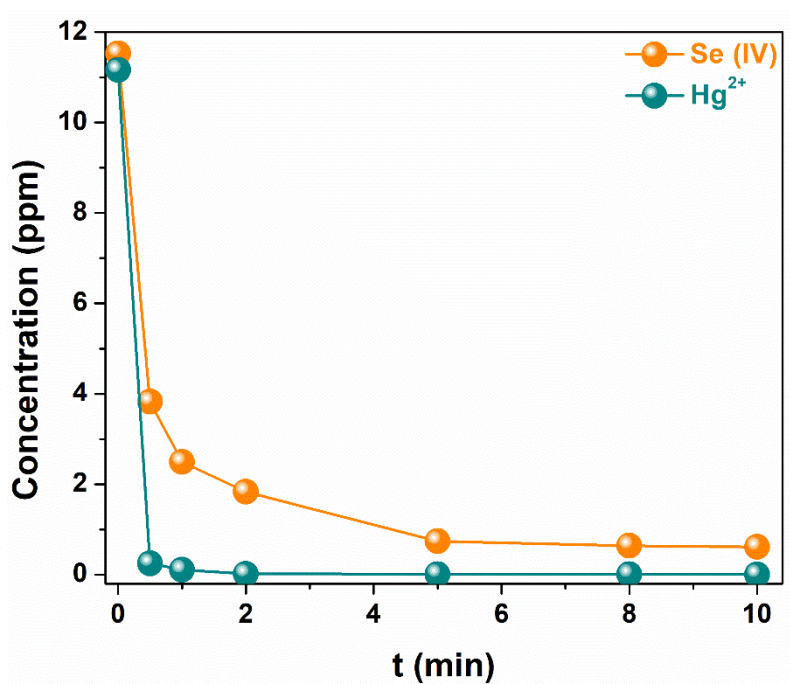
Appendix Figure 5.31. Selectivity study of Se (IV) by mPOP@MoS₄²⁻.



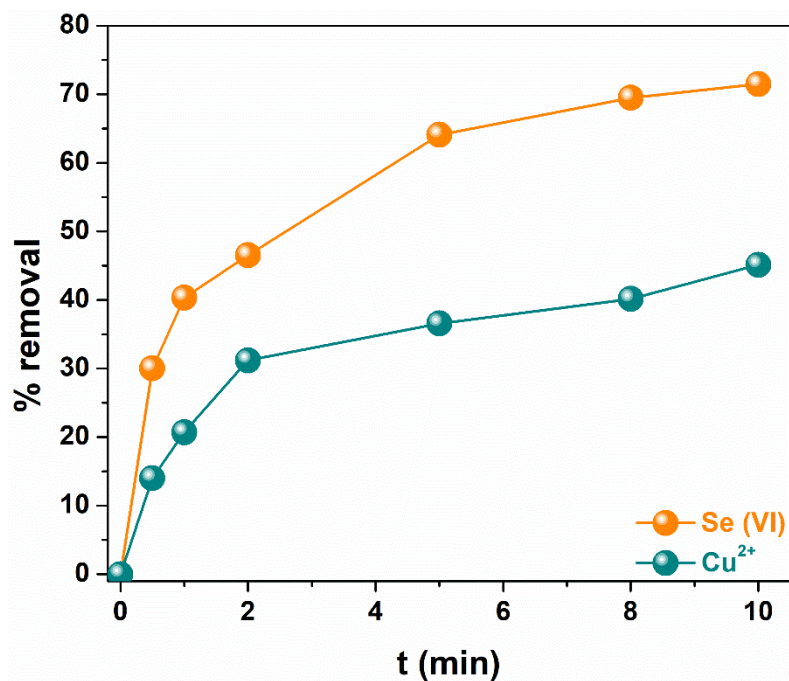
Appendix Figure 5.32. Selectivity study of Se (VI) by mPOP@MoS₄²⁻.



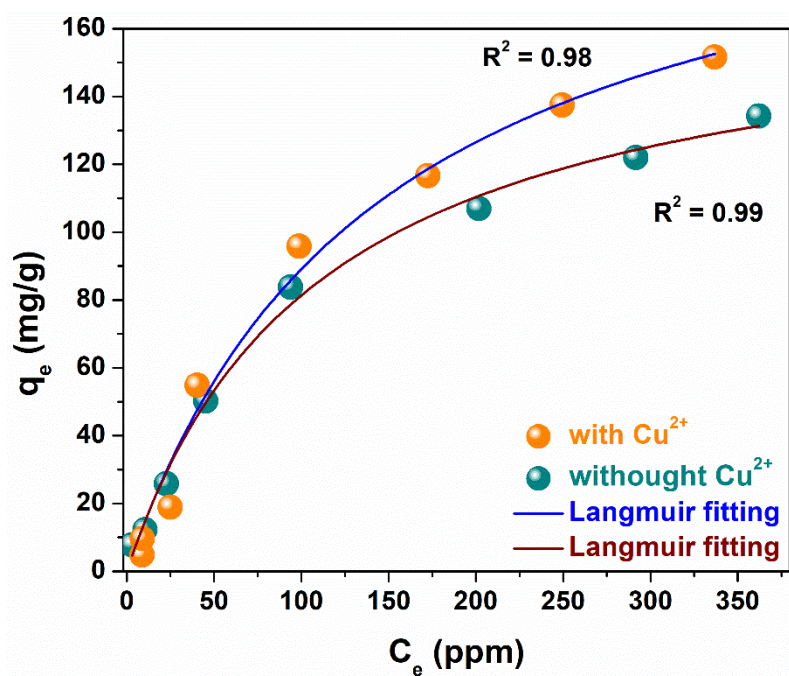
Appendix Figure 5.33. Low concentration (1ppm) Kinetics of Se (IV) & Se (VI) by mPOP@MoS₄²⁻.



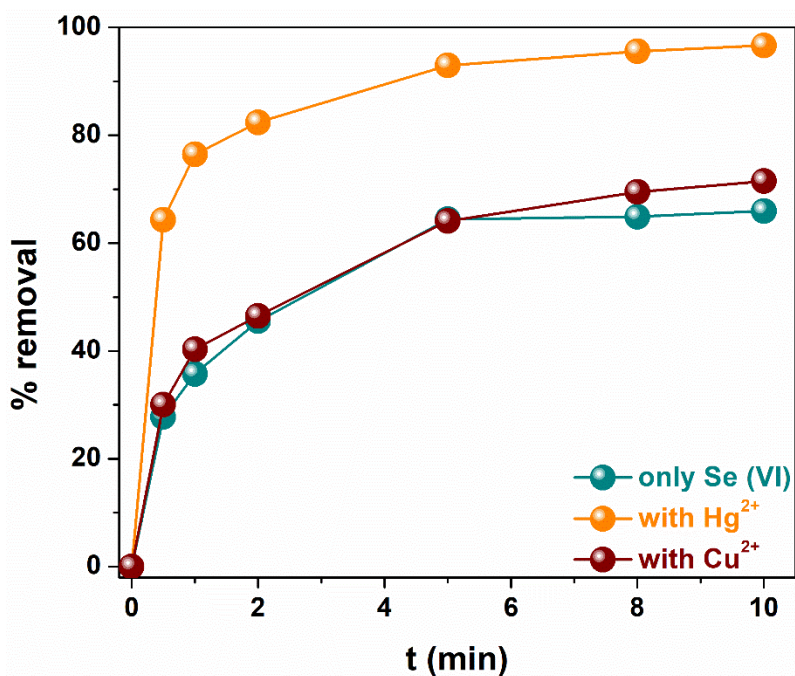
Appendix Figure 5.34. Simultaneous change in concentration Of Se (IV) & Hg²⁺ with time.



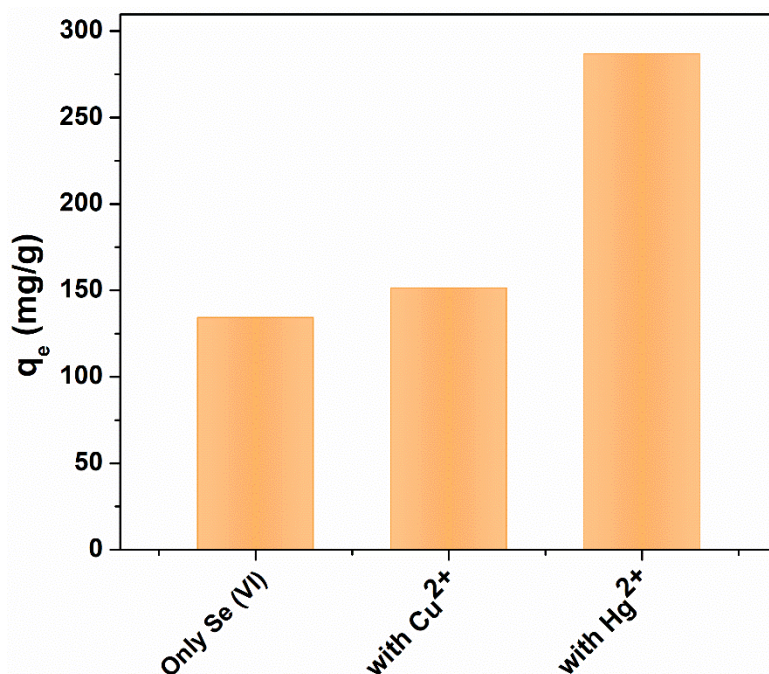
Appendix Figure 5.35. Sorption kinetics curves for Cu²⁺ (10 ppm) and Se (VI) (10 ppm) during Cu/Se coadsorption.



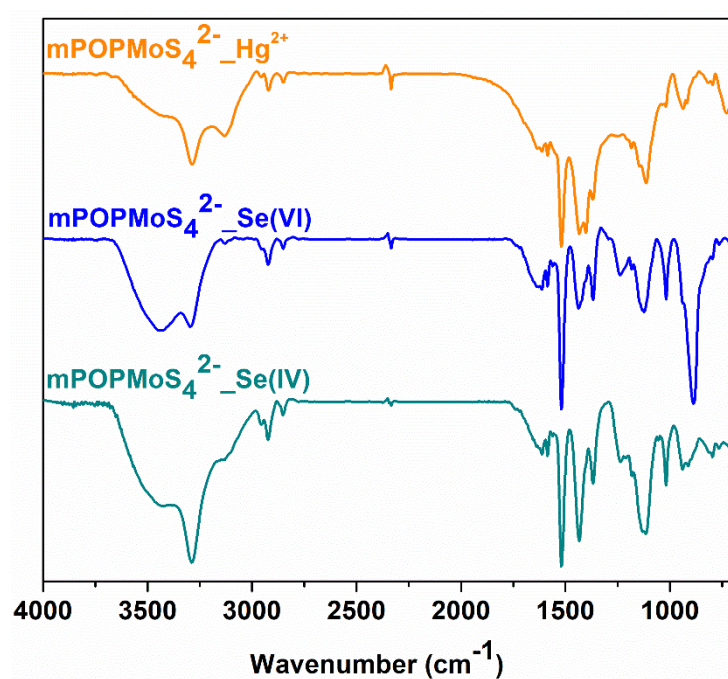
Appendix Figure 5.36. Sorption isotherms for Se (VI) with and without 20 ppm of Cu²⁺ by mPOP@Mos₄²⁻



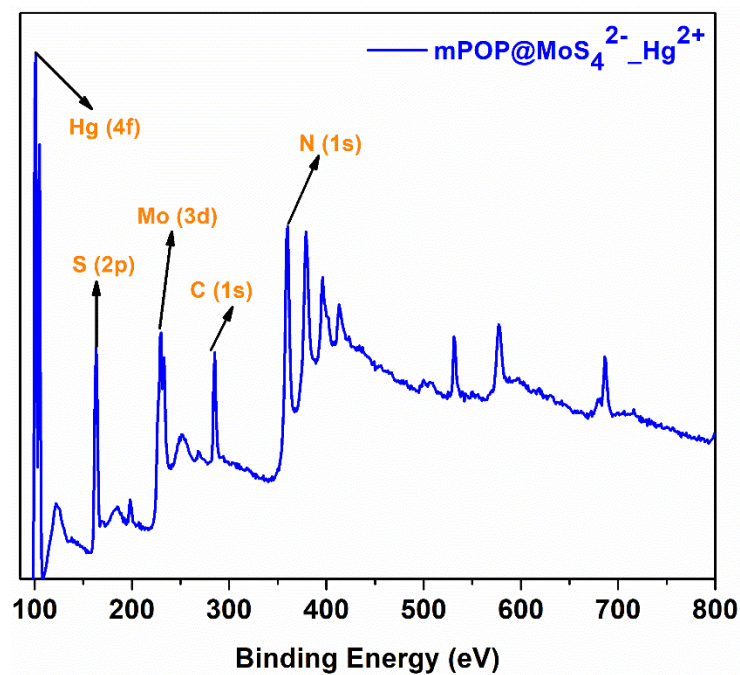
Appendix Figure 5.37. Kinetics comparison with individual Se (VI), with 20 ppm Hg²⁺ & 20 ppm Cu²⁺.



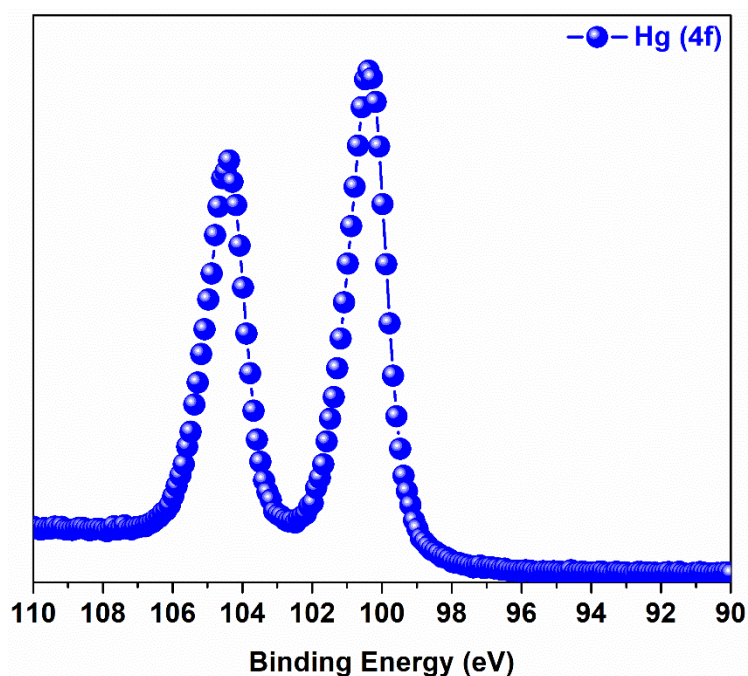
Appendix Figure 5.38. Uptake capacity for individual Se (VI), with 20 ppm Hg²⁺ & 20 ppm Cu²⁺.



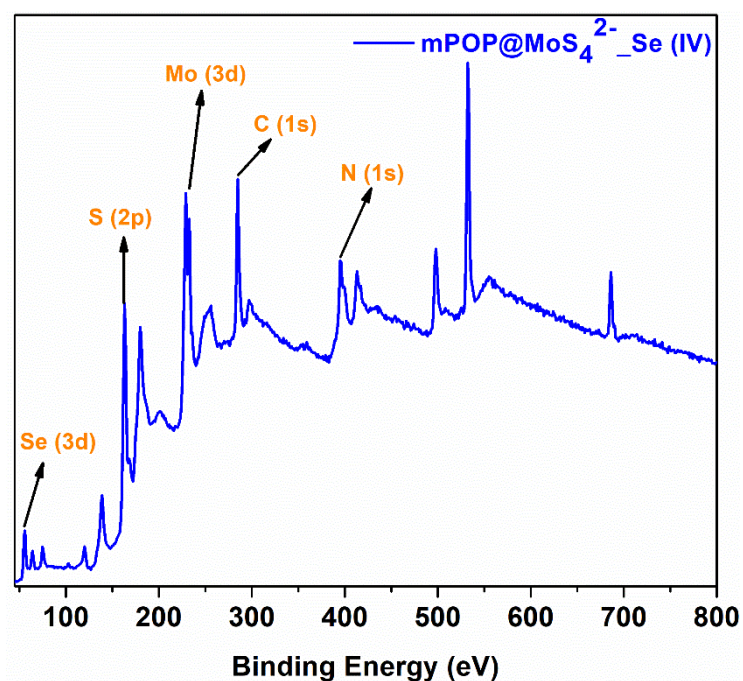
Appendix Figure 5.39. FT-IR spectra of mPOP@MoS_4^{2-} after Se (IV) (cyan), Se (VI) (blue) & Hg^{2+} (orange) adsorption.



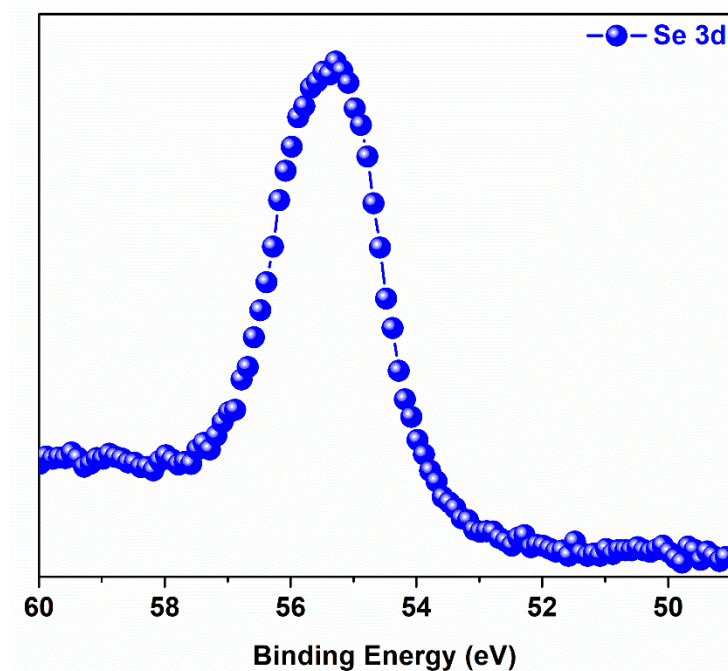
Appendix Figure 5.40. XPS survey scan of mPOP@MoS_4^{2-} after Hg^{2+} adsorption.



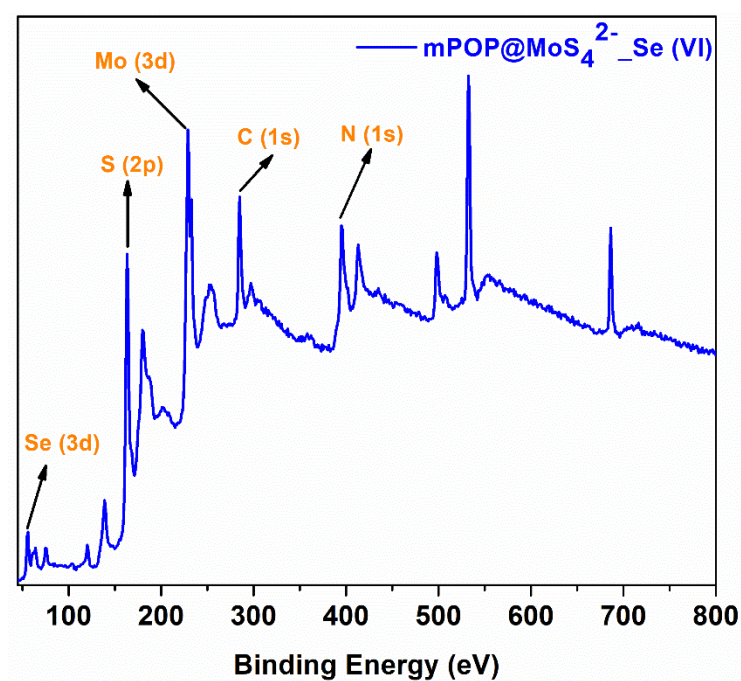
Appendix Figure 5.41. Hg (4f) XPS spectrum of mPOP@MoS_4^{2-} after Hg^{2+} adsorption.



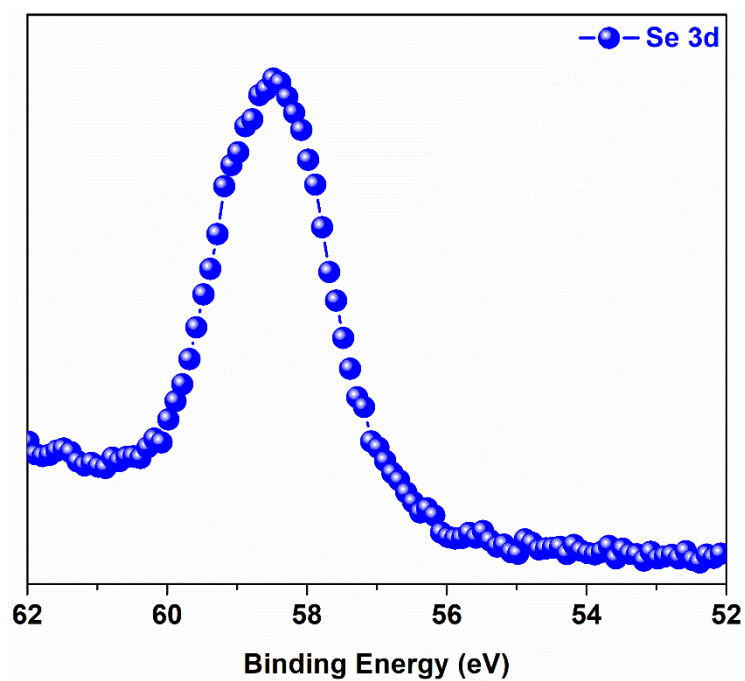
Appendix Figure 5.42. XPS survey scan of mPOP@MoS_4^{2-} after Se (IV) adsorption.



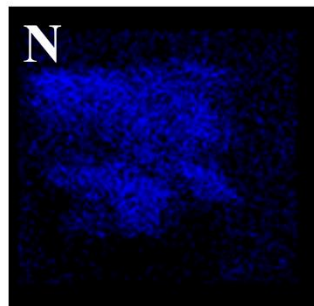
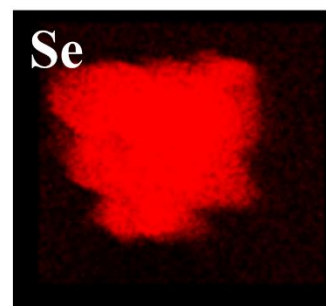
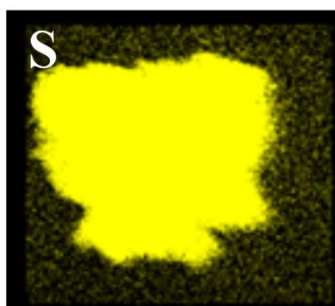
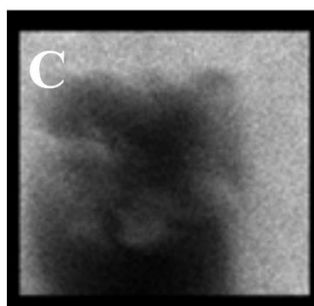
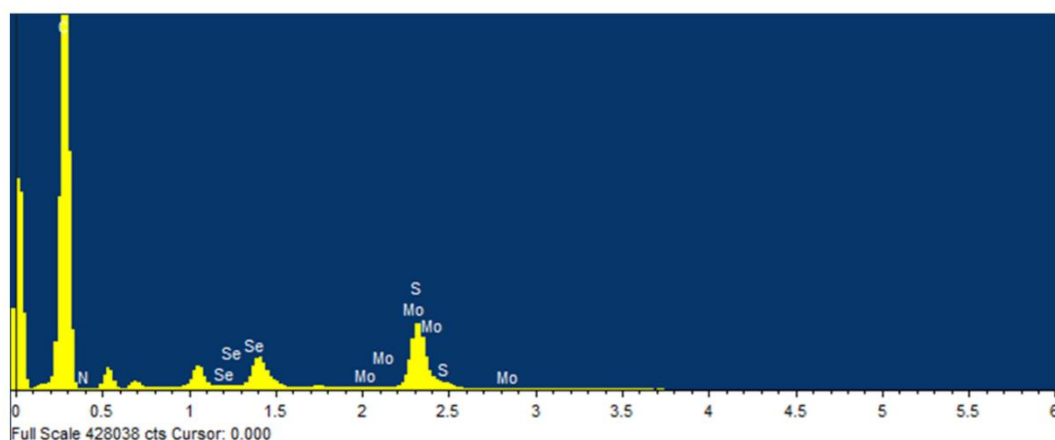
Appendix Figure 5.43. Se 3d XPS spectrum of mPOP@MoS₄²⁻ after Se (IV) adsorption.



Appendix Figure 5.44. XPS survey scan of mPOP@MoS₄²⁻ after Se (VI) adsorption.

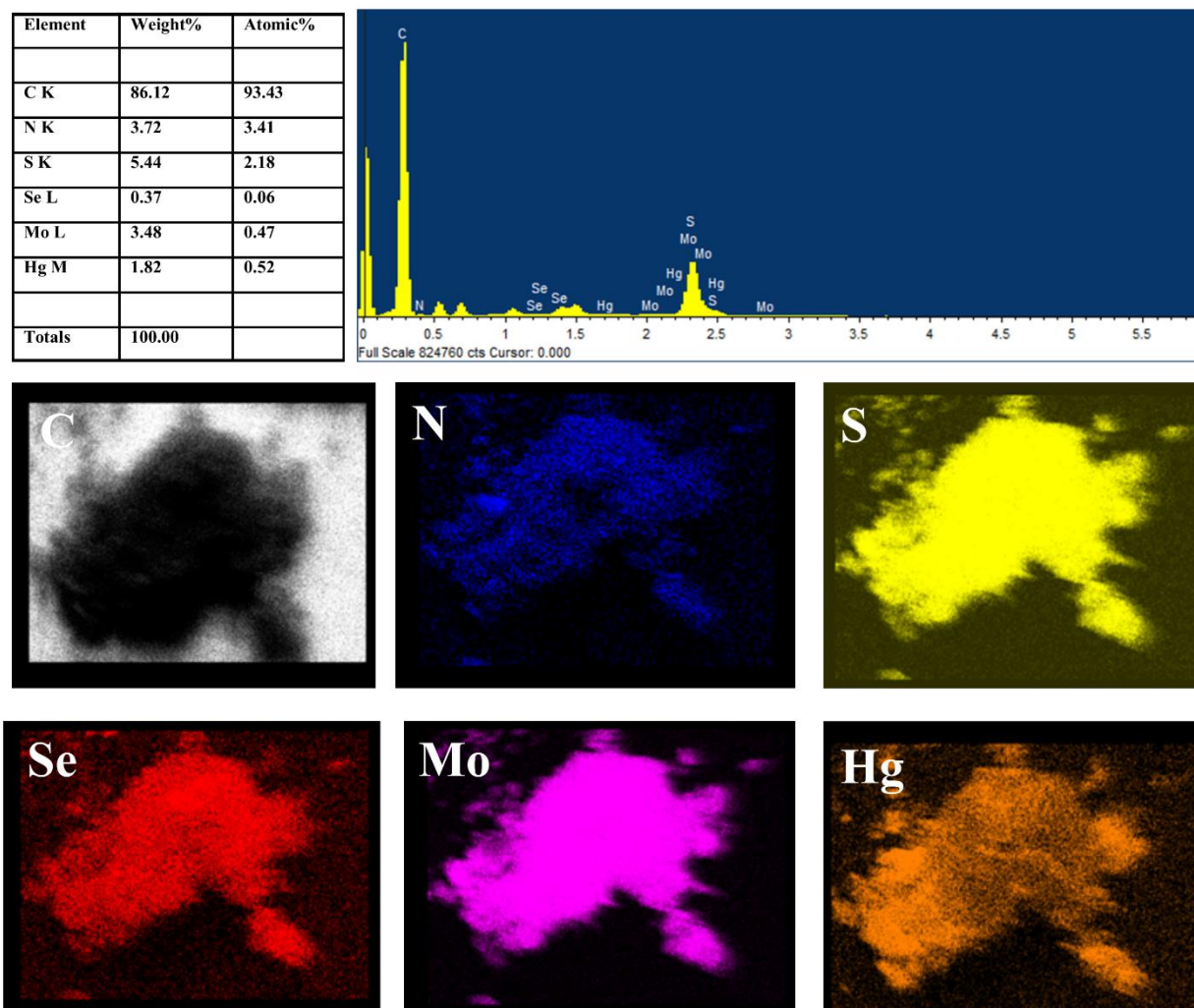


Appendix Figure 5.45. Se 3d XPS spectrum of mPOP@MoS₄²⁻ after Se (VI) adsorption.



Element	Weight%	Atomic%
C K	89.75	97.06
N K	0.38	0.36
S K	4.32	1.75
Se L	2.74	0.45
Mo L	2.82	0.38
Totals	100.00	

Appendix Figure 5.46. Elemental mapping and EDS spectra of mPOP@MoS₄²⁻ after Se (VI) adsorption.



Appendix Figure 5.47. Elemental mapping and EDS spectra of mPOP@MoS₄²⁻ after Se (VI) & Hg²⁺ adsorption.

Appendix Table 1: Comparison of the Se(IV) sorption capacities of mPOP@MoS₄²⁻ with those of other state-of-the-art sorbents:

Sorbent	Capacity (mg/g)	Equilibrium time	pH	Selectivity	Reference
MgAl-MoS ₄ -LDH	294	24 h	6-9	NA	<i>J. Am. Chem. Soc.</i> , 2017 , 139, 12745–12757.
Thiourea-formaldehyde (TUF) Resin	833.3	78 h	<1	NA	<i>J. Appl. Polym. Sci.</i> , 2011 , 122, 1134–1141.
HMBA incorporated into mesoporous inorganic silica	93.56	40 min	1.5	vs. various anions	<i>Sensors Actuators, B Chem.</i> , 2015 , 209, 194–202.
Mg–Al–CO ₃ layered double hydroxide	160	NA	5-8.5	NA	<i>J. Mater. Chem. A</i> , 2014 , 2, 15995-16007.
NU-1000	102	<1 min	6	NA	<i>J. Am. Chem. Soc.</i> , 2015 , 137, 7488–7494.
MOF-808	133	5 min	NA	NA	<i>CrystEngComm</i> , 2018 , 20, 6140–6145.
BUT-MOF	270	3 min	1-10	vs. NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , HCO ₃ ⁻	<i>J. Mater. Chem. A</i> , 2021 , 9, 3379-3387
ET-MOF	234	-	-	vs. NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , HCO ₃ ⁻	<i>J. Mater. Chem. A</i> , 2021 , 9, 3379-3387
PROP-MOF	259	-	-	vs. NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , HCO ₃ ⁻	<i>J. Mater. Chem. A</i> , 2021 , 9, 3379-3387
SBUT-MOF	210	-	-	vs. NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , HCO ₃ ⁻	<i>J. Mater. Chem. A</i> , 2021 , 9, 3379-3387
Y ₂ (OH) ₅ Cl·1.5H ₂ O	207	5 h	7-9	vs. NO ₃ ⁻ , Cl ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , HPO ₄ ²⁻	<i>Environ. Sci. Technol.</i> , 2017 , 51, 8606–8615.
mPOP@MoS₄²⁻	286.8	2 min	7	Vs Cl⁻, NO₃⁻, SO₄²⁻	This work

Appendix Table 2: Comparison of the Se(VI) sorption capacities of mPOP@MoS₄²⁻ with those of other state-of-the-art sorbents:

Sorbent	Capacity (mg/g)	Equilibrium time	pH	Selectivity	Reference
Thiourea-formaldehyde (TUF) Resin	526.3	78 h	< 0	NA	<i>J. Appl. Polym. Sci.</i> , 2011 , 122, 1134–1141
H ⁺ -diaminofunctionalized MCM-41	123	10 h	6.5	Vs NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻	<i>Bull. Chem. Soc. Jpn.</i> , 2003 , 76, 2225–2232.
Fe ³⁺ - diamino-functionalized MCM-41	117	10 h	6.5	Vs NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻	<i>Sensors Actuators, B Chem.</i> , 2015 , 209, 194–202.
Mg–Al–CO ₃ layered double hydroxide	90	NA	5-8.5	NA	<i>J. Mater. Chem. A</i> , 2014 , 2, 15995–16007.
Polyamine-type Ion Exchange Resin (Eporasu K-6)	243	<1 min	3 h	NA	<i>Sep. Sci. Technol.</i> , 2007 , 42, 3155–3167
NU-1000	62	5 min	NA	NA	<i>CrystEngComm</i> , 2018 , 20, 6140–6145.
MOF-808	118	5 min	NA	NA	<i>CrystEngComm</i> , 2018 , 20, 6140–6145.
Y ₂ (OH) ₅ Cl·1.5H ₂ O	124	5 h	7-9	vs. NO ₃ ⁻ , Cl ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , HPO ₄ ²⁻	<i>Environ. Sci. Technol.</i> , 2017 , 51, 8606–8615.
UiO-66	34.3	>10h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
UiO-66-HCl	86.8	5h	3-7	vs. NO ₃ ⁻	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
UiO-66-Ac	45.6	10h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
UiO-66-36Dif	55.1	10h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
UiO-66-12Trif	62.9	5h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
UiO-66-36Trif	70.8	10h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.
NU-1000	78.8	<3h	6.8	-	<i>Chem. Eng. J.</i> , 2017 , 330, 1012–1021.

iMOF-1C	100	60 min	6.8	vs. various anions	<i>Angew. Chemie - Int. Ed.</i> , 2020 , 59, 7788–7792
mPOP@MoS ₄ ²⁻	268.1	2 min	7	Vs Cl⁻, NO₃⁻, SO₄²⁻	This work

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Chapter 6

Summary and Perspectives

6.1 Summary and Perspectives

Porous organic polymers (POPs) have earned tremendous research attention as class of advanced porous materials (APMs) 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 POPs. 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. 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 section of the thesis work focuses on rational design of ultra-stable & low density high performance POP based nanotraps to segregate toxic and hazardous water contaminants. In this regard, a magnetically separable cationic porous polymer composite was employed to capture several organic micropollutants from water with fast kinetics and high capacity. Following this, nature inspired Hg-Se antagonism was exploited to harness biological antagonism triggered water detoxification in a cationic macroporous polymer. Thus developed material was utilized in swift and efficient removal of Hg^{2+} and Se (IV)/Se (VI) from water. Interestingly, simultaneous capture of these toxic pollutants was also achieved where enhanced performance of selenium oxy-anions were observed in presence of Hg^{2+} . Exceptional uptake capacity along with admirable performance in trace amount capture as well as real world samples advocated the sorbent's competency. This study highlights one of the rare examples of trapping both cationic & anionic contaminants in a cationic sorbent material.

Strategic design and syntheses of materials that combine the advantages of structural robustness, function-led design and enhanced performance is a key take-away of the current thesis work. In addition, a major pitfall of powder materials in terms of Processability is addressed through different composite preparation such as beads and aerogels. The importance of judicious structural modifications is also punctuated by fabricating three different functional polymer composites from the same parent polymer to be applied in distinct applications with excellent potency. The crux of all the scientific works carried out in this thesis has been rendering task-specific functionality aimed at target-specific applications. Imparting iconicity in POPs can work as a boon but still remain less explored and require more research. Also, working on performance retention under operational conditions in the long run as well as cost-effective scalability is very important and needs significant attention. Thus, the next few years hold great promise for researchers to build on and contribute in developing task-specific POPs to address important industrial & environmental concerns.

Research Publications

([†] - indicates equal contribution)

Included in Thesis:

1. Palladium anchored N-Heterocyclic Carbene in a Porous Organic Polymer (POP): An Efficient Heterogeneous Composite Catalyst for Eco-Friendly C-C Coupling.
Sumanta Let,[†] Gourab K. Dam,[†] Sahel Fajal, Partha Samanta, Subhajit Dutta and Sujit K. Ghosh.
J. Org. Chem. **2022**, 87, 24, 16655–16664.
2. All Organic Porous Heterogeneous Composite with Antagonistic Sites as Cascade Catalyst for Continuous Flow Reaction.
Sumanta Let, Gourab K. Dam, Sahel Fajal and Sujit K. Ghosh.
(*Manuscript under revision*).
3. Magnetic Nanoparticle-Embedded Ionic Microporous Polymer Composite as an Efficient Scavenger of Organic Micropollutants.
Sumanta Let, Subhajit Dutta, Partha Samanta, Shivani Sharma and Sujit K. Ghosh.
ACS Appl. Mater. Interfaces, 2021; 13, 51474–51484.
4. Harnessing bio-inspired antagonism in a charged macroporous organic polymer toward enhanced pollutant segregation from water.
Sumanta Let, Sahel Fajal, Writakshi Mandal and Sujit K. Ghosh.
(*Manuscript under Preparation*).

Not Included in Thesis:

5. A Dye@MOF Composite as Luminescent Sensory Material for Selective and Sensitive Recognition of Fe (III) ions in Water.
Sumanta Let, Partha Samanta, Subhajit Dutta and Sujit K. Ghosh.
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6. A Luminescent Water-Stable Cationic MOF for Bimodal Recognition of Cr (VI) and As (V & III) Oxo-anions in Water.
Subhajit Dutta,[†] **Sumanta Let,**[†] Mandar M. Shirolkar, Aamod V. Desai, Partha Samanta, Sahel Fajal, Yogeshwar D. More and Sujit K. Ghosh.
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7. A Crown tethered Porous Organic Polymer (POP) as a Heterogeneous Triphasic Phase Transfer Catalyst.
Sumanta Let, Gourab K. Dam and Sujit K Ghosh.
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8. A Crown Ether Integrated Porous Organic Polymer (POP) toward Efficient Cs & Sr sequestration from Radioactive-waste.
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(*Manuscript under Preparation*).
9. Rapid, selective capture of toxic oxo-anions of Se (IV), Se (VI) and As(V) from water by an ionic metal-organic framework (iMOF).
Shivani Sharma, **Sumanta Let**, Aamod V. Desai, Subhajit Dutta, Gopalsamy Karuppasamy, Mandar M. Shirolkar, Ravichandar Babarao and Sujit K. Ghosh.
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Gourab K. Dam, Sahel Fajal,[†] Subhajit Dutta,[†] **Sumanta Let**, Aamod V. Desai and Sujit K. Ghosh.
ACS Appl. Opt. Mater., **2023** (Just accepted).



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Evolution of porous materials from ancient remedies to modern frameworks

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Palladium-Anchored N-Heterocyclic Carbenes in a Porous Organic Polymer: A Heterogeneous Composite Catalyst for Eco-Friendly C–C Coupling



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Magnetic Nanoparticle-Embedded Ionic Microporous Polymer Composite as an Efficient Scavenger of Organic Micropollutants

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Palladium-Anchored N-Heterocyclic Carbenes in a Porous Organic Polymer: 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*



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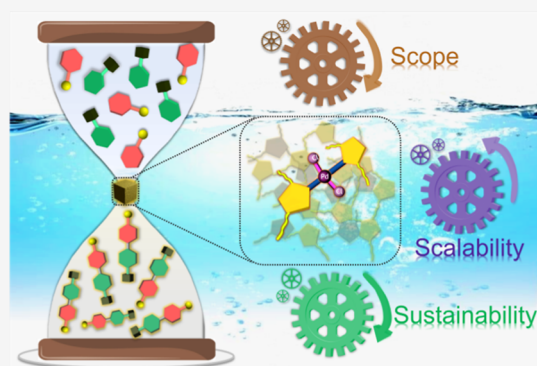


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Supporting Information

ABSTRACT: Aggregation-induced catalyst deactivation during the reaction in supported metal catalysts prevails as one of the pitfalls toward their practical implementation. Herein, a homogeneously dispersed palladium-coordinated N-heterocyclic carbene (NHC) was strategically integrated inside a microporous hyper-cross-linked polymer via post-synthesis structural modulation. Successful immobilization of spatially isolated Pd (II) units onto the polymer scaffold yielded highly robust heterogeneous catalysts 120-MI@Pd NHC and 120-EI@Pd NHC, respectively. 120-EI@NHC Pd (4.41 wt % Pd) illustrated a remarkable catalytic potency (yield up to >99%) toward the eco-friendly Suzuki–Miyaura coupling (SMC) reaction at room temperature. The superior catalytic efficiency of 120-EI@Pd NHC is further highlighted from its excellent functionality tolerance over 42 substrates bearing electronic diversity and a turnover frequency value reaching up to $4.97 \times 10^3 \text{ h}^{-1}$ at a very low catalyst dosage of 0.04 mol %. Pertaining to heterogenization, the polymer catalyst could be easily reused with intact catalytic efficiency for at least 10 cycles. The catalytic competence of 120-EI@NHC Pd in terms of scope, scalability, and sustainability advocates its proficiency, while processability was achieved by crafting 3D aerogel monoliths. The conceptual feasibility was further investigated by devising a cup-based nano-reactor with gram-scale product isolation over three catalytic cycles.



INTRODUCTION

The present-day life is unthinkable without catalysis which has come forth as an indispensable technology toward the fundamental requisites of life such as energy, food, and water. Catalysis lies at the very heart of chemical products and the industries thereof constituting a rudimentary branch of contemporary scientific research with tremendous importance and conceptual bottlenecks.¹ With thriving economy and an upsurge in global population together with downsizing of raw materials, manufacturing via a more sustainable and greener approach is of paramount importance where catalysis has a pivotal role to play. This is further punctuated in the 9th principle of green chemistry stated as “Catalytic reagents, as selective as possible, are superior to stoichiometric reagents”.² Organometallic catalysis using metal-containing complexes to drive an organic transformation has become a significant area of research in organic chemistry. In particular, the Suzuki–Miyaura coupling (SMC) reaction, since its inception in 1979, has emerged as one of the potent, versatile, and straightforward methodologies for crafting carbon–carbon (C–C) bonds and has intrigued both industry and academia.^{3–6} Over the years, the SMC reaction has been successfully employed toward the selective construction of C–C bonds in pharmaceuticals, natural product synthesis, materials science, supramolecular chemistry, as well as various advanced functional materials.^{7–12}

Hitherto, in recent times, numerous palladium-based (Pd) homogeneous catalysts inclusive of palladium chloride along with palladium–phosphine complexes, ancillary ligands such as N-containing complexes, N-heterocyclic carbenes (NHCs), acyclic diaminoboranes (ADCs) as well as bipyridines have been documented for the SMC reaction.^{13–18} These catalysts usually proceed efficiently in harmful organic solvents under inert conditions. In general, homogeneous catalytic systems furnished with uniform and systematic active sites display quality performance, excellent yields, and great selectivity along with a high turnover frequency (TOF).^{19,20} However, utilization of costly ligands, complexity in the isolation of the catalyst and product, and metal leaching combined with toxic Pd contamination in the reaction products have greatly muted their application in academia and chemical industry.^{21,22} To circumvent these impediments, substantial efforts have been made worldwide in developing heterogeneous Pd-based catalysts. Palladium immobilization onto the insoluble support

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Magnetic Nanoparticle-Embedded Ionic Microporous Polymer Composite as an Efficient Scavenger of Organic Micropollutants

Sumanta Let, Subhajit Dutta,[§] Partha Samanta,[§] Shivani Sharma, and Sujit K. Ghosh*

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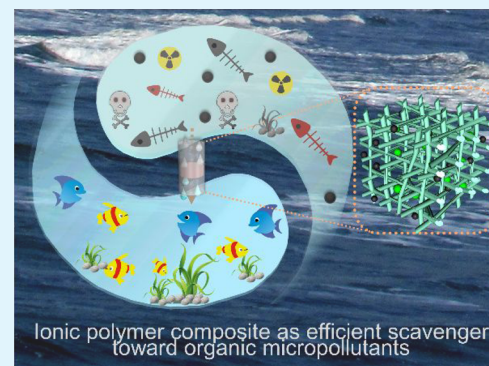
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Supporting Information

ABSTRACT: A cationic microporous composite polymer (120-TMA@Fe) bearing free exchangeable chloride anions alongside easy magnetic separation was crafted through post-polymerization structure modulation. The precursor polymer 120-Cl was synthesized via an “external cross-linking” strategy in a straightforward one-pot Friedel–Crafts reaction. Subsequently, a cationic network accommodating magnetic Fe₃O₄ nanoparticles, viz., 120-TMA@Fe was fabricated through chemical modifications. 120-TMA@Fe displayed excellent adsorption proficiency both in terms of rapid kinetics and maximum uptake capacity when screened for a wide range of organic micropollutants of various categories. Amongst the tested pollutants, including anionic dyes, aromatic models, plastic components, and pharmaceuticals, 120-TMA@Fe illustrated exceptional performance in removing all of these model pollutants with adsorption equilibrium reaching within only 5 min. The Langmuir adsorption isotherm model determined the theoretical maximum uptake capacity ($q_{\text{max,e}}$) of 120-TMA@Fe to be 357 mg g^{−1} for methyl orange dye, 555 mg g^{−1} for plasticizer bisphenol A, and 285 mg g^{−1} for antibiotic ibuprofen. Additionally, 120-TMA@Fe showed unaltered performance upon harsh chemical treatment as well as in complex real-world samples. The potency of 120-TMA@Fe was further supported by its outstanding regeneration performance up to 10 cycles.

KEYWORDS: composite polymer, organic micropollutant, uptake capacity, adsorption, regeneration



INTRODUCTION

Environmental pollution, by definition, is the accumulation of any contaminant, either in the form of a substance or energy, at a faster kinetics than its decomposition or dilution into nontoxic products.¹ The gravity of environmental pollution and its after effects are so appalling that unrestricted access to clean freshwater along with good health and well-being features as the sustainable development goals of the United Nations.² In particular, water pollution has grown into a genuine concern for the global population and has attracted consequential research interest worldwide.^{3–5} Recognizing this issue, the World Health Organization (WHO) reckons that 3 billion people around the globe lack access to safe drinking water.⁶ Organic micropollutants, a myriad array of molecules comprising organic dyes, pharmaceuticals, hormones, pesticides, and industrial chemicals, are dominant contributors toward water pollution.^{7,8} Of 100,000 commercially available dyes having a production rate over 7×10^5 tons annually, around 2% are discharged into various water bodies.⁹ Many, amongst these micropollutants, especially aromatic molecules, are biologically nondegradable and can have detrimental effects on the environment, aquatic ecosystem, and human health even when present at negligible concentrations owing to their mutagenic as well as carcinogenic nature.^{10,11} Additionally, there are organic micropollutants identified to be endocrine

disruptors, while several others can cause severe aesthetic complications well as chronic toxicity when enriched in surplus amounts in humans and animals.^{12,13} On the other hand, categorically nonsteroidal anti-inflammatory drugs (NSAIDs) as anti-inflammatory and analgesic remain amongst the most prominently used pharmaceuticals. Statistically, a study implemented by the U.S. Department of Health and Human Services under The National Health Interview Survey disclosed that nearly 72 million adults (31.1% of U.S. population) conform to the regular usage of NSAIDs in 2010, accounting for a 40% increase after 2005.¹⁴ Furthermore, the large-scale and increasing production of NSAIDs with ever-increasing consumption intensifies the discharge of these pharmaceuticals, the aftermath being the continuous documentation of the emergence of these materials in various water bodies, for example, groundwater, surface water, and sewage water.^{15,16} As a result, the accumulation of these leaked NSAIDs known as “emerging pollutants” could prove poisonous toward the

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