

**Advanced Porous Materials for Environmentally
Relevant Toxic Pollutants Detection and
Sequestration**

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

A thesis submitted in partial fulfilment of the requirements of the
degree of Doctor of Philosophy

द्वारा / By
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शोध प्रबंध पर्यवेक्षक: प्रो. सुजीत के. घोष
/ Thesis Supervisor: Prof. Sujit K. Ghosh



भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे
INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2023

Dedicated to

Maa, Baba

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-Writakshi Mandal



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

Certificate

It is hereby certified that the work described in this thesis entitled “*Design, Syntheses and Functional Studies of Advanced Porous Materials for Environmentally Relevant Toxic Pollutants Detection and Sequestration*” submitted by *Ms. Writakshi Mandal* 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: 20/09/2023

A handwritten signature in black ink, likely belonging to Dr. Sujit K. Ghosh, positioned above a horizontal line.

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Declaration

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

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Writakshi Mandal

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6. Summery and Perspectives

Synopsis

The prime motivation of our research work which are included in the thesis is to design and synthesize of functional porous materials for the remediation of toxic water pollutants. In the field of porous materials metal-organic framework (MOFs), porous organic polymer (POPs) and lately evolved covalently linked porous organic material (covalent-organic frameworks (COFs)) and hybrid composite materials have seen immense progress in recent years. Due to large surface area, pore functionality and tuneable pore surface etc. porous materials have become one of the pioneer in the field of material science. Porous materials have wide range of applications in the field of gas and solvent separation, gas storage, heterogeneous catalysis, adsorption of pollutants, recognition of small molecules, drug delivery etc. In my thesis work I have demonstrated both recognition of toxic water pollutant by porous materials (MOF and POP) as well as sequestration of toxic heavy metal-based oxoanions and radioactive oxo-pollutants from water/nuclear waste by porous framework materials (ionic POP (iPOP) and hybrid composite materials).

Chapter 1. Introduction

In this section a brief discussion about porous materials, including metal-organic framework (MOF), porous organic polymer (POP), covalent organic framework (COF), metal-organic cage (MOC), hybrid composite and their various potential applications are included. Different classification of MOFs, COFs, MOCs and POPs have been discussed further. One of the main uses for porous materials is as a tool for the identification and removal of various water contaminants that contribute to a clean environment has been included. Definition, types and origins of water pollution by various hazardous and toxic chemicals have been discussed elaborately. Moreover, scope of strategically designed and synthesis of various functionalized porous materials for the remediation of water has been discussed.

Part-I: Luminescent Porous Materials for Recognition Based Applications

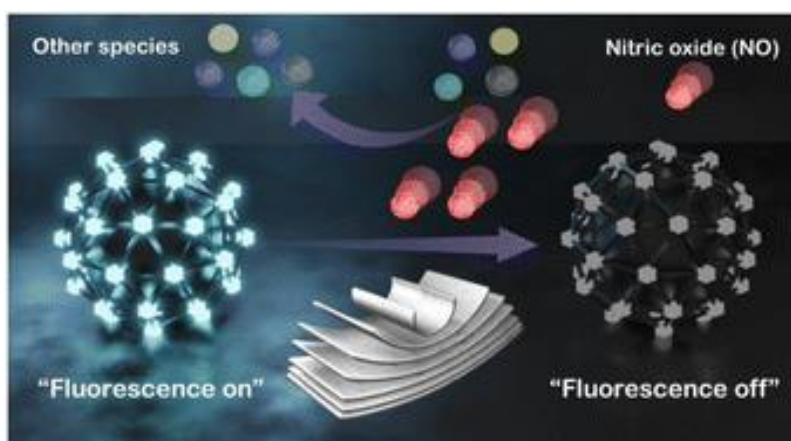
Luminescent porous materials such as luminescent MOFs (L-MOFs) and luminescent POPs are recently emerging as promising materials towards molecular recognition application owing to the advantages including specific design, tunable surface functionality as well as simplicity in terms of applications. A fast and precise reaction to the incoming guest analyte is determined by the host-guest interaction within the porous scaffold of these materials, offering considerable promise for real-time application. The aforementioned section of the thesis contains two chapters i.e. chapter-2 and chapter-3. In chapter-2, a post-synthetically modified MOF-808 with para amino benzoic acid is utilized as a probe to detect nitric oxide (NO), a toxic gas and water pollutant. Next, in chapter-3, a chemically stable highly luminescent

porous organic polymer (POP) is utilized to detect biologically and environmentally relevant molecules, such as antibiotics and pesticides in water medium.

Chapter 2. Post Engineering of a Chemically Stable MOF for Selective and Sensitive Sensing of Nitric Oxide.

Nitric oxide (NO) sensing is a crucial process in various biological systems. Nitric oxide is a gaseous signalling molecule that plays a fundamental role in several physiological and cellular processes. In this chapter, a functionalized metal-organic framework (MOF) has been synthesized for the detection of nitric oxide (NO) in water. A hydrolytically stable PABA@MOF-808 has been synthesized and further has been characterized for the detection of nitric oxide in water. Para-amino benzoic acid (PABA) was incorporated to the Zr-SBU of the MOF-808 to selectively detect the NO in water medium by chemodosimetric approach. The -NH_2 group of PABA and the NO undergo a chemical reaction as a result of the chemodosimetric method, quenching the luminous intensity. In addition to check the selectivity of the probe PABA@MOF-808 was tested with various other interfering analytes which are coexist with the NO like HOO^- , OCl^- , NO_3^- , NO_2^- , O_2^{2-} etc. PABA@MOF-808 shows selective response towards NO in the presence of above other interfering analytes. The limit of detection of the probe towards NO was $0.715\ \mu\text{M}$ which is one of the best value in the domain of this NO sensing. Along with this, the probe exhibited very high “turn-off” or quenching constant (K_{sv}) value.

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Chapter 3. Selective and Sensitive Recognition of Specific Types of Toxic Organic Pollutants with a Chemically Stable Highly Luminescent Porous Organic Polymer (POP)

In this chapter a chemically stable highly luminescent porous organic polymer (IP_{POP}-1) has been synthesized for selective detection of micropollutants in water. Owing to its electronically rich character, IP_{POP}-1 shows selective quenching response towards electron deficient antibiotics (NFT, NFZ) and pesticides (CHPS, Nitrofen) in water. The detection limit of IP_{POP}-1 towards antibiotics: NFT and NFZ are 0.046 and 0.045 mM respectively. On the other hand, in case of pesticides the limit of detection towards chloropyriphos and nitrofen are 0.470 and 0.471 mM respectively. After the detection study the compound further recycled for few cycles and it can be used without any apparent loss of function. The reason behind such strong quenching response was found as both fluorescence resonance energy transfer (FRET) and photoinduced electron transfer (PET). Further isothermal titration calorimetry (ITC) was carried out in order to explore the thermodynamic feasibility of the quenching mechanism. Also, to mimic the real-time antibiotic sensing the photoluminescence study was carried out with the real hospital waste water. Finally, IP_{POP}-1 based mixed matrix membranes (MMMs) were fabricated for the practical devised-based application.

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Part-II: Functional Porous Materials for Sequestration Based Applications

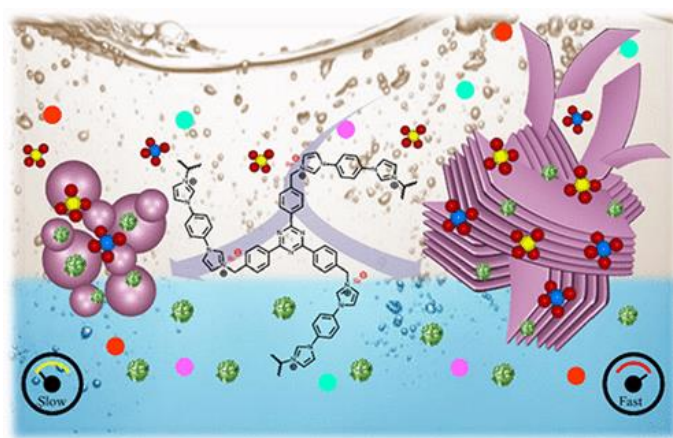
Functional porous materials play a crucial role in various sequestration-based applications by efficiently sequestering and storing specific target molecules or substances. These materials have a high surface area, large pore volume, and are engineered to possess specific functionalities that enable them to interact selectively with the desired species. Due to their multifunctional characteristics, hybrid composite porous material and porous organic polymer (POP) stand out among the others as having exceptional characteristics. These materials are used in applications that rely on sequestration because of their strong chemical stabilities and distinctive qualities. This section of the thesis contains two

chapters i.e. chapter-4 and chapter-5. In chapter 4, a series of ionic imadazolium functionalized POP were synthesized and used for selective extraction of heavy metal-based oxoanions (CrO_4^{2-} and ReO_4^-) from contaminated water. In chapter 5, highly efficient and selective entrapment of radioactive oxo-pollutants (TcO_4^-) has been demonstrated by a rationally designed multifunctional hybrid composite-based membrane, constructed by covalent joining of metal-organic cage with ionic COF material.

Chapter 4. Unveiling the Impact of Diverse Morphology of Ionic Porous Organic Polymers with Mechanistic Insight on the Ultrafast and Selective Removal of Toxic Pollutants from Water

Water pollution due to heavy metal based toxic oxo-pollutants have recently gained significant research attention. Therefore, selective extraction of these hazardous species from different water medium has become a topical research interest. With this aim, in this work, an imadazolium-functionalized ionic porous organic polymer (iPOP) has been synthesized and further utilized for sequestration of heavy metal-based toxic oxo-pollutants, such as chromate [Cr(VI)] and perrhenate [Re(VII)] from water. It has been demonstrated how altering morphologies can increase a material's effectiveness towards separation of these oxoanions. Among various morphologies, the flake-like iPOP demonstrated faster ultrafast capture of both oxoanions in water than a spherical one. Further, the flake-like iPOP exhibited highly efficient separation in a wide pH range as well in various water system. Moreover, to mimic the real time studies a breakthrough experiment has been performed to selectively entrap the CrO_4^{2-} anions. The in situ self-exfoliation of flakes into thin nanosheets with a larger surface area is the fundamental mechanism that underlies the ultrafast dynamics. To supplement the experimental results, thorough theoretical binding energy calculations were also carried out.

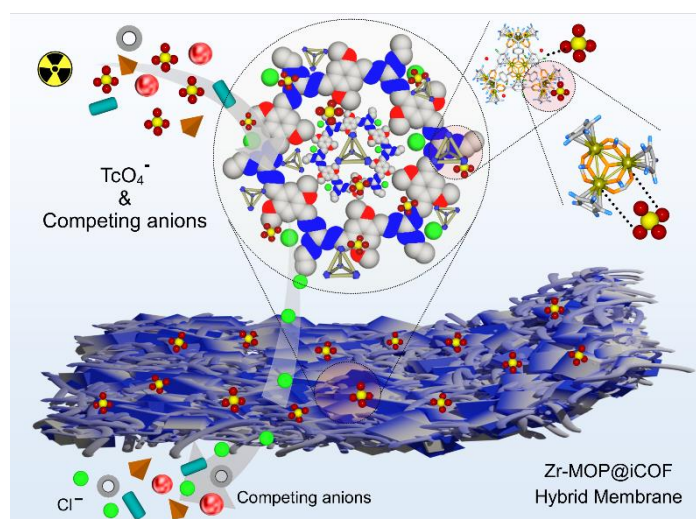
ACS Appl. Mater. Interfaces 2022, 14, 17, 20042–20052



Chapter 5. Nanotrap Infused Ultrathin Hybrid Composite Material for Highly Selective Entrapment of Radioactive TcO_4^-

^{99}Tc is one of the toxic radioactive substances due to its long half-life and high environmental mobility. Disposal of ^{99}Tc during the Vitrification process of nuclear waste becomes very challenging as there is generation of volatile Tc_2O_7 . Hence removal of ^{99}Tc from radioactive waste is very challenging at the same time utmost necessary. In previous works mostly we have synthesized MOF and polymers for detection and removal of toxic pollutants from water but these materials have some drawbacks like stability issue, work performances etc. To mitigate those issues, now in this work a hybrid composite material has been synthesized to get efficient uptake performances. In this work a hybrid composite material Zr-MOP@iCOF has been synthesized by covalent joining of a chemically stable anionic MOP with a negatively charged COF, where ample number of Cl^- ions are free that can exchange with the TcO_4^- anion. Moreover, this composite material has Zr-SBU which electrostatically interacts with TcO_4^- oxoanions and also have free amine group that can interact with the selective TcO_4^- through H-bonding. The composite material shows rapid entrapment of TcO_4^- from simulated nuclear waste as well as from different water systems in a highly selective manner. Moreover, for real time application, a membrane has been fabricated with the composite to perform the breakthrough-based flow-through TcO_4^- capture from waste-water system.

Manuscript submitted.



Abbreviations

DMF	N,N'-dimethylformamide
DMAc	N,N'-dimethylacetamide
MeOH	Methanol
EtOH	Ethanol
THF	Tetrahydrofuran
mg	Miligram
g	Gram
SCXRD	Single-Crystal X-Ray Diffraction
RT	Room Temperature
min	Minutes
mL	Milliliter
mmol	Milli moles
MOF	Metal-Organic Framework
MOP	Metal-Organic Polyhedra
MOC	Metal-Organic Cage
COF	Covalent-Organic Framework
HCP	Hyper-cross-linked polymer
PXRD	Powder X-Ray Diffraction
FT-IR	Fourier transform infra-red spectroscopy
TGA	Thermo-gravimetric Analysis
UV	Ultraviolet
FE-SEM	Field Emission Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance
EDX	Energy Dispersive X-ray Analysis
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
CP-MAS	Cross-Polarization Magic-Angle-Spinning
AFM	Atomic force microscopy
HRTEM	High-resolution transmission electron microscopy
DRS	Diffuse Reflectance Spectroscopy
ITC	Isothermal Titration Calorimetry

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Research Publications

(† indicates equal contribution)

Included in the thesis:

1. Post engineering of a chemically stable MOF for selective and sensitive sensing of nitric oxide. **Writakshi Mandal**, Dipanjan Majumder, Sahel Fajal, Sumanta Let, Mandar M. Shirolkar, Sujit K. Ghosh.
Mol. Syst. Des. Eng., 2023, 8, 756-766.
2. Selective and Sensitive Recognition of Specific Types of Toxic Organic Pollutants with a Chemically Stable Highly Luminescent Porous Organic Polymer (POP). **Writakshi Mandal**, Sahel Fajal, Partha Samanta, Subhajit Dutta, Mandar M. Shirolkar, Yogeshwar D. More, Sujit K. Ghosh.
ACS Appl. Polym. Mater. 2022, 4, 11, 8633–8644.
3. Unveiling the Impact of Diverse Morphology of Ionic Porous Organic Polymers with Mechanistic Insight on the Ultrafast and Selective Removal of Toxic Pollutants from Water. **Writakshi Mandal**, Sahel Fajal, Samraj Mollick, Mandar M. Shirolkar, Yogeshwar D. More, Satyam Saurabh, Debanjan Mahato, Sujit K. Ghosh.
ACS Appl. Mater. Interfaces 2022, 14, 17, 20042–20052.

4. Nanotrap Embedded Chemically Stable Hybrid Composite Membrane for Selective Entrapment of Radioactive TcO_4^- from Simulated Nuclear Waste.
Writakshi Mandal, Sahel Fajal, Dipanjan Majumder, Mandar M. Shirolkar, Sumanta Let, Sujit K. Ghosh.
[Manuscript submitted.](#)

Not included in the thesis:

5. Selective and Ultrafast Sequestration of Radioactive Oxo-pollutants by a Chemically Stable Ionic Organic Network: The Study of Shape Template Effect
Writakshi Mandal, Sahel Fajal, Dipayan Ghosh, Mandar M. Shirolkar, Sujit K. Ghosh.
[Manuscript under preparation.](#)
6. Unfolding the Role of Building Units of MOFs with Mechanistic Insight Towards Selective Metal Ions Detection in water.
Sahel Fajal†, **Writakshi Mandal**†, Dipanjan Majumder, Mandar M. Shirolkar, Yogeshwar D. More, Sujit K. Ghosh.
[Chem.Eur.J. 2022, 28, e20210417.](#)
7. Luminescent cationic MOF and its polymer composite membrane elicit selective sensing of antibiotics and pesticides in water.
Subhajit Dutta†, **Writakshi Mandal**†, Aamod V. Desai, Sahel Fajal, Gourab K. Dam, Mandar M. Shirolkar, Soumya Mukherjee, Sujit K. Ghosh.
[Mol. Syst. Des. Eng., 10.1039/D3ME00008G](#)
8. Trap Inlaid Cationic Hybrid Composite Material for Efficient Segregation of Toxic Chemicals from Water
Sahel Fajal, **Writakshi Mandal**, Samraj Mollick, Yogeshwar D. More, Arun Torris, Satyam Saurabh, Mandar M. Shirolkar, Sujit K. Ghosh.
[Angew. Chem.Int. Ed. 2022, 61, e2022033.](#)
9. Ordered Macro/Microporous Ionic Organic Framework for Efficient Separation of Toxic Pollutants from Water
Sahel Fajal, Atikur Hassan†, **Writakshi Mandal**†, Mandar M. Shirolkar, Sumanta Let, Neeladri Das, Sujit K. Ghosh.
[Angew. Chem.Int. Ed. 2023, 62, e2022140.](#)
10. Luminescent metal–organic frameworks (LMOFs) as potential probes for the recognition of cationic water pollutants.
Partha Samanta, Sumanta Let†, **Writakshi Mandal**†, Subhajit Dutta and Sujit K. Ghosh.
[Inorg. Chem. Front., 2020, 7, 1801–1821.](#)
11. Benchmark uranium extraction from seawater using an ionic macroporous metal–organic framework
Samraj Mollick, Satyam Saurabh, Yogeshwar D. More, Sahel Fajal, Mandar M. Shirolkar, **Writakshi Mandal** and Sujit K. Ghosh
[Energy Environ. Sci., 2022, 15, 3462–3469.](#)

12. Ionic metal–organic frameworks (iMOFs): progress and prospects as ionic functional materials
Subhajit Dutta, Yogeshwar D. More, Sahel Fajal, **Writakshi Mandal**, Gourab K. Dam and Sujit K. Ghosh.
Chem. Commun., 2022, 58, 13676–13698.
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Debanjan Mahato, Sahel Fajal, Partha Samanta, **Writakshi Mandal** and Sujit K. Ghosh.
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Yogeshwar D. More, Samraj Mollick, Satyam Saurabh, Sahel Fajal, Michele Tricarico, Subhajit Dutta, Mandar M. Shirolkar, **Writakshi Mandal**, Jin-Chong Tan and Sujit K. Ghosh.
Small 2023, 2302014.
15. Nano-snare Implanted Ultralight Crystalline Hybrid Composite Material for Multiple Cooperative Interactions Mediated Efficient Sequestration of Radioiodine
Sahel Fajal, **Writakshi Mandal**, Arun Torris, Dipanjan Majumder, Sumanta Let, Mandar M. Shirolkar, Sujit K. Ghosh.
Manuscript submitted.
16. Unraveling Mechanistic Insights in Covalent Organic Frameworks for Highly Efficient Sequestration of Organic Iodides from Simulated Nuclear Waste
Sahel Fajal, Dipanjan Majumder, **Writakshi Mandal**, Sumanta Let, Gourab K. Dam, Mandar M. Shirolkar, Sujit K. Ghosh.
Manuscript submitted.
17. Efficient Selective Removal of Toxic Se(IV), Se(VI) and Hg(II) From Water by MoS₄²⁻@POP Composite: The Role of Antagonistic Effect
Sumanta Let, Sahel Fajal, **Writakshi Mandal**, Sujit K. Ghosh.
Manuscript submitted.
18. Nonfluorinated superhydrophobic MOP@Foam composite material for effective removal of oil from oil-water emulsion
Dipanjan Majumder, Sahel Fajal, **Writakshi Mandal** and Sujit K. Ghosh.
Manuscript submitted.

Chapter 1

Introduction

1.1 Porous Materials

An interesting class of substances known as porous materials is distinguished by its distinctive structure, which has linked pores or voids throughout its composition. The enormous interior surface area of these materials offers plenty of room for the adsorption or absorption of gases, liquids, or even other solids. They have excellent qualities due to their porous structure, including high surface area-to-volume ratios and variable pore sizes, which allow them to be used in a variety of different disciplines. Porosity can be found in rocks, biological tissues, soil, and zeolites as it is inherent property of nature.^[1] Strategically design and inauguration of porosity in framework material by mimicking nature has drawn a significant position in science. A variety of porous materials have unrolled in the last few decades.^[2] Porous materials can be classified based on their pore sizes; materials with pore size less than 2 nanometer (nm) is called microporous materials, while the materials with pore sizes between 2 nm to 50 nm is called the mesoporous materials. When the pore size is above 50 nm then it is called macroporous materials.^[3] Porous materials have a critical role in tackling environmental, industrial, and technical concerns, from water purification and air filtering to catalysis, energy storage, and medication delivery systems. As scientists and engineers work to harness their potential for sustainable developments in a variety of industries, their adaptability and ability for customisation make them a key field of research and innovation. In the earlier stage porous materials mainly comprise of Aluminophosphates (ALPOs) and zeolites assembled from covalent bonding between inorganic nodes.^[3-5] However, there are many different types of porous materials, each with its own characteristics and uses. Activated carbon, which is made up of carbon particles with a high porosity, is one of the most popular varieties. Due to its extraordinary adsorption ability for pollutants and contaminants, it is widely employed in the filtration of water and air. Zeolites, another important class of porous materials, are crystalline aluminosilicates with uniform pore structures. They are used as ion-exchange agents in water softening operations and as catalysts in the petrochemical sector. Mesoporous silica materials can be used for a wide range of applications, from drug carriers in medicines to catalysts and component parts in advanced coatings. With such conventional porous materials, however, target-specific applications are practically difficult because the structure-property link is still unidentified. Therefore, it is crucial to find a new class of porous materials where it is simple to fine-tune order and functions at the atomic level. Porous materials are still revolutionizing several industries and advancing sustainable technology thanks to ongoing research and development. In this view, advanced functional porous materials (AFPMs), which majorly include metal-organic frameworks (MOFs), metal-organic polyhedra (MOPs) porous organic polymers (POPs), covalent organic frameworks (COFs), and their hybrid composite materials represent an advanced class of porous materials with tunable structures, allowing for tailored pore sizes and surface chemistries. A revolution in chemistry and material engineering has resulted from the discovery of

AFPMs at the tail end of the 1980s. Compared to conventional porous solids, a new class of porous materials that are potentially complimentary and even much more desirable are made possible by the specific arrangement of organic, inorganic, or a combination of both moieties. A general scheme which shows the overall classification of different types of porous materials, including pure inorganic, pure organic and inorganic-organic hybrid materials has been presented in figure 1.0. These materials hold great promise in different field of applications, which are discussed below.

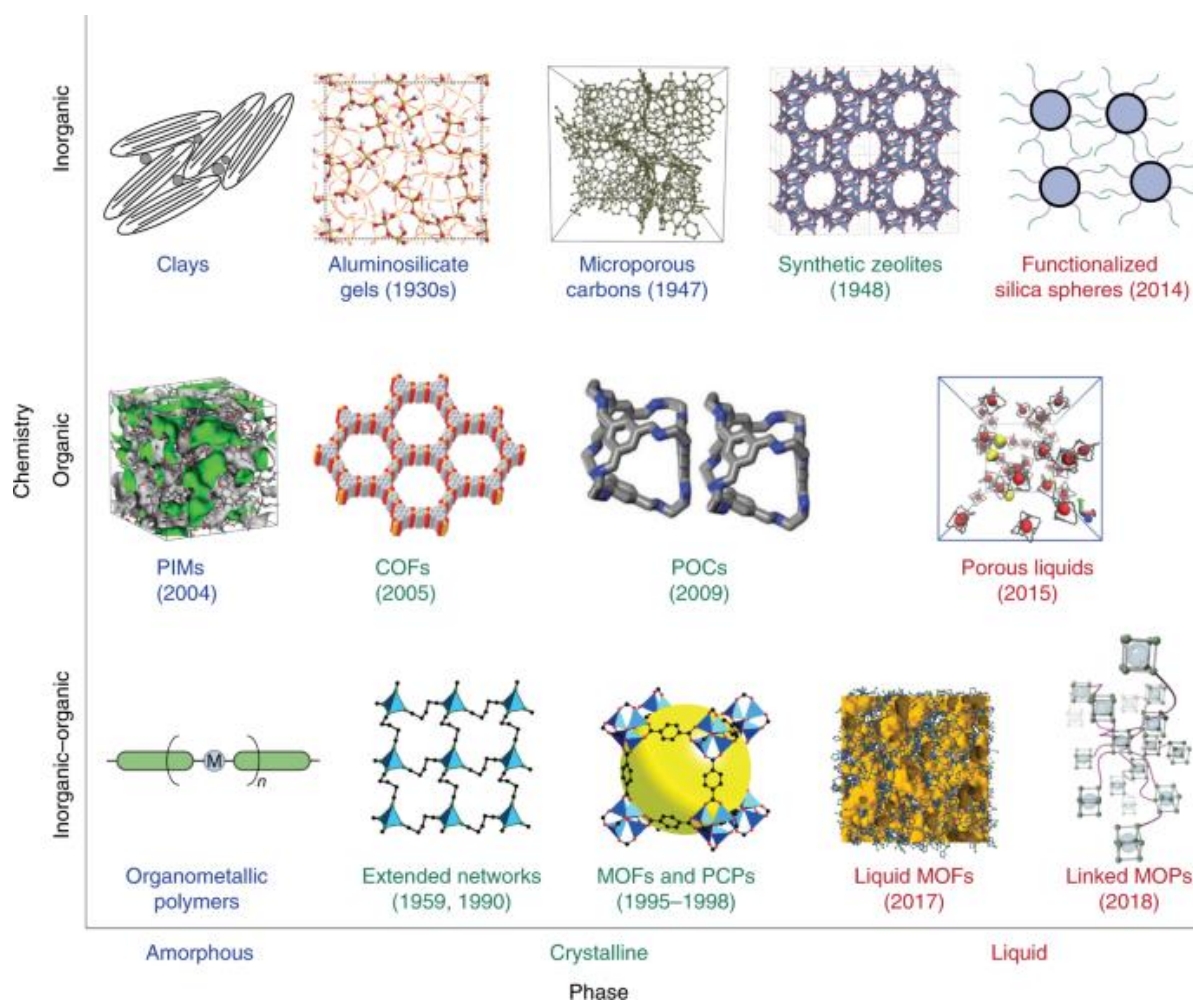


Figure 1.0 Schematic representation of general classification of different types of porous materials with their years of discovery. (Reproduced with permission from reference 69)

1.2 Advanced Functional Porous Materials (AFPMs)

In the last two decades witnessed a strategic elevation in the synthesis of new class of materials through uses of strategic and functional building blocks to formation of a new class of materials namely advanced functional porous materials. (AFPMs).^[1, 6] The building of these materials accomplished in two strategies. A) Employment of functional organic synthons and inorganic nodes to form organic-inorganic hybrid porous structure, B) Utilisation of organic functionalized building unit via linking through covalent and noncovalent interactions to the formation of metal free porous organic framework. The former class comprises of metal-organic frameworks (MOFs), metal-organic polyhedra (MOPs), and metal-organic gel (MOG). On the other hand, the later includes functionalized porous organic materials (POMs).^[7-11] Porous organic materials comprise of crystalline porous organic architectures like covalent organic frameworks (COFs), hydrogen bonded organic frameworks (HOFs), porous organic cages (POCs) as well as amorphous porous organic systems which includes different porous organic polymer (POPs) (**Figure 1.1**).^[12-15] The key benefit of using the aforementioned methodologies is that they enable careful selection of functional moieties for the synthesis of AFPMs, resulting in the task specific nature of such materials. The building blocks are designed in a way that an application specific functionality is included to create an interactive porous scaffold that is functional and adapted to the applications needs.^[6, 7] Such fabrication of porous materials generates two kinds of porosity a) extrinsic porosity b) intrinsic porosity. Extrinsic porosity means the porosity generated in the molecular architectures as result of packing between the molecules, on the other hand intrinsic porosity means to the generation of pores as a consequence of the shape and geometry of the building block. The word extrinsic means “between the molecules” whereas intrinsic means “within the molecules”.^[16, 17] Another crucial property of AFPMs is their design flexibility, which allows for enormous surface area and clearly defined functional pores. Additionally, some of them are easily mouldable into thin films or membranes or other monolithic forms, which have significant advantages in a variety of real-world applications. Few of them can even be processed into usable forms and dissolved in a common solvent without losing their natural porosity, which is almost unimaginable with traditional porous solids. Additionally, the hybrid composites of these novel porous materials usually exhibited inventive, one-of-a-kind features that are typically not seen in traditional porous solids. Further discussion about individual class of AFPMs are listed below.

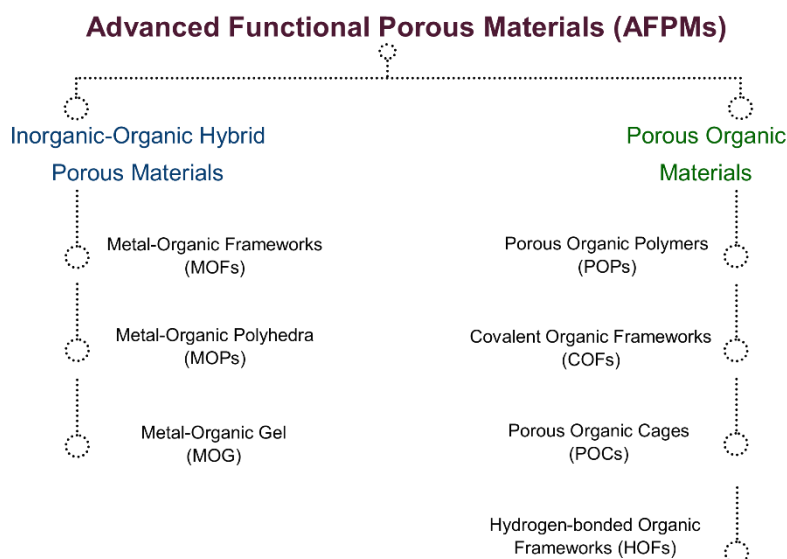


Figure 1.1 Scheme for classification of advanced functional porous materials.

1.2.1 Metal-Organic Frameworks (MOFs)

MOFs, a special class of AFPMs are unique subclass of co-ordination polymers consisting potential voids. Such porous structures are constructed from the co-ordination bond between inorganic metal nodes or clusters and organic struts.^[18, 19] MOFs are synthesized from organic ligand and metal precursors solutions at room temperature or solvothermal crystallization methods. The solvent molecules of the synthetic reaction media often occupy the voids of the framework material. In order to access the space, those guest solvents must be eliminated from the MOF pores by vacuum treatment or heating or both process. Based on these MOFs are classified in three different generations; namely first generation, second generations and third generations. After desolvation, the first-generation frameworks lose their structural integrity while the second generation retains its framework structure after desolvation. On the other hand, third generation is known as ‘Dynamic framework’ which after desolvation shows flexible behaviour by transforming into an alternate structure. Another key characteristic of these materials is their reversible dynamicity, which means that following resolution, the framework returns to its original structure.^[22] Another approach to synthesize functional MOFs is ‘post synthetic modification (PSM)’ where a MOF synthesized by aforementioned pre-synthetic strategy and having a functional subunit within the porous structure further it is utilised for chemical transformation to generate structurally similar but functionally different porous MOFs (**Figure 1.2**).^[23] The primary motif of PSM is that it helps in achieve those MOFs which are difficult to synthesize by conventional techniques.^[24]

Based on the charges functional MOFs can be classified in two categories neutral MOFs and ionic MOFs (*i*-MOFs).^[25] The organic linker utilised in MOF chemistry to bind the metal nodes generally consist of carboxylate (-COOH) group and different heterocyclic donors containing free N atoms for coordinating the metal centre.^[26-27] The framework's nature can be strategically modified depending on the type of organic counterpart used in MOF manufacturing. Using of carboxylate linker generally forms neutral MOFs as the binding occurs between cationic metal nodes with anionic functionalities leading to charge neutrality. Based on the electrostatic nature iMOFs can be classified into cationic and anionic frameworks. Cationic MOFs are formed when there is an excess of positive charge in the framework along with presence of additional counter anion to retain the charge neutrality. This types of frameworks are formed by neutral nitrogen donor based ligand systems where the positive charge of the metal centre is not neutralised after co-ordination by neutral nitrogen atoms of the ligand. On the other hand, anionic frameworks are formed when the ligand contains multiple anionic sites so that metal nodes post coordination fails to fulfil the condition of charge neutrality and excess counter cations are required additionally to be present within the framework to satisfy the charge of the framework (**Figure 1.2**).^[25]

MOFs are used in a wide range of applications due to their structural properties and large surface area. The pore dimension associated with MOFs as well as pendant functionalities in the framework's backbone provide a platform for host guest chemistry. MOFs are frequently used for gas storage as well as difficult separation of gases or solvents from mixtures of gases or liquids, all of which are significant from an industrial standpoint. The most important application of MOFs is the separation of carbon dioxide, a well-known greenhouse gas, from mixtures of gases such as nitrogen, methane and hydrogen which solves carbon capture and sequestration (CCS) difficulties.^[29] Also MOFs have important role on separation of xylene isomers, styrene and ethylbenzene as well as benzene and cyclohexane molecules.^[30-31] Because of their similar boiling points, separation of the aforementioned triad and pairs is extremely difficult using traditional distillation procedures. On the other hand, luminescent MOFs (LMOFs) have the additional property of emitting light when excited by an external energy source, such as UV light or visible light. The luminescence can arise from the intrinsic properties of the metal ions or ligands, or from interactions between them. The emission wavelengths can be controlled by the choice of metal ions and organic ligands used in the MOF synthesis. The porous cavity contained in LMOFs is also used for host guest recognition leading to sensing of various incoming analytes such as cationic and anionic species, gas molecules, explosives, and biomolecules.^[32] MOF can operate as a carrier molecule in drug delivery-based biocompatible applications due to the encapsulation of analytes within the porous spaces.^[33] However, the presence of functional nodes inside the porous structures of MOFs allows it to function as a tool for heterogeneous catalytic applications.^[34] In case of ionic framework the extra counter ions present in the framework leads to ion exchange that is highly relevant

in case of environment friendly molecular recognition and sequestration of toxic hazardous pollutants. [35] MOFs are one of the pioneer in development of materials for clean energy based applications. [36] Such materials can also be used as conductors and electrochemical applications based materials including supercapacitor. [37] Encapsulation of guest species such as nano particles and functional molecules also leads to the formation of composite materials, which are used in energy and environmental applications. [38]

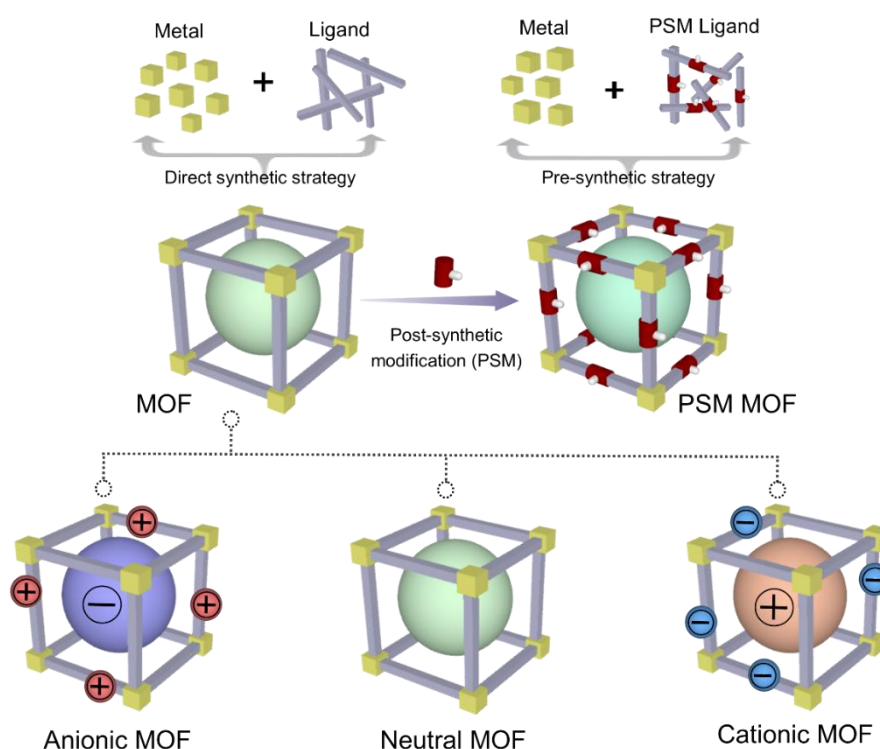


Figure 1.2 Schematic representation of various types of MOFs based on synthetic preparation and charge specificity.

1.2.2 Metal-Organic Polyhedra (MOPs)

In the early 21st century the term metal-organic polyhedra (MOPs) was first introduced. Metal-organic polyhedra, as opposed to MOFs, are discrete molecular entities formed by the coordination aided self-assembly of metal ions or metal clusters and organic building blocks with symmetric well-defined geometries and restricted cavities with numerous pore apertures (Figure 1.3). [47] MOPs are also known as nanoballs, nanospheres, nanocapsules and nanocages. MOP research has increased rapidly in the recent two decades due to its diverse uses in catalysis, sensing, host-guest chemistry, separation and

storage, drug delivery, ion channels, and many other fields. ^[48] Furthermore, MOP's solubility provides significant advantages over other APMs in the manufacture of thin films, membranes, ion channels, and other biological applications, among other things. ^[49] Supramolecular chemists devised a number of design methodologies for the synthesis of MOPs, including directed bonding, molecular library, symmetry interaction, molecular panelling, weak-link, reticular chemistry, supramolecular blueprint, and bridging ligand replacement procedures.

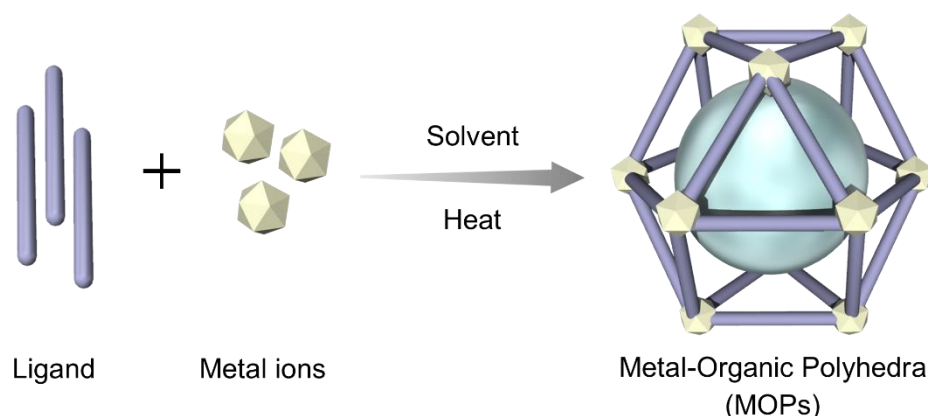


Figure 1.3 Schematic representation of general synthesis of MOPs.

1.2.3 Porous-Organic Polymer (POPs)

Porous organic polymers are a diverse family of amorphous AFPMs formed by covalently anchoring functional organic moieties such as heterocycles, macrocycles, and fused aromatic system (**Figure 1.4**). ^[39] These class of polymers comprised of polymers of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), hyper crosslinked polymers (HCPs), covalent triazine frameworks (CTFs) and porous aromatic frameworks (PAFs). These organic compounds are synthesized through various types of organic reactions, both in solution and solid state, such as Friedel crafts reactions in the case of HCPs, trimerisation of nitrile functionalities in the case of CTFs, and various types of organometallic cross-coupling reactions for PIMs, PAFs, and CMPs such as Sonogashira-Hagihara coupling, Yamamoto coupling, and Suzuki coupling. ^[10, 15, 39] The strategic use of functional synthons with many reaction sites enables the spread of infinite network structure. Materials can be of two-dimensional or three dimensional in nature depending on the structure of the building blocks and the free rotation of the pendant chemical bonds. ^[40] Another classification of POPs that can be made depending upon their charge specificity. Among them, neutral polymers do not contain any charged species, whereas ionic POPs (iPOPs) are polymers with ionic sites in their structural backbone. In addition, iPOPs can be categorised as cationic or anionic depending on the nature of the charge present

on the backbone of the polymeric material. If the charge of the polymeric background is positive then it will be called as cationic polymer. On the other hand if the charge of the polymeric backbone is negative then it will be called as anionic polymer. Free counter ions built into the framework are exchangeable and thus applicable for various applications that rely on the ion-exchange process, such as waste-water treatment, gas separation, etc. The fundamental benefit of POPs is that they combine the characteristics of porous materials and organic polymers. The existence of porous gaps creates enough space for host guest interaction, whereas the presence of polymeric backbones creates rigid structural topologies. Porosities in this sort material can be adjusted and controlled by varying the following factors: monomer structure and shape, synthetic method, and component reactivity.^[39,41] The reaction parameters, which include the initial material concentration, the amount of solvent and catalyst utilised, and the temperature, can have a minor effect on the porous character of the porous solids. Having high surface area of POP leading to generation of excellent porosity and also the robust nature of the polymer results in good stability in a variety of chemical environments. POP's metal-free nature also allows them to operate as low density materials, and in some situations, the short range order in their structures caused by the nature of packing at the molecular level allows them to attain solution processibility.^[40]

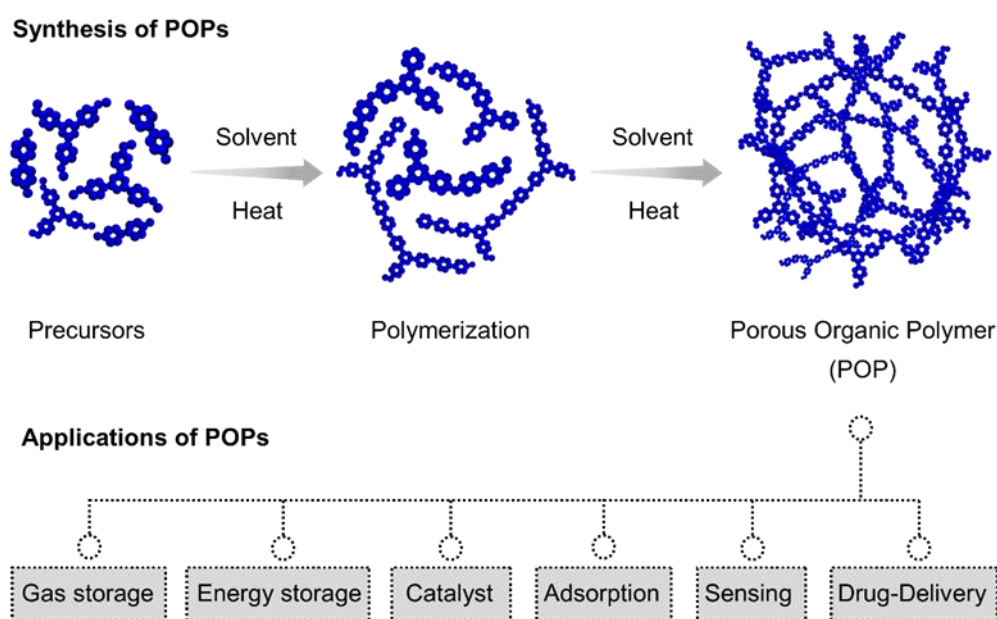


Figure 1.4 Schematic representation of general synthesis and applications of POPs.

This is significant for real-time applications since such materials can be used in both solution and solid states, as well as thin films.^[15] Like MOFs, POPs have also several applications in different fields, e.g. storage of multiple gases like hydrogen, methane as well as separation of gases from the mixture of gases. Because of the availability of large pores that can accept functional molecules required for

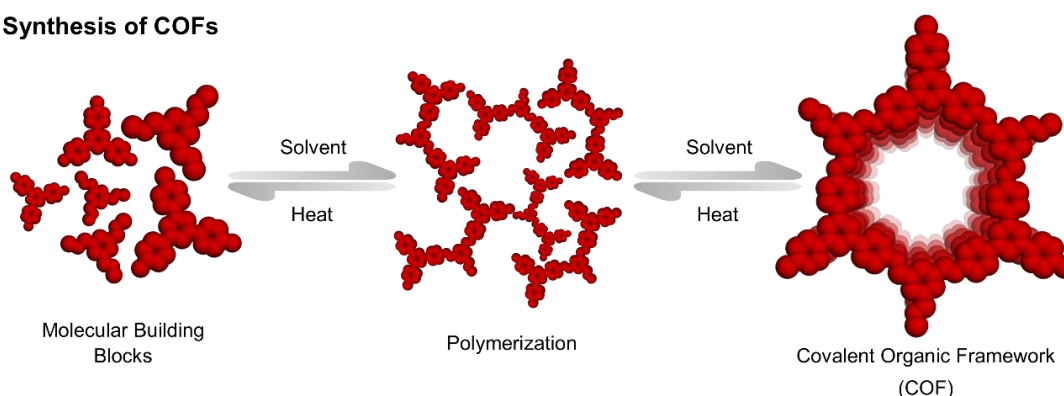
catalytic applications, as well as structural stability and great reusability, POPs are used as a scaffold for heterogeneous catalysis. In the case of POPs, the inclusion of both hydrophilic and hydrophobic functions within the pores can result in the incorporation of both types of entering guest molecules. This has implications for molecular identification applications such as molecular separation, sensing, and selective capture of a specific molecule from both aqueous and organic media. [39, 43-44] The existence of prolonged conjugation within the backbones of POPs aids in the achievement of various photophysical and light harvesting applications, while the selective insertion of relevant functional moieties propels these materials to be used in various electrochemical applications (**Figure 1.4**). [39, 45-46]

1.2.4 Covalent Organic Frameworks (COFs)

Covalent organic frameworks (COFs), a class of porous organic polymer are constructed through strong covalent bonds between organic building blocks, resulting in a well-defined three-dimensional network with precise control over pore size, shape, and surface functionality. COFs are a type of crystalline porous organic polymer that allows for the atomically accurate integration of organic building blocks to form predesigned structures with nanopores (**Figure 1.5**). [50] A team led by Yaghi demonstrated the value of the topological design principle in the synthesis of covalent organic frameworks (COFs), the first instance of which was successful, in 2015. [51] Because they are composed of light weight components joined by robust covalent bonds, COFs have low mass densities, high thermal stabilities, and permanent porosity. COFs are classified as two-dimensional (2D) or three-dimensional (3D) depending on the dimensions of the building blocks. In 2D COFs, the 2D sheets that make up the covalently bound framework can be stacked on top of one another to create a layered eclipsed structure with periodically aligned columns. However, 3D COFs, which expand this framework in three dimensions through a building block containing a sp^3 carbon or silane atom, typically have large surface areas, open sites, and low densities. COFs can be classified into two groups: neutral and ionic COFs, depending on their charges. According to how charged they are, ionic COF is further divided into the categories cationic COF and anionic COF. Due to the exceptional structural versatility and tailorability, making them highly desirable for various applications. COFs are excellent options for renewable energy storage and environmental cleanup because of their exceptional gas storage and separation characteristics. Their employment in catalysis for effective chemical transformations is made possible by their large surface area and customizable electronic characteristics. In optoelectronics, where COFs may find use in sensors and light-emitting diodes (LEDs), they have also demonstrated promise. COFs have also been investigated for medication delivery in biomedical applications because of their biocompatibility and controlled release characteristics (**Figure 1.5**). These many uses highlight the

enormous potential of covalent organic frameworks as a cutting-edge class of materials that can significantly boost a number of different businesses and scientific fields.

Synthesis of COFs



Applications of COFs

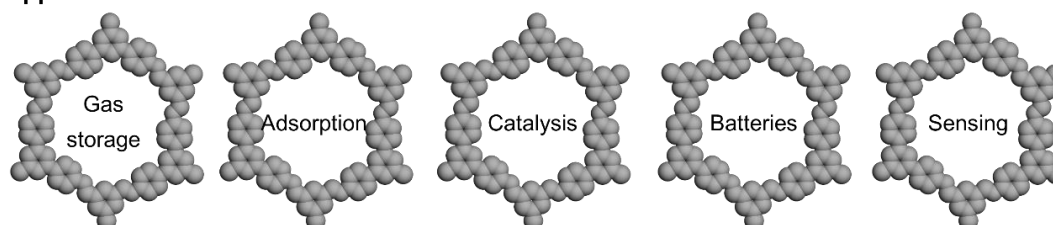


Figure 1.5 Schematic representation of general synthesis and applications of COFs.

1.2.5 Hydrogen Bonded Organic Frameworks (HOFs)

Hydrogen-bonded organic frameworks (HOFs) are a type of porous molecular material that uses hydrogen-bonding interactions to assemble organic building blocks to construct two-dimensional (2D) and three-dimensional (3D) crystalline networks. As the hydrogen bonds are reversible in nature; HOFs accredits of solution processability and simple regeneration.⁷¹ Furthermore, HOFs can be formed as high-quality single crystals for unambiguous superstructure determination via single-crystal X-ray diffraction, which is critical for investigating superstructure property interactions. Marsh and Duchamp reported the first hydrogen-bonded crystalline network in 1969 as a 3D superstructure of polycatenated hexagonal networks formed from trigonally shaped trimesic acid (TMA) linked by the $R_2^2(8)$ hydrogen-bonded motif provided by the carboxyl (COOH) groups. Significant progress has been made in realizing stable HOFs with permanent porosities over the last decade by focusing on the design of molecular building blocks to introduce rigidity, auxiliary $[\pi-\pi]$ interactions, and interpenetration of their frameworks to sustain the extended networks.

1.2.6 Porous Liquids

Porous liquids are a novel type of substances that is liquid at room temperature and has persistent porosity. In 2007, the introduction of new liquid molecules that exhibit permanent porosity while retaining their fluidity properties, dubbed 'porous liquid,' altered our perspective on non-porous fluids, challenging the notion that only solid porous materials can be used for size- and shape-selective adsorption and separation. Porous liquids are of three types; Type 1, neat host liquid incapable of collapsing or interpenetration, Type 2 and Type 3, which are rigid hosts with microporous frameworks dispersed in sterically hindered solvents. The main fundamental difference between a porous liquid and solid is fluidity which opens up various process advantages.⁷²

1.3 Composite material

A composite material is a combination of two or more substances that retains their intrinsic identity, or in certain cases, demonstrates greater and unique features than the individual components utilised alone.^[52,53] The properties of composite materials depend on several factors: a) individual components properties b) component's relative amounts c) size, shape and distribution of the components, d) the degree of interactions between the parental components, etc. Composite materials, in general, are made up of a host matrix and functional guest species, where the guests are used for their greater activity and the host matrix is frequently used as a support for the guests. As a host matrix for support media, a variety of porous materials are often utilised. These porous matrices immobilise the functional guest components and limit both leaching and aggregation tendencies, resulting in a significant increase in their reactivity.^[54] Furthermore, the host matrices can provide additional active sites that collaborate with the guest in the composite material. Because of the customizable pore environment, consistent pore topologies, multiple functional locations, and framework flexibility, AFPMs are an excellent candidate as a host matrix for the encapsulation of various functional guests.^[55] The selection of an acceptable host matrix can be accomplished by utilising a large library of AFPMs, while simulation approaches are frequently utilised as an effective screening method.

Synthesis strategies of composite materials

The efficiency of the composite materials depends upon its shape, size and distribution of guest species into the host matrix. The development of simple manufacturing processes effects these critical characteristics and, as a result, the overall performance efficiency of composite materials to a large extent. Few strategies are there for the immobilization of guest species into the host matrix (**Figure 1.6**).

(A) Assembly of guest species inside the pre-synthesized host cavity: The functional guest species are generated in this technique by immobilising the guest precursors within the pre-synthesized host matrix.^[56] This extensively used tactic is known as “ship-in-bottle” strategy. In this process, the guest precursors are first impregnated into an AFPM matrix using various techniques such as vapour deposition, solid grinding, and solution infiltration, and then reduced to the required guest material. The host pores limit the expansion of the guest species in this approach, allowing them to remain confined within the pores. However, there are some challenges still remain in this technique. I) The host matrix should be stable under the synthetic condition of guest species. II) Due to the formation of larger size guest species there is partial degradation of host species. III) It is difficult to exact control over the interior location, composition, and structure of guest species within the host cavity. Several methods are there for the infiltration of guest precursors into the host matrix as follows (**Figure 1.7**).

(I) Chemical vapour deposition (CVD): This method is one of the oldest methods known for the encapsulation of guest species into the host matrix. In this method, precursor molecules are initially impregnated into the pores of a host matrix via sublimation, followed by breakdown via heat or photochemical conditions. Because no solvents are used in this approach, the guest species can be loaded into the host matrix to the greatest extent possible. However, the major shortcomings in this process is the larger sized guest species compared to the host matrix that resulting partial disruption of the framework. Moreover, this process has still not been investigated fully due to its difficulty in controlling the deposition process in a reproducible manner.

(II) Solution infiltration method: The following method involves the use of precursor solutions for liquid phase impregnation. The solution of the guest precursors is immersed in an adequate solution to infiltrate into the vacant cavity of the host matrix during this process. Following that the precursors are reduced in order to produce the required guest species. The solubility of the guest precursors in the solution determines the loading capacity. The distribution of guest species inside the host matrix is determined by both the guest antecedents and the nature of the host matrix. The creation of a wide range of particle sizes within the host matrix is a shortcoming of this approach. Under the severe conditions of external reducing agents such as NaBH_4 or hydrazine, the host matrix may occasionally collapse.

(III) Incipient wetness impregnation: The only difference between this approach and solution impregnation is that the precursor solution of the guest is decreased to a minimum level. Although the maximal loading of guest species is achievable in this procedure without decomposing the framework, it is restricted by the solubility of guest precursors in acceptable solvents.

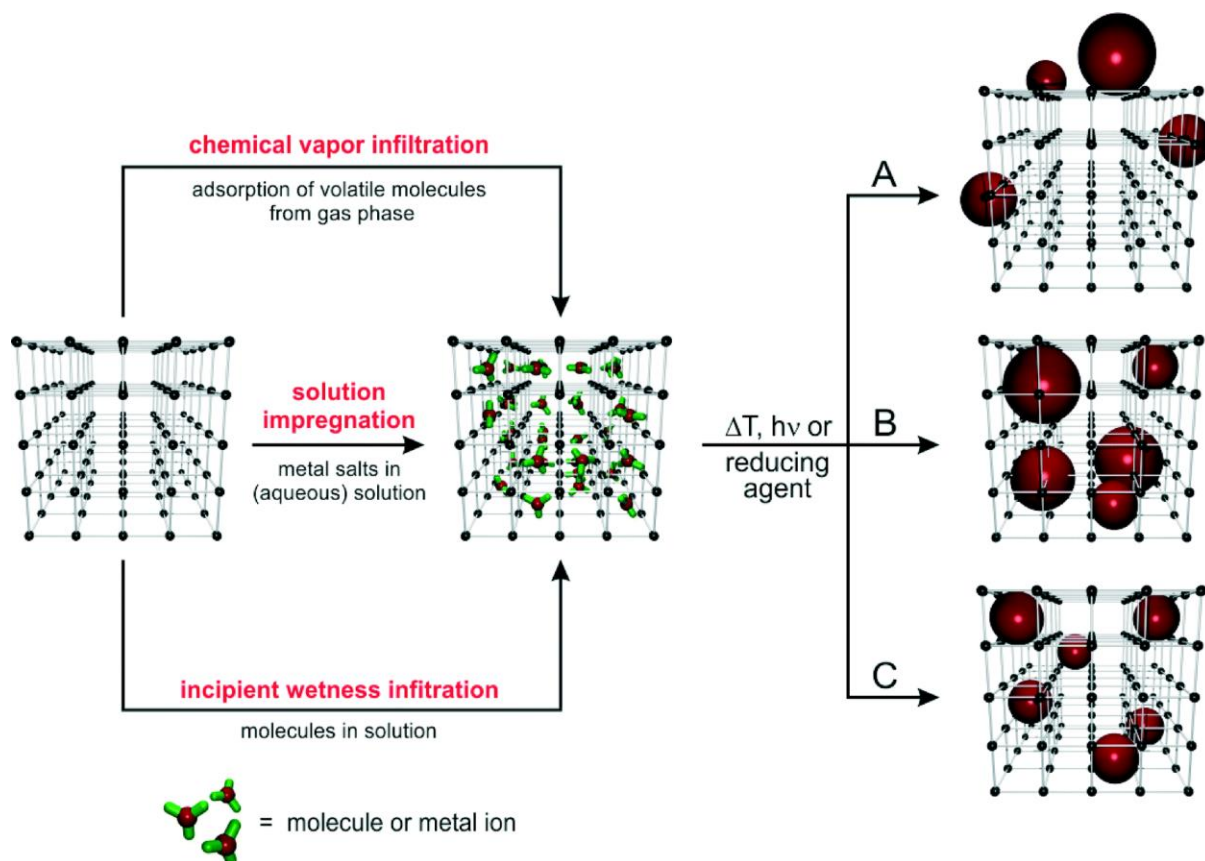


Figure 1.6 Schematic representation of general synthesis of functional guest species into a pre-synthesized host cavity. (Reproduced with permission from reference 70)

(IV) Solid-state grinding: Solid-state grinding of volatile guest precursors without the use of any solvents can also be used to achieve infiltration of guest species into the porous host matrix. During the grinding process, the volatile guest precursors sublime to vapour and infiltrate into the voids of the host matrix, resulting in well-distributed deposition of precursor molecules. Following that, the embedded guest precursors are reduced to produce small-sized desired guest species throughout the host matrix. The grinding process is a reasonably simple and effective method for creating the guest loaded host matrix without the use of solvents or after-infiltration washing operations.

(B) Assembly of host around the guest species: This is a “bottle-around-ship” or template synthesis technique, in which the desired composite is built by self-assembling a host matrix around the pre-synthesized functional guest species.^[57] In general, pre-synthesized guest species are not found in the host matrix's cavities, but are instead covered by the host framework. This technique not only overcomes frequent difficulties, such as the aggregation of guest species on the exterior surface and partial damage to the host framework, but it also preserves the composition, size, and morphology of the guest species.

The particle size of the guest species is not limited to the aperture size of the host frameworks because they are synthesised prior to encapsulation. However, with this method, guest species generally self-nucleate outside of the host matrix. Furthermore, in most circumstances, guest elements are unable to withstand the reaction state of the host matrix (**Figure 1.7**).

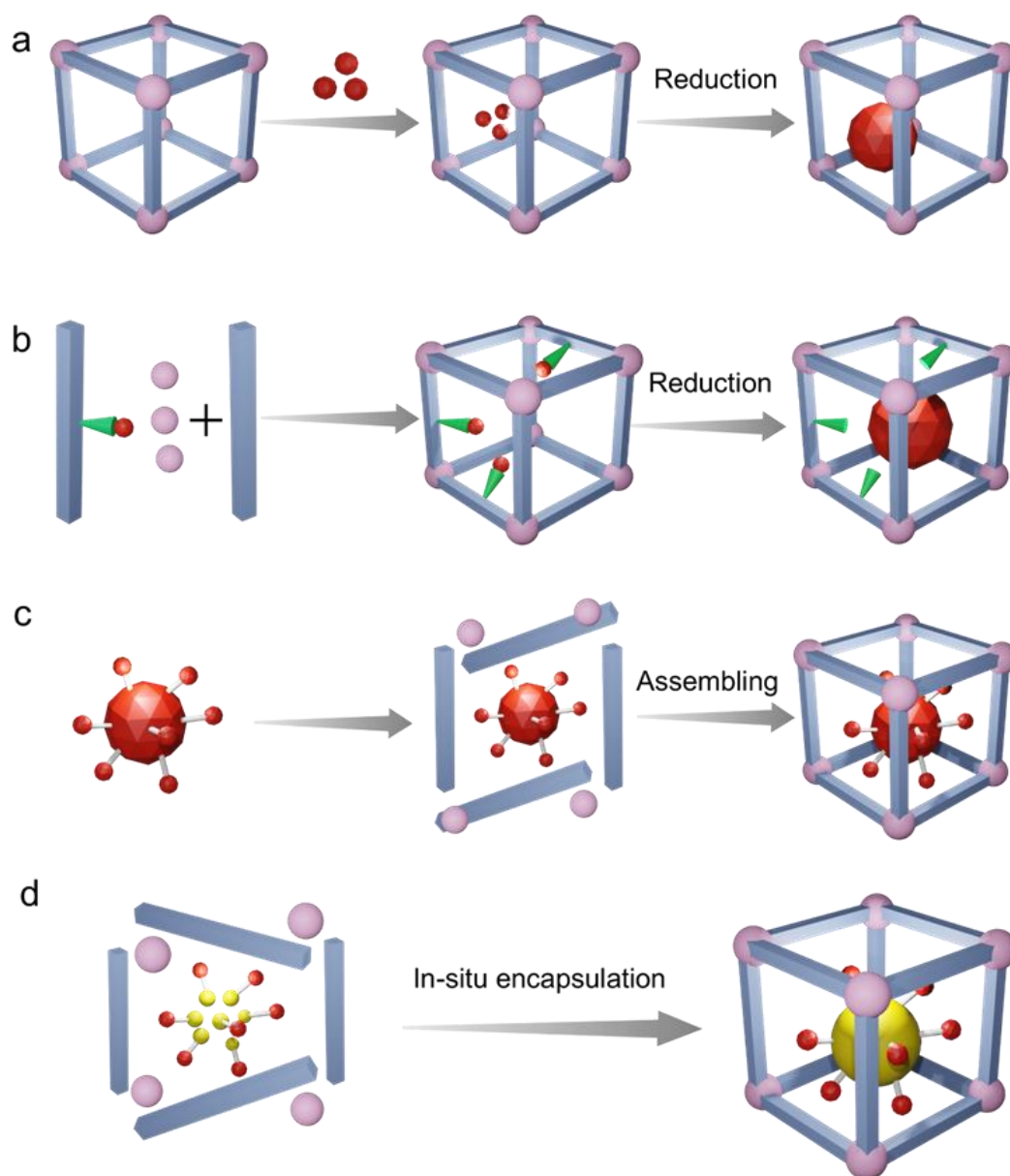


Figure 1.7 Schematic representation of general synthesis composite materials.

(C) Sandwich assembly strategy: In this approach, guest species are impregnated between the two shells of the porous host matrix.^[58] This novel strategy entails preparing a host core, infiltrating chosen

guest species, and then overgrowing a porous host shell onto the guest-deposited host core. By repeating both stages, functional guest deposition and host overgrowth, multi-layered composite materials can be created. This method allows for precise control over the position, form, and composition of the guest species in the intended composite material. The most difficult aspect of this approach is the formation of a fracture-free shell on the core. When a selected matrix has mismatched topologies, additional surfactant capping agents are required to produce a fracture-free shell on the guest deposited host core (**Figure 1.7**).

(D) *In situ* encapsulation strategy: This technique requires combining all of the ingredients of the host matrix as well as functional guest precursors in a suitable solution, where the guest species and host framework form concurrently. ^[59] The balance of nucleation rates of both materials is substantially influenced by numerous parameters, including precursor concentrations, solvent selection, reaction temperature, and modulators. Because of its simplicity, cheap production cost, and reproducibility, this recently invented one-pot synthesis process is well suited for composite materials in practical applications. Nonetheless, because both the guest species and the host matrix form synchronously under the same reaction setting, controlling the growth of these two separate complexes is a difficult challenge (**Figure 1.7**).

1.4 Applications of Advanced Functional Porous Materials (AFPMs)

Porous materials have been explored in diverse field of applications (**Figure 1.8**) such as, ^[60,61]

Gas storage

Separation of gases and industrially important liquids

Biomedical applications

Pollutants sequestration

Carbon capture and conversion

Heterogeneous catalysis

Sensing of toxic species

Electrochemical applications

Fuel cell applications

Gas Storage and Separation:

Advanced porous materials play a pivotal role in gas storage and separation applications due to their unique structural properties and high surface area. These materials, which include metal-organic frameworks (MOFs), porous organic polymers (POPs), covalent organic frameworks (COFs) and other, offer an extensive internal network of pores and tailored chemical functionalities. In gas storage, they enable the efficient adsorption and storage of gases such as hydrogen, methane, and carbon dioxide, critical for clean energy and environmental solutions. Moreover, these materials excel in gas separation by selectively adsorbing specific molecules, facilitating processes like natural gas purification, carbon capture, and air separation. Their tunable pore sizes and surface chemistries make them versatile tools for addressing pressing energy and environmental challenges by enhancing the efficiency and sustainability of gas storage and separation processes. Moreover, gas and liquid separation are critical industrial process for the production of chemicals, fuels, plastics, and polymers but it is also an energy-intensive process due to classical cryogenic distillations. Advanced functional porous materials can potentially fulfil the energy efficient separation cost.

Sensing:

Advanced functional porous materials have found promising applications in sensing applications owing to their exceptional surface properties and selective adsorption capabilities. Materials like metal-organic frameworks (MOFs), porous organic polymers (POPs) and covalent organic frameworks (COFs) are especially well-suited for this purpose. Their high surface area and tunable pore structures enable them to selectively recognize specific molecules or ions, making them valuable components in gas and chemical sensors. MOFs, for instance, can be tailored to detect various gases, including toxic pollutants or volatile organic compounds, while POPs can be designed to sense specific chemicals or biomolecules. These advanced porous materials provide a platform for highly sensitive, selective, and rapid detection methods, opening doors to applications in environmental monitoring, healthcare diagnostics, and industrial safety, where precise and reliable sensing capabilities are paramount.

Biomedical application:

Advanced porous materials have revolutionized biomedical applications by offering a diverse range of functions and properties that address critical healthcare challenges. Metal-organic frameworks (MOFs), for instance, are being explored for drug delivery systems due to their high surface area and tunable pore sizes, enabling the controlled release of therapeutics with precision. POPs or COFs have shown promise in tissue engineering and regenerative medicine, as their biocompatibility and porous structures can support cell growth and tissue regeneration. Zeolites and mesoporous silica materials have been used as drug carriers and imaging agents in cancer therapy and diagnostics, while porous hydrogels

have been employed for wound healing and drug delivery applications. These advanced porous materials are driving innovations in drug delivery, tissue engineering, diagnostic tools, and personalized medicine, offering novel solutions to improve patient care and outcomes in the field of biomedicine.

Heterogeneous Catalysis:

Advanced porous materials have emerged as crucial catalysts in heterogeneous catalysis applications, catalysing a wide range of chemical reactions with improved efficiency and selectivity. MOFs, POPs and COFs, with their well-defined pores and tunable chemical functionalities, are particularly valuable in this context. MOFs, for example, offer a versatile platform for immobilizing metal catalysts, enabling precise control over reaction conditions and enhanced catalytic performance. POPs and COFs, known for their ordered microporous structures, are used extensively in the petrochemical industry for catalytic cracking and hydrocracking processes, facilitating the conversion of feedstock into valuable products like gasoline and petrochemicals. Additionally, covalent organic frameworks (COFs) have shown promise in catalysing various reactions due to their robust structures and adaptable chemistry. These advanced porous materials are driving advances in green and sustainable chemistry by enabling more efficient and environmentally friendly catalytic processes in industries such as energy production, petrochemicals, and fine chemicals manufacturing.

Magnetism:

Magnetic property is very important for many applications viz. high-density information storage, quantum computing, magnetic resonance signal enhancer and many more. Advanced porous materials are increasingly finding applications in the field of magnetism, contributing to a wide range of technological innovations. One notable example is the use of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) as platforms for magnetic nanomaterials. These porous materials can be functionalized with magnetic nanoparticles, enabling them to be employed in various areas such as magnetic resonance imaging (MRI) contrast agents and targeted drug delivery systems. Additionally, some porous materials themselves exhibit interesting magnetic properties, making them suitable for spintronic devices and data storage applications. For instance, certain spin-crossover MOFs can switch between magnetic states under external stimuli, holding potential for next-generation memory devices. These developments in the magnetism of advanced porous materials open up exciting opportunities in medical diagnostics, information technology, and materials science, promising enhanced performance and novel functionalities in a wide array of applications.

Pollutants sequestration:

In the field of pollutant sequestration, porous materials have become potent tools with a variety of uses for tackling environmental contamination issues. They are extremely effective at adsorbing, capturing,

and removing a variety of pollutants from water and air sources because to their distinctive structural characteristics, which include large surface area and specialized pore sizes. Organic pollutants, heavy metals, and volatile organic compounds are frequently removed from industrial effluent and exhaust gases using porous adsorbents like activated carbon and metal-organic frameworks. These materials can be customized to selectively target particular contaminants, offering effective and affordable options for the filtration of water and air. Additionally, porous materials have played a crucial role in tackling new environmental problems, such as the collection and sequestration of greenhouse gases like carbon dioxide, which has aided in attempts to reduce climate change. In summary, porous materials' numerous pollutant sequestration properties highlight how important they are for protecting the environment and advancing environmentally friendly methods of pollution control and mitigation.

Electrochemical applications:

Due to their distinct structural traits and adaptable qualities, advanced porous materials are crucial in a variety of electrochemical applications. These substances, which have a large surface area and a connected network of pores, make an excellent foundation for many electrochemical processes. One common use for porous electrodes is in energy storage systems like supercapacitor and batteries, where they increase the electroactive surface area and enable quicker ion diffusion and higher charge/discharge rates. Additionally, porous materials are essential for fuel cell technology because they operate as gas diffusion layers and catalyst supports to enhance electrochemical reactions. As the porous structure may be modified to accommodate particular analytes, they also find use in sensors and biosensors, where they improve sensitivity and selectivity. In conclusion, porous materials have shown to be crucial elements in many different electrochemical systems, advancing energy storage, renewable energy conversion, and analytical sensing technologies.

Electro-catalysis:

In the field of electro-catalysis, porous materials have become key players, enabling a wide range of applications that promote improvements in sustainable energy and environmental remediation. They are excellent candidates for supporting electro-catalysts, which quicken chemical processes at the electrode-electrolyte interface thanks to their naturally high surface area and customizable pore structure. Porous materials serves as catalyst supports in the field of fuel cells, improving the effectiveness of oxygen reduction and hydrogen oxidation reactions. Additionally, they are essential for electrochemical water splitting, which makes it possible to produce clean hydrogen for the storage of renewable energy. Porous materials can be specifically designed to selectively absorb and catalytically breakdown target pollutants in electrochemical sensors and pollution treatment systems. In conclusion,

porous materials continue to spur electro-catalysis innovation, easing the transition to more environmentally friendly and sustainable energy conversion and pollution control procedures.

Although these materials are widely being used in such above said applications, but not very well explored for the capture of toxic and hazardous pollutants. In this regard, porous materials have been found to be potential candidate for environmental applications. Luminescent metal-organic frameworks (LMOFs) have showed tremendous potential in the detection of environmentally harmful and toxic species. But very often MOFs have shown stability issues like poor chemical stability and less hydrolytic stability. Due to this poor stability, it hinders their applications related to the remediation of water pollutants. On the other hand, porous organic material can be excellent candidate for the sequestration of environmentally hazardous water contaminants due to their high physiochemical stability.

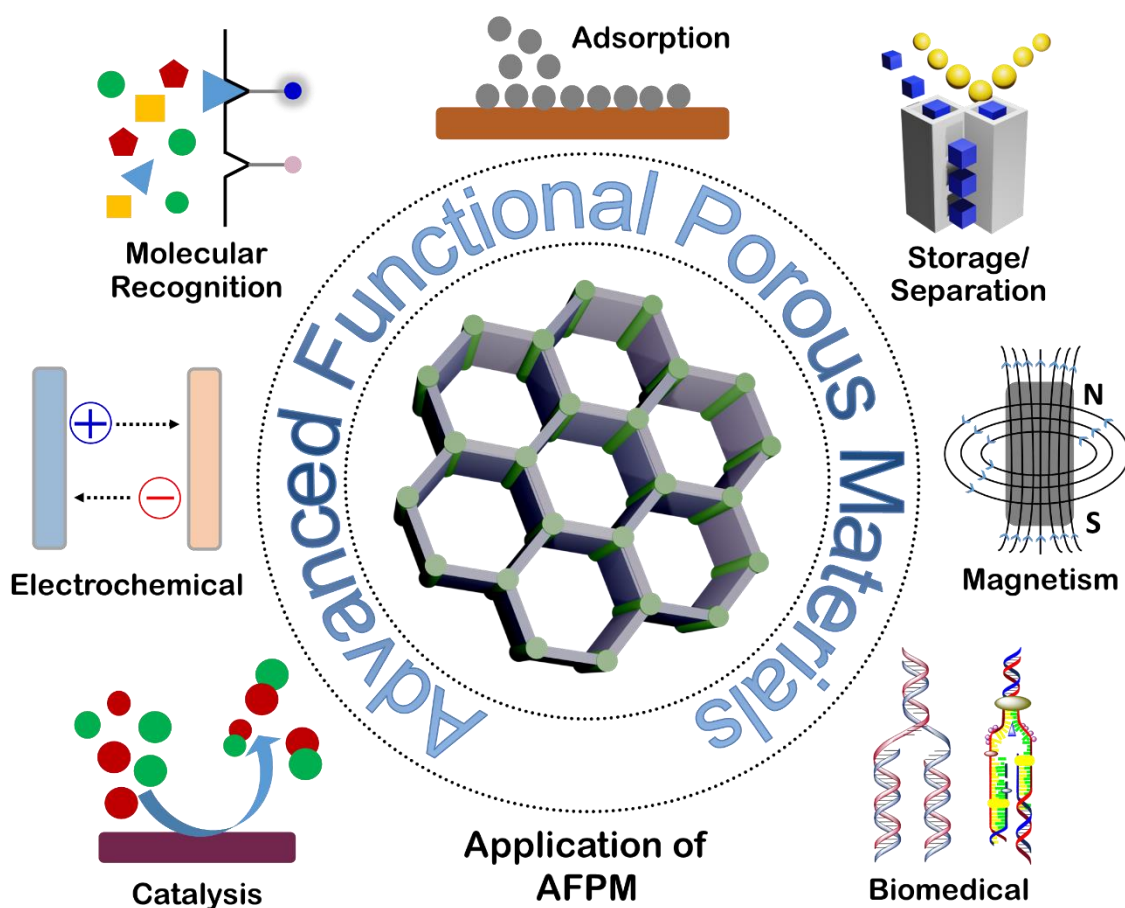


Figure 1.8 Schematic representation of various application of advanced functional porous materials (AFPMs).

1.3 Water Pollution and Remediation

The gradual growth in environmental pollution has become a global concern, and significant attention is being dedicated worldwide to pollutant clean-up. By creating such pollutions, advanced civilizations and global industrializations have had a major negative impact on the ecosystem.^[62] Water pollution has recently emerged as a key source of worry among all types of pollution. It has been noted that increased water pollution and excessive usage of fresh water have had a bigger impact on the Earth's water system.^[63] As a result, almost half of the world's population has been discovered to be living in areas designated as water stressed zones. According to recent figures, almost 1 billion people do not have access to safe drinking water. This situation is projected to deteriorate worse in the near future. According to a recent assessment, the United Nations (UN) estimates that there will be a 40% shortage of clean water in the next 15 years.^[64] Furthermore, it has been shown that nearly 2 million people die each year from waterborne diseases such as diarrhoea, poor hygiene, and so on, which are caused by widespread water contamination. The Safe Drinking Water Act (SDWA) generally defines water pollutants or contaminants as physical, chemical, or biological materials or substances present in water.^[65] Chemical water pollution, pathogen contamination, physical water pollution, and other types of water pollution are well known and are generating substantial difficulties. Water pollution caused by numerous harmful and hazardous compounds has been identified as one of the most dangerous and threatening to life systems. Water pollution caused by chemicals has been observed to gradually increase as dirty waste waters from various sources are released straight into effluents (**Figure 1.8**). Chemical water pollutants have been further broadly classified into organic and inorganic pollutants.^[65,66] In the case of organic pollutants, this subgroup of water pollutants includes a diversified and broad variety of organic molecules. Different types of dye molecules, herbicides/pesticides, oils, pharmaceutical goods, personal care products, polyromantic hydrocarbons, detergents, and other organic pollutants are the most frequent and well-known.^[67] Organic pollutants have been discovered to be emitted through a variety of residential activities, industry, agricultural fields, and so on. On the other hand, inorganic pollutants include different types of heavy metals (e.g., Hg^{2+} , Pb^{2+} , Cd^{2+} etc), oxo-anion (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, AsO_4^{3-} , SeO_3^{2-} , SeO_4^{2-} etc.), radionuclides (e.g., ^{99}Tc , ^{131}I , ^{129}I , ^{137}Cs , ^{89}Sr , ^{235}U etc) etc.^[68] Organic pollutants have a greater variety and number of inorganic contaminants. However, inorganic contaminants last far longer in the environment than organic pollutants. Furthermore, inorganic contaminants are extremely difficult to breakdown or convert into eco-friendly species. Organic pollutants, on the other hand, are less persistent in the environment and more easily degraded. Furthermore, organic pollutants have been labelled as pseudo-persistent pollutants to our environment because a large number of organic materials have been discovered to be discharged into various water effluents. In nature, all of these inorganic and organic contaminants are poisonous, harmful, and carcinogenic. Chemical water contamination causes a number of deadly diseases.

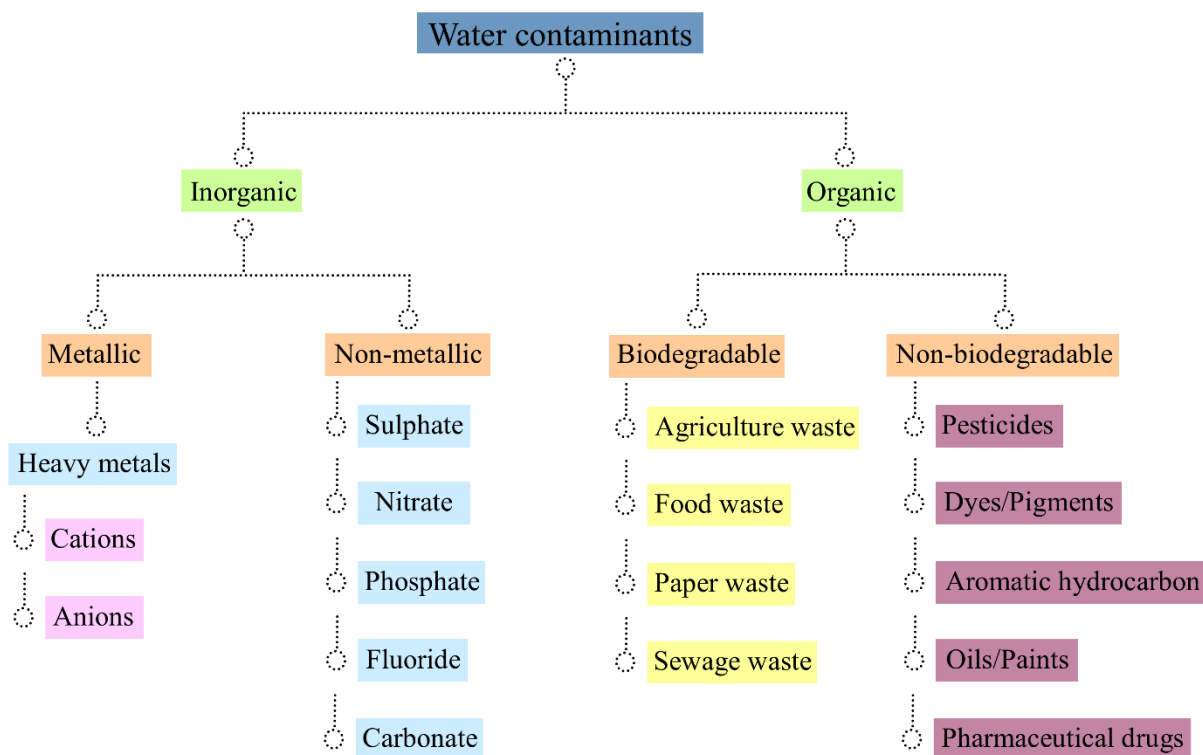


Figure 1.8 Schematic representation of classification of various water contaminants.

Recognising the dangers of water contamination, the United Nations developed the Sustainable Development Agenda in order to offer universal access to safe drinking water. Desalination of saltwater for freshwater or clean water harvesting from groundwater has emerged as a top goal in this regard. However, for real-time applications, these strategies must be efficient and economical globally. Furthermore, widespread use of such approaches may cause a crisis in groundwater levels, and desalination plants for seawater treatment may cause contamination in coastal areas. ^[63a, 67d] In this context, aside from purification of groundwater and seawater, reuse of water has emerged as one of the most promising avenues for addressing the water crisis. Water reuse is increasing popularity, and several forms of technologies are being used to achieve this goal. Precipitation, flocculation/coagulation, membrane technology, sedimentation, biological process, filtering, improved oxidation process, and other techniques are currently used to address water pollution. Although these aforementioned techniques are working, but there are several shortcomings like complicated handling, high operation cost, generation of secondary pollutants, unable to remove wastes completely from water etc. have led researchers to find an alternative solution. Adsorption-based techniques have emerged as an alternative to the aforementioned procedures in this regard. Adsorption-based processes have outperformed other conventional procedures because to their low operating costs, ease of regeneration for use in numerous cycles, comparatively low formation of secondary pollutants, higher waste removal

efficiency, and so on. To date, numerous materials, such as polymer resins, zeolites, activated carbons, mesoporous silica, mesoporous clay materials, and others, have been investigated for the removal of toxic and hazardous chemical waste from water by adsorption. However, the sluggish kinetics, limited capacity, comparatively complicated adsorbate production, poor selectivity, and other properties of the aforementioned materials have been discovered to be a challenge for real-time applications with improved efficiency. In recent years, advanced functional porous materials have been explored for the environmental remediation (**Figure 1.9**). Recognition and sequestration of toxic hazardous species by AFPMs has gained paramount interest.

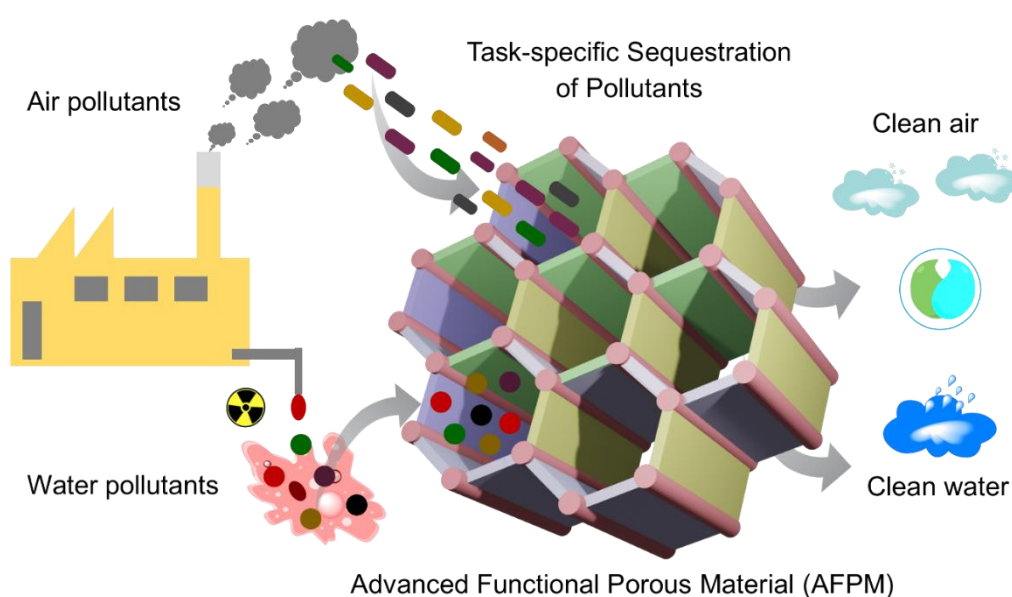


Figure 1.9 Schematic illustration of remediation of the water/air pollutants with advanced functional porous materials.

1.4 Thesis Overview

All of the scientific studies in this thesis are concerned with the use of AFPMs as a tool for the detection and sequestration of harmful environmental contaminants. Specific to the task, AFPMs are designed and synthesised to recognise and encapsulate harmful air and water contaminants. In the first part of the work, functionalized luminescent metal-organic framework and luminescent porous organic polymer have been synthesized for the detection of toxic hazardous pollutant from water. In the second part, a robust hydrolytically stable ionic porous organic polymer and a cationic hybrid composite materials have been synthesized for the selective sequestration of toxic pollutant (metal-based oxoanions) from water. To the best of our knowledge, such strategic studies related to the production and explorations of AFPMs as a tool for environmental remediation are studied relatively little in the literature.

In the second chapter, a hydrolytically stable luminescent MOF (MOF-808) has been synthesized. After that MOF-808 has been post synthetically modified by para-amino benzoic acid (PABA) and forms PABA@MOF-808. PABA@MOF-808 detects nitric oxide (NO) via chemodosimetric approach. Free amine groups are there in the pore of the MOF channel which sense NO via chemical reaction. This process is going through via deamination reaction and it selectively sense NO in both aqueous and gaseous phase in presence other interfering analytes. An exclusive fluorogenic turn-off response was observed with very good quenching constant (K_{sv}) and limit of detection (LOD) values. Furthermore, flexible mixed matrix membrane (MMM) has been fabricated with PABA@MOF-808, which can detect NO both in water medium and vapor phase.

MOFs have some drawbacks as it is not that much stable, in the third chapter, a neutral highly luminescent porous organic polymer (IP_{POP}-1) has been synthesized to overcome the shortcomings of the MOF compound for the detection of micropollutants in water. IP_{POP}-1 selectively detects electron deficient antibiotics (NFZ, NFT) and pesticides (CHPS, nitrofen) from water with a very good quenching constant (K_{sv}) and a good limit of detection value (LOD). The reason behind this good quenching is the charge transfer happens between the high electron dense compound (IP_{POP}-1) to electron deficient micropollutants (NFZ, NFT, CHPS and nitrofen). IP_{POP}-1 could be regenerated for ongoing usage after the detection test with no obvious loss of function. Finally, IP_{POP}-1 based mixed matrix membranes were fabricated and employed to mimic real-time antibiotic detection in water.

Detection of toxic materials from water is not the final solutions, extraction of those toxic pollutants from water is utmost necessary. For later part of this thesis work effective sequestration of toxic pollutants by ionic porous organic polymer and inorganic-organic hybrid composite materials have been discussed.

In the fourth chapter, a chemically stable ionic porous organic polymer (iPOP-5) has been synthesized for the selective sequestration of toxic CrO_4^{2-} , and ReO_4^- anions from water. In this work it has been shown that by changing the morphologies of the compound the efficiencies of the compound have been improved. Among different morphologies flake morphology [iPOP-5(F)] shows ultrafast kinetics over spherical [iPOP-5(S)] ones. Notably, in the presence of too many other anions, iPOP-5(F) selectively removed Cr(VI) and Re(VII). Additionally, the substance showed effective oxoanions separation over a wide pH range and in a variety of water systems, including potable, lake, river, sea, and tannery water. Also, a detail mechanistic analysis revealed that the ability to attain rapid sequestration efficiency is aided by the infrequent in situ exfoliation of flakes morphology of iPOP-5 into thin nanosheets.

In the last chapter, we have synthesized a hybrid composite material for selective entrapment of radioactive TcO_4^- ion from simulated nuclear waste. To overcome the shortcomings of single material in sequestration process now in this work we have explored a composite material. MOP@iCOF, a hybrid composite material has been synthesized where we have chosen the MOP and iCOF as a single component first. Zr-MOP has been chosen as guest due to the presence of its Zr-SBU which is well known for its interaction with the oxoanion. Apart from this Zr-MOP has some of the free NH_2 group which is aligned along the pore that can interact with the oxoanions through H-bonding, also it has free Cl^- anions which is exchangeable with the ReO_4^- anions. Moreover, we have chosen iCOF, due to its high chemical stability and ample number of free exchangeable Cl^- anions. MOP@iCOF entraps TcO_4^- very fast also it selectively captures ReO_4^- in presence of other interfering analytes. This material is highly recyclable also it shows very good removal efficiency in different water system (lake water, river water, sea water). Further we have fabricated this material into a mixed matrix membrane for real time applications.

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Chapter 2

Post Engineering of a Chemically Stable MOF for Selective and Sensitive Sensing of Nitric Oxide

2.1 Introduction

Nitric oxide is produced naturally by oxidation of amino acid (L-arginine to L-citrulline) with a heme-containing enzyme known as nitric oxide synthase (NOS).^[1] Nitric oxide (NO) works as a retrograde neurotransmitter, allows the blood flow in brain and also has significant roles in intercellular signaling.^[1,2] It can act as a regulatory agent in various physiological and pathological process e.g., leukocyte adhesion inhibition, bronchodilation, renal functioning etc.^[1,3] Owing to the immense importance of NO in various biological signalling process it has attracted much attention to the biologists, chemists, and medical researchers.^[4] On the other hand, excess concentration of NO in aqueous medium and air causes deleterious consequences to the living systems, especially for human being.^[5,6] Therefore, considering both the importance and adverse impacts of nitric oxide selective and sensitive monitoring of NO from water medium as well as vapour phase has become an imperative research topic, which is highly relevant to practical environmental surveillance. Moreover, in perspective of various biological and pathological process the selective identification of NO is also vital. However, owing to its very brief lifetime along with high diffusivity and volatility it is extremely difficult to precisely recognize NO.^[1,7] In this view, up until now, several efforts have been attempted to develop effective sensory materials for the specific recognition of nitric oxide from different medium. Also, various methods like calorimetry, electron paramagnetic resonance, electrochemical and chemiluminescence have been applied for the detection of NO.^[1,7] However, all these methods exhibited several limitations such as time consuming, less efficiency, expensive, complex technique etc.^[7] In regard with this, recently, fluorescence based detection methods have been considered as promising over other due to its unique properties including quick response time, easy simple economical operation, large Stokes shifts, high sensitivity towards real-time monitoring and non-invasive nature.^[8,9] Moreover, the optimal fluorescence probe should show a notable variation in fluorescence intensity along with high selectivity even in the presence of interfering analytes.^[10] Owing to these advantages, numerous small organic molecules and metal based fluorescent probes have been developed and further utilized for the detection of various environmentally relevant toxic species. Importantly, to our particular interest, ortho-diamine based fluorescent probes and metal based complexes are widely been used for NO sensing.^[11-16] However, in spite of substantial progress in the development of in vivo targeted synthetic probes, there are several intrinsic limitations including the water solubility and hydrolytic instability of the organic molecules based probes, which restricts their large-scale real-time sensing application. In order to overcome these shortcomings, development of suitable materials for efficient detection of toxic species such as NO is the primary aspect of current research in this domain.

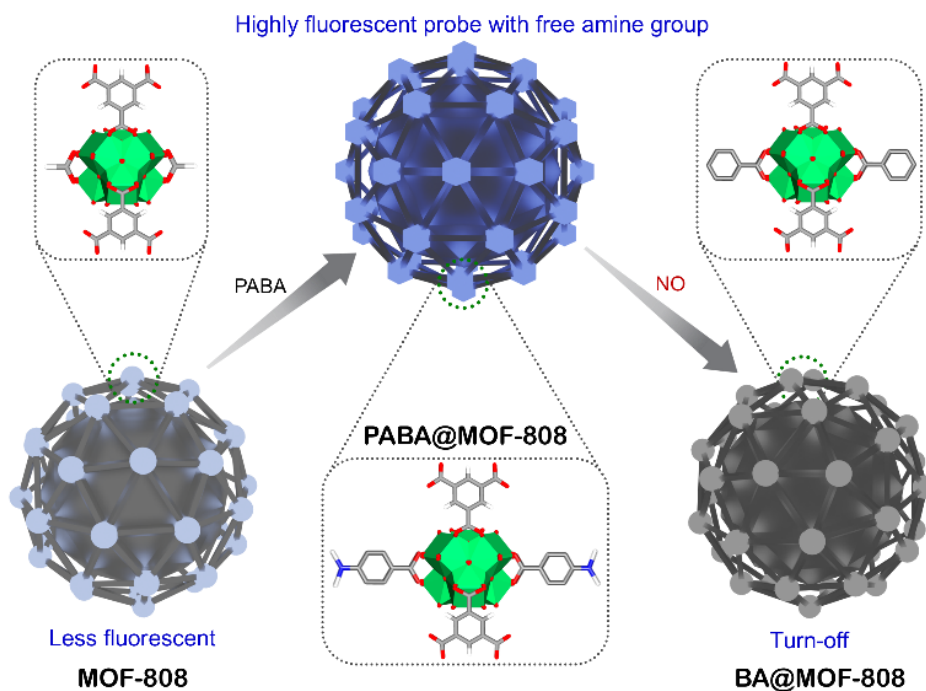
In this context, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have come up as a propitious and unique class of materials with crystalline architecture.^[17] MOFs are porous solid

materials, made up with coordination assembly of organic ligands and metal nodes or clusters, where organic ligands and the metal clusters can be functionalized in line with the desired applications. [18-20, 62] Moreover, because of their unique characteristics such as highly porous nature, large surface area, tunable functionality, structure-property correlation, MOFs have appeared as contender target specific guest approachable host system, and therefore received intense attention in different leading applications including gas storage, chemical separation, catalysis, electrochemistry, biology and most importantly sensing. [20-22] That being said, luminescent MOFs (LMOFs) a subclass of MOFs have extensively been studied for the chemical sensing application. Incorporating intense emissive guests, d^0 or d^{10} metal cations, and prudent selection of π -electron rich organic linkers are just a few of the deliberate strategies that have made LMOFs the frontrunner in the identification of numerous toxic substances. [23-25] Lower detection limits and quick response mechanisms are made possible by the combined advantages of molecular sieving and confinement effect in porous MOFs. These advantages include significant improvements in selectivity as well as host-guest interactions that initiate signal transduction in counter-reaction to a specific analyte. [26, 27]

Furthermore, the heterogeneous nature of MOFs makes it simple to recover for recycling purposes in such an application. [28] In addition, the facile design strategy with the judicious choices of linker to incorporate specific functionality into the framework conveyed high selectivity and sensitivity to the host framework towards the incoming analyte. [29] In this line, linker modulation imparts a great impact in the design of luminescent MOFs which can be easily achieved via post-synthetic modification of the organic ligand or especially the metal cluster of MOFs. [30, 31, 61]

The capability to detect low concentration of nitric oxide is of emerging importance. In order to monitor the water quality and air quality index, it is best to identify harmful NO in water and vapor as early as possible, before the concentrations rise, collect in the local environment, and result in significant harm. [14, 32-35] In the literature, majority of the NO sensing studies are depending upon electrochemical measurement, which required exclusive expert personnel, complex operation and high cost. [36-39] This has largely been limits the versatile easy sensing application. Therefore, techniques that can offer simple and economical way to detect NO with high sensitivity, selectivity and more importantly based on portable instrumentation is highly desirable. On the other hand, a material for target specific analyte detection in aqueous media must first be stable in water in order to be used in practice. [9] Along with this, considering the fact that the chemical environment of NO containing vapour is acidic, it is particularly important for the probe to be highly stable in extreme acidic condition. Furthermore, in the above mentioned reports, the NO sensing studies have been done with typical powder form, which further restricts the real-time practical monitoring. Therefore, development of highly efficient, chemically and hydrolytically stable luminescent MOF-based sensor in the form of device (such as

membrane) for the selective and sensitive detection of nitric oxide species is highly desirable. With this aim along with considering all the aforementioned discussion, in this work we have chosen Zr(IV)-based MOF-808 as a promising platform for developing an efficient sensor for NO detection by rational post integration of specific functionality, owing to its following unique properties. MOF-808 is a well-known high chemically, thermally and hydrolytically stable Zr(IV) metal cluster based porous MOF.^[40, 41] The presence of benzene core ligand together with d10 metal cations make MOF-808 as a luminescent probe, which further award utilization as a sensory material.^[42, 43] Moreover, the Zr⁶⁺-oxo cluster of MOF-808 offer tunable functionality in the framework by allowing simple yet versatile, facile induction of diverse functional moieties in its secondary building unit (SBU) by exchanging the formate linker.^[42-45] Furthermore, MOF-808 was found as an ideal MOF-candidature for the fabrication of mixed-matrix-membranes (MMMs), because of its special cluster coordination and the ensuing simplicity of adding more functional molecules.^[46] All these characteristics provide a unique scaffold that can be effectively used as per our targeted NO detection application. Following these guidelines, herein, we have embraced the chemodosimeter-based approach for demonstrating efficient detection of NO both from aqueous and vapour phase by fabricating a highly stable post-synthetically modified MOF-808-based luminescent probe. It should be mentioned, unlike chemosensors, the target analyte reacts with the dosimeter (probes) in the chemodosimeter in an irreversible manner to produce signals that are permanent.^[47] Because of this, it has been found that both the selectivity and sensitivity toward target analyte is higher for chemodosimeters with comparison to chemosensors.^[48] Therefore, in this work, we have developed a probe by post-synthetic modification of Zr⁶⁺-metal cluster of MOF-808 by coordination grafting with p-aminobenzoic acid (PABA) (Scheme-1, Figure 2.1a). This strategic engineering of MOF-808 with PABA helps to provide high luminescent nature along with target specific functionality (free amine group) in the probe (PABA@MOF-808). Based on the knowledge that NO react with free amine groups,^[7] we have deliberately incorporated free accessible amine group in the framework which can detect NO. Motivated by the strong luminescent nature with high chemical stability, we investigated the detection ability of PABA@MOF-808 towards NO in both water and vapour (Scheme-1). PABA@MOF-808 was found to exhibit highly sensitive and selective detection of NO over other relevant species with superior fluorescence quenching efficiency and low limit of detection (LOD) values. Furthermore, the in-depth mechanism of the fluorescence quenching phenomena of PABA@MOF-808 by NO was demonstrated with the help of the fluorescence resonance energy transfer (FRET), photoinduced electron transfer (PET), density functional theory (DFT) studies and the counter collision process between the fluorescent probe and the analyte. Finally, considering the real world application, a self-standing, flexible and processable mixed-matrix membrane (MMM) of PABA@MOF-808 was fabricated and was further applied for the effective detection of NO from water medium and qualitative identification from vapour phase.



Scheme 1. Schematic illustration of post engineering of chemically stable MOF and further detection of nitric oxide (NO) with free amine group containing fluorescent probe (PABA@MOF-808).

2.2 Experimental

Materials: 1,3,5 benzene tricarboxylic acid (BTC), DEA NONOate sodium salt hydrated, paminobenzoic acid (PABA) and NaClO were purchased from Sigma-Aldrich. ZrOCl_2 was purchased from Merck. All the dry solvents and other chemicals were obtained locally. These chemicals were used without further purification.

Physical Measurements: Powder X-ray diffraction patterns (PXRD) were measured on Bruker D8 Advanced X-Ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a tube voltage of 40 kV and current of 40 mA in 5° to 40° 2θ range. Thermogravimetric analyses were recorded on Perkin-Elmer STA 6000 TGA analyzer under N_2 atmosphere with a heating rate of $10^\circ \text{C min}^{-1}$. The Fourier transform infra-red (FT-IR) spectra were recorded on NICOLET 6700 FT-IR Spectrophotometer using KBr Pellets in $400\text{--}4000 \text{ cm}^{-1}$ range. 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. Morphologies of the crystalline materials were recorded with Zeiss Ultra Plus field-emission scanning electron microscopy (FESEM) with integral charge

compensator and embedded EsB and AsB detectors [Oxford X-max instruments 80 mm². (Carl Zeiss NTS, GmbH), Imaging conditions: 2 kV, WD = 2 mm, 200 kX, Inlens detector]. Solid state UV-visible spectra were recorded on Perkin-Elmer UV visible spectrometer. UV spectra were recorded on Shimadzu UV 2600 Spectrophotometer. ¹H NMR spectra were recorded on a JEOL 400 MHz or Bruker 400 MHz spectrometer. XPS studies was performed using K-Alpha+model (Thermo Fischer Scientific, UK) with Al K α source. Raman spectra were acquired with an Xplora PLUS Raman microscope (Horiba Company) (785 nm laser and a 1200 lines/mm grating). All fluorescence measurements were done on Jobin Yvon Fluoromax-4 spectrofluorometer with stirring attachment. The time correlated singlephoton counting method was used for the fluorescence lifetime measurement with the help of an Edinburgh Instrument Life-Spec II spectrometer.

Safety note: DEA NONOate sodium salt hydrated and few other chemicals used in this study are highly toxic in nature. Proper safety protocol should be followed before carefully handling these chemicals.

MOF-808 Synthesis: MOF-808 was synthesized following a reported protocol.^[49] At first, 537 mg of 1,3,5-benzenetricarboxylic acid (2.5 mM) and 2.42 gm of ZrOCl₂.8H₂O (7.5 mM) were dissolved in 160 ml of dimethylformamide (DMF). Then to this 160 ml of formic acid was added and the whole thing is capped in 500 ml screw capped glass jar heated at 130 °C for three days. After that a white precipitate was formed. Then it was collected by several washings and centrifuged. After that it was dried in an oven at 70 °C for 6 hours.

Synthesis of PABA@MOF-808: PABA@MOF-808 was synthesized following a reported protocol.^[50] At first MOF-808 (200 mg) was well dispersed in DMF (10 ml) ultrasonically, then PABA (0.72 g, 5.2 mM) was added to the dispersed phase of MOF-808 and reacted at 60 °C for 48 hours to obtain amino functionalized MOF-808. The desired product was washed thrice a times with water and ethanol respectively, then it was placed in an oven dried at 100 °C for 12 hours.

Preparation of PABA@MOF-808 based mixed matrix membranes (MMMs): The following reported standard protocol has been adopted for the fabrication of the MOF-polymer based membrane.^[51] To prepare the membrane, at first, a versatile polymer, PVDF (150 mg) was dissolved in 1.9 ml of DMF by stirring the mixture at room temperature for 24 hours. The PVDF-DMF mixture results a viscous sticky solution after one day. Then, a certain amount of fine powder of PABA@MOF-808 was added with the solution of thus prepared pure polymer to form a homogeneous mixture by stirring the whole solution for another 24 hours. After that, the mixture was casted onto aluminium foil by a regular scraper to make a flat thin-sheet membrane. Thus, fabricated system was then dried in a hot plate and further soaked in DI water, led to the fast delamination of the MMMs. Thus, obtained free-standing films were dried in air and further cut into small pieces for sensing application.

Preparation of the analytes:

DEA NONOate sodium salt hydrated (purchased from Sigma-Aldrich was used as received) was used as a source of NO. Gaseous nitric oxide was synthesized by the reaction between KI (1 M) and NaNO₂ (1 M) and catalyzed by acid. ^[52] Aqueous solutions of NO₂⁻ (nitrite) and NO₃⁻ (nitrate) were prepared from NaNO₂ and NaNO₃ respectively. Stock solution of 0.1 mM hydrogen peroxide (H₂O₂) was prepared by diluting 30% H₂O₂ solution. Aqueous solution of NaClO was used as a source of ClO⁻ (hypochlorite). Singlet oxygen (¹O₂) was generated from the reaction of hypochlorite and H₂O₂. ^[53]

Fluorescence Study: In typical experimental setup, 1 mg of MOF has been taken in a cuvette and 2 mL water has been added to that. Initial luminescence spectra of MOF in water has been recorded by exciting at different wavelength (spectra recorded in the range of wavelength ~300- 500 nm). Then to the dispersed MOF in water we have added the stock solution of NO in water (20 µL to 300 µL) and spectra were recorded for each addition. With each addition of NO, we found quenching in the fluorescence emission of MOF. For competing studies, we have taken NO₂⁻, NO₃⁻, H₂O₂, ClO⁻, ¹O₂ in water. In a typical way, for initial study we have taken 1 mg of MOF in 2 mL of water. To the dispersed MOF solution we have added 300 µL of the competing species from the stock solution and recorded the corresponding spectra to check the response of MOF. Later, in a similar way to the dispersed MOF (1 mg) in water medium (2 mL) we have added 300 µL of competing analyte and followed by the addition of 300 µL NO solution from the stock as prepared earlier. We have recorded both responses of MOF in presence of competing analytes and in presence of both competing analytes and NO. By combining these two responses we got the selectivity of MOF towards NO in presence of other competing analytes.

Quantum calculation method:

For further mechanistic insight into molecular level pathway for selective and dynamic photoluminescence quenching mediated by nitric oxide (NO) and other ROS/RNS species, we performed First-principle calculations based on density functional theory (DFT) and obtained HOMO – LUMO energy gaps for subunit of PABA@MOF-808 along with NO and other ROS/RNS species. Discovery Studio 2017 (Accelrys) program was used for DFT calculations. All the DFT calculations were performed at fine quality calculation level. The single-point energy calculations were performed using three parameters B3LYP function considering DMol3 code. In the beginning, the molecular structures of subunit of PABA@MOF-808, NO and other ROS/RNS species were fully relaxed using geometry optimization by keeping Auto mode Multiplicity factor, Double Numeric Plus Polarizing (DNP+) basis set and water as solvent. Subsequently, the structural simulation performed using

simulated annealing technique on geometry relaxed subunit of PABA@MOF-808 to find possible interaction site with NO and other ROS/RNS species.

2.3 Result and Discussion

In the starting, MOF-808 was synthesized via solvothermal reaction according to the reported protocol by reacting its precursors benzene-1,3,5-tricarboxylic acid and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.^[40] After synthesis, the powder compound was centrifuged and was washed thrice with DMF followed by water and acetone before dried in oven. Preliminary, to check the successful formation, structural integrity and crystallinity of the synthesized compound, the powder x-ray diffraction (PXRD) of as-synthesized phase was recorded and the pattern was found to well matched with the simulated pattern of MOF-808, which indicated formation of MOF-808 with bulk phase purity (Figure 2.1b). Next, to get the desolvated phase, the as-synthesized MOF-808 was dipped into methanol for 3-4 days, followed by activated at 100 °C for 12 hours under vacuum. The desolvated MOF-808 was again characterized by PXRD, which suggest similar crystallinity and structural integrity was retained in the activated phase (Appendix Figure 2.1). Thermogravimetric analysis (TGA) profile of desolvated MOF-808 shows no weight loss up to 240 °C indicates that there is no trapped solvent molecules present in the pores of the framework (Appendix Figure 2.2). Moreover, the TGA profile exhibited weight loss in two steps, ~11% and ~15% are observed in the temperature range of ~267 °C to ~355 °C and ~462 °C to ~614 °C, which corresponds to the loss of coordinate formate ion and the 1,3,5-benzenetricarboxylate (BTC) linker, respectively, in the SBU of the MOF.^[41, 42] Further, Fourier transform infrared spectroscopy (FT-IR) was applied to characterize the MOF-808. Strong adsorption band near 1443 cm^{-1} and 1600 cm^{-1} in the FT-IR spectra corresponds to the symmetric and asymmetric stretching frequencies of deprotonated carboxylate groups of BTC linker of the MOF, respectively (Figure 2.1c, Appendix Figure 2.3).^[42, 43, 46] This suggest the coordination bridging of BTC ligands with Zr(IV)-metal cations. Furthermore, the high porous nature of the MOF-808 was investigated by N_2 sorption measurement at 77K temperature. The N_2 uptake and corresponding BET surface area for MOF-808 at 1 atm pressure was found to be 763 mL/g and 2250 m^2/g , respectively (Figure 2.1e).

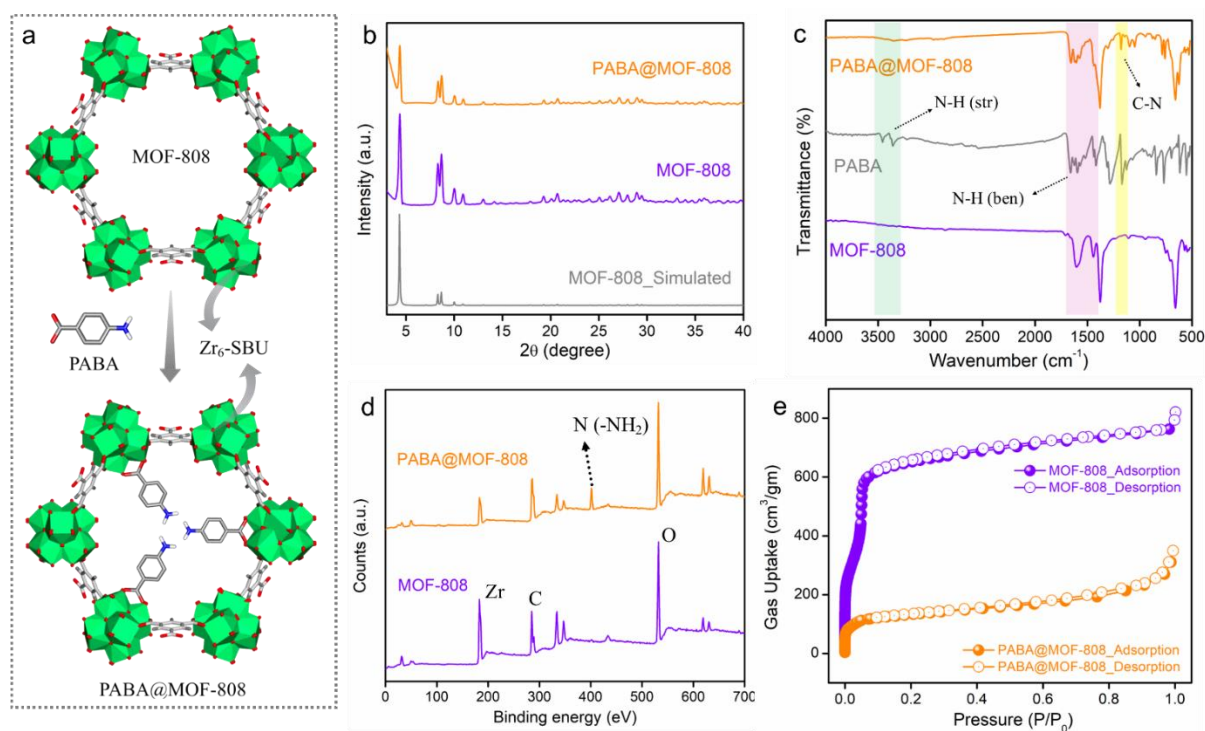


Figure 2.1 (a) Schematic representation of post-synthetic modification (PSM) of MOF-808 with *p*-aminobenzoic acid (PABA). (Colour code: grey-carbon, white-hydrogen, red-oxygen, blue-nitrogen and green-zirconium) (b) PXRD patterns, (c) FT-IR spectra (d) XPS survey spectra and (e) Nitrogen gas sorption data at 77K of pristine MOF-808 and PABA@MOF-808.

The pore size distribution (PSD) calculated for MOF-808 through nonlinear density functional theory (NLDFT) using N₂ adsorption data was found to be 2.01 nm (Appendix Figure 2.4). After these successful structural characterizations, the morphological features of MOF-808 were investigated with the help of field emission scanning electron microscopy (FESEM) analysis. The FESEM images infer the regular robust octahedron shape with smooth surface of the framework (Appendix Figure 2.5). Also, the energy dispersive spectroscopy (EDS) with elemental mapping image of MOF-808 shows that C, O, Zr elements are evenly distributed throughout the compound (Appendix Figure 2.6). After the establishment of the highly crystalline porous structure of MOF-808, it was subjected to post-synthetically modified with *p*-aminobenzoic acid (PABA) to get free amine (-NH₂) group containing probe - PABA@MOF-808, following a reported protocol (see experimental section for details).^[46] Thus synthesized compound was thoroughly characterized with following techniques. The PXRD patterns of PABA@MOF-808 were found to be identical to those of MOF-808, depicting the similar structural integrity and crystallinity with MOF-808 after the PSM method (Figure 2.1b). The TGA profile of

PABA@MOF-808 indicated almost similar thermal behaviour with MOF-808 (Appendix Figure 2.7). Now, in order to understand the successful coordinating grafting of PABA in MOF-808 by PSM process FTIR, Raman, X-ray photoelectron spectroscopy (XPS) analysis have been done. The IR spectra of PABA@MOF-808 showed appearance of new peaks at 1181 cm^{-1} which corresponds to the stretching frequency of C-N bond of PABA molecules (Figure 2.1c).^[46] In addition, the Raman spectrum of PABA@MOF-808 clearly shows a peak associated with the N-H bond of PABA at $\sim 1013\text{ cm}^{-1}$, which is not present in pure MOF-808 (Appendix Figure 2.8).^[46]

Moreover, the XPS survey spectra of PABA@MOF-808 indicated peak corresponding to the binding energy of nitrogen atoms at $\sim 401.1\text{ eV}$ compared with that of pristine MOF-808 (Figure 2.1d, Appendix Figure 2.9). All these results validate the successful incorporation of free -NH_2 group in the framework of MOF-808, which is beneficial for the selective NO sensing application. Furthermore, the FESEM images of PABA@MOF-808 revealed that the morphology was found to identical with that of the MOF-808 with a bit rougher surface, which depicted the structural robustness of the post-synthetically modified MOF (Appendix Figure 2.10). Moreover, the EDS and elemental mapping analysis of PABA@MOF-808 showed homogeneous distribution of all the relevant C, N, O and Zr elements (Appendix Figure 2.11). Further, the N_2 sorption data of PABA@MOF-808 showed gas uptake amount of 310 mL/g with BET surface area $472\text{ m}^2/\text{g}$, which was found significantly lower than the pristine MOF-808 (Figure 2.1e). This clearly depicted the incorporation of PABA moiety into the framework.

Now, as aforementioned for real-time aqueous phase detection, a potential sensory material should exhibit high hydrolytic stability. Henceforth to test the water-stability of PABA@MOF-808 was dipped in water for one week. After 7 days the material was filtered, dried and characterized with PXRD, TGA, FTIR and FESEM experiments. Both the PXRD pattern and FTIR spectra of water treated PABA@MOF-808 showed no change in the peak position with the pristine compound, depicted retention of structural integrity (Appendix Figure 2.12 and 2.13). The thermogram of water dipped compound displayed no significant changes suggested similar thermal stability (Appendix Figure 2.14). Moreover, the FESEM images along with EDS and elemental mapping data showed no morphological changes (Appendix Figure 2.15, 2.16a). Moreover, uniform dispersibility was illustrated by illuminating the MOF solution with 532 nm laser light which rendered the Tyndall effect. After 30 min of exposure the exhibition of Tyndall effect proves its stability toward the uniform dispersibility of the MOF dispersion (Appendix Figure 2.16b).^[60] All these results clearly indicated hydrolytic robustness of PABA@MOF-808 which is advantageous for the practical implementation of the probe for aqueous phase NO sensing study.

Apart from these structural and morphological characterizations, optical properties of PABA@MOF-808 was further investigated to check its ability towards sensing application. The solid powder

compound was found yellowish colour under the excitation of UV light. The solid-state UV-vis spectra of PABA@MOF-808 was recorded in the wavelength range of 200 nm to 800 nm, which revealed maximum absorbance of light at ~240 nm to ~290 nm (Appendix Figure 2.17).

Thereafter, the photoluminescence (PL) emission spectra of water-dispersed PABA@MOF-808 was recorded in the wavelength range of ~300 nm to ~500 nm upon excitation at 290 nm, which exhibited broad emission at 310 nm at room temperature (Appendix Figure 2.18). Enthuse from these luminescent properties, high structural stability along with functional recognition moiety (such as pendent $-NH_2$ group), we sought to investigate the sensing studies with PABA@MOF-808 towards NO in both water and vapour medium.

2.4 Sensing Studies

We have investigated the detail photoluminescence performances of PABA@MOF-808 towards NO sensing. First, for the detection of nitric oxide, in a typical sensing experiment 1 mg of PABA@MOF-808 was dispersed in 2 ml of water and the corresponding emission spectra was recorded (Appendix Figure 2.19a). After that certain amount of NO solution (with concentration 1 mmol) was added to it and the corresponding emission spectra was recorded. It was observed that the emission spectra of the probe was quenched rapidly upon addition of the NO solution (Appendix Figure 2.20). In a detail titration experiment, 1 mM aqueous solution of NO were added by incremental amounts of 20 μ L to a total of 300 μ L into the PABA@MOF-808/water dispersion. It was found that the fluorescence emission intensity of the probe was gradually quenched upon incremental addition of NO solution (Figure 2.2a). From this fluorescence quenching profile the quenching constant (K_{sv}) was calculated using the Stern-Volmer equation: $(I_0/I) = 1 + K_{sv}[Q]$, where K_{sv} is quenching constant, $[Q]$ is the molar concentration of the analyte, and I_0 and I are the luminescent intensities before and after addition of the analyte respectively. ^[54] The K_{sv} value of PABA@MOF-808 with a linear fitting at low concentration range for NO sensing was found as $6.10 \times 10^3 \text{ M}^{-1}$ (Figure 2.2b). This result explored the strong interaction between the $-NH_2$ group of the probe and NO. Interestingly, this value is found to be one of the best in the domain of MOF-based NO sensing studies. ^[23] Moreover, for a good sensory material, the limit of detection (LOD) is a necessary parameter in order to evaluate its detection ability for trace concentration. ^[55] The LOD value calculated for PABA@MOF-808 was of 0.715 μ M (21.45 ppb) (Figure 2.2c). These values clearly indicated the highly sensitive detection of NO molecules by the newly developed luminescent probe (PABA@MOF-808). On the other hand, apart from sensitivity, selective identification of targeted analytes is an essential criterion for an ideal sensor. Therefore, to test the selectivity of the probe, we have performed the similar sensing study with other relevant interfering

reactive nitrogen and oxygen species (RNS or ROS) such as nitrate (NO_3^-), nitrite (NO_2^-), hydrogen peroxide (H_2O_2), singlet oxygen ($^1\text{O}_2$), hypochlorite (OCl^-), etc. In the single analyte selectivity test, the solution of these species were individually introduced into the aqueous suspension of PABA@MOF-808 and the emission spectra were recorded before and after the addition. It was found that no any significant changes in the PL spectra of the PSM-MOF was observed after the addition of these species individually with compare to nitric oxide, which confirmed the selective NO detection ability of the probe (Figure 2.2d, Appendix Figure 2.21-2.26). This result invigorated us further to perform the binary selectivity detection test of NO in the concurrent presence of above RNS/ROS species, which is appraised an essential criterion for real world sensing application.

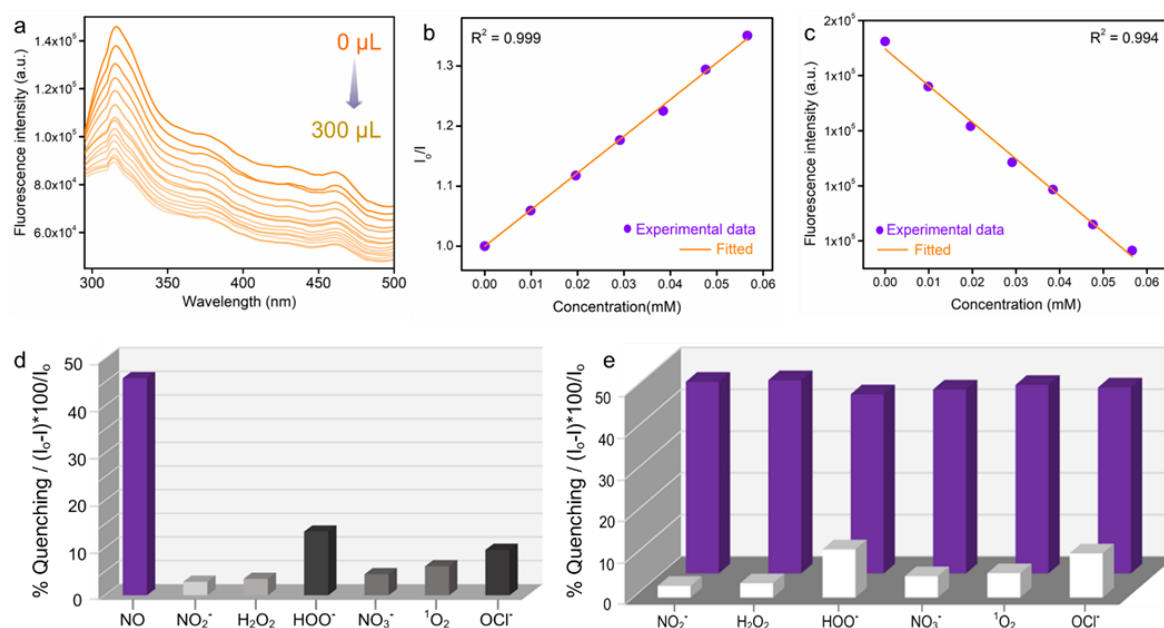


Figure 2.2 (a) Photoluminescence spectra of PABA@MOF-808 in water in the presence of different concentrations of NO. (b) Stern-Volmer (SV) plots for quenching of PL intensity of PABA@MOF-808 by NO. (c) LOD calculation plot (d) Relative fluorescence quenching response towards different RNS/ROS species in water, (e) Relative fluorescence quenching response towards different RNS/ROS species followed by addition of NO solution.

For this experiment, at first we collected the emission spectra of the pristine PABA@MOF-808/water dispersion followed by the addition of 300 μL interfering analytes (HOO^- , NO_2^- , NO_3^- , H_2O_2 , $^1\text{O}_2$, OCl^-). Thereafter, again the emission spectra of the mixture were recorded after introduction of equal amount of NO solution. As anticipated, the fluorescence intensity of PABA@MOF-808 was found to negligibly quench upon the addition of the aforementioned analytes apart from NO (Appendix Figure 2.21-2.26). However, interestingly, upon further addition of an equal amount of NO individually into those mixtures, the emission intensity was observed decrease rapidly (Appendix Figure 2.21- 2.26).

This finding affirmed that the coexisting of other relevant species does not disturb the quenching ability of NO for PABA@MOF-808, which further explored its high selective recognition potential (Figure 2.2e). All together, these observations make the current probe applicable for NO detection in complicated real-time biological systems, preventing off-target reactivity and erroneous responses.

2.5 Sensing Mechanism Studies

This results devoted us further to investigate the in-depth underlying mechanism behind the selective and sensitive detection of NO by PABA@MOF-808. Looking into literatures, it has been found that in general there might be several possibilities of fluorescence quenching, which are majorly includes rupture of MOF's structure in presence of analyte, diffusional interaction like fluorescence resonance energy transfer (FRET), non-diffusional interaction like photo induced electron transfer (PET).^[9] Now, to explore the mechanism, initially we recorded the PXRD of NO treated MOF that retained its crystallinity even after completion of sensing experiment (Appendix Figure 2.27). In addition, no changes in the TGA profile as well as FESEM images after the NO treatment of the MOF system indicated identical thermal stability and robust morphology, respectively (Appendix Figure 2.28, 2.29). From this observation, we discarded the possibility of quenching of PL emission due to the collapse in structure of the probe. After this, we focus into the remaining two probable mechanisms i.e., FRET and PET.

Resonance energy transfer is an excited state phenomenon that results in dynamic quenching occurring through energy transfer between fluorophore and quencher.^[23, 25, 51] To test whether there was any energy transfer between the probe and analyte (quencher), we compared the absorbance spectra of all the analytes and photo luminescent spectra of the probe. It was found that there was significant overlap between the PL spectra of the probe and absorbance spectra of nitric oxide (quencher) (Figure 2.3a). From this observation, it was quiet evident that the energy transfers between PABA@MOF-808 and nitric oxide (NO), is one of the factor in quenching mechanism. Moreover, we moved ahead to check photo induced electron transfer (PET) process as another reason behind this quenching. In the PET process, the excited electron from the probe absorbs light and moves to the analyte's lowest unoccupied molecular orbital (LUMO). Thereafter the probe's ground state is reached by these excited electrons through a nonradiative drop, which further reduces the fluorescence intensity.^[9, 56] To test PET, we performed the DFT theoretical calculation, which provided the HOMO – LUMO energy gaps for unit of PABA@MOF-808 and the RNS/ROS species including NO using B3LYP - D3/SDD - 6– 31G(d) (Figure 2.3b) (see experimental section for details). It was found that among all the species, the LUMO of NO lies between the valance band and conduction band of the probe, which is close to the HOMO of the probe. This enables the electron transfer from the HOMO of PABA@MOF-808 to the LUMO of NO (Figure 2.3b). This result validated the photo triggered electron transfer process between the NO

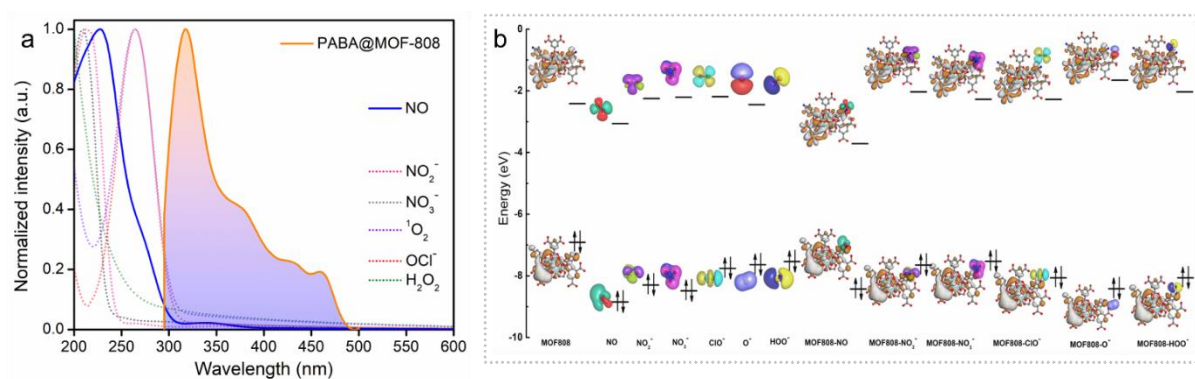


Figure 2.3 (a) Spectral overlap between UV-vis spectra of different ROS/RNS species and photoluminescence (PL) emission spectra of PABA@MOF-808. (b) HOMO and LUMO energy levels of unit of PABA@MOF-808 and different ROS/RNS species along with NO.

and PABA@MOF-808 as another plausible mechanism for quenching of fluorescence intensity. Again, to test the nature of the quenching process, lifetime measurement of the probe before and after NO treatment was performed using time resolved fluorescence experiment. It was observed that the average lifetime of the probe was slightly changed after the treatment of NO solution (Appendix Figure 2.30). This observation suggests the presence of dynamic quenching process behind the fluorogenic turn-off response.

In addition to this, further we assume that there might be some ground state interaction that operates the quenching mechanism. To verify this, we performed solid-state UV-vis spectroscopy study individually with MOF and NO treated MOF samples. After comparing the absorption spectra of the samples before and after NO addition, it was come to our notice that significant change in the UV-Vis spectra with disappearance of ~240 nm peak in case of NO treated MOF (Appendix Figure 2.31). This result clearly suggested that there must be strong ground-state interaction present between the quencher and fluorophore. To validate this conclusion, further, we performed ¹H NMR and FT-IR studies. The ¹H NMR spectra indicated that PABA@MOF-808 contain characteristics peaks of 4-aminobenzoic acids moiety, Whereas NO treated PABA@MOF-808 showed the characteristic peaks of benzoic acid (Appendix Figure 2.32). Moreover, the FTIR spectra suggested the absence of peak at ~1181 cm⁻¹ in the NO treated sample (Appendix Figure 2.33). Also, the XPS spectra indicated disappearance of binding energy peak associated with nitrogen atom in the NO treated MOF powder (Appendix Figure 2.34). All these data indicated that NO underwent fast chemical reaction with the free amino group of 4-aminobenzoic acids moiety present in the luminescent framework resulting in formation of benzoic

acids and thus reduced the luminescent intensity of the probe.^[33] All these studies supported the presence of both static and dynamic quenching mechanism behind the fluorescence-off response of PABA@MOF-808 upon NO addition.

2.6 Mixed-Matrix-Membrane-based sensing studies

Inspired by the above sensing results, we sought to explore the potential of the developed sensor (PABA@MOF-808) towards specific recognition of NO by fabricating a device for the real-time sensing investigation. That being said, although luminescent MOFs have been extensively studied for the detection of various environmentally relevant chemicals, their typical powder-form owing to their high crystalline nature, LMOFs are mostly found as unable to explore its full potential towards sensing application. This is because of the less contact of the probe with the analytes solution due to the nonhomogeneous dispersion of the powder MOFs. Such a phenomenon broadly restricts the maximum probe-analytes interactions which further create less sensitivity, low detection ability as well as inaccuracy in the sensing result.^[9, 10, 57]

Therefore, it is particularly important to develop processable form of LMOFs for the practical sensing application. In this regard, fabrication of LMOFs-based membranes or films, or more especially mixed-matrix-membranes (MMMs) is recently considered as promising strategy for various potential applications.^[58] Albeit, in recent years, significant research has been done to demonstrate MOF-based films or membranes for various utilizations, the exploration of LMOF-based MMMs towards detection of toxic NO gas has largely been unexplored. The development of MOF-based MMMs offer manipulation, easy handling, flexibility and processability of the materials for the practical application. Furthermore, the superior crack resistance ability, high flexibility and processability allowing them to be molded into different device form.^[59] Moreover, the homogeneous distribution of the probes (LMOFs) throughout a large area of the MMM offer high solvent permeation flux and exposed most of the interactive sites of the probe towards upcoming analytes. This increase the analyte-probe (LMOFs) interaction to enhance the sensitivity of the detection.^[59]

Keeping all the consideration in mind, in this work, we developed a mixed-matrix-membrane based on a composite mixture of PABA@MOF-808 with a widely used polymer, poly (vinylidene fluoride) [PVDF] and further used for efficient detection of nitric oxides in gaseous phase as well as in aqueous medium. We have adopted the well-known drawdown coating (doctor-blading) method for the fabrication of luminescent MMMs. In a typical procedure, at first a suspension of PVDF in DMF solvent was prepared.

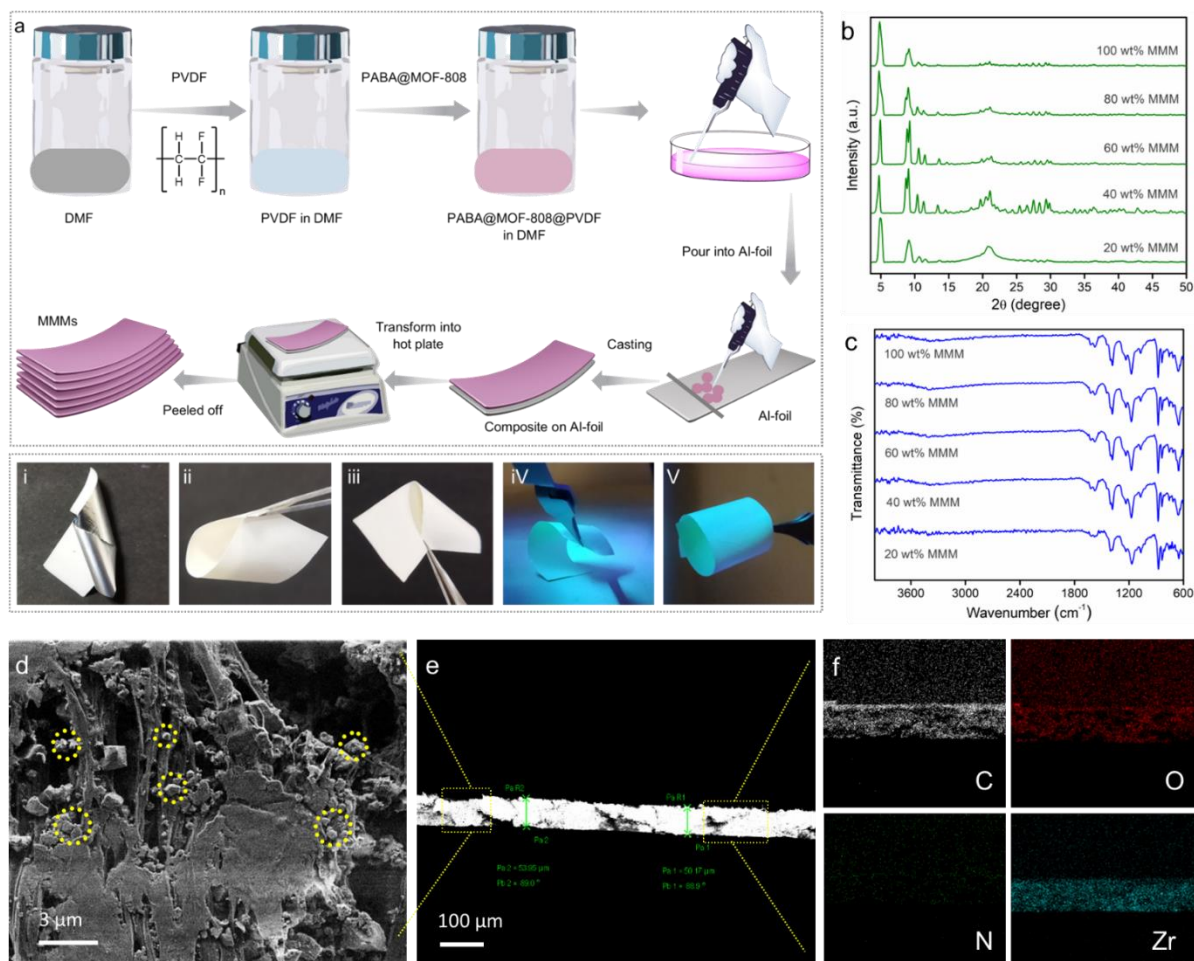


Figure 2.4 (a) Schematic illustration of MMM fabrication procedure by drawdown coating (doctor-blading) method. (b) PXRD patterns and (c) FT-IR spectra of the PABA@MOF-808@PVDF MMMs with different MOF ratio. (i-v) Digital images of the 80 wt% MMM showing its self-standing, mechanical stability and highly luminescent nature under UV light. (d) FESEM top view image of 80 wt% MMM. (e) FESEM cross-section image of 80 wt% MMM. (f) FESEM elemental mapping images of the respective elements (C: carbon, O: oxygen, N: nitrogen, Zr: zirconium).

Then a certain amount of PABA@MOF-808 was mixed in the above suspension and make a homogeneous dispersion by mixing overnight. Thereafter, this mixture was casted onto the Al-foil by hand with the help of a glass substrate to make a homogeneous film. Next, this coated PABA@MOF-808@PVDF films were heated on a hot-plate to finally prepare the self-standing MMMs as schematically represented in figure 2.4a (see Appendix section for details). It is noteworthy to mention that in order to understand the role of the amount of MOFs upon NO sensing study, a series of MMMs have been fabricated with the similar above protocol taking different loading contain of PABA@MOF-808 (20, 40, 60, 80 and 100 wt% (in mg)) in the PVDF solution. Thus developed MMMs were found

to stand-alone, macroscopic defect or cracks free, and mechanically stable and highly luminescent in nature, which are beneficial for the real-time NO sensing study (Figure 2.4(i-v)). After the fabrication, the MMMs were thoroughly characterized by PXRD, FT-IR, TGA and FESEM analysis. The PXRD patterns of all the MMMs indicated the presence of highly crystalline PABA@MOF-808 with no structural changes in the PVDF composite (Figure 2.4b). Further, upon increasing the amount of the MOF nanocrystals in the MMMs the amorphous nature of the PVDF polymer become weaken and consequently, the peaks of the MOFs become sharp (Figure 2.4b). This result suggests the robust structural integrity with bulk-purity of the probe in the MMMs. The corresponding distinguished peaks in the FT-IR spectra of all the MMMs clearly indicated the stable existence of PABA@MOF-808 binded with PVDF polymer (Figure 2.4c). The TGA profiles of the MMMs revealed the improved thermal behaviour with compare to the pristine powder materials because of the high thermal stability of PVDF polymer (Appendix Figure 2.35). After these structural characterizations, the morphological investigation has been done with the help of FESEM analysis. As a representative example we select 80 wt% MMM for this analysis. The front view of the FESEM images of PABA@MOF-808@PVDF MMM clearly showed the presence of octahedral morphology of the MOFs throughout the polymeric phase of PVDF membrane (Figure 2.4d, Appendix Figure 2.36). Moreover, intact robustness of the sensing probe along with the minimal aggregation of MOF particles can be observed from the FESEM images (Figure 2.4f, Appendix Figure 2.37). In addition, the cross-section images of the MMM exhibited a thickness of ~60 to ~80 μm (Figure 2.4e, Appendix Figure 2.38). The energy dispersive X-ray spectroscopy (EDS) analysis indicated the presence of all the relevant elements along with zirconium (Zr) and nitrogen (N), which suggest successful grafting of PABA@MOF-808 in the PVDF membrane (Appendix Figure 2.39). Also, these elements were found to homogeneously distribute throughout the large surface of the membrane, which suggest no obvious aggregation of MOF nanoparticles (Figure 2.4f, Appendix Figure 2.40). Furthermore, the porous nature of this MMM was confirmed from the nitrogen gas sorption measurement at 77K, which provided the surface area as 62.76 m^2/g (Appendix Figure 2.41). This data also indicated lowering in the total gas uptake and thus reduced in the surface area with compare to the powder MOF samples. ^[52]

After the successful characterizations, we moved ahead to perform the NO sensing studies by these MMMs both from aqueous and vapour phase. From a preliminary screening test, it was observed that the MMM made up with 80 wt% PABA@MOF-808 exhibited highest emission intensity under excitation of 290 nm UV radiation (Appendix Figure 2.42). Now, the above sensing study and the insight mechanism revealed upon treatment of NO, the amino benzoic acid group of the highly luminescent probe (PABA@MOF-808) converted into benzoic acid group which is found to be less luminescent in nature. Therefore, in order to test the feasibility of the developed MMM towards efficient

detection of NO, we have performed a titration study for aqueous phase sensing. At first, the emission profile of the 80% MMM was recorded which exhibited a broad spectrum with a maximum of ~ 325 nm

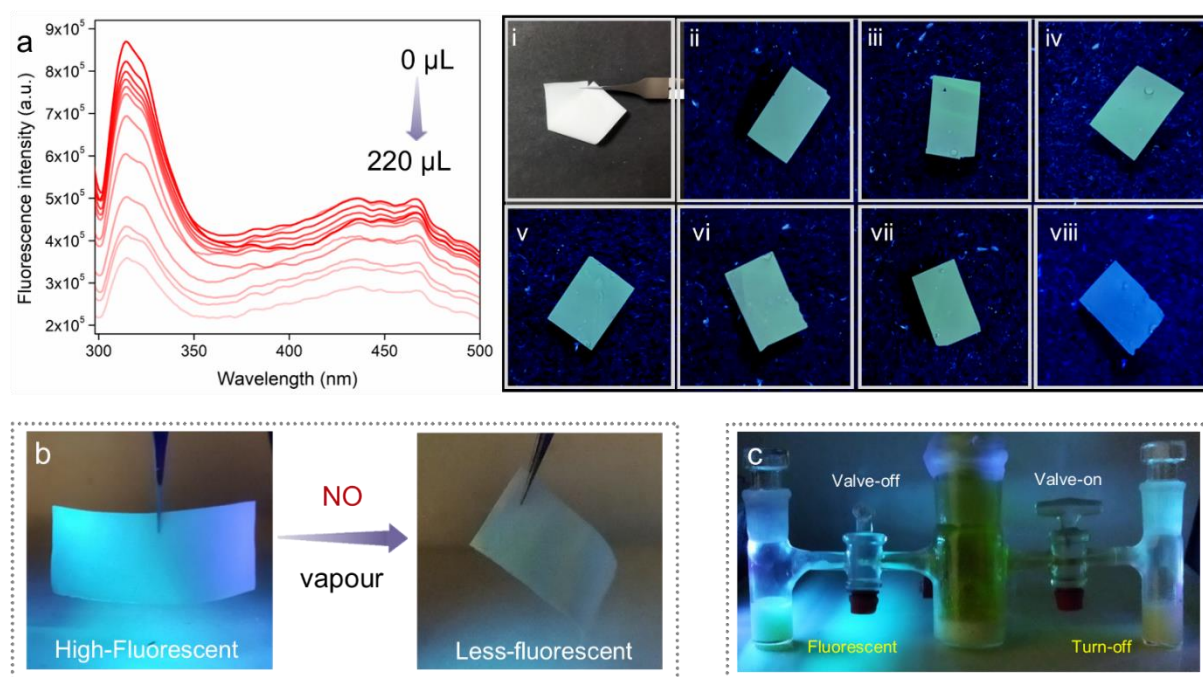


Figure 2.5 (a) Photoluminescence spectra of PABA@MOF-808-MMM in water in the presence of different concentrations of NO. (i) Pristine MMM, (ii) H_2O_2 , (iii) $^1\text{O}_2$, (iv) NO_2^- , (v) NO_3^- , (vi) OCl^- , (vii) HOO^- , (viii) NO treated MMM. (b) Digital images of luminescent quenching response of the self-standing MMMs upon treatment of NO vapour, under UV light. (c) Demonstration of “turn-off” behaviour of PABA@MOF-808/water in contact with NO vapour.

upon excitation at ~ 290 nm (Appendix Figure 2.42). Interestingly, the high emission intensity of the MMM was found to significantly quenched when treated into 1 mmol aqueous NO solution. Motivated by this observation, we adopted a typical soaking method for the through titration sensing study. In this method, a small piece of the MMM was dipped into the different concentration of aqueous solution of the salt for a certain time and the respective fluorescent intensities were recorded before and after NO treatment. It was found that upon dipping of the MMM into the NO solution, the high emission intensity of the MMM decreased gradually with increasing the concentration. From figure 2.5a it was calculated as near about 59% emission intensity of the MMM was quenched upon treatment of 220 μL 1 mmol NO solution. This quenching phenomena of the MMMs can also be visualized from the digital images (Figure 2.5-viii). Thereafter, from this fluorescence quenching profile the quenching constant (K_{sv}) was calculated. The K_{sv} value of the MMM for NO was found as $4.15 \times 10^3 \text{ M}^{-1}$ (Appendix Figure 2.43). Furthermore, the LOD value of this MMM was calculated as 0.715 μM (Appendix Figure 2.44). Both

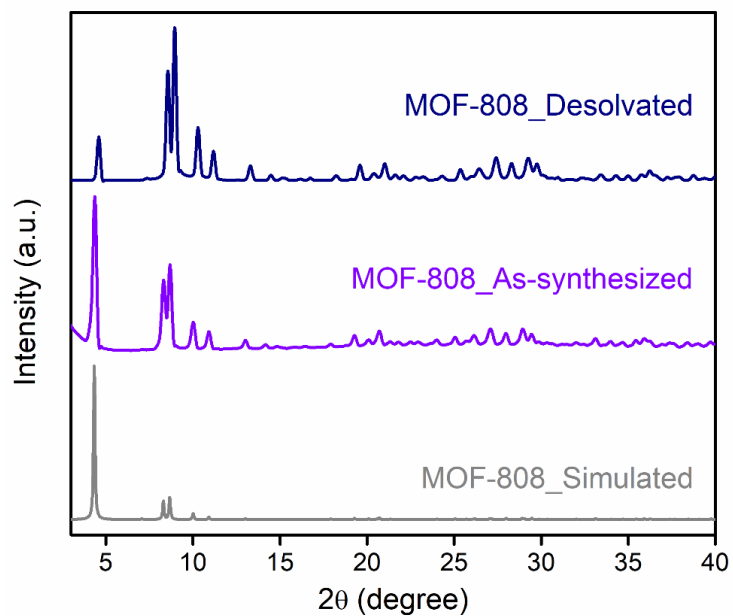
these K_{sv} and LOD values of the MMM for NO sensing were also found to be well comparable with the other literature reports. Along with high sensitivity, the selective detection of targeted species is also an important parameter for an effective sensor. Therefore, we performed the selectivity test of the MMM for NO sensing along with the other aforementioned interferences with the similar soaking method. As anticipated, the MMM was found to exhibit qualitative quenching response in case of NO only, whereas, other interferences were observed to be unable to change the emission intensity of the MMM (Figure 2.5(i-viii)). These results clearly indicated the potential of the PABA@MOF-808-based MMM towards real-time aqueous phase selective and sensitive NO sensing. Enthused by the above result, as a proof of concept, we also looked at the practical application and proceeded on to investigate the vapour phase NO sensing by the MMM. As a quantitative test, we made a set-up for the demonstration of vapour phase NO detection by the self-standing MMM (Appendix Figure 2.45). As shown in figure 5b the MMM in the prototype device exhibit rapid identification of NO gas generated from the reaction of KI and NaNO_2 (see Appendix Section for detail). Similar turn-off response was observed in the case of aqueous suspension of powder sample upon exposure of NO vapour (Figure 2.5c). This impressive finding suggested a potential use for the PABA@MOF-808-based MMMs in both aqueous and vapour phase practical detection of toxic NO. The improved sensitivity of the MMM towards NO might be caused by triggered interactions between the NO molecules and functional recognition sites of the sensor, which is generated due to the homogenous distribution of the probe throughout the membrane matrix.

2.7 Conclusions

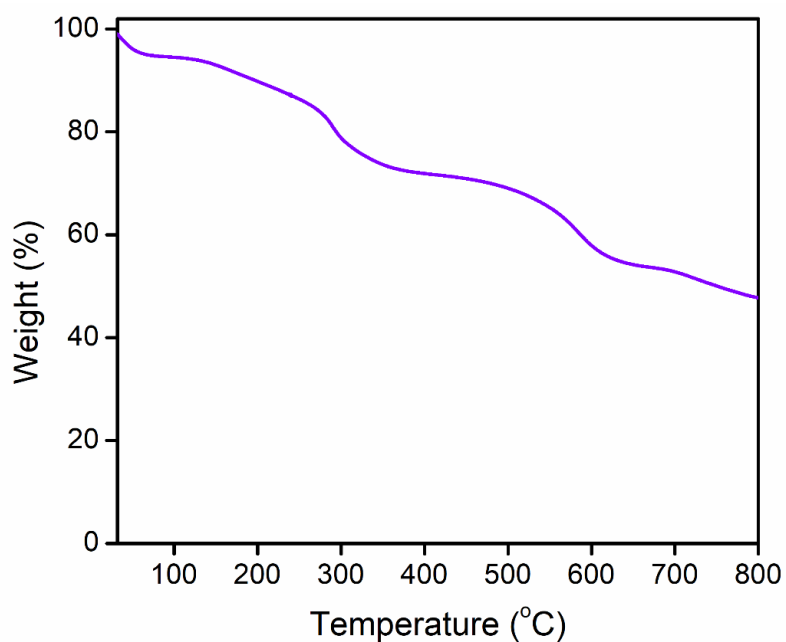
To summarize, in this work we have presented a straightforward way of crafting functionality tailored MOF to act as a molecular flask for monitoring the presence of NO. Judicious choice of amine group bearing organic linker was introduced inside porous cavity of MOF-808 Zr-SBU cluster via post-synthetic modification as a versatile tool yielded PABA@MOF-808. Thus prepared amine functionalized MOF was found to show rapid and sensitive recognition of NO in dual phase. Aside from fluorescence quenching through a “turn-off” signal response, presence of NO could also be realized under UV light to the naked eye. The potency of PABA@MOF-808 is further highlighted by its high K_{sv} value ($6.10 \times 10^3 \text{ M}^{-1}$) and excellent LOD of $0.715 \mu\text{M}$. Further, the sensing response was exclusive toward the target analyte even in presence of interfering RNS/ROS species making it a superior sensory probe. To gain mechanistic understanding of NO detection, in-depth experimental and DFT theoretical studies were also carried out. Keeping in mind the practical applicability, a self-standing flexible mixed-matrix membrane was also fabricated for qualitative NO sensing in water as well as vapour phase. We believe this work can actuate further research in developing task-specific functionalized MOF based sensory materials with the objective of accomplishing suitable probes for detecting biologically important molecules.

Appendix Section

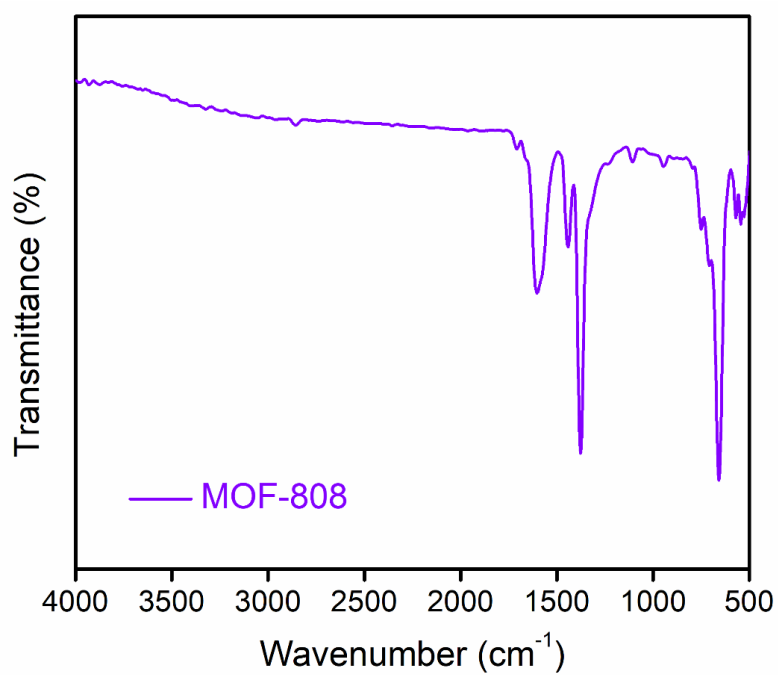
Appendix Section 1: Structural characterizations of MOF-808 & PABA@MOF-808.



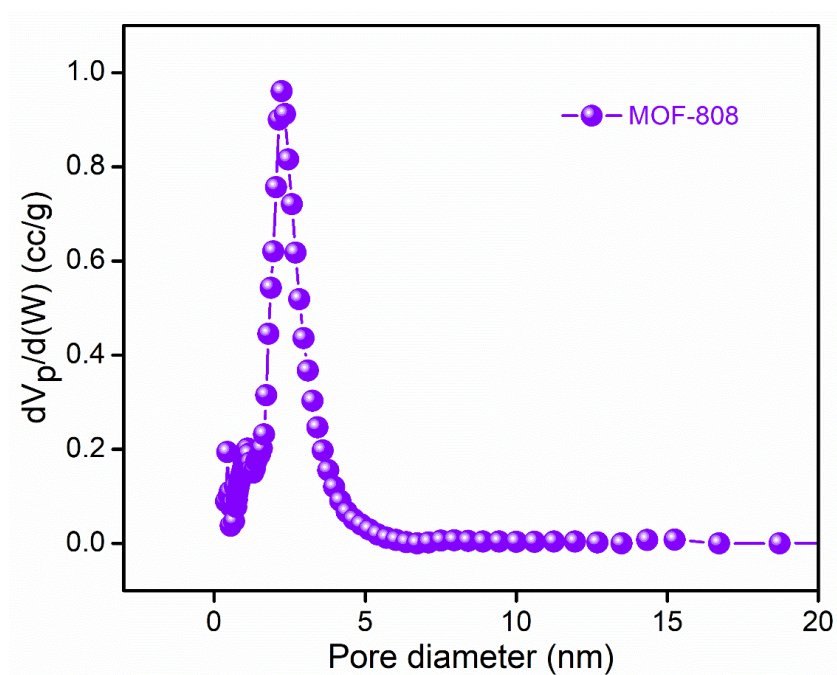
Appendix Figure 2.1: PXRD pattern of as-synthesized and desolvated phase of MOF-808.



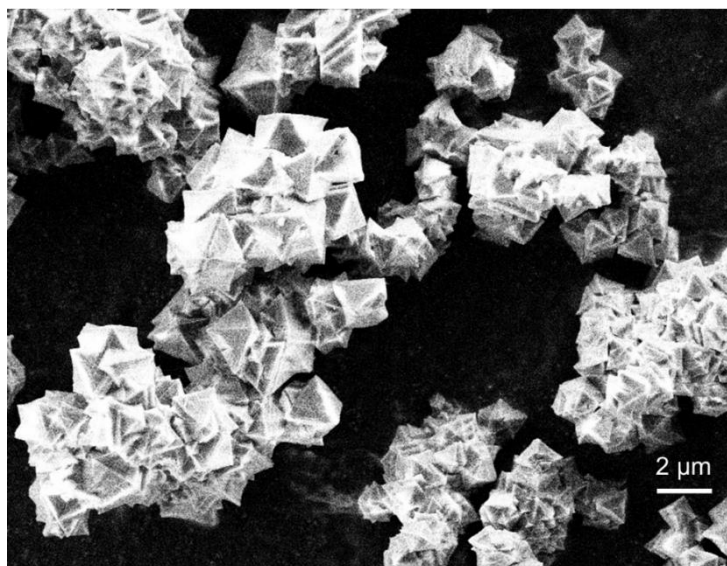
Appendix Figure 2.2: Thermogravimetric (TGA) profile of desolvated MOF-808.



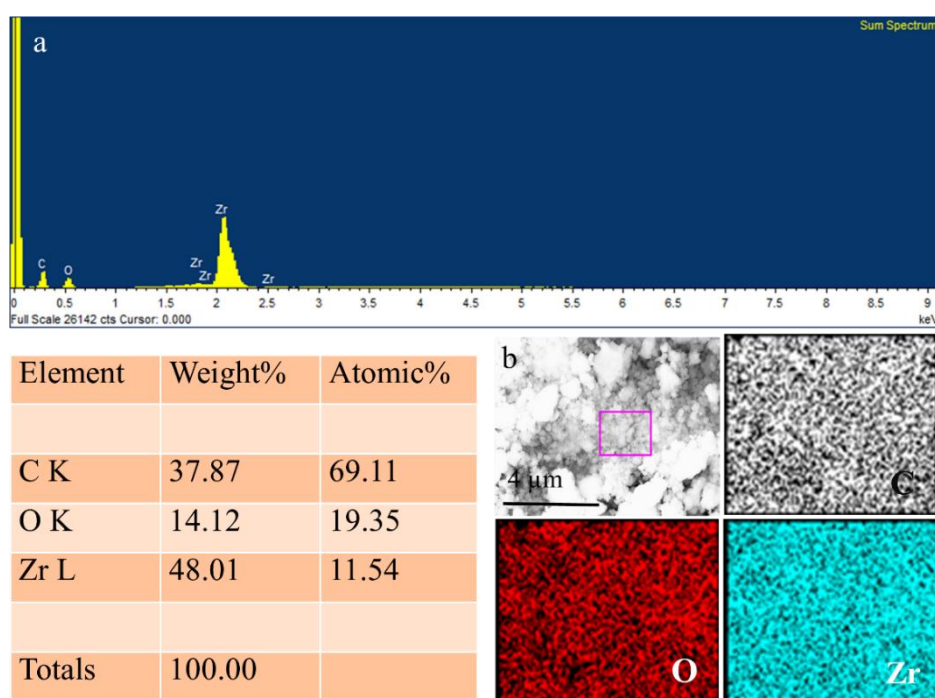
Appendix Figure 2.3: FTIR spectra of MOF-808.



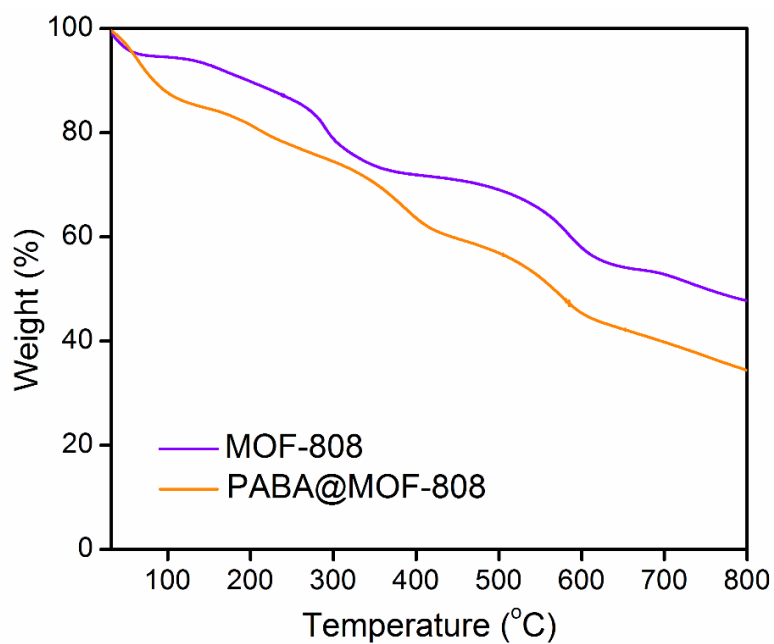
Appendix Figure 2.4: Pore size distribution profile of MOF-808 from N_2 sorption measurement.



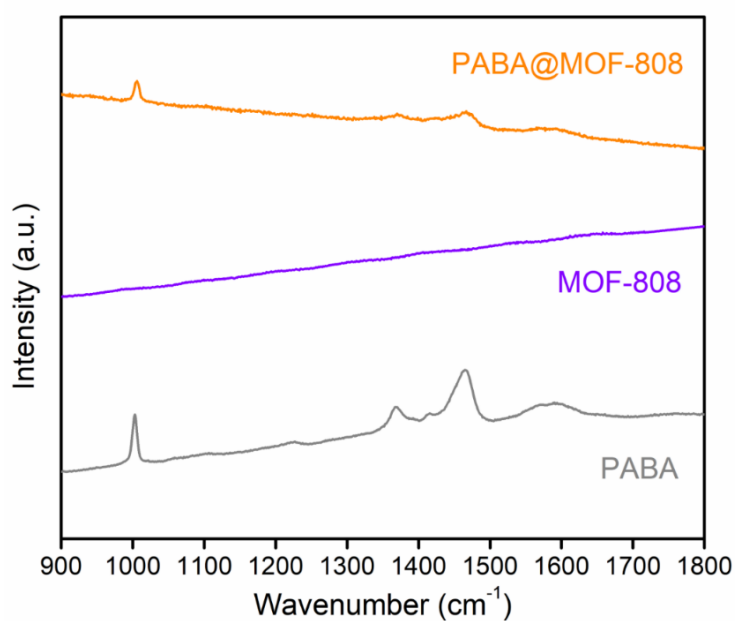
Appendix Figure 2.5: FESEM Image of MOF-808.



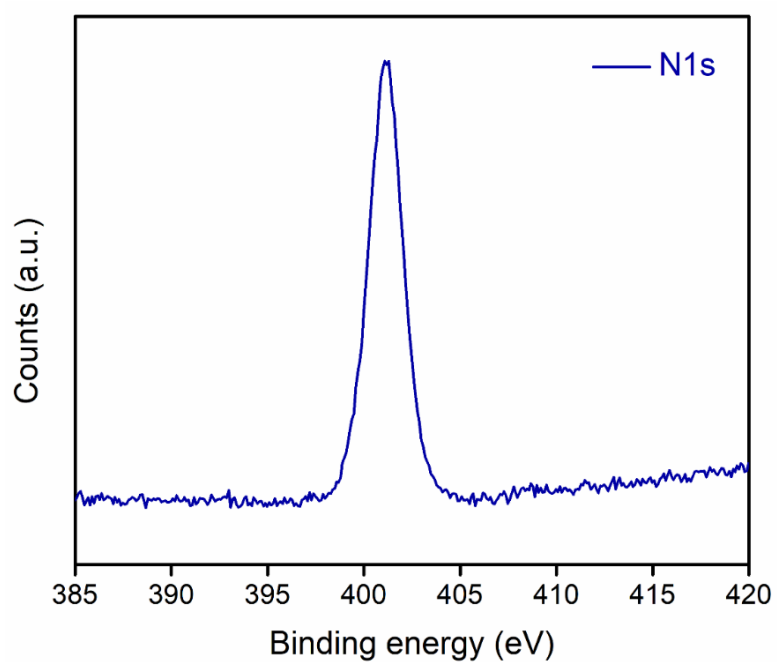
Appendix Figure 2.6: (a) EDX data and (b) Elemental mapping image of MOF-808.



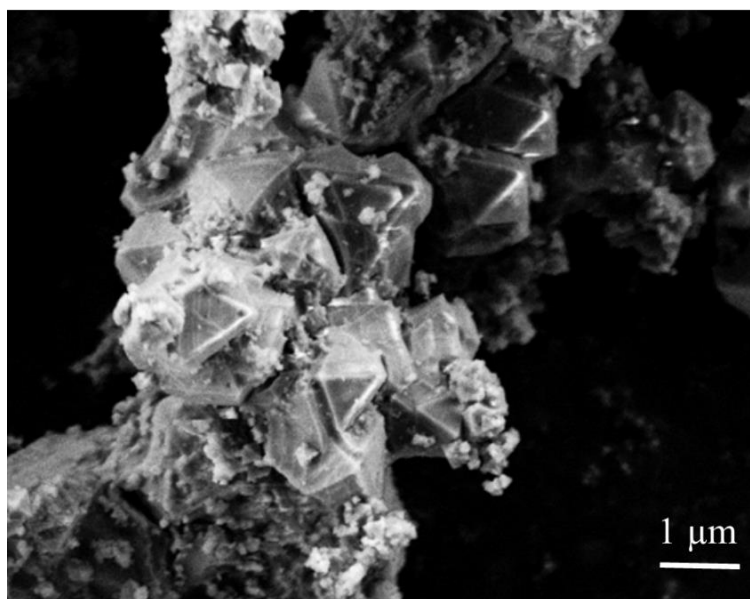
Appendix Figure 2.7: Thermogravimetric (TGA) profile of PABA@MOF-808 along with MOF-808.



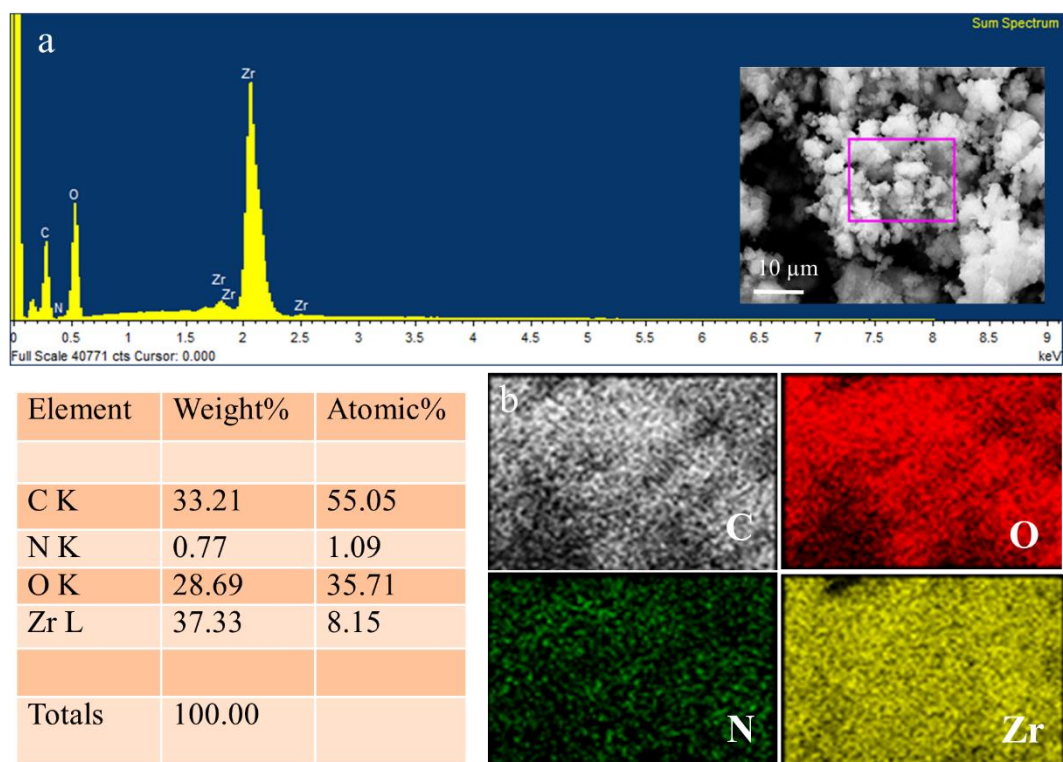
Appendix Figure 2.8: Raman Spectra of MOF-808 and PABA@MOF-808.



Appendix Figure 2.9: XPS Spectra of nitrogen (N) 1s orbital of PABA@MOF-808.

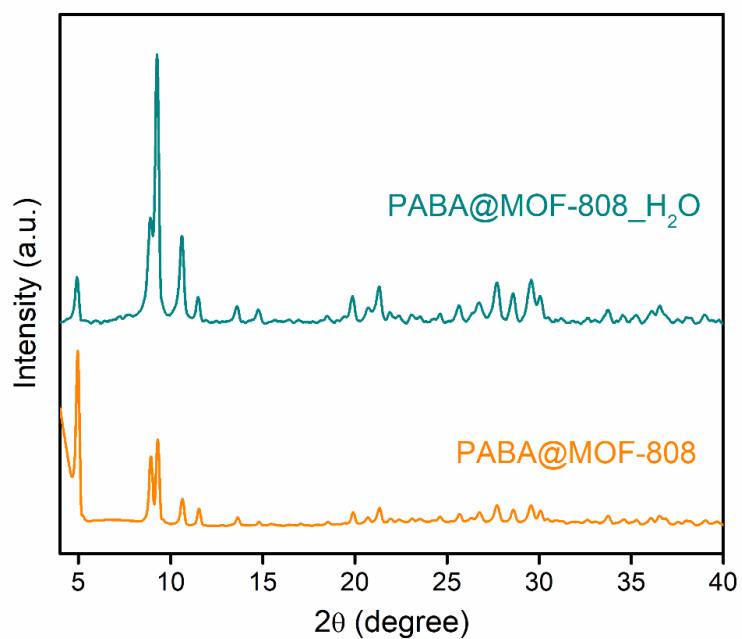
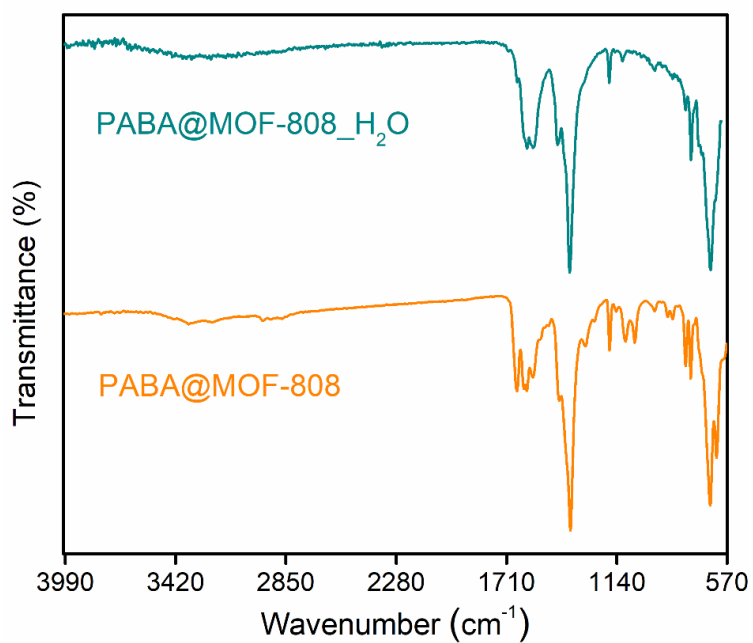


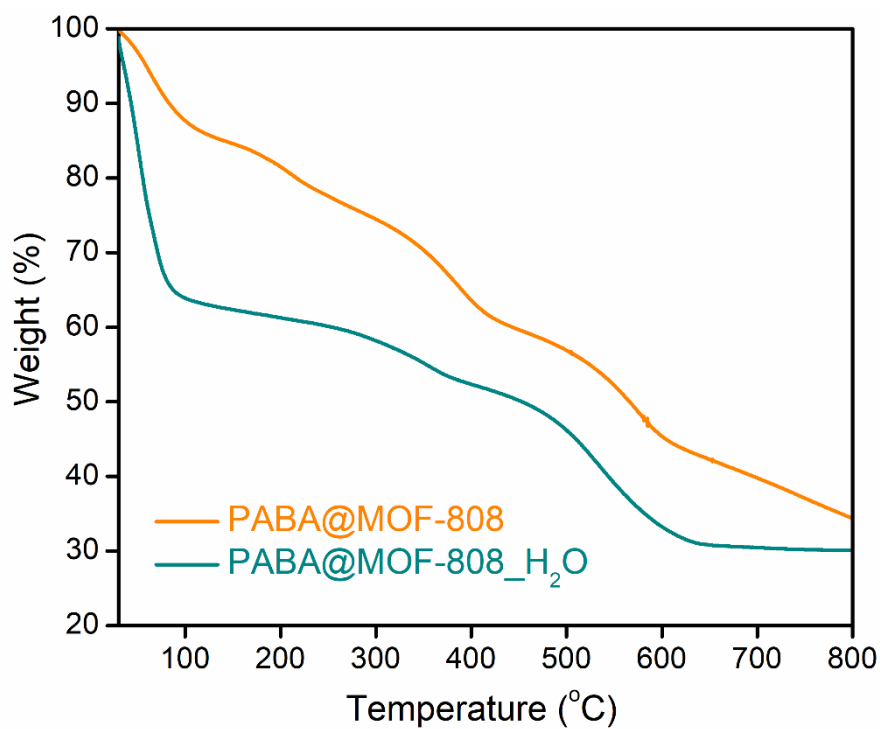
Appendix Figure 2.10: FESEM image of PABA@MOF-808.



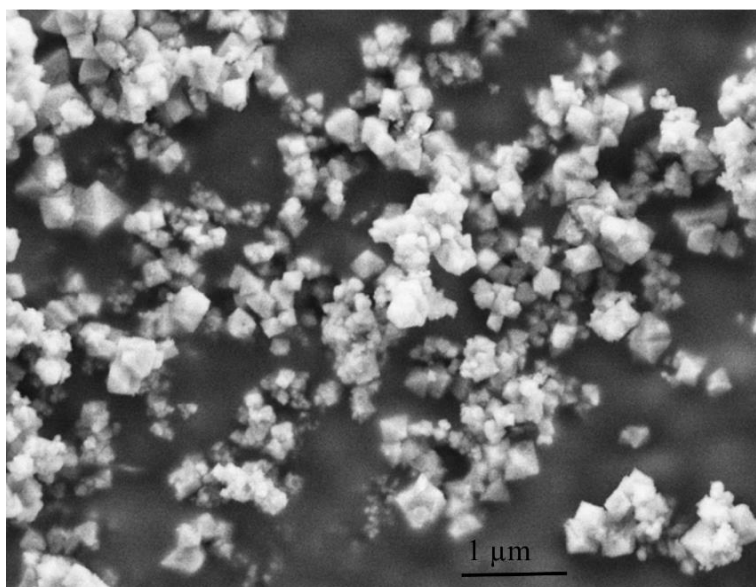
Appendix Figure 2.11: (a) EDX data and (b) Elemental mapping image of PABA@MOF-808.

Appendix Section 2: Hydrolytic Stability of PABA@MOF-808

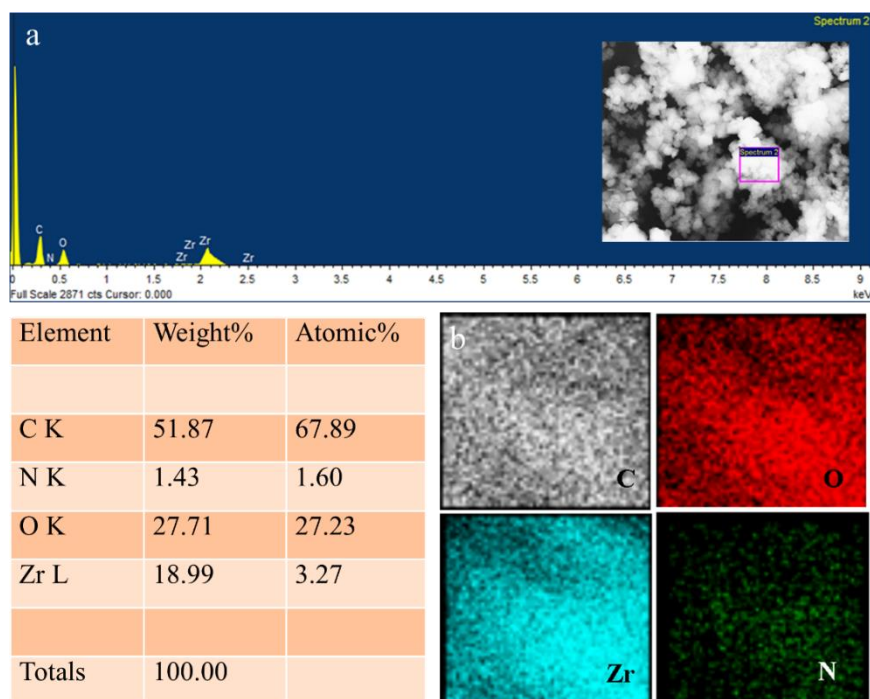
**Appendix Figure 2.12:** PXRD pattern of water treated PABA@MOF-808.**Appendix Figure 2.13:** FTIR Spectra of water treated PABA@MOF-808.



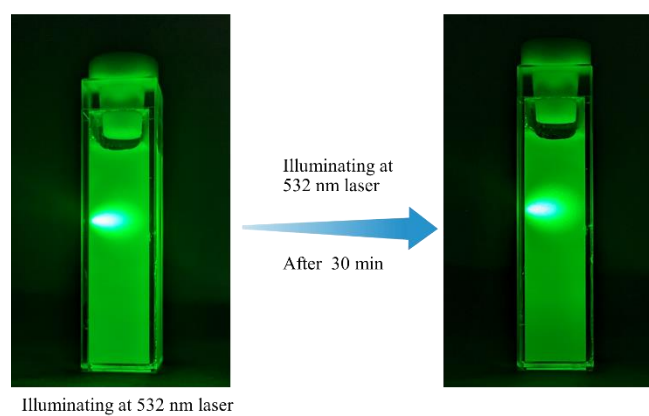
Appendix Figure 2.14: Thermogravimetric (TGA) profile of water treated PABA@MOF-808.



Appendix Figure 2.15: FESEM image of water treated PABA@MOF-808.

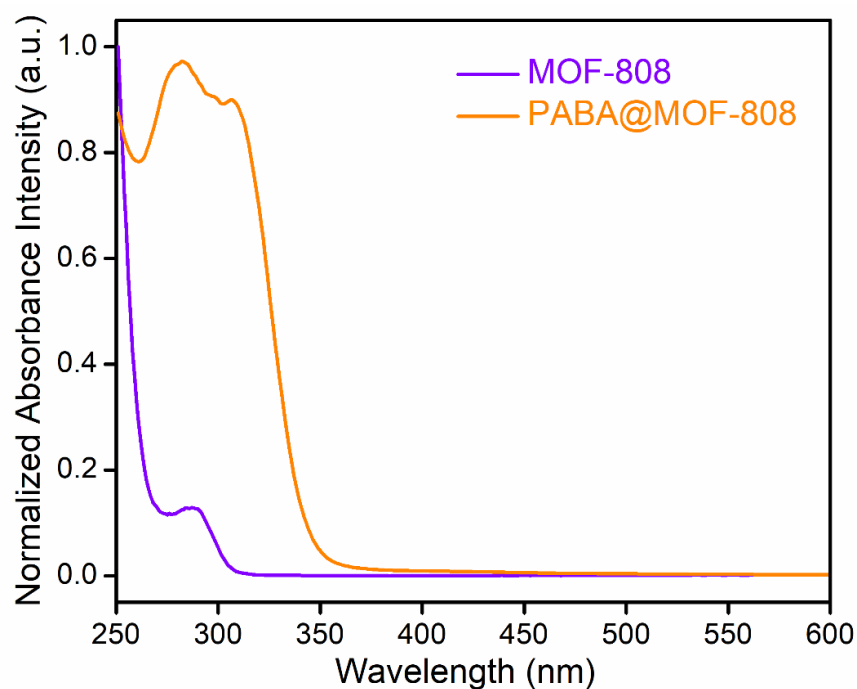
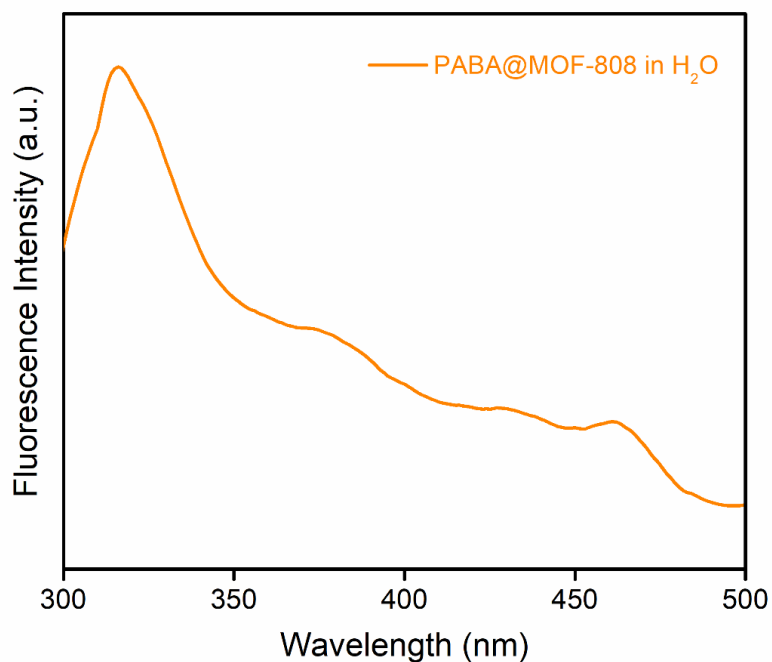


Appendix Figure 2.16a: EDX data, Elemental mapping image of water treated PABA@MOF-808.

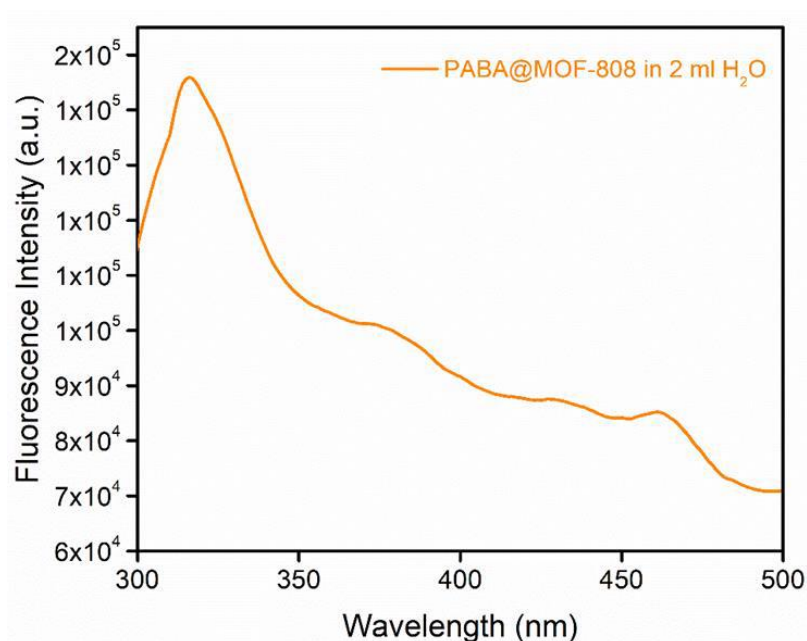


Appendix Figure 2.16b: Tyndall effect of PABA@MOF-808 dispersion in water (initial and after 30 min of laser exposure).

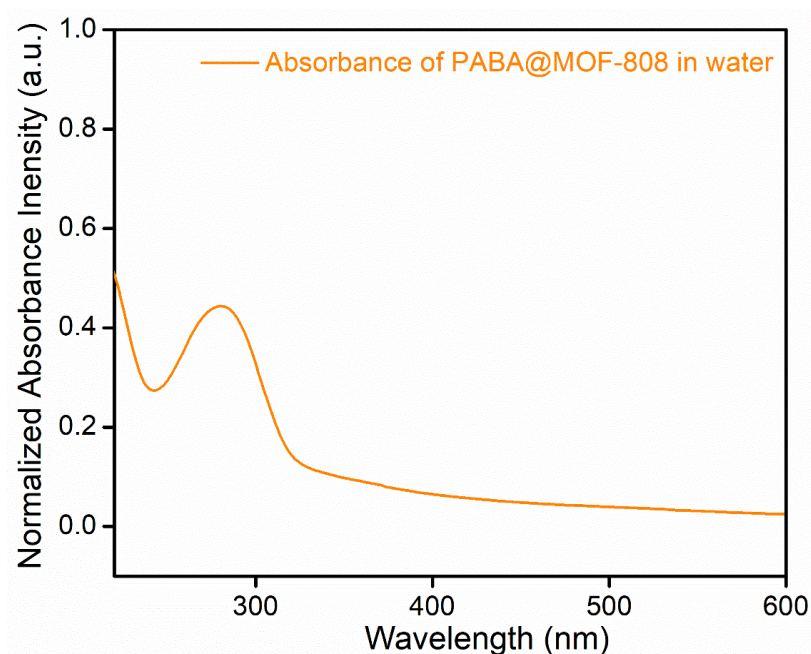
Appendix Section-3: Optical Characterizations of PABA@MOF-808

**Appendix Figure 2.17:** Diffuse reflectance UV-vis spectra of PABA@MOF-808 and MOF-808.**Appendix Figure 2.18:** Photoluminescence emission spectra of water dispersed PABA@MOF-808.

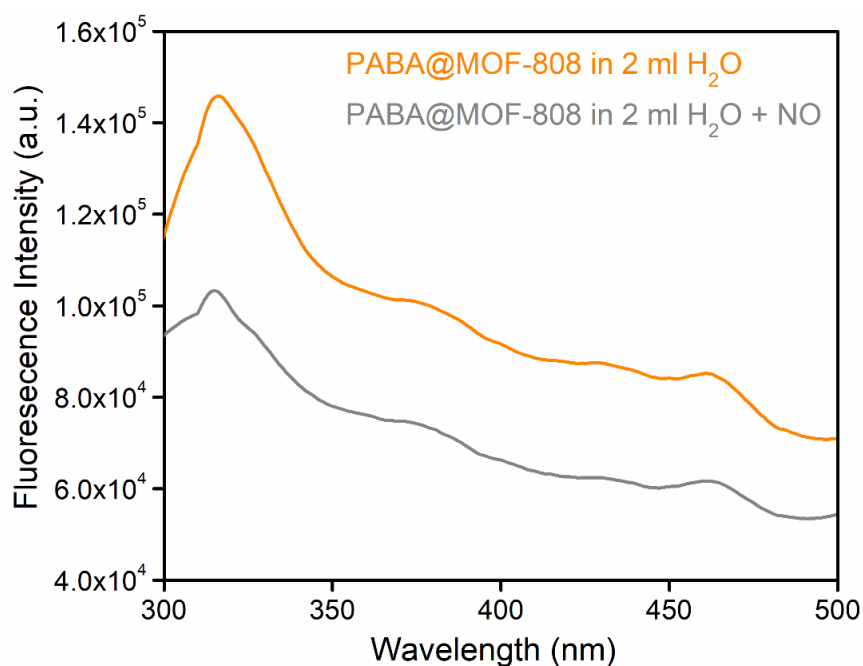
Appendix Section-4: Sensing Studies of PABA@MOF-808



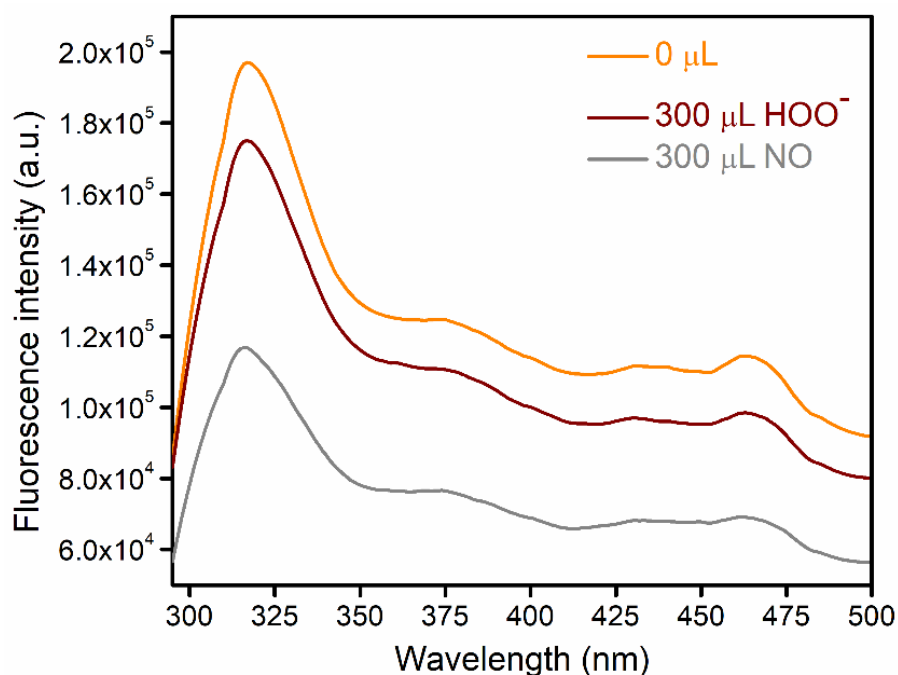
Appendix Figure 2.19a: Photoluminescence emission spectra of PABA@MOF-808 dispersed in 2 mL water.



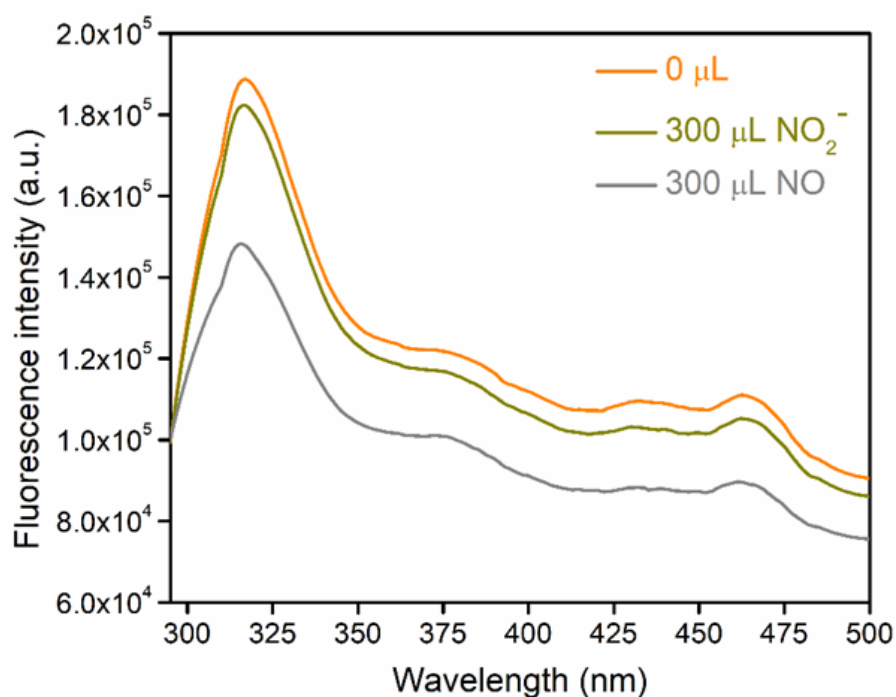
Appendix Figure 2.19b: Absorption spectra of PABA@MOF-808 dispersed in 2 mL water.



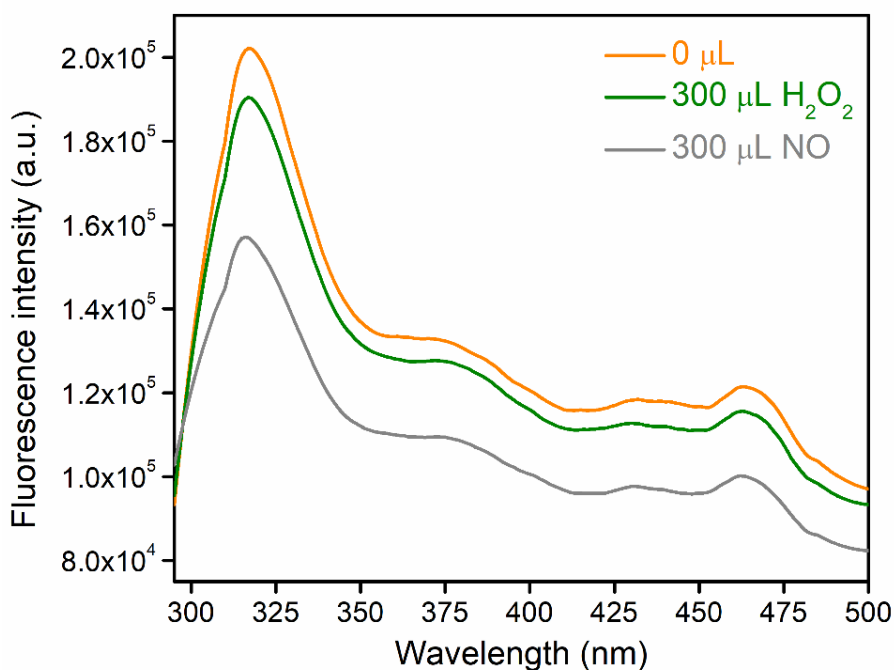
Appendix Figure 2.20: Change in PL intensity after addition of certain amount of NO aqueous solution.



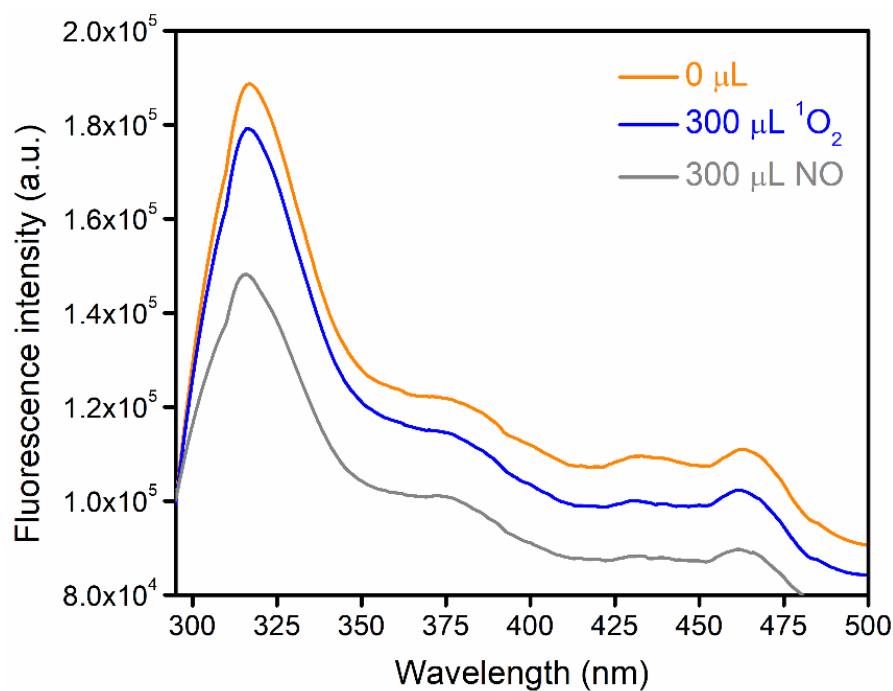
Appendix Figure 2.21: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous HOO⁻ solution, followed by the addition of 300 μL of NO aqueous solution.



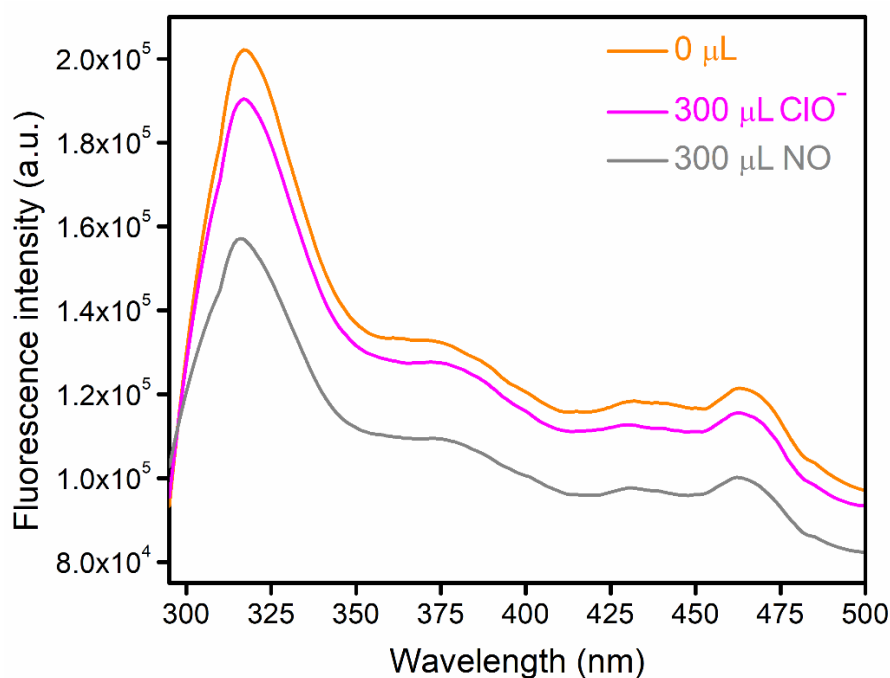
Appendix Figure 2.22: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous NO_2^- solution, followed by the addition of 300 μL of NO aqueous solution.



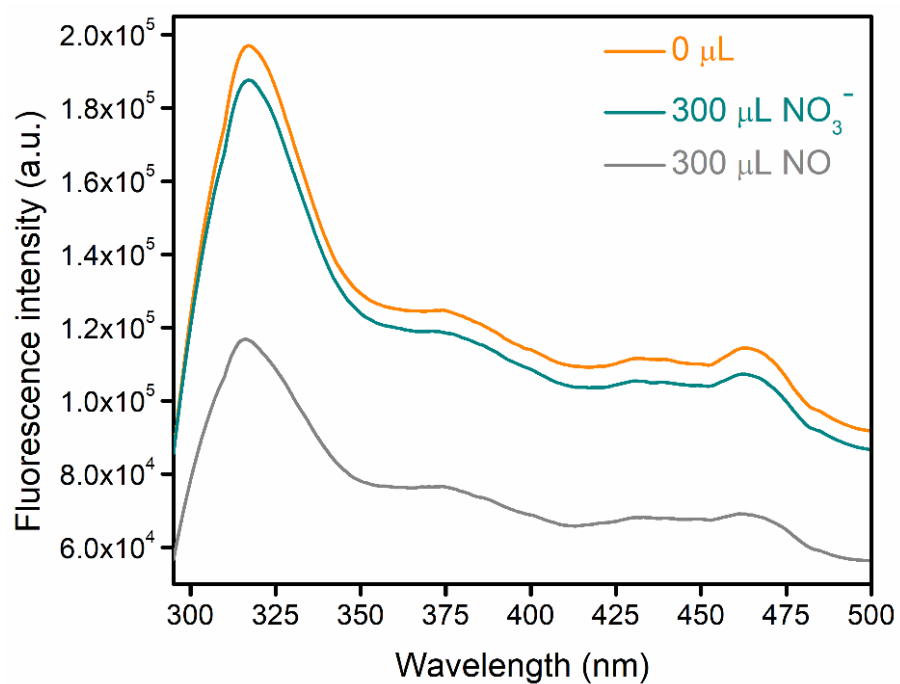
Appendix Figure 2.23: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous H_2O_2 solution, followed by the addition of 300 μL of NO aqueous solution.



Appendix Figure 2.24: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous $^1\text{O}_2$ solution, followed by the addition of 300 μL of NO aqueous solution.

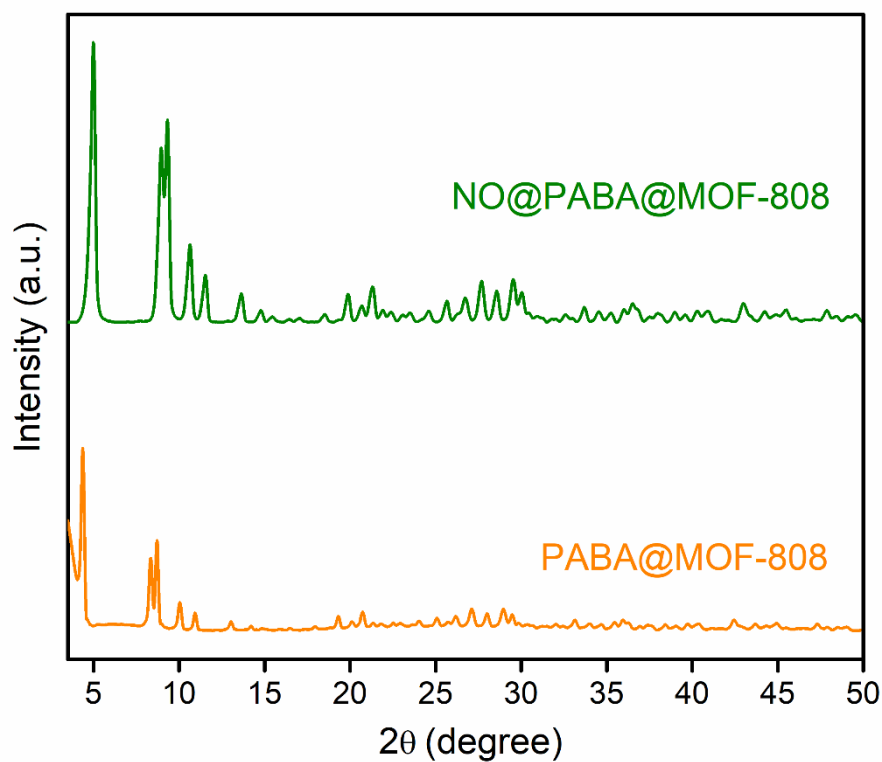
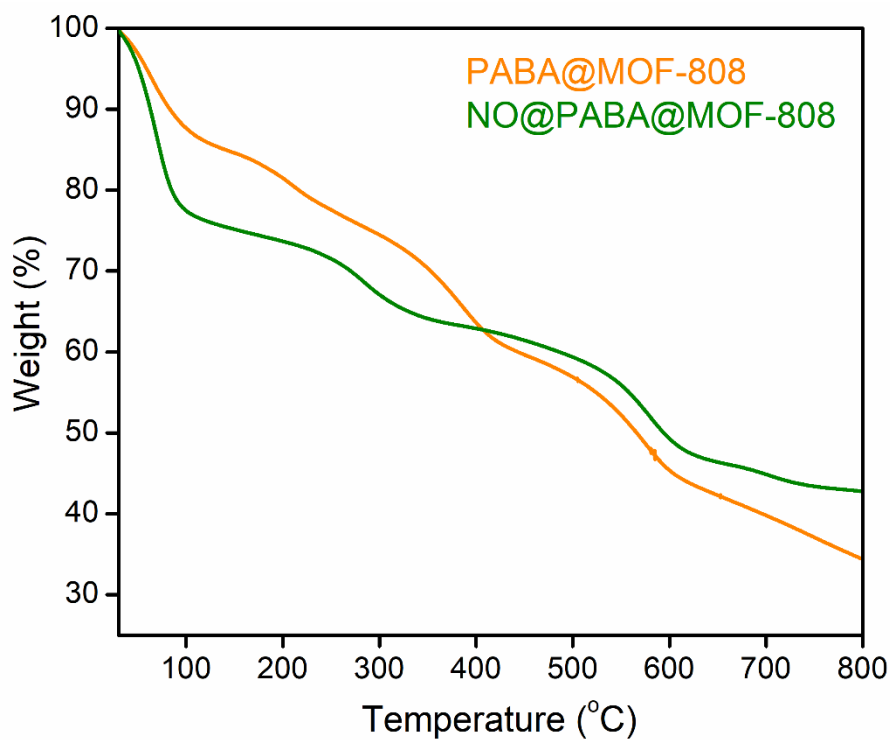


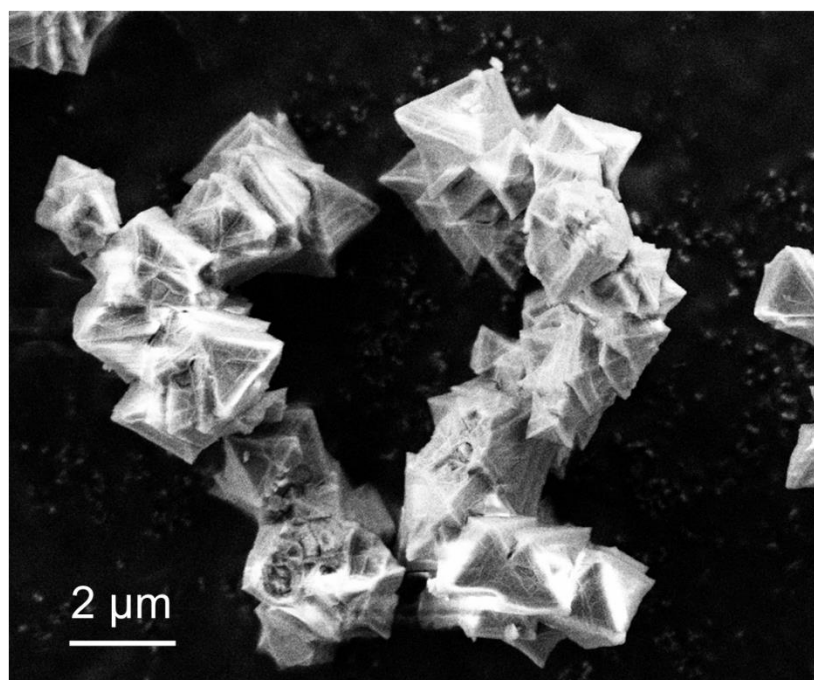
Appendix Figure 2.25: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous ClO^- solution, followed by the addition of 300 μL of NO aqueous solution.



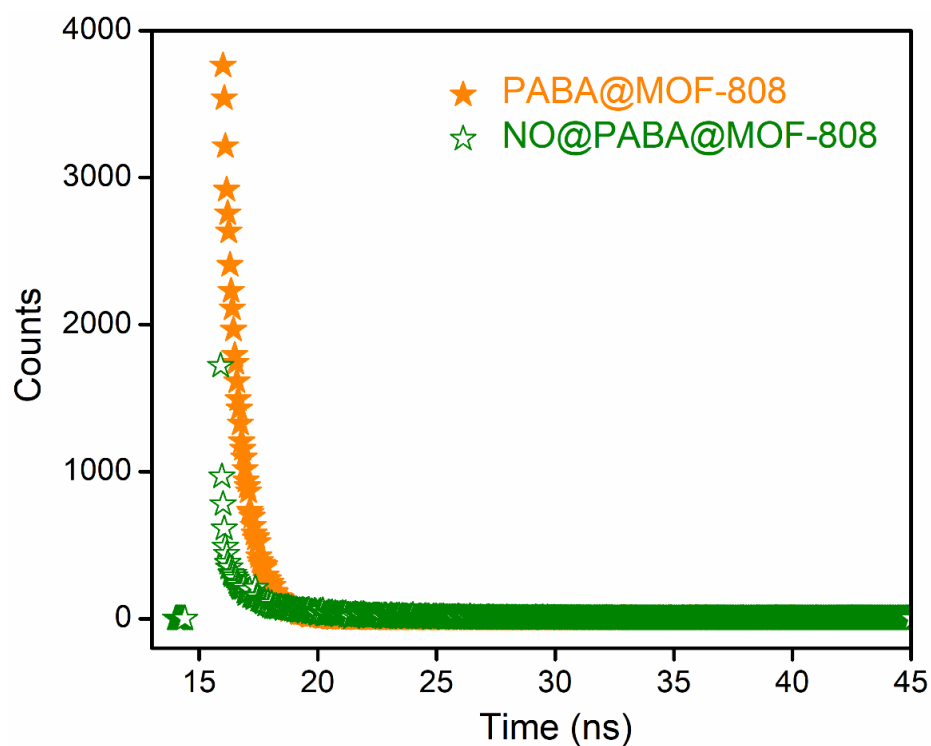
Appendix Figure 2.26: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous NO_3^- solution, followed by the addition of 300 μL of NO aqueous solution.

Appendix Section-5: Sensing Mechanism Studies of PABA@MOF-808

**Appendix Figure 2.27:** PXRD profile of PABA@MOF-808 before and after treatment of NO solution.**Appendix Figure 2.28:** TGA profile of PABA@MOF-808 before and after treatment of NO solution.



Appendix Figure 2.29: FESEM image of PABA@MOF-808 after treatment of NO solution.



Appendix Figure 2.30: Time-resolved fluorescence decay profile of PABA@MOF-808 before and after NO treatment.

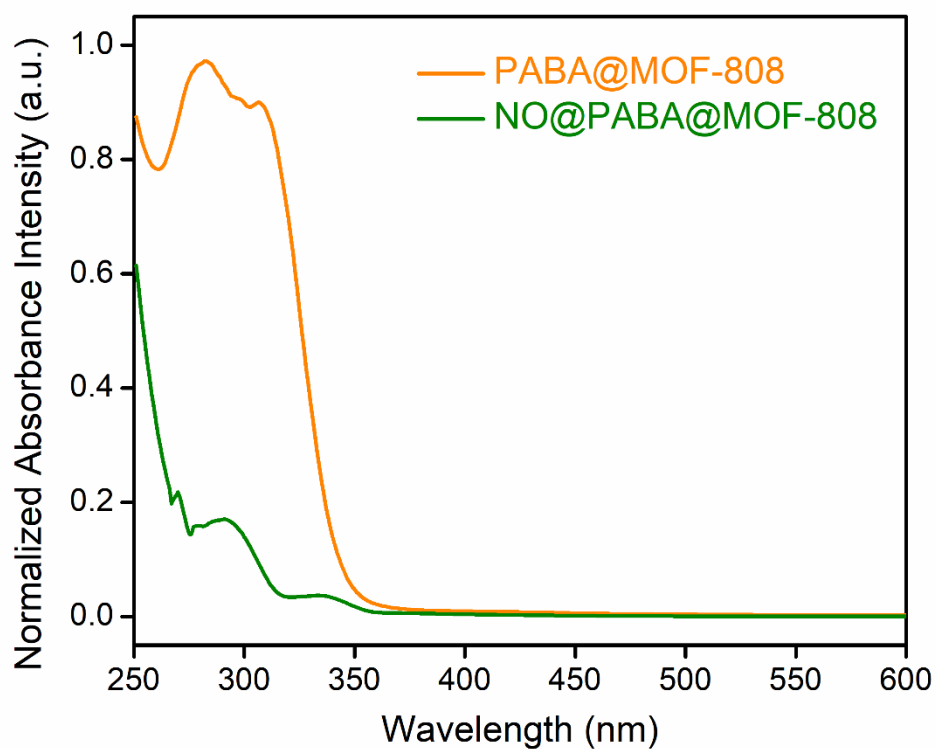
Appendix Table-1: The values of different parameter for the lifetime measurements.

Compound	$\alpha_1(\%)$	$t_1(\text{ns})$	$\alpha_2(\%)$	$t_2 (\text{ns})$	$t_{av} (\text{ns})$	R^2
PABA@MOF-808	100	0.71	--	--	0.71	0.99
NO@PABA@MOF-808	10.7	1.18	89.3	0.04	0.93	0.99

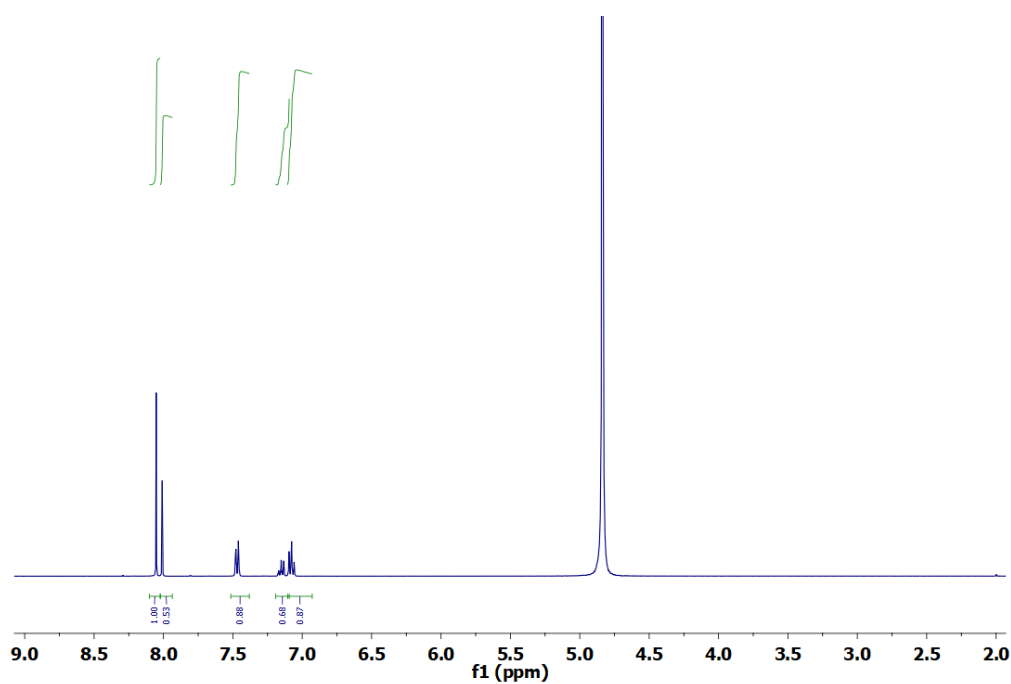
If t_1 and t_2 are PL lifetimes for bi-exponential decay with weightage α_1 and α_1 respectively then PL decay can be fitted using- $I(t) = \sum_i \alpha_i e^{(t/t_i)}$; $i = 1, 2$.

And the average PL would be lifetime, $t_{av} = \frac{\alpha_1 t_1^2 + \alpha_2 t_2^2}{\alpha_1 t_1 + \alpha_2 t_2}$.

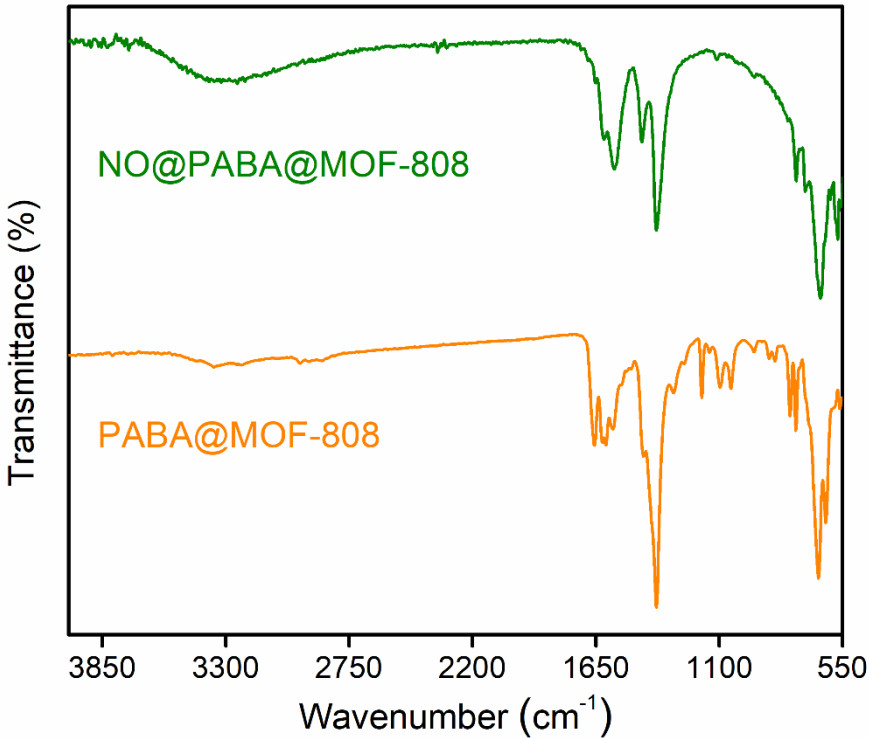
Excitation Wavelength: 285 nm; Detection wavelength: 316 nm; τ (Average lifetime) = 0.93 ns [NO treated PABA@MOF-808]; $\chi^2 = 0.99$



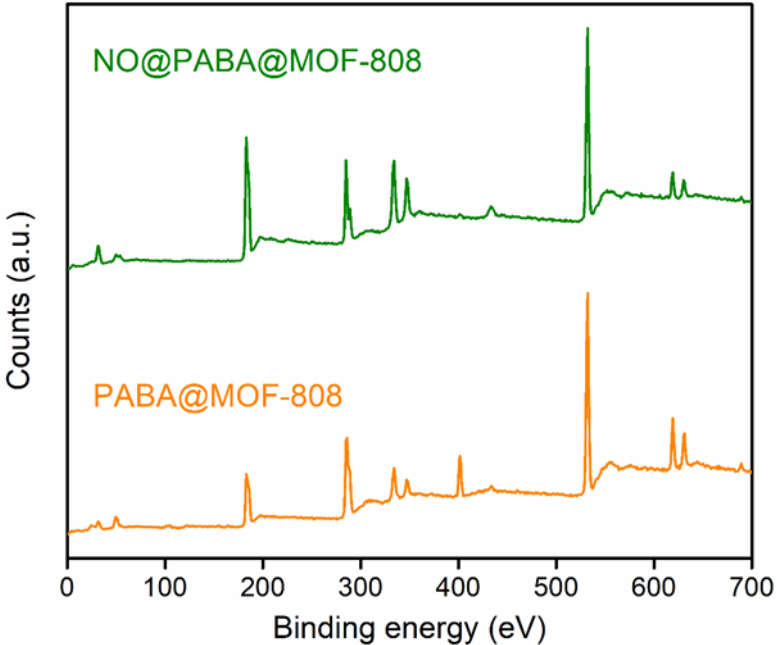
Appendix Figure 2.31: Diffuse reflectance UV-vis spectra of PABA@MOF-808 before and after NO treatment.



Appendix Figure 2.32: ^1H NMR spectra of PABA@MOF-808 after NO treatment.

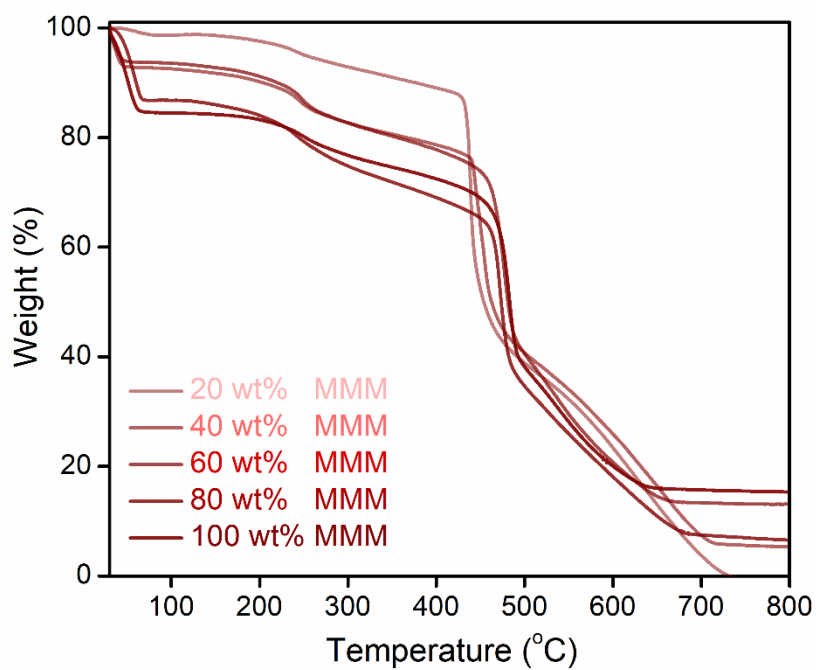


Appendix Figure 2.33: FT-IR spectra of PABA@MOF-808 before and after NO treatment.

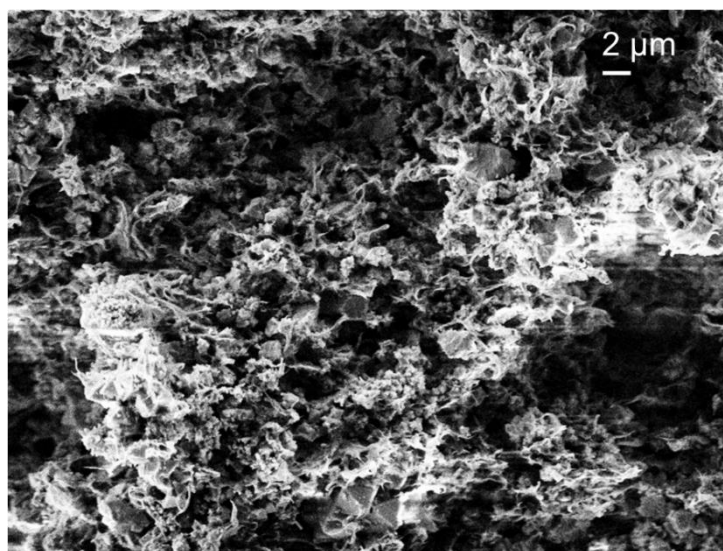


Appendix Figure 2.34: XPS survey spectra of PABA@MOF-808 before and after NO treatment.

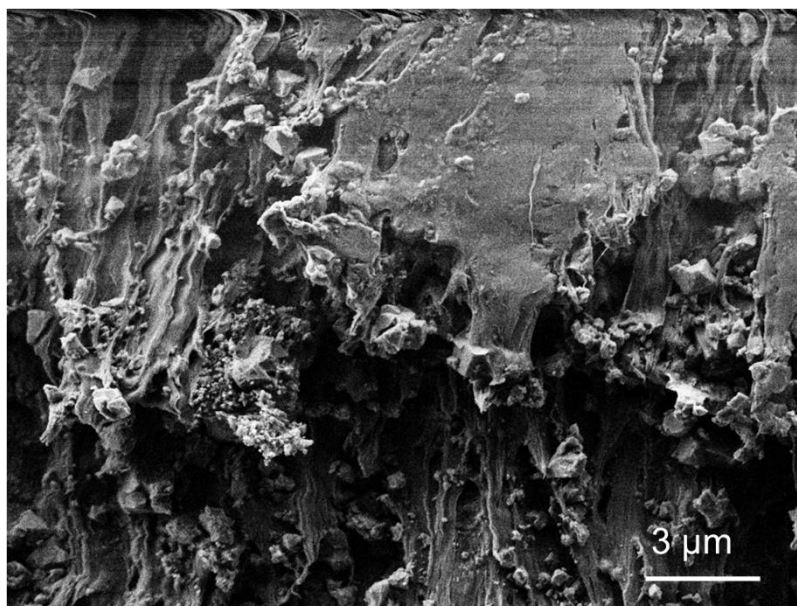
Appendix Section-6: Mixed Matrix Membrane based sensing studies.



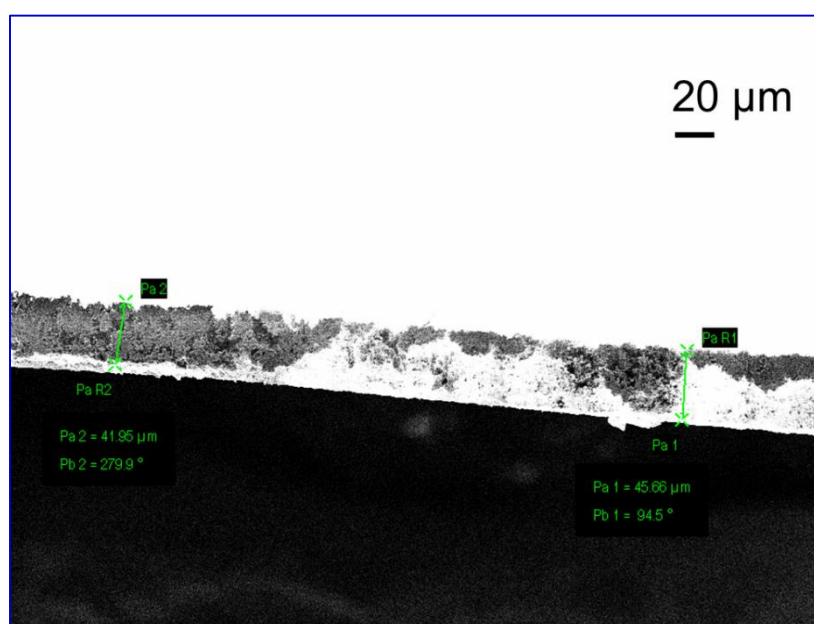
Appendix Figure 2.35: TGA spectra of PABA@MOF-808@PVDF MMMs with different MOF ratio.



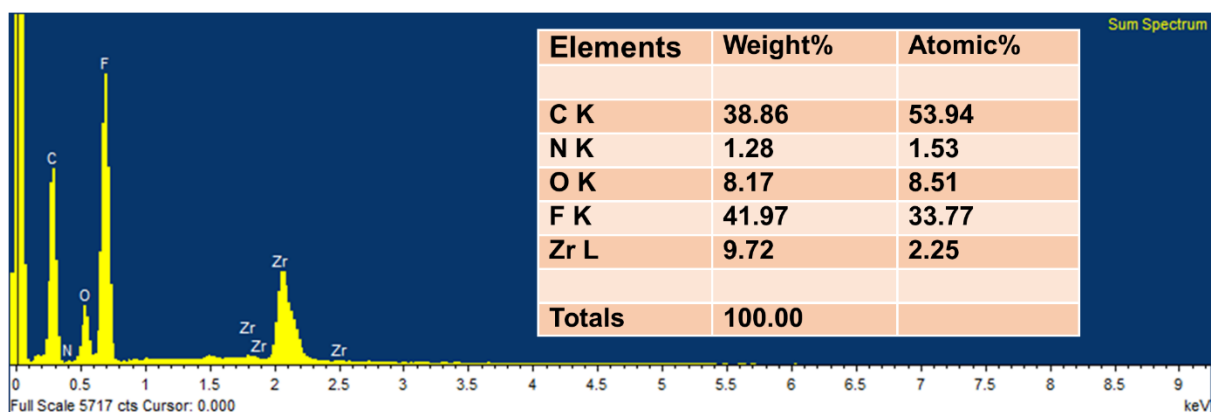
Appendix Figure 2.36: FESEM image of front view of PABA@MOF-808@PVDF MMMs



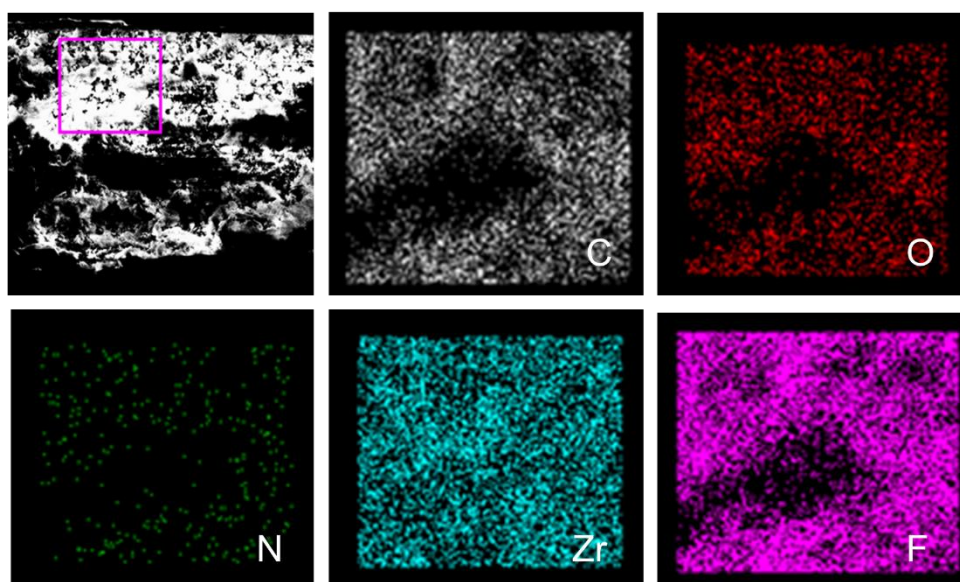
Appendix Figure 2.37: FESEM image of PABA@MOF-808@PVDF MMMs.



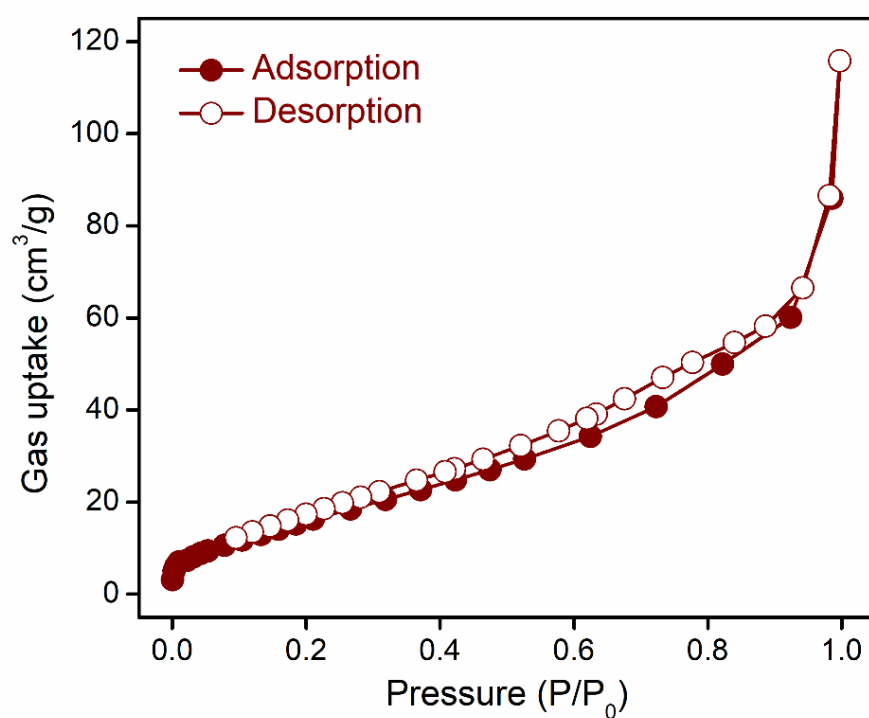
Appendix Figure 2.38: FESEM image of cross-section view of PABA@MOF-808@PVDF MMM.



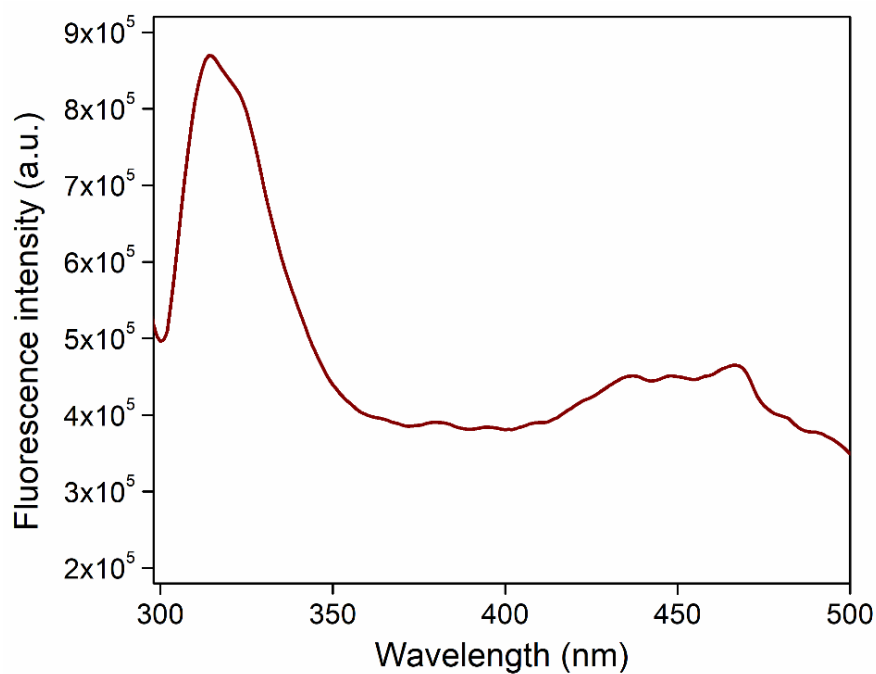
Appendix Figure 2.39: Energy dispersive X-ray spectroscopy (EDS) data of PABA@MOF-808@PVDF MMM.



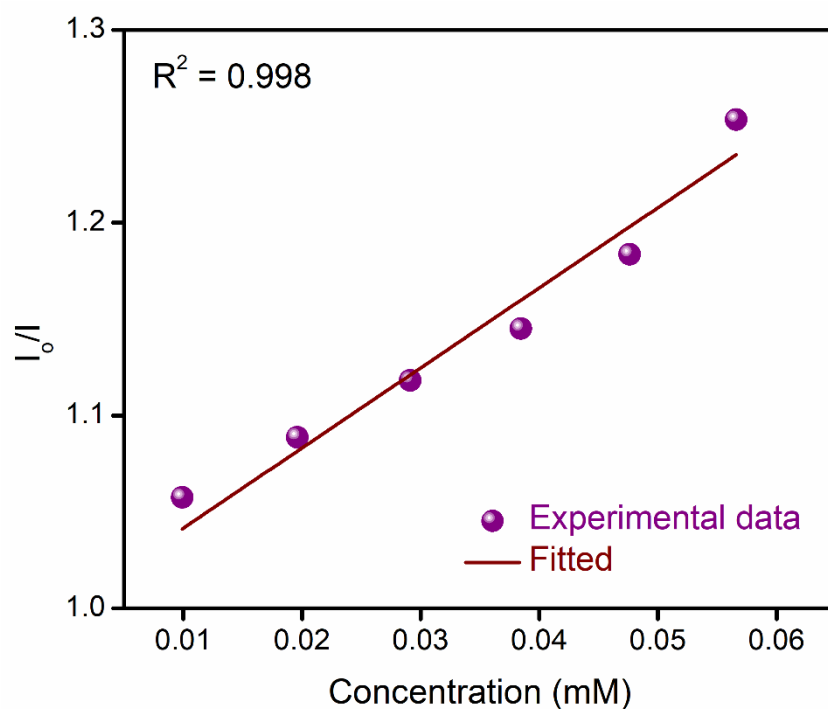
Appendix Figure 2.40: Elemental mapping images of PABA@MOF-808@PVDF MMM



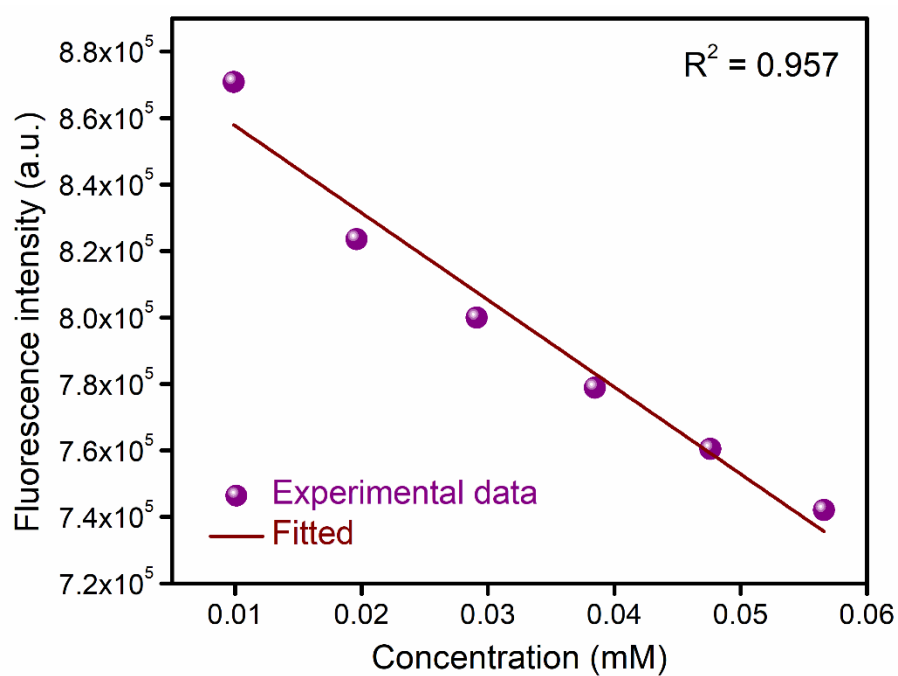
Appendix Figure 2.41: Nitrogen gas sorption data of PABA@MOF-808@PVDF MMM.



Appendix Figure 2.42: Photoluminescence emission spectra of PABA@MOF-808@PVDF MMM.



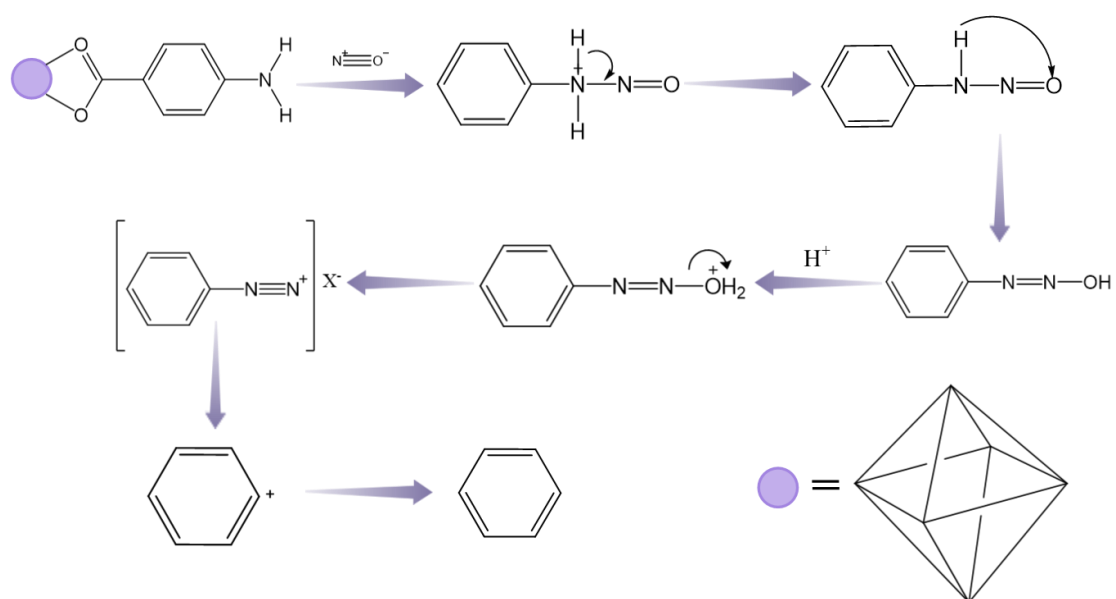
Appendix Figure 2.43: Stern-Volmer (SV) plots for quenching of PL intensity of PABA@MOF-808@PVDF MMM by NO.



Appendix Figure 2.44: Plot for calculation of LOD of PABA@MOF-808@PVDF MMM towards NO detection.



Appendix Figure 2.45: Digital image of set-up for demonstration of NO vapour detection by PABA@MOF-808@PVDF MMM.



Appendix Figure 2.46: Schematic presentation of the chemical reaction between free amino groups of MOF composite and NO which leads to the formation of benzoic acid.

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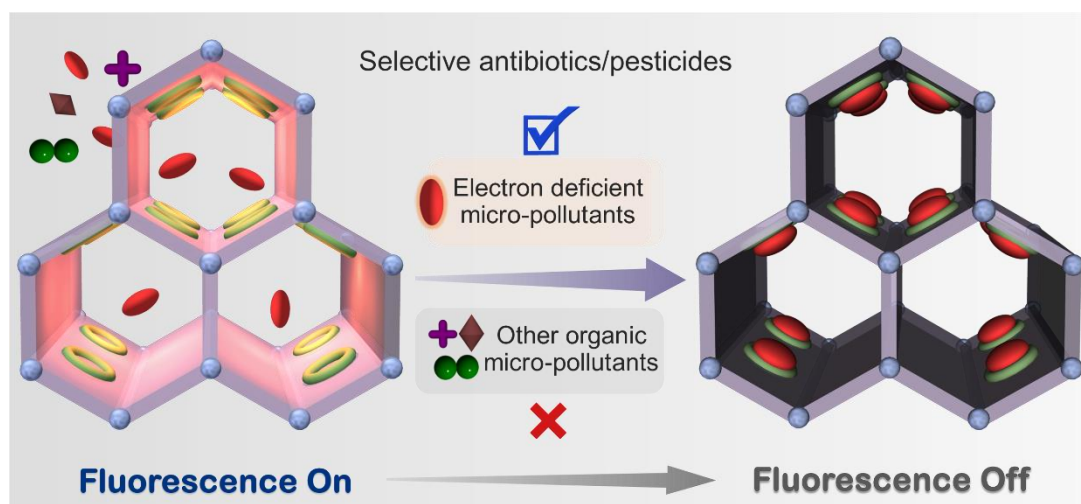
Chapter 3

Selective and Sensitive Recognition of Specific Types of Toxic Organic Pollutants with a Chemically Stable Highly Luminescent Porous Organic Polymer (POP)

3.1 Introduction

In the 21st century, the drinking water crisis has emerged as a serious issue across many regions of the world.^[1,2] With ever increasing populations and urbanization, water pollution is becoming a great threat to the entire ecosystem.^[3] Anthropogenic water pollutants, such as emerging organic contaminants, contribute a major portion to water pollution.^[4] The Safe Drinking Water Act (SDWA) defines the term “contaminant” as any foreign physical, chemical, radiological, or biological substance in water.^[5] Among anthropogenic wastes, antibiotics and pesticides are considered two major pollutants that cause severe water pollution.^[6] Since the discovery of penicillin, a well-known antibiotic used as an antimicrobial substance active against bacteria, it has been used widely as a medicine in hospitals for humans and also as veterinary medicine owing to its ability to inhibit the growth of various pathogens.^[7,8] Apart from this, with the development of agricultural production, it is also used in agricultural fields for food production, aquaculture, beekeeping, etc.^[6,9,10] However, the excessive use of antibiotics causes bacterial drug resistance and antibiotic resistance. In line with this, the abuse or misuse of such species also further results in severe environmental pollution.^[11-13] On the other hand, pesticides, another class of potential organic contaminants, have become a “matter of concern” in recent times. Pesticides have been extensively used in modern agriculture to raise production.^[6,14,15] Not only are pesticides extremely toxic in nature to agricultural pests, but also their residues in water bodies cause serious water pollution.^[16,17] Prolonged exposure to these hazardous species causes serious problems to living organisms by affecting their nervous systems, respiratory systems, and reproductive systems.^[18] Considering the detrimental consequences as well as high levels of risk of these aforementioned organic contaminants in water, systematic and regular monitoring of these species has emerged as a fundamental research problem. Over the past few decades, many analytical techniques like mass spectroscopy (MS), Raman spectroscopy (RS), liquid chromatography–tandem mass spectrometry (LC-MS), LC with UV detection (LC-UV), and ion mobility spectroscopy (IMS) have been employed for detection of these toxic species.^[19-22] However, all of these methods exhibited limitations, such as lower efficiency expensiveness, being time consuming, complexity of the technique, and need for expert personnel. Hence, developing a simple, cost-effective, fast response, highly sensitive method for selective identification of toxic species has become a topical research interest. In this view, fluorescence-based detection techniques have drawn attention because of their high sensitivity, selectivity, quick sensing response, ease of operation, and low cost.^[23-25]

Recently, the luminescent porous material based fluorescence technique for the detection of target-specific environmental contaminants has received special research attention, owing to its pre-concentration effect, high sensitivity, selectivity, reusability, low fabrication and operational costs, etc.^[26-29] Compared to traditional porous materials, such as activated carbon, zeolites, and resin,



Scheme 3.1 Schematic representation of detection of selective organic micro pollutants.

advanced porous materials such as metal–organic frameworks (MOFs) and porous organic polymers (POPs) have recently been shown to be promising toward sensing application because of their improved sensitivity, high selectivity, and fast response. [27,30]

Although several MOF-based antibiotic and pesticide sensing studies have been reported, [6–11, 25] the detection of these species with low-cost and thermally and chemically stable highly luminescent POPs is very rarely explored. [27,31] POPs are a class of porous materials constructed with strong covalent bonds between various pure organic building blocks as a potential scaffold, featuring highly tunable porosity and excellent chemical and thermal stability. [32–35] The successful development of such materials with the aforementioned properties along with rational incorporation of fluorophores also offers advantages toward construction of efficient sensory materials. The high porosity and large surface area of these materials allow fast mass diffusion and strong interaction of the probes with the targeted analytes and thus further result in rapid detection and sensitivity, respectively. [36–28] Moreover, the heterogeneous nature coupled with high chemical stability of these materials enables the easy and superior recyclable detection ability of these probes, making them useful for different environments. [39, 40]

Keeping the target in mind for the selective and sensitive detection of specific antibiotics and pesticides in water and considering the facts of developing a low-cost, easy-operation, portable, reliable, highly stable, efficient point-of-use sensory material, we strategically chose POPs as a potential stable sensory material for the specific task of sensitive detection of antibiotics and pesticides in water (Scheme 3.1). For this, we revisited the chemical structures of the selected contaminants, and we found that these antibiotics and pesticides can be classified depending upon their electronic properties. For example, a

few of them are electron deficient and others are electron rich. Guided by this information, we envisioned that development of electron-rich moieties containing materials could be beneficial in respect of both inducing a highly luminescent nature and easily differentiating between tunable electronic configuration-based contaminants.

Considering this, in this work, a robust highly luminescent POP (IP_{POP-1}) is reported for the sensitive and selective detection of specific antibiotics and pesticides in water (Scheme 3.1). The rational construction of the chemically stable POP (IP_{POP-1}) as a fluorophore was carried out by utilizing the nucleophilic aromatic substitution reaction between 2,4,6- tris(4-fluorophenyl)-1,3,5-triazine (TFPT) and [1,1'-biphenyl]- 4,4'-diol (BPDO) monomers (Figure 1a) (see the experimental section for details). We reasoned that this in situ fabricated ether-linkage electronically rich covalent network results in intense luminescence properties in water along with high thermal and chemical stabilities in both acidic and basic media. Inspired by such a strong luminescent nature owing to the electron-rich moieties together with high stability, we investigated the detection ability of IP_{POP-1} toward a group of antibiotics and pesticides in an aqueous medium. Among various antibiotics, the compound exhibited selective detection capability toward electron-deficient nitrofurazone (NFZ) and nitrofurantoin (NFT) with superior fluorescence quenching efficiencies (2.75×10^4 and 1.6×10^4 M⁻¹, respectively) and lower limit of detection (LOD) values (0.046 and 0.045 mM respectively). Similarly, the compound showed a high degree of fluorescence selective quenching efficiency toward electron deficient pesticides like chloropyriphos (CHPS) and 2,4- dichloro-1(4-nitrophenoxy)-benzene (nitrofen) in an aqueous medium with appreciable LOD values. Thereafter, the mechanism of the fluorescence quenching phenomenon of IP_{POP-1} by the selected antibiotics and pesticides was demonstrated with the help of the fluorescence resonance energy transfer (FRET), photoinduced electron transfer (PET), and counter-collision processes between the targeted analytes and the probe. Again, the density functional theory (DFT) was applied to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and theoretically investigate the insight behind such a quenching response, which validated the strong interaction between the electron-deficient analytes and the π - electron-rich polymeric backbone. Moreover, such a strong interaction was found to be thermodynamically favourable, which was further investigated by isothermal titration calorimetry (ITC). Finally, considering real-world application, a mixed-matrix membrane (MMM) of IP_{POP-1} was fabricated and was further applied in the detection of selected antibiotics in a simulated water sample along with a real antibiotic contaminated hospital wastewater system.

3.2 Experimental

3.2.1. Materials: All the reagents, starting materials and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals, Alfa aesar depending on their availability and used without further

purification. 4,4-dihydroxybiphenyl was bought from Sigma-Aldrich. All antibiotics and pesticides are toxic in nature and proper protective gear (masks, gloves) is always to be used.

3.2.2 General Characterization and Physical Measurements:

3.2.2.1 Fourier transform infrared spectroscopy (FT-IR): The Fourier transform infra-red (FT-IR) spectra were recorded on NICOLET 6700 FT-IR Spectrophotometer using KBr Pellets. FT-IR data are reported with a wave number (cm^{-1}) scale in 500-4000 cm^{-1} range.

3.2.2.2 Thermogravimetric analysis (TGA): Thermogravimetric analyses were recorded on PerkinElmer STA 6000 TGA analyzer by heating the samples from 40 °C to 800 °C under N_2 atmosphere with a heating rate of 10 °C min^{-1} .

3.2.2.3 Scanning electron microscopy (SEM): The morphology of the crystalline materials was recorded with a Zeiss Ultra Plus field-emission scanning electron microscope (FESEM) with an integral charge compensator and embedded EsB and AsB detectors (Oxford X-max instruments 80 mm^2 (Carl Zeiss NTS, GmbH). The samples were sputter-coated with a 5 -10 nm Au film to reduce charging. The elemental analysis was carried out using voltage of 15 KV equipped with an EDX detector. Data acquisition was performed with an accumulation time of 600 s.

3.2.2.4 Transmission electron microscopy (TEM): TEM imaging and STEM-EDS were performed on the HRTEM (JEM-2200FS, JEOL) operating at an acceleration voltage of 200 kV. For TEM analysis, all the samples were dispersed in isopropanol and sonicated. Then, the samples were left for 2 min, and the upper part of the solution was taken for preparing TEM samples on a lacey carbon coated copper grid (Electron Microscopy Science, 200 mesh).

3.2.2.5 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.

3.2.2.6 ^{13}C Solid-state Nuclear magnetic resonance (NMR): ^{13}C solid-state NMR spectra were recorded on Bruker 500 MHz NMR spectrometer. The chemical shifts are expressed in parts per million (δ scale).

3.2.2.7 Confocal laser scanning microscope (CLSM): Confocal laser scanning microscope (Zeiss, Oberkochen, Germany Model LSM 10) was used to achieve background free high-resolution images of all the compounds.

3.2.2.8 Photoluminescence study: All fluorescence measurements were done on Jobin Yvon Fluoromax-4 spectrofluorometer (HORIBA Scientific) with stirring attachment.

3.2.2.9 UV-visible absorption study: UV-vis absorption studies were performed on a Shimadzu UV 3600 UV /vis /NIR spectrophotometer in an optical quartz cuvette (10 mm path length) over the entire range of 200-800 nm.

3.2.2.10 Steady state photoluminescence study: The steady-state photoluminescence studies were recorded on a Fluorolog-3 spectrofluorometer (HORIBA Scientific).

3.2.2.11 Isothermal Titration Calorimetry (ITC): The ITC experiments were performed on a Malvern MicroCal PEAQ-ITC microcalorimeter having 20 (19+1) injection cycle method capacity, the sample volume of 280 μL with a sample cell size of 200 μL and injection syringe volume of 40 μL for each set of experiments.

ITC experiment quantitatively provides the change in enthalpy, entropy and Gibbs free energy associated with the adsorption process between adsorbent and adsorbate. In this typical experiment, first, the reference cell was filled with deionized water, and a homogeneous aqueous suspension of adsorbate (IP_{POP}-1) (which was grounded into fine powder) was poured into the sample cell and the 1 mmol concentration of adsorbent (NFT) aqueous solution was placed into the syringe, while the complete mixture was stirring at 750 rpm. In this study, we recorded the thermograms of NFT adsorption in the IP_{POP}-1. The first injection of each titration was fixed at 0.4 μL . At least two titrations for each analyte-compound pair were collected. Data analysis was performed in y. MicroCal PEAQ-ITC analysis software. The heats of injection for blank titrations (analyte (NFT)) into blank) were subtracted from the heats of injection into compound suspensions.

3.2.3 Quantum calculation method:

For further mechanistic insight into molecular level pathway for selective and dynamic photoluminescence quenching mediated by antibiotics and pesticides, we performed First-principle calculations based on density functional theory (DFT) and obtained HOMO – LUMO energy gaps for subunit of POP and subunit for different antibiotics and pesticides. Discovery Studio 2017 (Accelrys) program was used for DFT calculations. All the DFT calculations were performed at fine quality calculation level. The single-point energy calculations were performed using three parameters B3LYP function considering DMol3 code. In the beginning, the molecular structures of POP, antibiotics and pesticides were fully relaxed using geometry optimization by keeping Auto mode Multiplicity factor, Double Numeric Plus Polarizing (DNP+) basis set and water as solvent. Subsequently, the structural simulation performed using simulated annealing technique on geometry relaxed POP to find possible interaction site of the antibiotics and pesticides.

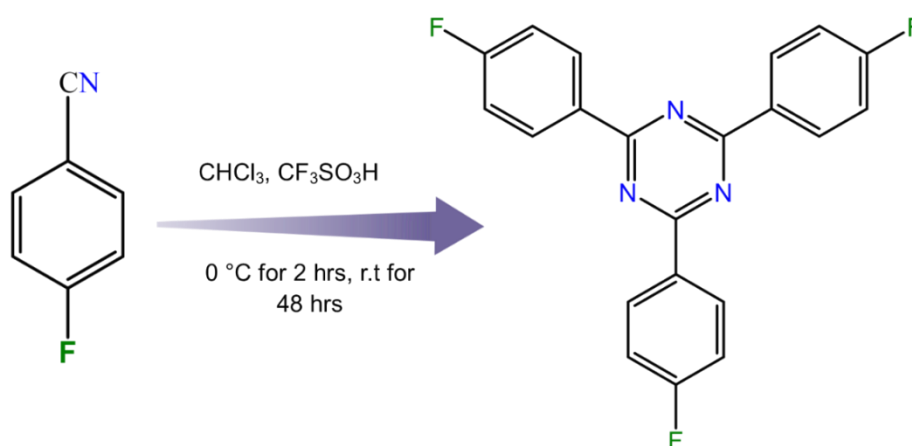
3.2.4 Optical properties simulation:

The optical properties were simulated using CASTEP code. The geometry optimized POP subunit – specific antibiotic/pesticide obtained above was considered for the calculations. The calculations were performed with Norm conserving pseudopotentials, Koelling – Harmon relativistic treatment, 600 eV energy cutoff, self – consistent dipole correction and 2×2×2 Monkhorst – Pack grid.

3.2.5 Detail Synthetic Procedures

3.2.5.1 Synthesis of precursor 1:

2,4,6-tris(4-fluorophenyl)-1,3,5-triazine (TFPT) was synthesized according to the reported protocol without any further modifications.^[41] Briefly, trifluoromethanesulfonic acid (11 ml, 124.6 mM) was taken in a dry CHCl₃ (30 ml) and was stirring at 0 °C for sometimes then 4-fluorobenzonitrile (3.5 g, 28.8 mM) in dry CHCl₃ was added to the stirred reaction vessel at 0 °C and for two hours and further at room temperature for 48 hours. After completion of the reaction the reaction mixture was poured into water containing sodium bicarbonate. After that the reaction mixture was filtered off and dried in vacuum; a white solid compound was obtained which was recrystallized from chloroform for further use.

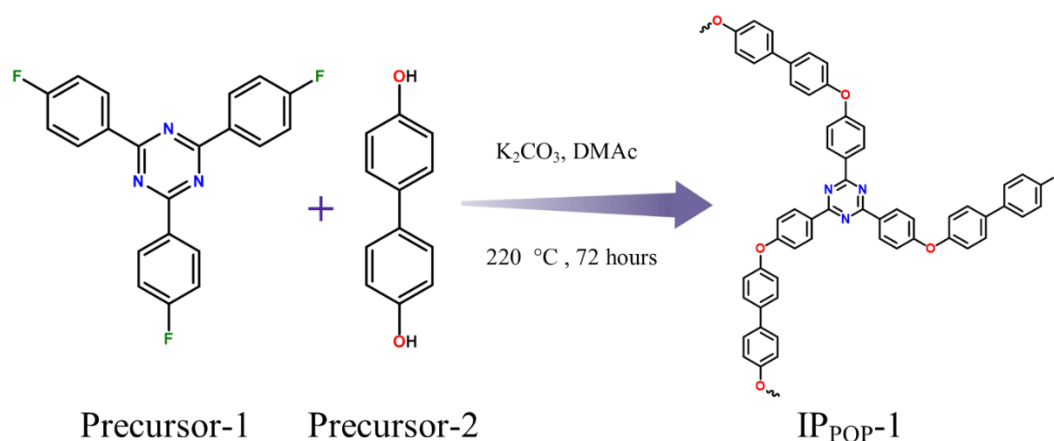


Scheme 3.2.5.1: Synthesis scheme of precursor-1.

3.2.5.2 Synthesis procedure of the polymer (IP_{POP-1}):

At first 0.256 g of 4,4'-dihydroxybiphenyl and 1.9 g of potassium carbonate were taken in 30 ml of Dimethylacetamide (DMAc) in a 100 ml of round bottom flask then it was heated at 120 °C for 2-3 hours under nitrogen atmosphere. Then 0.5 g of TFPT was dispersed in 20 ml of DMAc and it was added into the reaction medium followed by increase the temperature to 220 °C for 72 hours. After completion of the reaction, it was cooled and the reaction mass was poured into ice-cold water; a light-

yellow precipitate was obtained which was filtered off. To check whether the polymer was formed or not it was washed for several times by various organic solvents like DCM, CHCl_3 , DMF, EtOH, THF, ACN, MeOH and acetone. Insolubility into those solvents has been proven the formation of polymer material. It was then dried in oven, and then dipped into CHCl_3 : THF (1:1) solvent for three days with changing the solvent mixture once in a day. After three days it was filtered off and activated at 120°C for 24 hours.



Scheme 3.2.5.2: Synthesis scheme of IP_{POP}-1.

3.2.5.3 Synthesis procedure of IP_{POP}-1-based mixed matrix membranes (MMMs) or films: The following standard reported protocol has been adopted for the fabrication of the IP_{POP}-1/polymer-based membrane.^[42] To prepare the membrane, at first, a widely used polymer, PVDF, ~160 mg was dissolved in 1.9 ml DMF by stirring the mixture at room temperature for more than 24 h. The PVDF-DMF mixture results a viscous sticky solution after one day. After that, ~10 mg of fine powder of IP_{POP}-1 was added with the solution of thus prepared pure polymer to form a homogeneous mixture by stirring the whole solution for another 24 h. After that, the mixture was casted onto a clean glass slide by a regular scraper to make a flat thin-sheet membrane. Thus, fabricated system was then dried under ambient condition and further soaked in DI water. This led to the fast delamination of the MMMs. Thus, obtained free-standing films were dried in air and then in oven, and further cut into small pieces for sensing application.

3.2.6 Photoluminescence study

Analyte Preparation:

First stock solutions of all antibiotics and pesticides were prepared in water of concentrations 1 mM each.

Fluorescence Study:

In typical experimental setup, 1 mg of IP_{POP}-1 has been taken in a cuvette and 1.2 ml water and 0.8 ml acetonitrile were added to that. Initial luminescence spectra of IP_{POP}-1 in water acetonitrile medium have been recorded by exciting at different wavelength (spectra recorded in the range of wavelength 320-650 nm). Then to the dispersed IP_{POP}-1 in water acetonitrile medium we have added the stock solution of each antibiotic and pesticides (20 μ L to 300 μ L) and the spectra were recorded for each addition. With each addition of nitrofurantoin (NFT, NFZ) antibiotics and nitrofen and chlorpyrifos pesticides, there are gradual quenching in the fluorescence emission of the polymer but in case of other antibiotics and pesticides there are very minimal quenching of the spectrum. For competing studies, we have done the binary selectivity with rest of other non-quenching antibiotics (CHMP, AMP, SGD, STH, SPD) with NFZ and NFT individually. Similar competing experiment have done with the pesticides also. In this experiment we have taken 1 mg of IP_{POP}-1 in 2 ml of water acetonitrile mixture (3:2), then to this 200 μ L of one non quenching antibiotic was added. After that, to this solution again 200 μ L of NFZ was added. We have recorded both the responses of polymer in presence of competing antibiotics and pesticides. By combining two responses we got the selectivity of IP_{POP}-1 towards antibiotic (NFZ, NFT) and pesticides (nitrofen, chlorpyrifos) in presence of other competing antibiotics and pesticides.

Recyclability Test:

After the first detection cycle of NFT, the polymer was recovered by centrifugation in a 2 ml Eppendorf from the suspension. After that the settled compound was washed with water, followed by acetone and then allowed to dry at room temperature for overnight. After finally drying in oven at 75 °C for 2 hours, the polymer powder was again suspended in water acetonitrile (3:2) mixture, which was then used for the next antibiotic (NFT, NFZ) and pesticide (nitrofen, chlorpyrifos) detection investigation, following the identical sensing titration experiment. Thereafter, for the rest of remaining sensing cycles we repeated the similar procedure.

Chemical stability test:

To test the chemical (acid-base) stability of the compound, IP_{POP}-1 was treated with 1M HCl and 1 M NaOH solution for one week. After seven days the compound was separated and characterized with FT-IR, TGA, FESEM experiments.

3.3 Results and Discussion

The reaction of the monomers TFPT and BPDO in the presence of the solvent dimethylacetamide (DMAc) and a potassium carbonate (K_2CO_3) base yielded a highly luminescent polymer (IP_{POP-1}) as a light-yellow product with a high yield, as illustrated in Figure 1a (Schemes 3.2.5.1 and 3.2.5.2) (see the experimental section for details). Then, the synthesized IP_{POP-1} polymer was thoroughly washed with

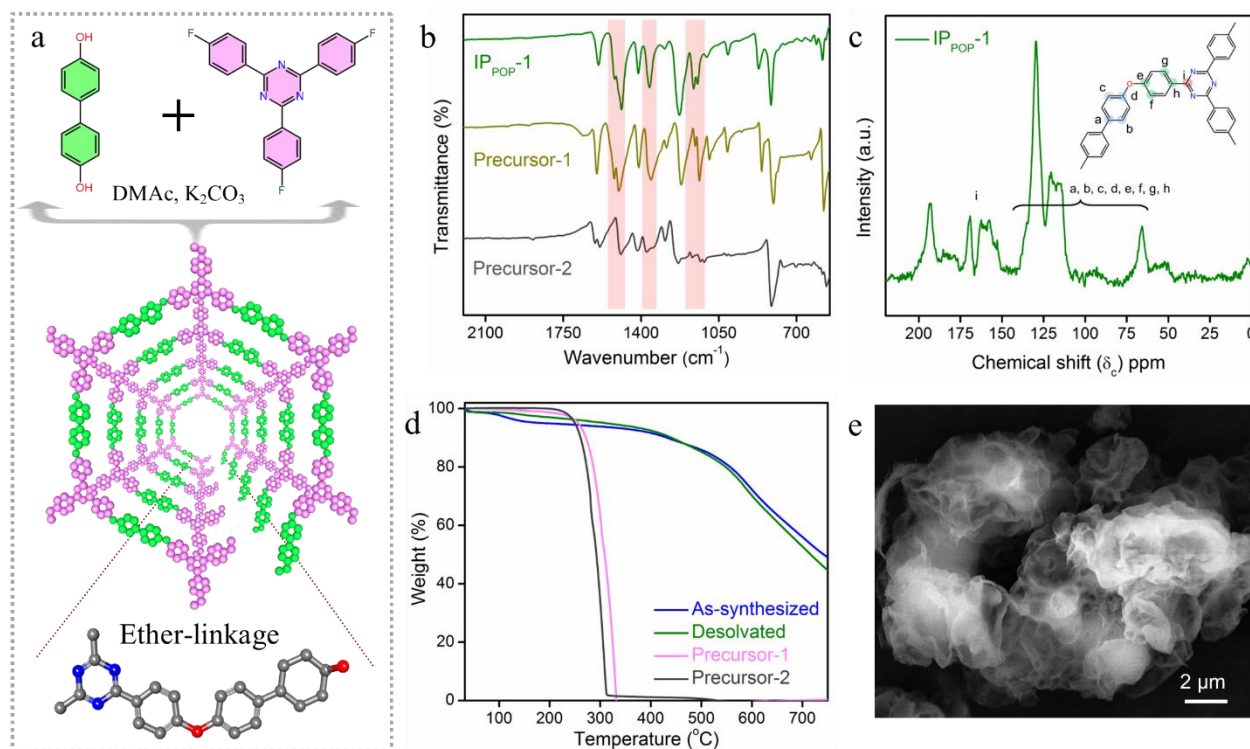


Figure 3.1 (a) Schematic representation of synthetic preparation of IP_{POP-1} , (b) FT-IR spectra of the IP_{POP-1} along with its respective precursors, (c) Solid-state ^{13}C NMR spectra of IP_{POP-1} , (d) TGA profile of IP_{POP-1} along with precursors, (e) FESEM image of IP_{POP-1} .

various solvents such as water, dimethylformamide (DMF), methanol (CH_3OH), ethanol (EtOH), tetrahydrofuran (THF), chloroform ($CHCl_3$), and hexane. The insolubility of the compound in the above solvents primarily indicated the formation of an extended framework material, connected via covalent linkages. Thereafter, multiple characterization techniques, viz., Fourier transform infrared (FT-IR), solid-state ^{13}C NMR (SS ^{13}C -NMR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM), were performed to confirm the structural as well as morphological features of the formed polymeric network. In the FT-IR spectra, a distinct peak at $\sim 1103\text{ cm}^{-1}$ appeared, which corresponds to the stretching of the ether linkage (C-O) in the polymer backbone of the material (Figure 3.1b).^[43] The aforementioned peak was

exclusively found for the compound IP_{POP}-1 and not for its respective monomers. Moreover, intense characteristic peaks at $\sim 1359\text{ cm}^{-1}$ (C-N) and at $\sim 1487\text{ cm}^{-1}$ (C=N) in the FT-IR spectra indicate the presence of triazine ring stretching in the polymer (Appendix Figure 3.1).^[44,45] Further, molecular level characterization of IP_{POP}-1 was done by employing SS ^{13}C NMR. In the SS ^{13}C NMR spectra of the compound, the peak at $\sim 169\text{ ppm}$ corresponds to the sp^2 carbon atom of the triazine ring (Figure 3.1c). On the other hand, the peaks from 110 to 130 ppm are ascribed to the carbon atoms of the aromatic moiety of IP_{POP}-1. Moreover, the signal at $\sim 66.5\text{ ppm}$ in the spectra corresponds to the carbon atom of the adjacent ether linkage (Figure 3.1c).^[45-47] Thereafter, to check the thermal behaviour of IP_{POP}-1, we carried out TGA, which indicated that there was a slight weight loss up to 100°C , which corresponds to the loss of trapped chloroform and THF solvent molecules in the as-synthesized phase of the compound (Figure 3.1d). Again, the compound exhibited no weight loss up to 500°C , as revealed from the TGA profile of the desolvated compound (Figure 3.1d). Apart from these structural characterizations, surface morphological investigation was carried out with the help of FESEM and TEM. IP_{POP}-1 demonstrated a thin-flake-shaped morphology, as observed in the FESEM image (Figure 3.1e). Furthermore, the TEM image of IP_{POP}-1 indicated a similar morphology for the compound (Appendix Figure 3.2).

Moreover, the elemental mapping analysis from the FESEM experiment on IP_{POP}-1 revealed the presence of all relevant elements (carbon, nitrogen, and oxygen) and a homogeneous distribution throughout the polymeric network (Appendix Figure 3.3). A similar result was observed from the energy-dispersive spectroscopy (EDS) data of the FESEM analysis (Appendix Figure 3.4a). The powder X-ray diffraction (PXRD) spectra of the polymer indicated the amorphous nature of the compound (Appendix Figure 3.4b). Now, in order to elucidate the porous nature of the compound, low-temperature (77 K) N_2 sorption measurement was performed. The nitrogen sorption isotherm of IP_{POP}-1 suggested the existence of porosity in the compound (Appendix Figure 3.5a, b). The hysteresis pattern in the nitrogen gas desorption profile can be explained in terms of network swelling in the presence of condensed nitrogen. Moreover, low-temperature (at 195 K) CO_2 gas adsorption measurement was performed, which displayed an uptake of $\sim 63\text{ cm}^3\text{ g}^{-1}$ (Appendix Figure 3.6). All of these characterization techniques validated the successful formation of the porous polymeric framework material.

That being said, for a real-time potential sensor, the sensory material should exhibit high chemical stability. Therefore, to test the chemical (acid - base) stability of the compound, IP_{POP}-1 was treated with a 1 M HCl and a 1 M NaOH solution for 1 week. After 7 days, the compound was separated and characterized with FT-IR, TGA, and FESEM experiments. The FT-IR spectra of the acid-base-treated IP_{POP}-1 indicated no change in the peak position from that of the pristine compound, suggesting

retention of structural integrity (Appendix Figure 3.7). Moreover, the identical TGA profile and PXRD spectra showed similar decomposition temperatures and the amorphous nature of the compound, respectively, after acid-base treatment (Appendix Figure 3.8a, b). FESEM and TEM images of acid-base-treated IP_{POP}-1 showed no morphological changes (Appendix Figure 3.9). These results clearly revealed the high chemical stability of IP_{POP}-1, which is beneficial toward aqueous-phase sensing application.

Apart from these structural characterizations, the optical properties of IP_{POP}-1 were further examined in order to investigate its ability toward sensing application. The solid powder compound (IP_{POP}-1) was found to exhibit intense blue fluorescence emission under a UV lamp (Appendix Figure 3.10a). A similar result was observed in the case of the fluorescence microscopy images (Appendix Figure 3.11 and 3.12). This observation drove us to check the absorbance and emission maxima of the compound. IP_{POP}-1 exhibited a broad absorption band from 200 to 410 nm with a maximum at 330 nm, as revealed from the diffuse reflectance UV-vis spectra (Appendix Figure 3.13). Meanwhile, upon excitation at 330 nm, the compound displayed an emission spectrum from 390 to 610 nm with a maximum at 470 nm in the solid-state photoluminescence spectra (Appendix Figure 3.14).

Now, keeping two considerations in mind, one of which is the target for aqueous-phase real-world sensing application and the other the high hydrolytic stability of IP_{POP}-1, we examined the photoluminescence response of IP_{POP}-1 in a water medium, which exhibited a relatively lower emission intensity. However, owing to the hydrophobic nature of the compound along with improved emission spectra with a high emission intensity centered at ~470 nm, we collected the final PL spectra of IP_{POP}-1 by dispersing it in a H₂O (1.2 mL) and ACN (0.8 mL) mixture (Appendix Figure 3.15). The compound in the aforementioned solvent mixture displayed an intense sky-blue emission (Appendix Figure 3.10b), which suggested that IP_{POP}-1 would be suitable for potential use as an efficient detection material toward sensing of environmentally relevant organic species, such as selected antibiotics and pesticides, in an aqueous medium.

3.4 Sensing Studies

Encouraged by the intense fluorescent nature and high hydrolytic as well as chemical stability of IP_{POP}-1, we examined in detail the performance of IP_{POP}-1 for the photoluminescence detection of specific organic micropollutants in a water medium. For this study, as potential microcontaminants, a variety of antibiotics and pesticides were chosen as emerging toxic organic substances in water. First, eight most commonly used antibiotics, namely, NFT and NFZ (class: nitrofurans), chloramphenicol (CHMP) (class:

chloramphenicol), ampicillin (AMP) (class: penicillin), sulfaguanidine (SGD) (class: sulfonamide), sulfathiazole (STH) (class: organosulfur), and sulfapyridine (SPD) (class: sulfonamides), Spectinomycin (SPCT), and five pesticides (CHPS, 2,4-dichloro-1(4-nitrophenoxy)- benzene (nitrofen), fenazaquin (FZQ), cypermethrin (CPM), and 2,6-dichloro-4-nitroaniline (DCNA)) were chosen for the sensing study (Appendix Figure 3.16).^[6,7,14] First, for the detection of the aforementioned antibiotics, in a typical titration experiment, 1 mg of IP_{POP}-1 was well dispersed in 2 mL of a H₂O/ACN (3:2) mixture, and the corresponding emission spectrum was recorded (Appendix Figure 3.15). Thereafter, 300 μ L of all of the selected aqueous solutions of antibiotics (with a concentration of 1 mmol each) was added into the mixture individually and the corresponding emission spectra were recorded. It was found that the high fluorescence emission of IP_{POP}-1 was quenched mostly and rapidly upon addition of the antibiotics NFZ and NFT only (Appendix Figures 3.17 and 3.18).

Meanwhile in the case of other antibiotics, the emission of IP_{POP}-1 was observed to be slightly decreased (Appendix Figure 3.19). This observation clearly indicated the selective quenching response of IP_{POP}-1 to the nitrofurantoin class of antibiotics, such as NFZ and NFT. Motivated by this result, we further compared the quenching efficiencies of IP_{POP}-1 for those antibiotics to which it exhibited lower quenching responses along with NFZ and NFT, individually (Figure 3.2a, b).

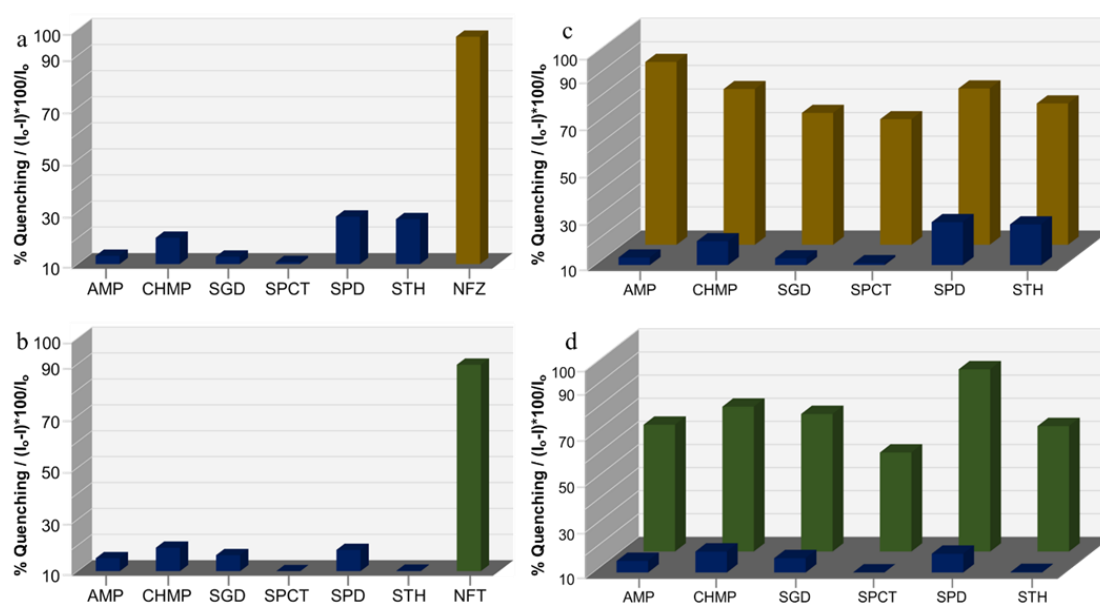


Figure 3.2 (a, b) Selective fluorescence quenching response of IP_{POP}-1 by NFZ and NFT, respectively, with compare to other selected antibiotics. (c, d) Binary selective quenching response of IP_{POP}-1 by NFZ and NFT, respectively, in the presence of other antibiotics. [Colour codes: Brown for NFZ, Olive green for NFT, and Dark blue for other antibiotics]

Moreover, this selective detection response inspired us to explore the binary recognition ability of IP_{POP-1} for these antibiotics in an aqueous medium, which is considered an essential criterion for real-world sensing application. For this experiment, first, we recorded the emission spectra of pristine IP_{POP-1} followed by the addition of equal amounts of other antibiotics along with NFZ and NFT, individually. It should be pointed out that the antibiotics, such as SPCT, STH, CHMP, AMP, SGD, and SPD, were added before the addition of NFZ or NFT to the IP_{POP-1} dispersion, because of the easy access of the free interaction binding sites of the polymer by those antibiotics. It was found that the fluorescence emission of IP_{POP-1} was slightly quenched upon the addition of 300 μ L of the aforementioned antibiotics apart from NFZ or NFT (Appendix Figures 3.20 and 3.21). Interestingly, upon further addition of an equal amount of NFZ or NFT, individually, in the previous mixture, the high emission intensity was found to decrease rapidly (Appendix Figures 3.20 and 3.21).

This observation suggested the binary selectivity of IP_{POP-1} toward the sensing of NFZ and NFT in the presence of other several antibiotics (Figure 3.2c, d). The aforementioned result reasoned the further explorations of sensing study of IP_{POP-1} toward NFZ and NFT with the following details: In a typical titration experiment, 1 mg of IP_{POP-1} was well dispersed in 2 mL of the H₂O/ACN mixture, and the corresponding emission spectra were recorded. Then, 1 mmol concentration aqueous solutions of both NFZ and NFT were individually added into the polymer suspension by incremental amounts of 20 μ L to a total of 300 μ L. It was found that the high fluorescence emission of IP_{POP-1} was gradually quenched upon incremental addition of both the NFZ and NFT antibiotics (Figure 3.3a, d). From the fluorescence quenching profiles of IP_{POP-1} for NFZ and NFT, the quenching constant (K_{sv}) was calculated, using the Stern-Volmer equation: $(I_0/I) = 1 + K_{sv}[Q]$, where K_{sv} is the quenching constant, $[Q]$ is the molar concentration of the analyte, and I_0 and I are the luminescent intensities before and after addition of the analyte, respectively. ^[48] The K_{sv} values for NFZ and NFT was found as high as 2.75×10^4 and $1.6 \times 10^4 \text{ M}^{-1}$, respectively, which are believed to be some of the highest values in the regime of porous materials (Figure 3.3b, e) (Appendix Table 1).

In addition, it is worth mentioning that the Stern-Volmer (SV) plot for NFZ was found to be linear in the whole concentration range; however, in the case of NFT, there was a deviation from linearity at the higher concentration range (Figure 3.3b, e). This deviation in the SV plot in the case of NFT might be attributed to the adsorption or triggered charge transfer process between IP_{POP-1} and NFT. ^[25] Moreover, for a good sensory material, the LOD is an important parameter for sensing applicability. ^[49] The LOD values were calculated as 0.046 and 0.045 mM for NFT and NFZ, respectively (Figure 3.3c, f). These LOD values of IP_{POP-1} for NFZ and NFT were also found to be well comparable with other literature reports. Furthermore, as aforementioned, apart from antibiotics, pesticides are another class of environmentally relevant toxic micro contaminants.

As similarly done for antibiotics, for the sensing of pesticides, we performed the same titration experiment, taking all of the selected pesticides against an aqueous suspension of IP_{POP}-1, individually. First, fresh 1 mmol aqueous solutions of each pesticide (CHPS, FZQ, CPM, DCNA, and nitrofen) were prepared.

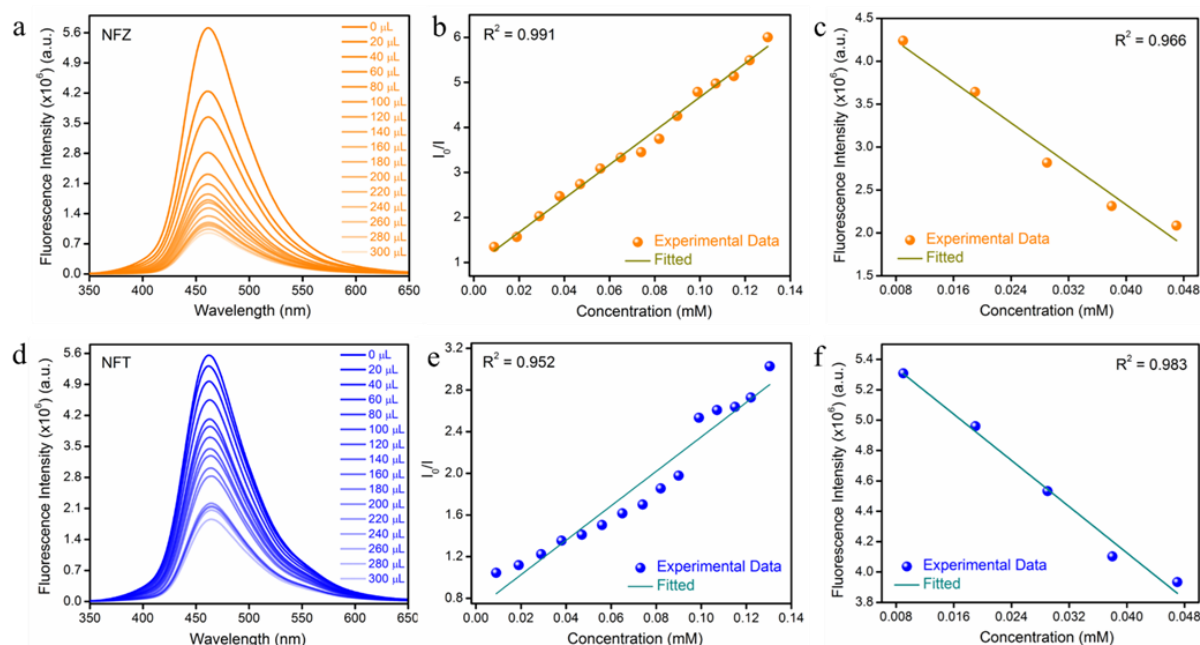


Figure 3.3 Sensing studies of antibiotics: (a, d) Fluorescence emission spectra of IP_{POP}-1 in different concentrations of NFZ and NFT aqueous solutions. (b, e) The corresponding Stern-Volmer plots of IP_{POP}-1 in different concentrations of NFZ and NFT aqueous solutions, respectively. (c, f) LOD calculation plot for quenching response towards NFZ and NFT, respectively.

Thereafter, upon addition of a total of 300 μ L of each pesticide solution into a suspension of IP_{POP}-1, the maximum emission of the luminescent polymer was found to be greatly quenched by CHPS and nitrofen only (Appendix Figures 3.22 and 3.23), whereas the emission spectra of IP_{POP}-1 were slightly decreased upon addition of other pesticides (Appendix Figure 3.24). Encouraged by this result, we further compared the quenching efficiencies of IP_{POP}-1 for the classes of pesticides that exhibited lower quenching responses with those for CHPS and nitrofen, individually (Appendix Figures 3.25 and 3.26). Moreover, this selective detection response motivated us to further explore the binary recognition ability of IP_{POP}-1 for these pesticides in an aqueous medium. As similarly done for antibiotics, in this experiment, first, we recorded the emission spectra of pristine IP_{POP}-1 followed by the addition of other pesticides along with CHPS and nitrofen, individually.

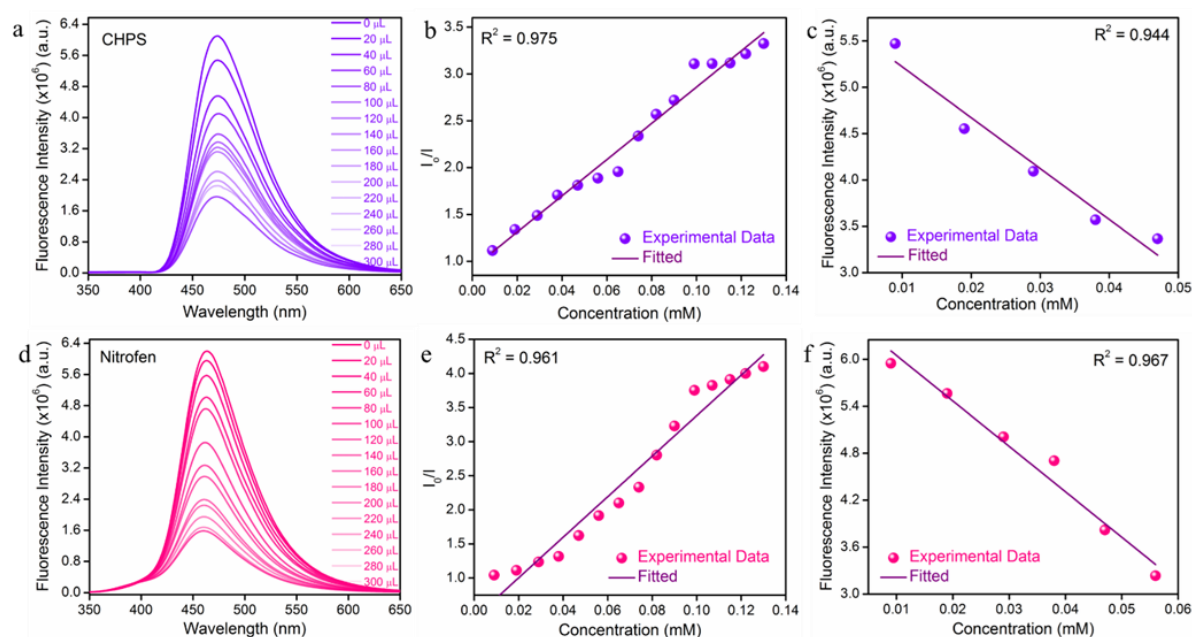


Figure 3.4 Sensing studies of pesticides: (a, d) Fluorescence emission spectra of IPPOP-1 in different concentrations of CHPS and nitrofen aqueous solutions. (b, e) The corresponding Stern-Volmer plots of IPPOP-1 in different concentrations of CHPS and nitrofen aqueous solutions, respectively. (c, f) LOD calculation plot for quenching response towards CHPS and nitrofen, respectively.

It was observed that the fluorescence intensity was slightly quenched upon addition of 300 μL of these pesticides without CHPS and nitrofen (Appendix Figure 3.27). However, upon further addition of an equal amount of CHPS or nitrofen, individually, in the previous mixtures, the high intensity was found to decrease abruptly (Appendix Figure 3.27). This observation motivated us to study the binary selectivity of IPPOP-1 toward sensing of CHPS and nitrofen in the presence of other pesticides.

Following the similar binary sensing experiment on antibiotics, in the case of pesticides, we found that IPPOP-1 exhibited selective quenching responses to both CHPS and nitrofen in the presence of other pesticides (Appendix Figures 3.28 and 3.29). This observation suggested that IPPOP-1 can be used as a potential sensing platform for the selective detection of specific pesticides along with targeted antibiotics in a water medium. This result further inspired us to investigate in detail the sensing by IPPOP-1 of the pesticides CHPS and nitrofen. For this, we performed a thorough titration experiment by incremental addition of 20 μL of 1 mmol aqueous solutions of the selected pesticides into a suspension of IPPOP-1. As anticipated, the emission spectra of IPPOP-1 were found to decrease gradually upon cumulative addition of both CHPS and nitrofen, individually (Figure 3.4a, d). From the fluorescence quenching profiles of IPPOP-1 for both CHPS and nitrofen, the quenching constant value K_{sv} was

calculated (Figure 3.4b, e). The K_{sv} values for CHPS and nitrofen were found to be 1.38×10^4 and $2.75 \times 10^4 \text{ M}^{-1}$, respectively. In addition to this, the respective LOD values for CHPS and nitrofen were calculated by plotting the decrease in the fluorescence intensity of IP_{POP}-1 against the concentration of the added analytes (Figure 3.4c, f). Significant LOD values of 0.470 and 0.471 mM were found for CHPS and nitrofen, respectively.

3.5 Mechanism Studies

Further, with the intention of in-depth understanding of the quenching responses of IP_{POP}-1 to the antibiotics NFZ and NFT and the pesticides CHPS and nitrofen, we explored the underlying mechanism with the help of the following experimental and theoretical investigations: In accordance with the literature, the quenching of the luminescent intensity of this type of material mainly takes place either due to structural deformation or due to the weak coordinative interaction (energy transfer and electron transfer) between the probe and the incoming analytes.^[50-52] Therefore, to investigate the mechanism we performed following experiments. First, no structural as well as morphological changes were observed after the sensing experiment as revealed from the FT-IR and FESEM images of the post-sensing experiment (Appendix Figures 3.30-3.32). This data indicated that the quenching of IP_{POP}-1 did not occur due to structural or morphological deformation or monomer dissociation. At this point, it can be said that the quenching of IP_{POP}-1 against selected antibiotics and pesticides is due to the suitable interactions (either energy transfer or electron transfer or both) between the probe and the analytes. Thereafter, to explore the nature of such a quenching process, the lifetime decay along with the FRET and PET processes were elucidated. A time-resolved fluorescence experiment was carried out in order to investigate the collision encounter mechanism between the excited state of IP_{POP}-1 and the antibiotics (NFZ and NFT) and pesticides (CHPS and nitrofen). The luminescence lifetime decay profiles indicated no significant change in the average lifetime between the pristine polymer and the IP_{POP}-1 treated with the antibiotic NFZ and the pesticides CHPS and nitrofen, which exhibited the presence of a static quenching mechanism behind such a response (Figure 3.5a, b).^[53, 54] This result further indicated the formation of a nonfluorescent ground-state complex between IP_{POP}-1 and those analytes.^[55] However, in the case of NFT, at low concentrations, only static quenching was observed when it was treated with IP_{POP}-1, which validated the presence of strong hydrogen-bonding interactions (Figure 3.5a). Nevertheless, at high concentrations, a significant varying degree of attenuation was observed when NFT was added with IP_{POP}-1 (Figure 3.5a and Appendix Figure 3.33). This result supports the existence of dynamic quenching, owing to the collisional interaction between NFT and IP_{POP}-1.^[56, 57] All of these

results of lifetime decay were well corroborated by the SV plots of the respective analytes with IP_{POP-1}.

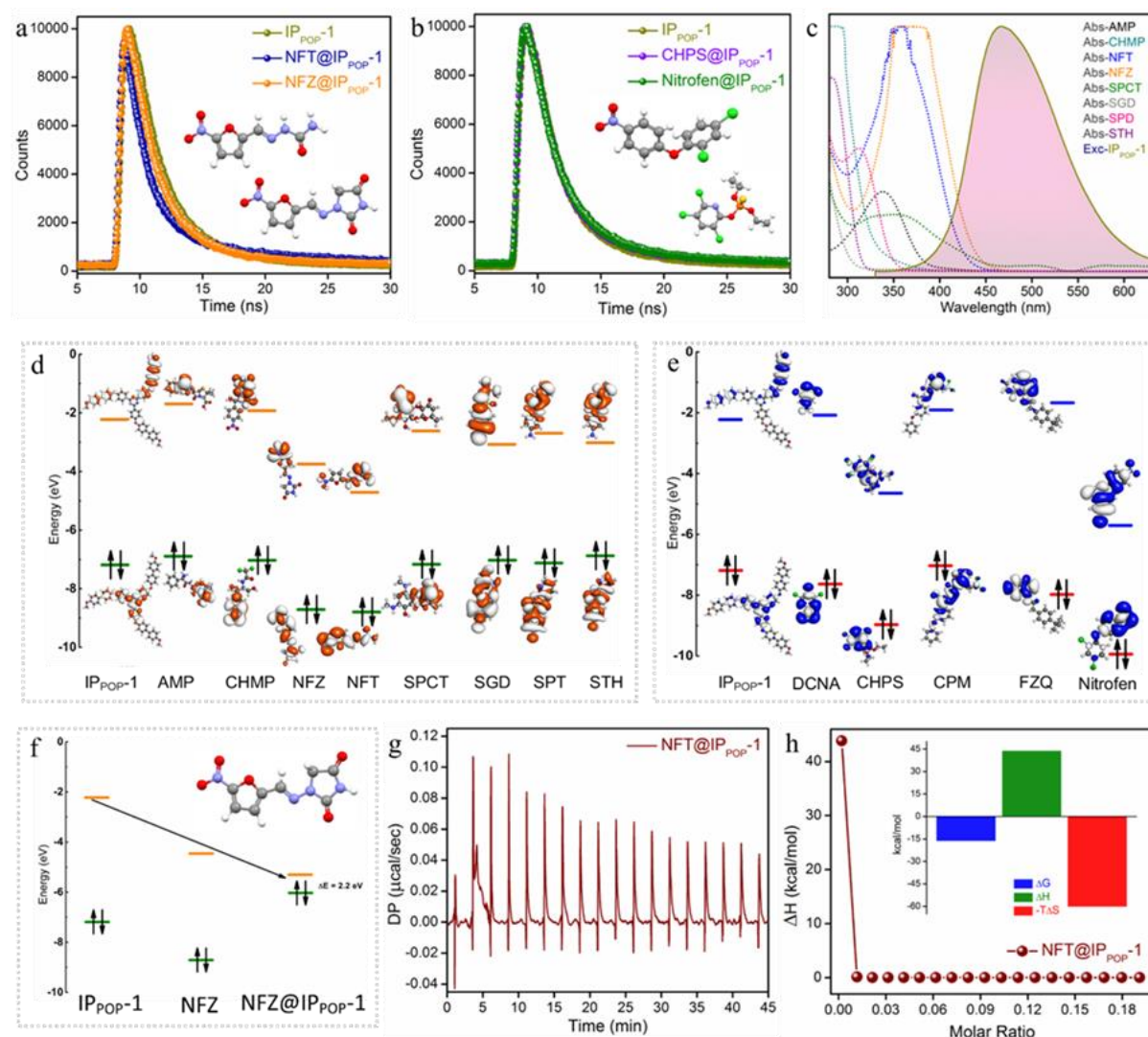


Figure 3.5 Lifetime decay profiles of IP_{POP-1} before and after treatment of high concentration of (a) NFZ and NFT antibiotic solution, and (b) CHPS and nitrofen pesticides solution. (c) Spectral overlap between UV-vis spectra of different antibiotics and fluorescence emission spectra of IP_{POP-1}. (d) HOMO-LUMO energy levels of unit of IP_{POP-1} and different antibiotics. (e) HOMO-LUMO energy levels of unit of IP_{POP-1} and different pesticides. (f) PET process during quenching of fluorescence intensity of IP_{POP-1} with NFZ. (g) ITC thermogram and (h) ITC heat exchange profile of interaction between aqueous solution of NFT and suspension of IP_{POP-1}. (Inset: thermodynamic parameters for the interaction).

Furthermore, the SV plots for both antibiotics (NFZ and NFT) and pesticides (CHPS and nitrofen) also suggest the presence of energy transfer phenomena between these analytes and IP_{POP-1}. Therefore, to validate the FRET process, the emission spectra of IP_{POP-1} and the UV-vis absorption spectra of all of the analytes (antibiotics and pesticides) were recorded, individually. Thereafter, when we plotted the emission spectra of IP_{POP-1} against the absorption spectra of all antibiotics and pesticides, in the case of antibiotics, a significant overlap between the emission spectra of IP_{POP-1} and absorption spectra of NFT and NFZ was observed (Figure 3.5c). Meanwhile, no such overlap was observed in the case of other antibiotics. This result clearly indicated the energy transfer between NFZ or NFT and IP_{POP-1}, which further caused the selective quenching response in the fluorescence intensity of IP_{POP-1}.^[58] However, in the case of pesticides, a similar type of spectral overlap was observed between the UV-vis absorption spectra of the CHPS and nitrofen pesticides and emission spectra of IP_{POP-1} (Appendix Figure 3.34). This whole observation suggests that in the case of both antibiotics and pesticides, the FRET process is one of the possible rationales behind the fluorescence quenching of IP_{POP-1}.

Thereafter, to get a more in-depth insight into the sensing mechanism, apart from the energy transfer, whether the fluorescence quenching of IP_{POP-1} by the selected antibiotics and pesticides was caused by the PET process or not, we carried out DFT calculations. In the PET process, after absorbing light, the electrons of the probe get excited and transfer to the LUMO of the quenching agent. Then, with the help of various nonradiative pathways, these excited electrons move down to the ground state of the probe. This further generates turn-off fluorescence response.^[51, 59] Further, to get mechanistic insight into the PET process, the HOMO and LUMO energy gaps for the units of IP_{POP-1} and various antibiotics as well as pesticides were calculated using DFT at a theoretical level of B3LYP - function DMol3 (Figure 3.5d) (see the experimental for details). It is worth mentioning that if the LUMO of the quenching agent lies in between the valance band and conduction band of the fluorophore or the probe, this enables the electron transfer from the HOMO of the probe to the LUMO of analytes (Figure 3.5f, Appendix Figures 3.35 and 3.36). Herein, in the case of antibiotics, the simulation calculation indicated that among all of the selected antibiotics, the LUMOs of NFT and NFZ were found to lie closest to the HOMO of the unit of IP_{POP-1} (Figure 3.5d). This result indicated the presence of strong intermolecular hydrogen bonding interactions between NFT or NFZ and IP_{POP-1}, which stabilized the LUMO energy and confined it on NFT and NFZ (Appendix Figure 3.37). This further facilitates the electron transfer process from the LUMO of IP_{POP-1} to the LUMO of NFT or NFZ and resulted in a quenching response (Appendix Figure 3.38).^[60, 61] A similar observation was found in the case of the pesticides, as among all of them, the LUMOs of CHPS and nitrofen were found to be the closest to the HOMO of IP_{POP-1} (Figure 3.5e and Appendix Figure 3.39), which enabled the electron transfer process selectively between CHPS or nitrofen and IP_{POP-1}, further causing fluorescence quenching (Appendix Figures 3.40 and 3.41). Therefore, along with energy transfer, the PET process was found to be one of the prominent

mechanisms behind the selective emission quenching of IP_{POP-1} by NFT, NFZ, CHPS, and nitrofen in water.

Apart from the above discussion, it is worth mentioning that IP_{POP-1} was also found to adsorb NFT from the water medium (Appendix Figure 3.42). Now, to identify whether this adsorption process is thermodynamically favourable or not, we performed an ITC experiment. ITC offers direct quantification of the Gibbs free energy (G), enthalpy change (H), change in entropy (S), and information about the binding energy constant (K_a) of a chemical process.^[62, 63] In this study, we carried out ITC by treating a 0.1 mmol NFT solution with an IP_{POP-1} aqueous suspension (see the experimental section for details). The resulting thermogram indicated a weak but prominent negative peak, which suggests the presence of a host-guest interaction with a favourable exothermic binding mode (Figure 3.5g). In addition, the interaction of NFT with the surface of IP_{POP-1} was found to be both kinetically as well as thermodynamically favoured, owing to the positive binding constant and negative Gibbs free energy change (Figure 3.5h and Appendix Figure 3.43).^[64] This result suggests that the adsorption of NFT with IP_{POP-1} is a thermodynamically driven process.

From the viewpoint of practical application, the regeneration ability is reasonably significant for a real-time chemosensor. Hence, an experiment on the recyclability of the sensing of IP_{POP-1} was carried out up to four cycles. The first cycle of the reuse of the polymer was done after recording the fluorescence intensities of an aqueous suspension of 1 mg of IP_{POP-1} followed by the addition of the analytes. After the first cycle, IP_{POP-1} was recovered by washing with water and acetone followed by centrifugation. Then, it was dried in an oven and further used for the next cycles with the same protocol. All fluorescence intensity data were collected and plotted against the number of cycles and compared. From the plots, it was obvious that the patterns are similar up to four cycles, which evidenced the high level of the recyclability of IP_{POP-1} for the detection of NFZ and CHPS (Figure 3.6a, b). Furthermore, taking two considerations into account, one of which is the mandatory requirement of a potential sensory material for detection of harmful micropollutants in water and the other the high detection ability of IP_{POP-1}, we performed real-world sensing studies of antibiotics, by treating IP_{POP-1} with real hospital wastewater spiked with NFZ antibiotics.^[64-68] For this, a similar thorough sensing titration experiment was conducted. The fluorescence emission profile of IP_{POP-1} was found to decrease rapidly upon treatment with the aqueous NFZ solution of a real hospital wastewater system (Figure 3.6c). However, we observed a slight raise in the K_{sv} value in the case of the simulated real water system compared to that of the synthetic antibiotic solution (Appendix Figure 3.44).

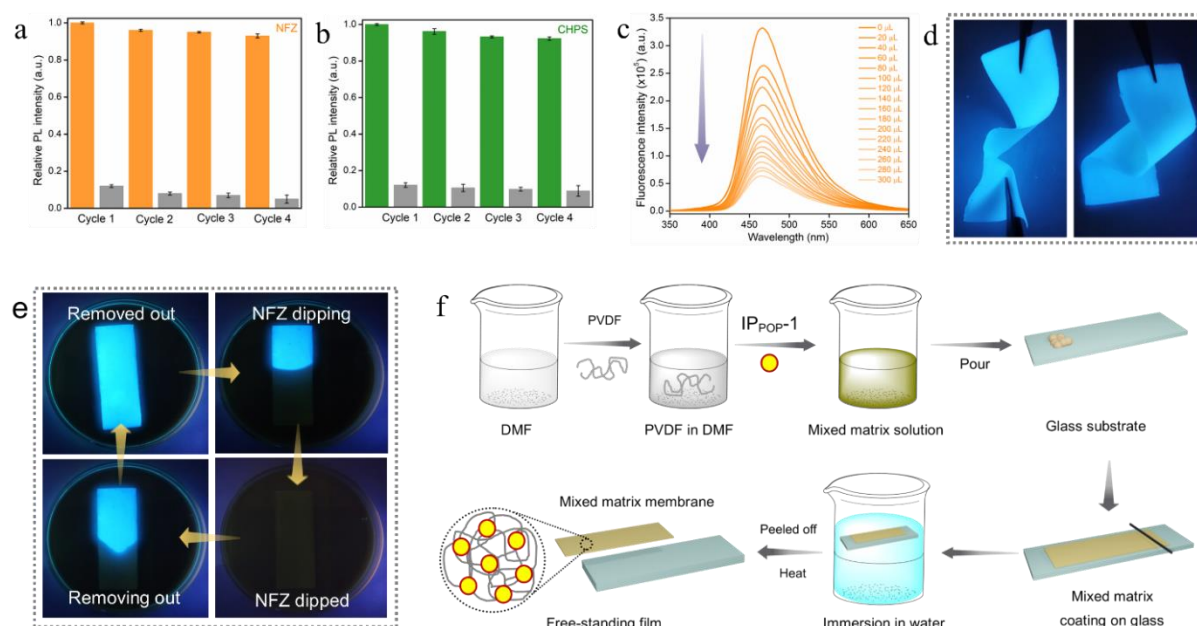


Figure 3.6 Other sensing performance: (a, b) Recyclability test for NFZ antibiotic and CHPS pesticide detection performance by IP_{POP}-1, respectively (orange and green colour indicates the intensities of pristine or regenerated POP, and the grey colour indicates intensity of the POP after analytes treatment). (c) Emission profile of IP_{POP}-1 upon treatment of NFZ in real-water (hospital) system. (d) Digital images of self-standing IP_{POP}-1-based MMMs under UV light. (e) Application of IP_{POP}-1@PVDF films for the detection of NFZ under UV light (f) Schematic illustration of the fabrication of IP_{POP}-1 @PVDF film, PVDF stands for polyvinylidene fluoride.

This alteration in the quenching efficiency of IP_{POP}-1 might be due to the coexistence of other excess anions (such as hydroxy ions) in the real hospital water, which interact with the active sites of the probe and further affect the interaction between the surface of the polymer and the antibiotics. A similar result was observed in the case of NFT as the fluorescence emission of IP_{POP}-1 was found to be quenched (Appendix Figures 3.45 and 3.46). This data indicated the potential use of IP_{POP}-1 for the efficient fluorescence detection of antibiotics in a real water system.

Encouraged by the above results, along with the consideration of practical application, as a proof of concept, we further moved ahead to explore MMM-based micropollutant sensing by IP_{POP}-1. First, for this qualitative detection experiment, IP_{POP}-1-based films were fabricated with the help of the PVDF polymer (see the experimental section in the Supporting Information for details) (Figure 3.6f).^[42] The IP_{POP}-1@PVDF MMMs exhibited a strongly luminescent as well as self-standing nature under UV light as shown in Figure 3.6d and Appendix Figure 3.47. Now, in order to test the response of the films

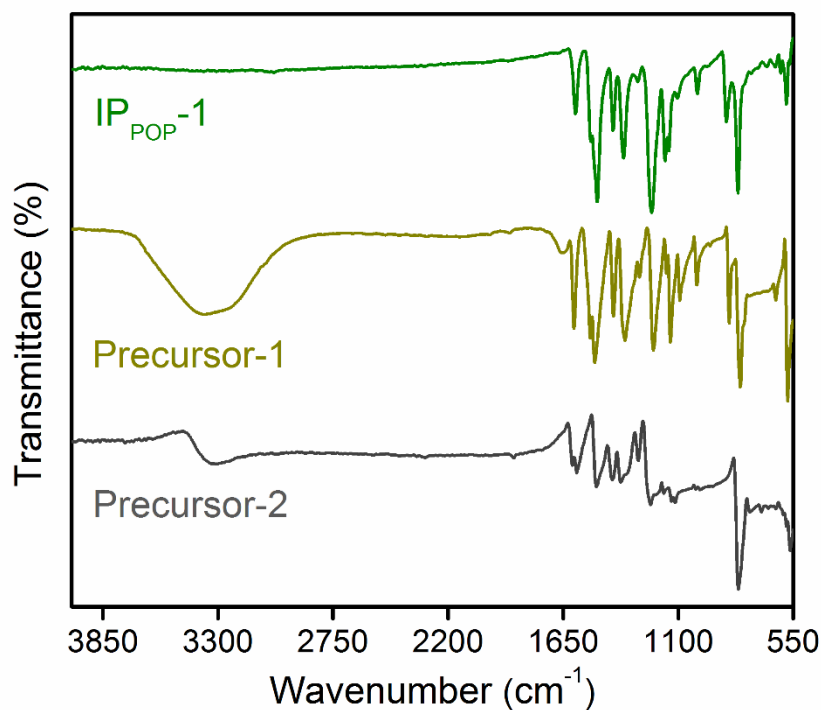
toward antibiotic sensing, the prepared MMMs were treated with an aqueous solution of NFZ. An interesting observation was found that the strongly luminescent nature of the IP_{POP}-1@PVDF films got rapidly quenched upon incorporation into the aqueous solution of NFZ (Figure 3.6e). Meanwhile, the emission of the MMM was regenerated upon removal of the films from the solution (Figure 3.6e). This observation indicated the potential application of IP_{POP}-1-based MMMs toward practical aqueous-phase detection of specific micro-contaminants in a reversible manner.

3.6 Conclusions

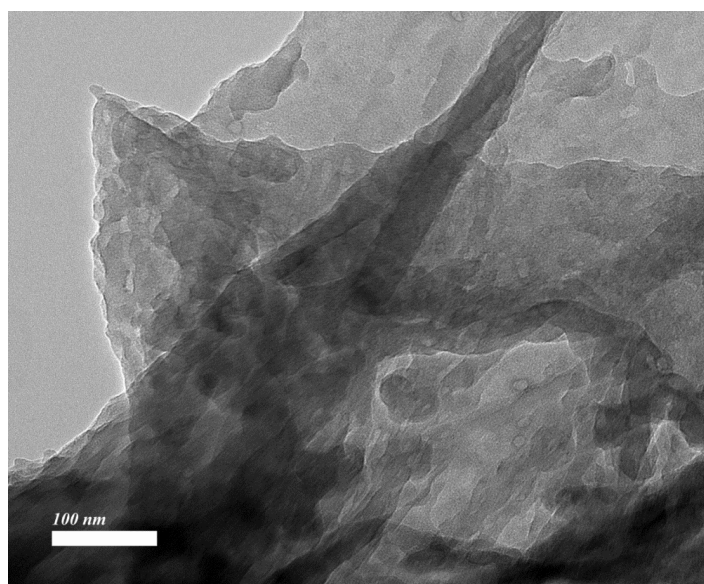
In conclusion, guided by the suitable interactions between electron-rich and electron-deficient moieties, in this work, systematic sensing studies of electronically unsaturated toxic organic substances, such as selected antibiotics and pesticides, were carried out by developing a low-cost, highly luminescent, and chemically stable electron-rich ether linkage-based POP (IP_{POP}-1). The POP was synthesized in a simple single-step reaction and was found to be highly luminescent as well as hydrolytically and chemically stable in nature. Thorough sensing studies revealed that the polymer had a highly sensitive and selective detection ability toward the antibiotics NFT and NFZ and the pesticides nitrofen and CHPS, among others, with recommended K_{sv} values and LOD values. Detailed experimental and theoretical calculations were carried out in order to examine the underlying mechanism. This suggests that the contribution of both the PET and FRET processes between the hosts to guest system was responsible behind such quenching phenomena of IP_{POP}-1 by selected antibiotics and pesticides in water. Moreover, IP_{POP}-1 was found to exhibit a similar detection capability toward trace antibiotics in a simulated hospital real water system. Furthermore, to mimic real-time sensing application, IP_{POP}-1-based MMMs were prepared and applied as a proof of concept toward recognition of antibiotics in water. We believe that these findings on employing a chemically stable, highly luminescent electronically tunable porous polymer for recognition of target specific toxic organic substances pave the way for the advancement of new efficient stable probes for the fluorescence-based detection of other environmentally relevant toxic species.

Appendix Section

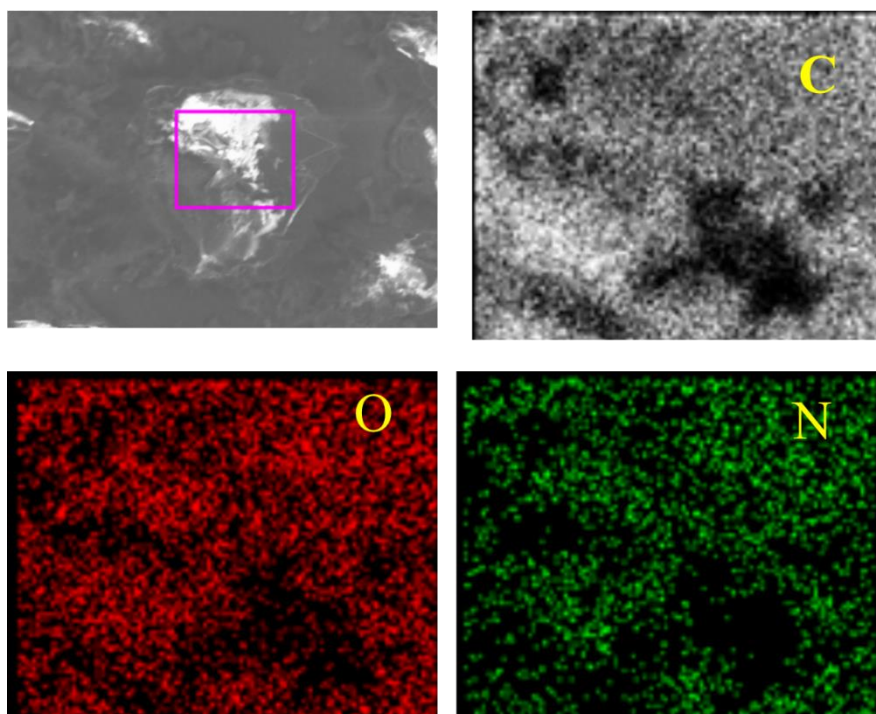
Appendix Section 1: Structural and Optical Characterizations of IP_{POP}-1



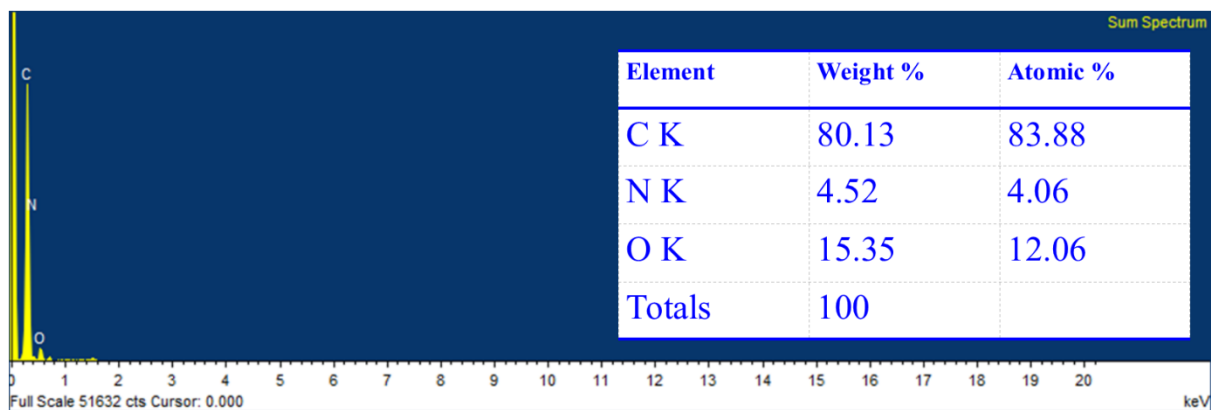
Appendix Figure 3.1: FT-IR spectra of IP_{POP}-1 with its precursor-1 and precursor-2.



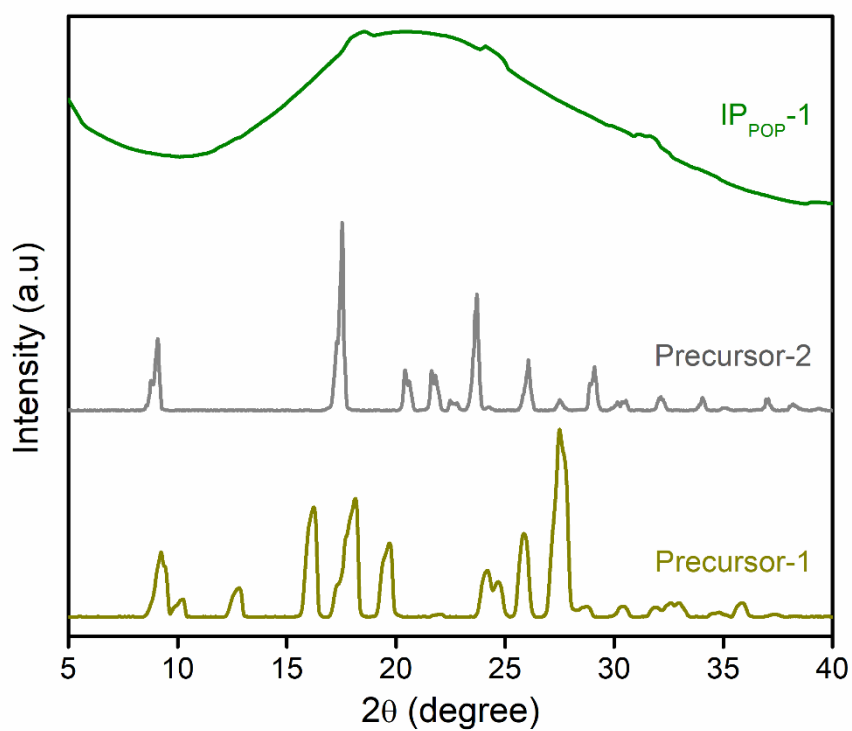
Appendix Figure 3.2: Transmission electron microscopy (TEM) image of IP_{POP}-1.



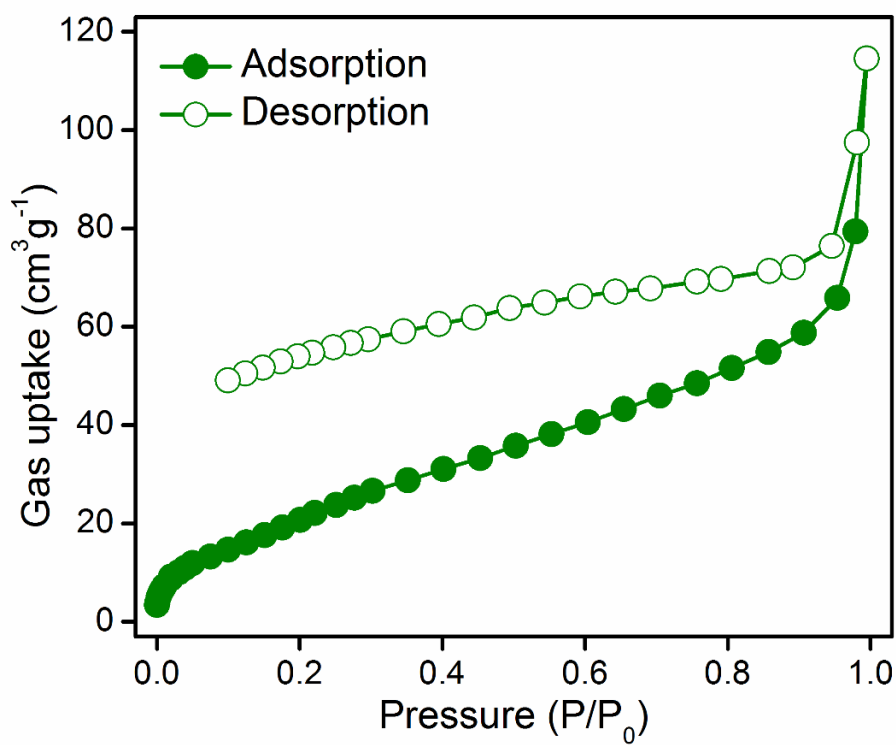
Appendix Figure 3.3: Elemental mapping analysis from FESEM experiment of IP_{POP}-1.



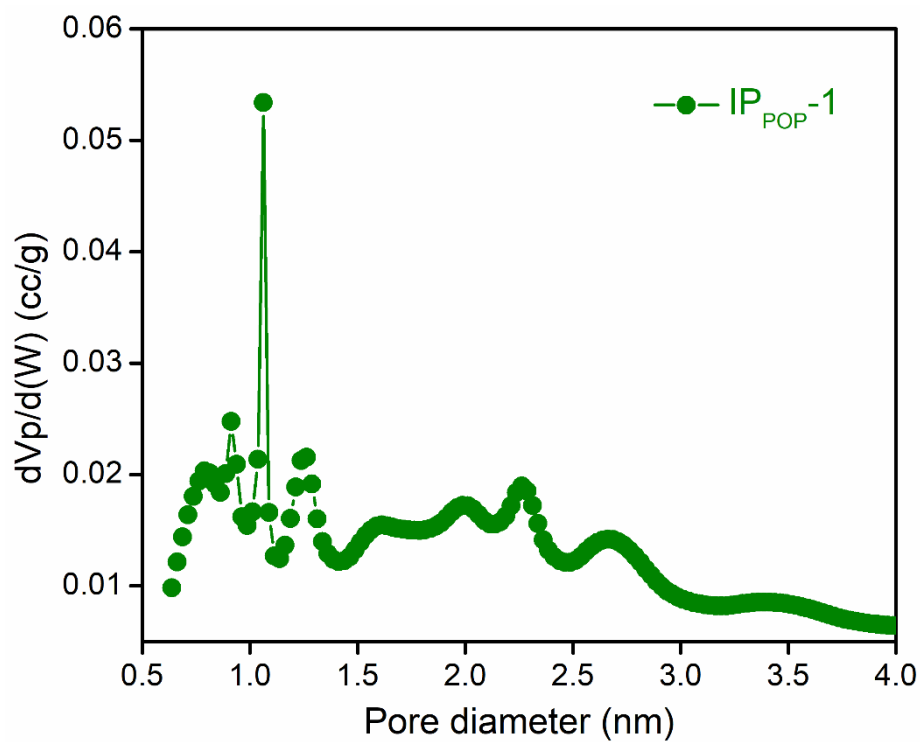
Appendix Figure 3.4: FESEM-EDS data of IP_{POP}-1.



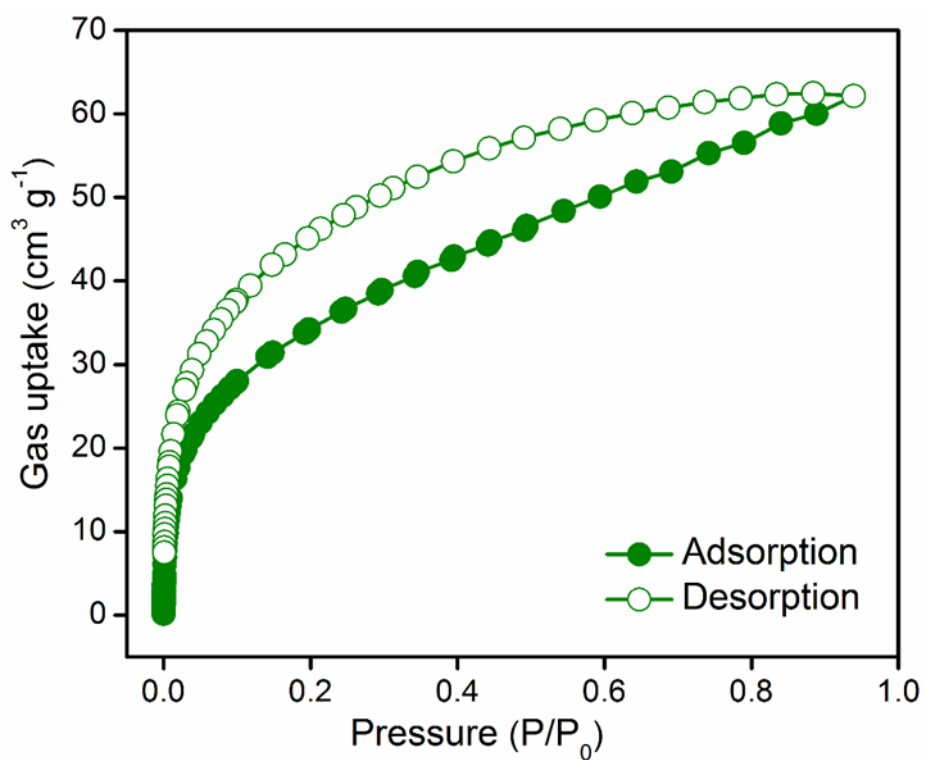
Appendix Figure 3.5: PXRD profile of IP_{POP-1} along with its precursors.



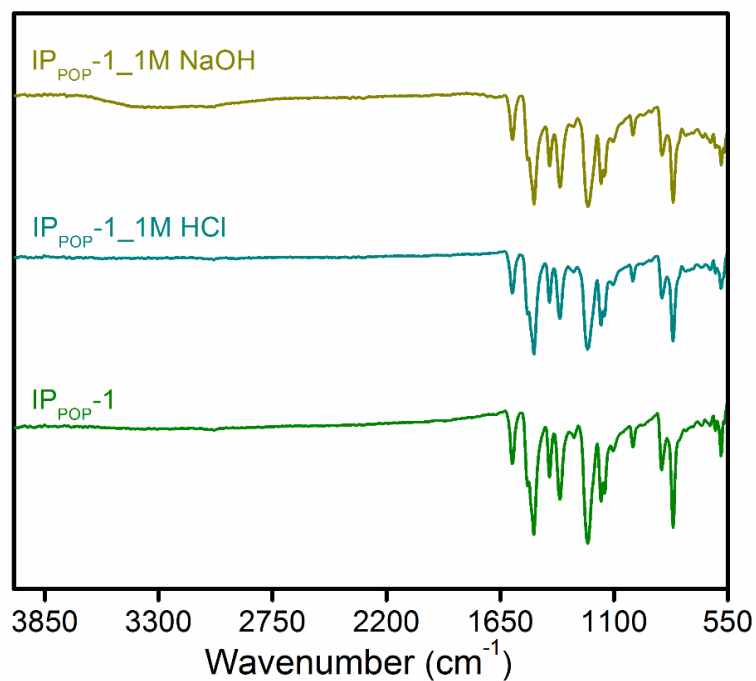
Appendix Figure 3.6: Nitrogen gas adsorption-desorption of IP_{POP-1} at 77 K.



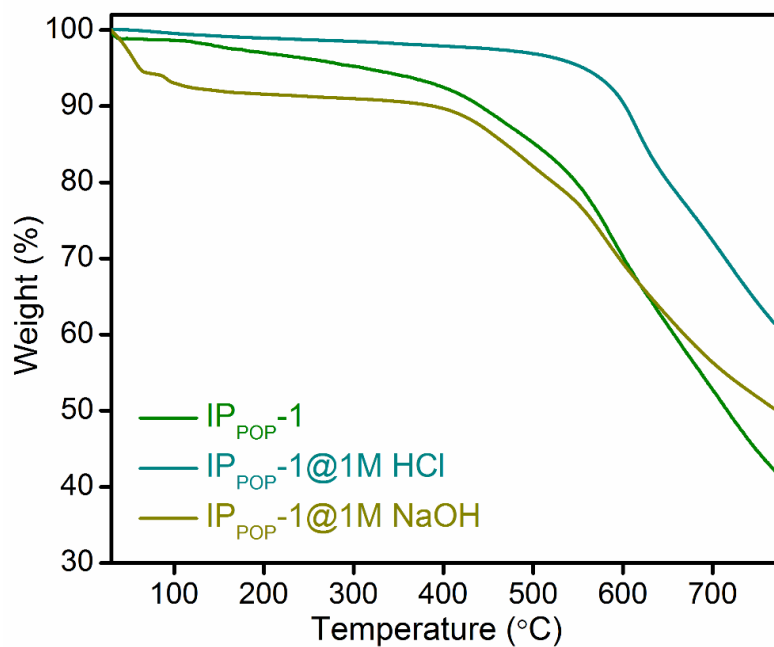
Appendix Figure 3.7: Pore size distribution profile of IP_{POP}-1.



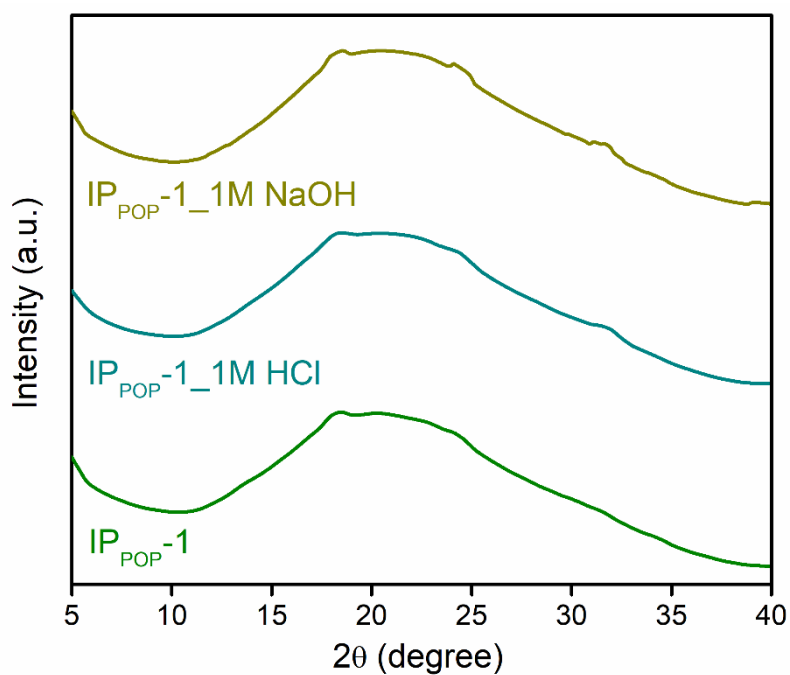
Appendix Figure 3.8: Carbon dioxide (CO₂) gas adsorption-desorption of IP_{POP}-1 at 195 K.

Appendix Section 2: Chemical Stability Test of IP_{POP}-1.

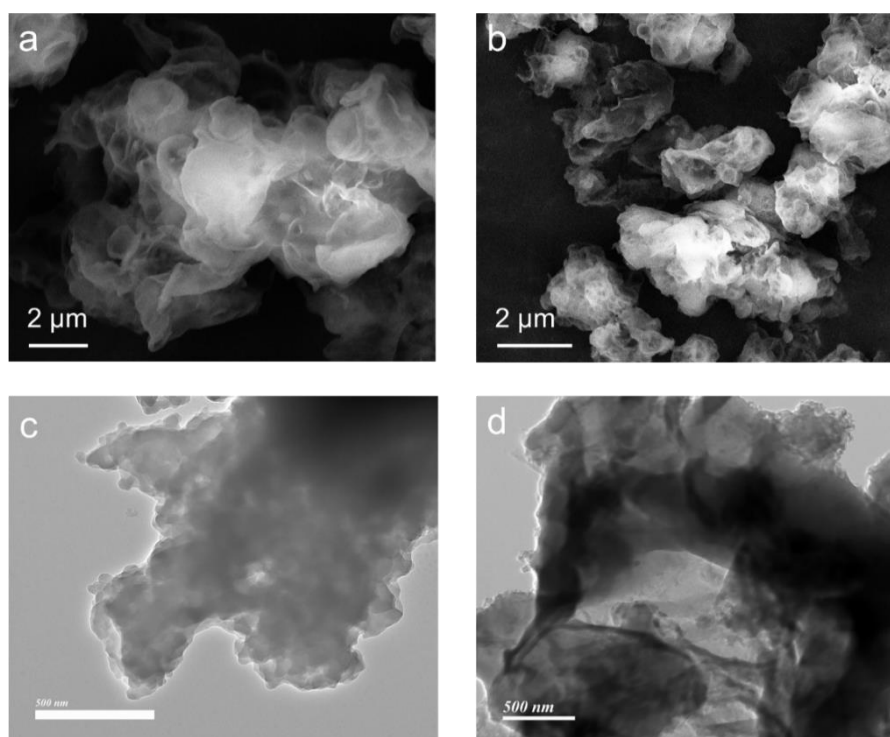
Appendix Figure 3.9: FTIR spectra of IP_{POP}-1 at different chemical environment: 1 M HCl and 1M NaOH.



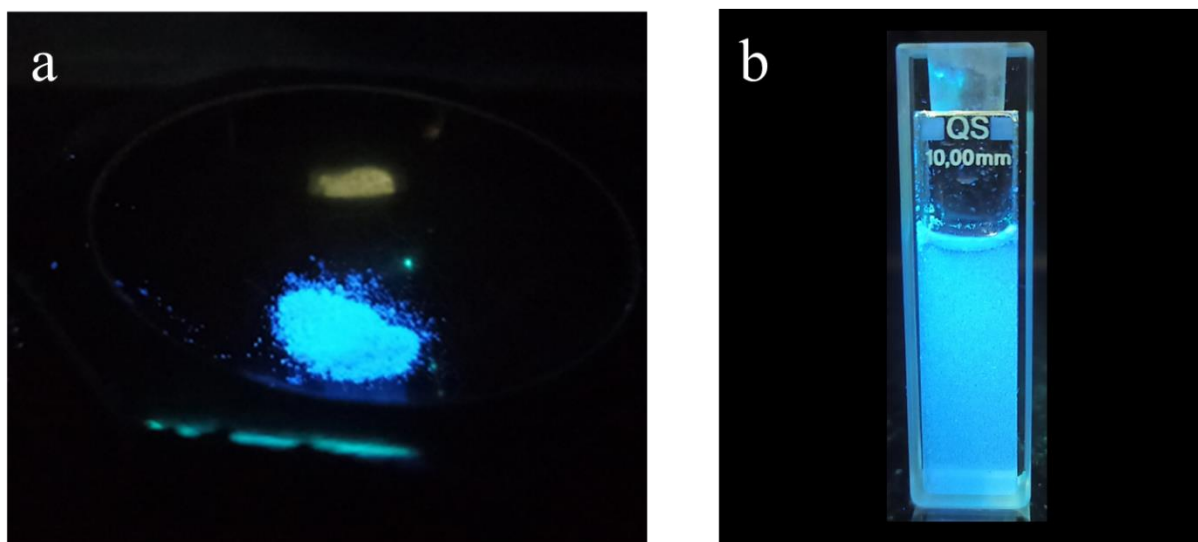
Appendix Figure 3.10: TGA analysis of IP_{POP}-1 at different chemical environment: 1 M HCl and 1M NaOH.



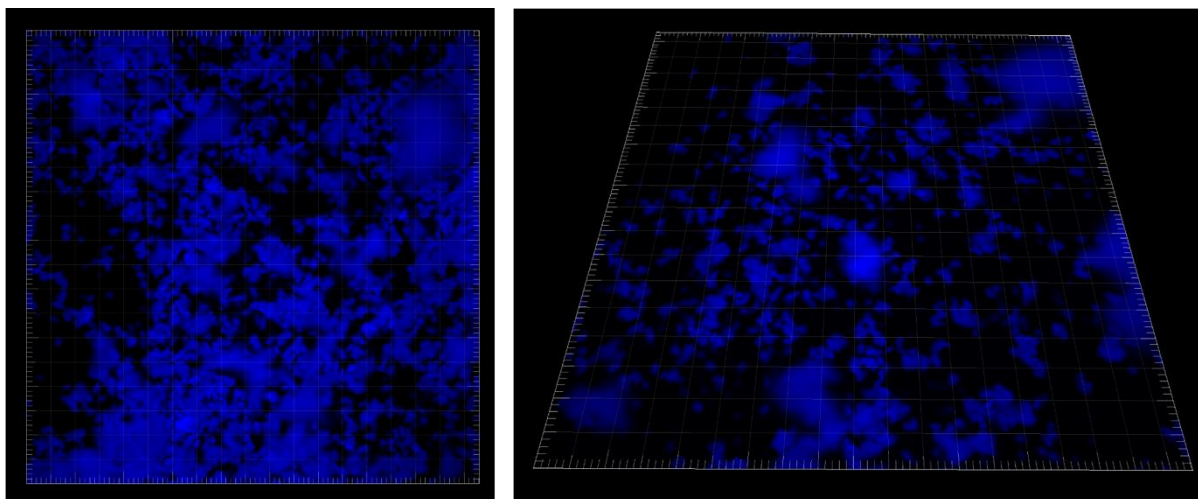
Appendix Figure 3.11: PXRD profile of IP_{POP}-1 at different chemical environment: 1 M HCl and 1M NaOH.



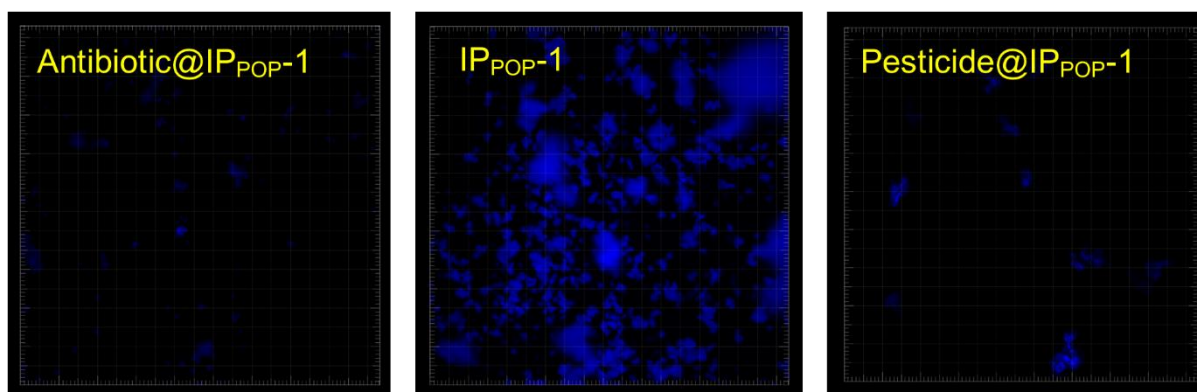
Appendix Figure 3.12: (a, b) FESEM and (c, d) TEM images of 1M HCl and 1M NaOH treated IP_{POP}-1, respectively.

Appendix Section 3: Optical Characterizations of IP_{POP-1}.

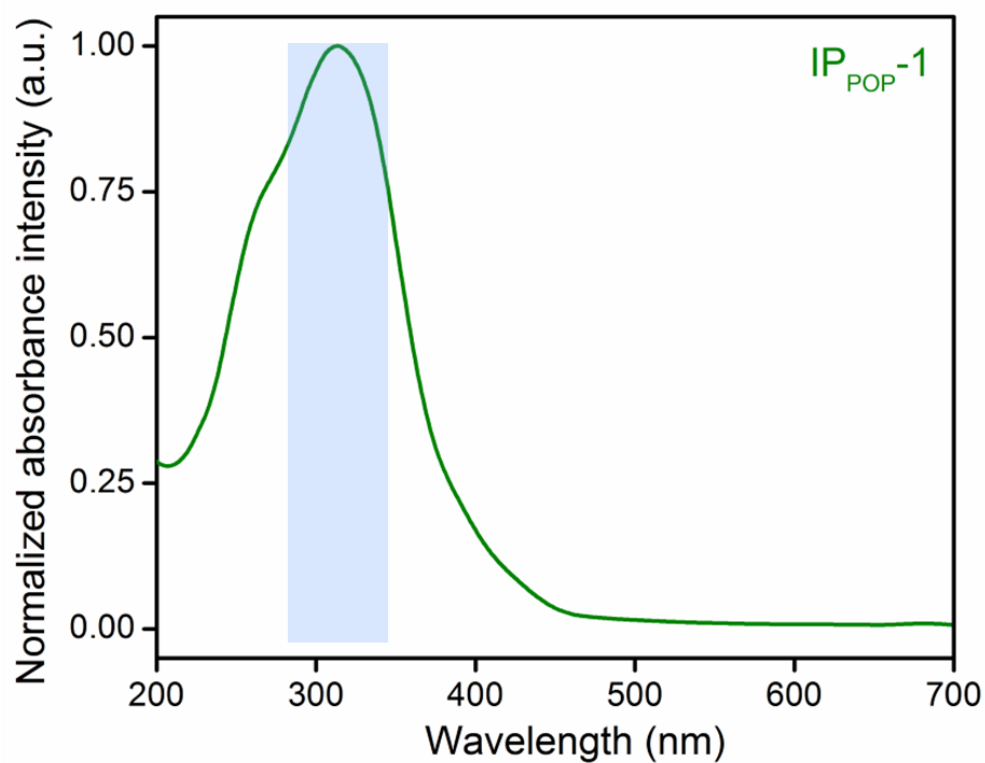
Appendix Figure 3.13: Digital image of (a) solid powder IP_{POP-1} and (b) dispersed IP_{POP-1} in water-acetonitrile solvent mixture, under UV lamp.



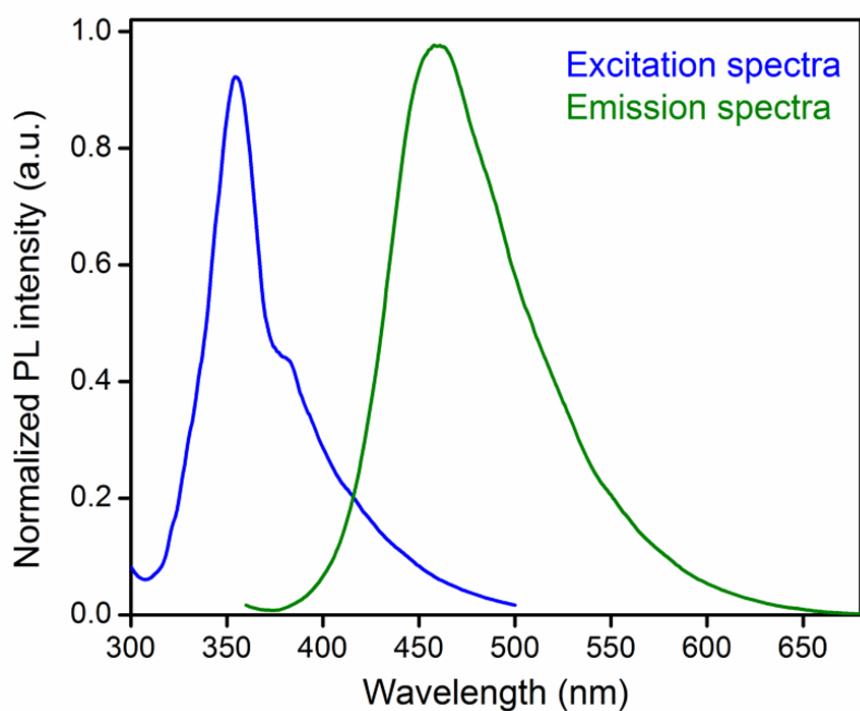
Appendix Figure 3.14: Fluorescence microscopy images of IP_{POP-1}.



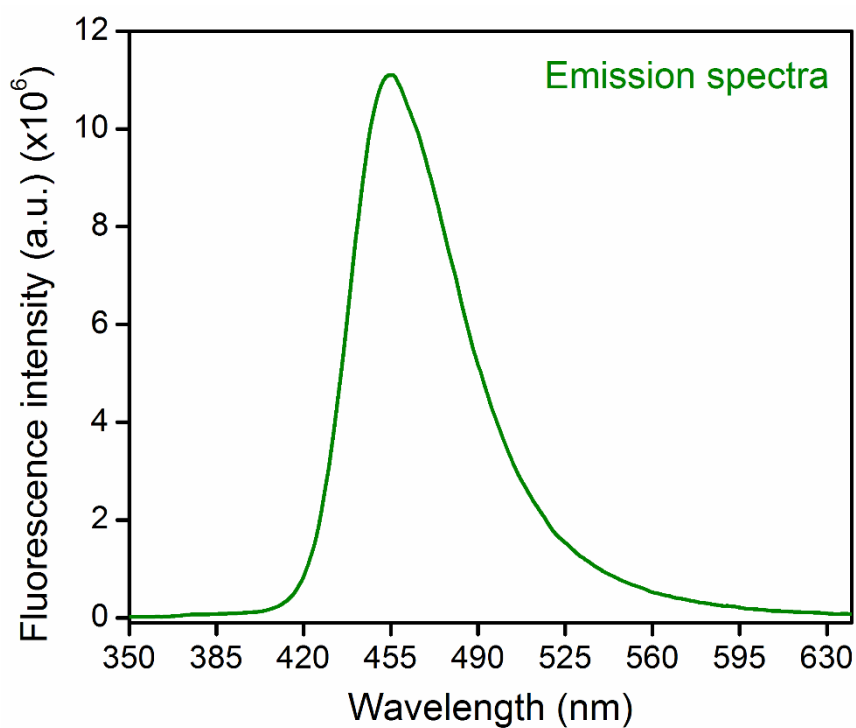
Appendix Figure 3.15: Fluorescence microscopy images of IP_{POP}-1 before and after sensing study.



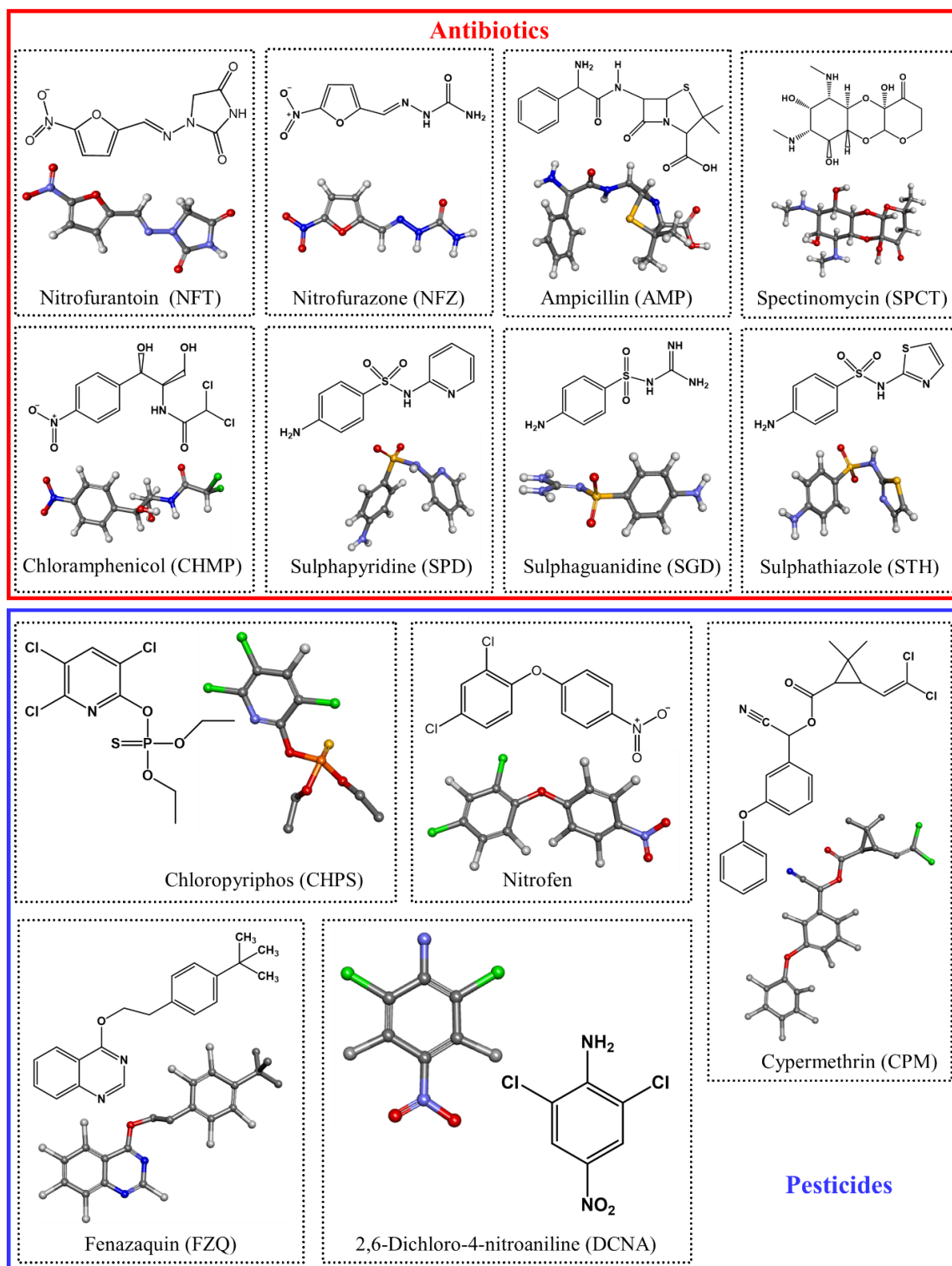
Appendix Figure 3.16: Diffuse reflectance UV-vis spectra of IP_{POP}-1.



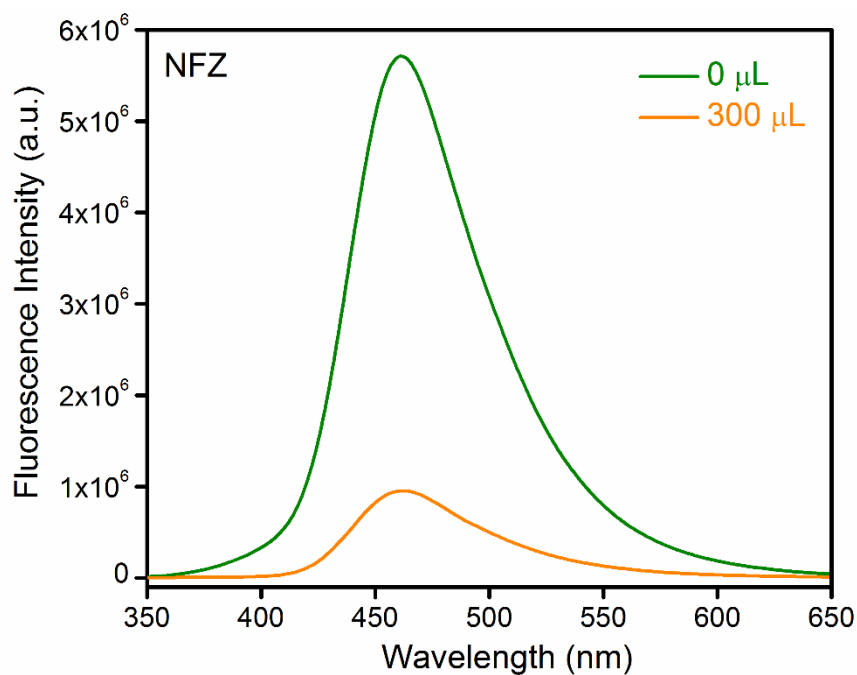
Appendix Figure 3.17: Solid-state photoluminescence excitation and emission spectra of IP_{POP}-1.



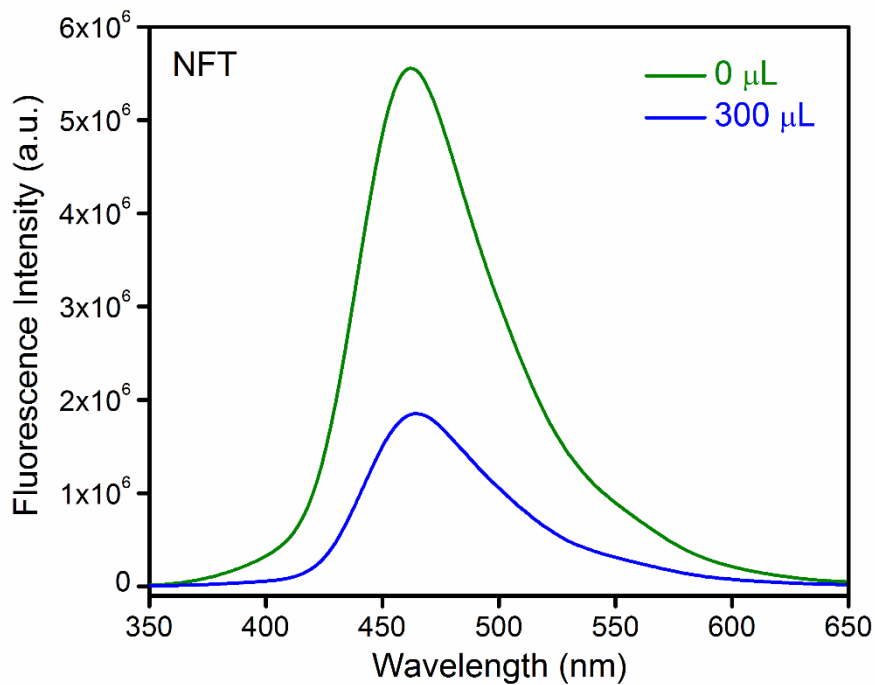
Appendix Figure 3.18: Photoluminescence emission spectra of IP_{POP}-1 dispersed in H₂O/ACN solvent mixture.



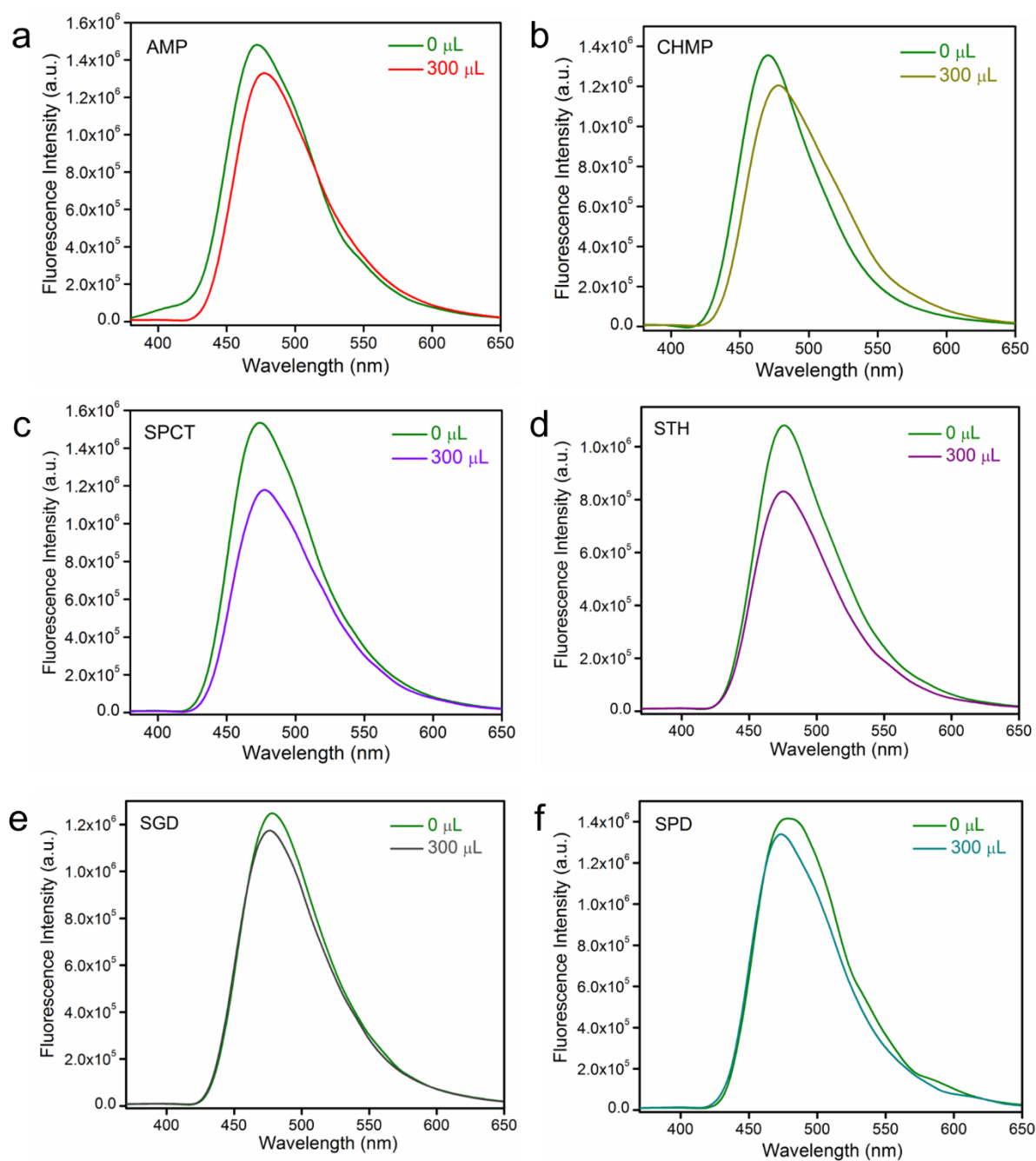
Appendix Figure 3.19: Chemical structure of various antibiotics and pesticides used in this sensing study. (Colour codes: Carbon-Gray, Nitrogen-Blue, Oxygen-Red, Chlorine-Green, Sulphur-Yellow, Phosphorus-Orange, Hydrogen-White).

Appendix Section 4: Sensing Studies of IP_{POP-1}

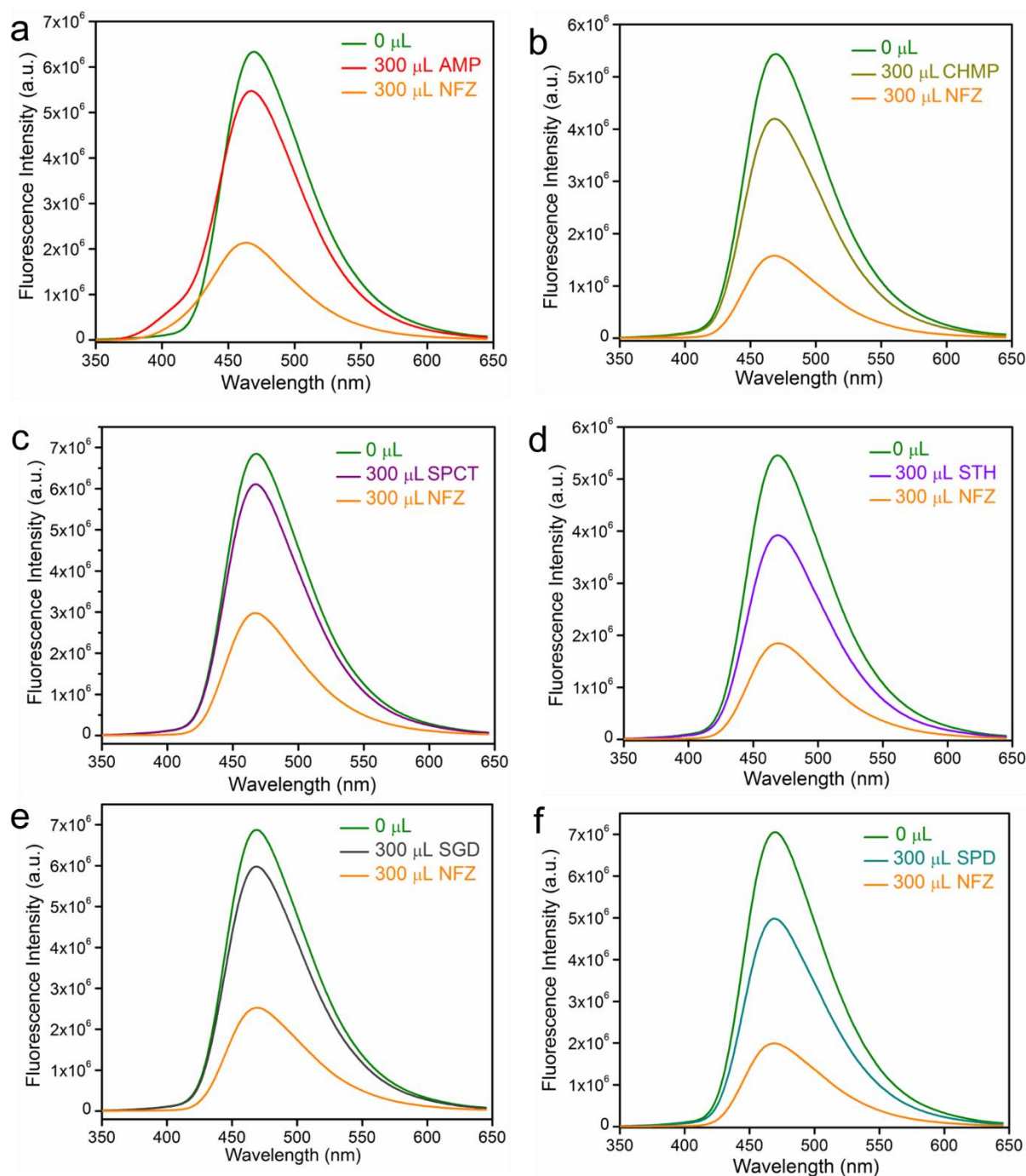
Appendix Figure 3.20: Fluorescence quenching response of IP_{POP-1} upon treatment of 300 μL of NFZ.



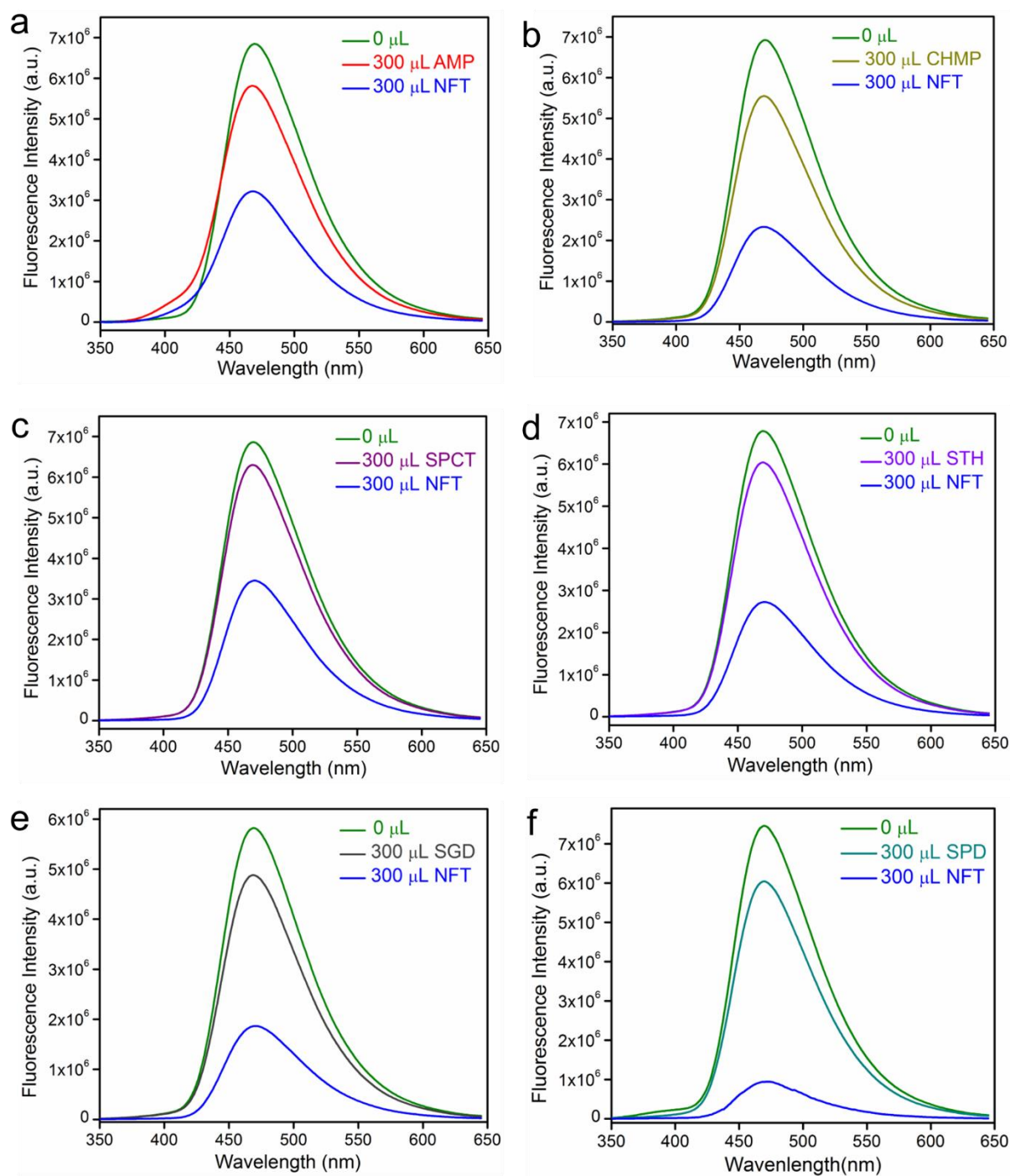
Appendix Figure 3.21: Fluorescence quenching response of IP_{POP-1} upon treatment of 300 μL of NFT



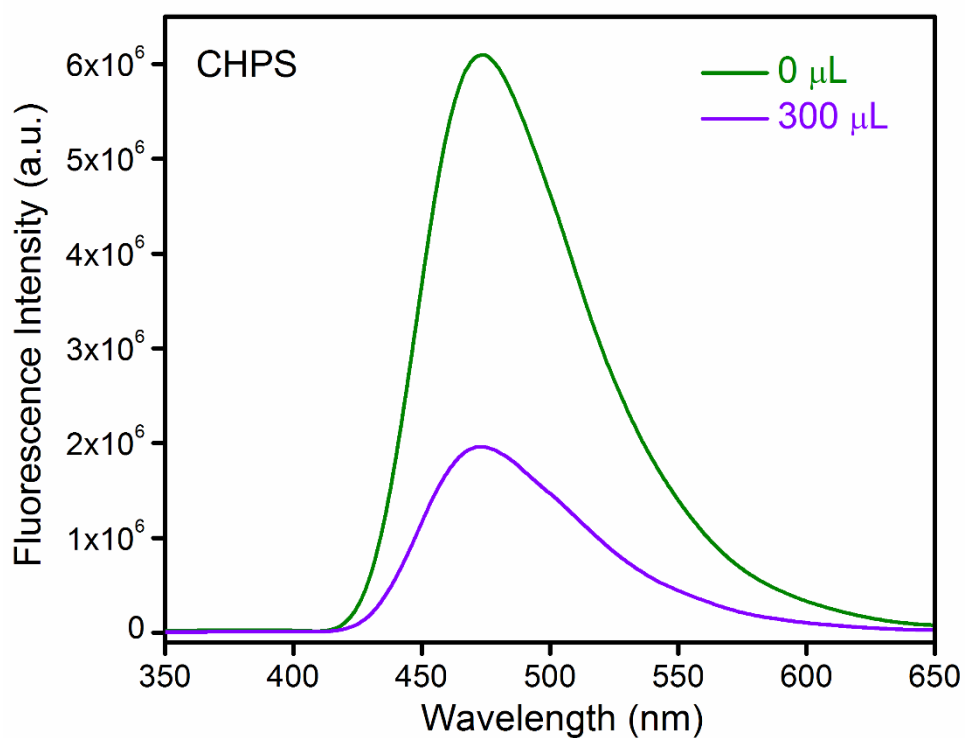
Appendix Figure 3.22: Fluorescence quenching response of IPPOP-1 upon treatment of 300 μL of (a) Ampiciline (AMP), (b) Chloramphenicol (CHMP), (c) Spectinomycin (SPCT), (d) Sulfathiazole (STH), (e) Sulphaguanidine (SGD), (f) Sulphapyridine (SPD).



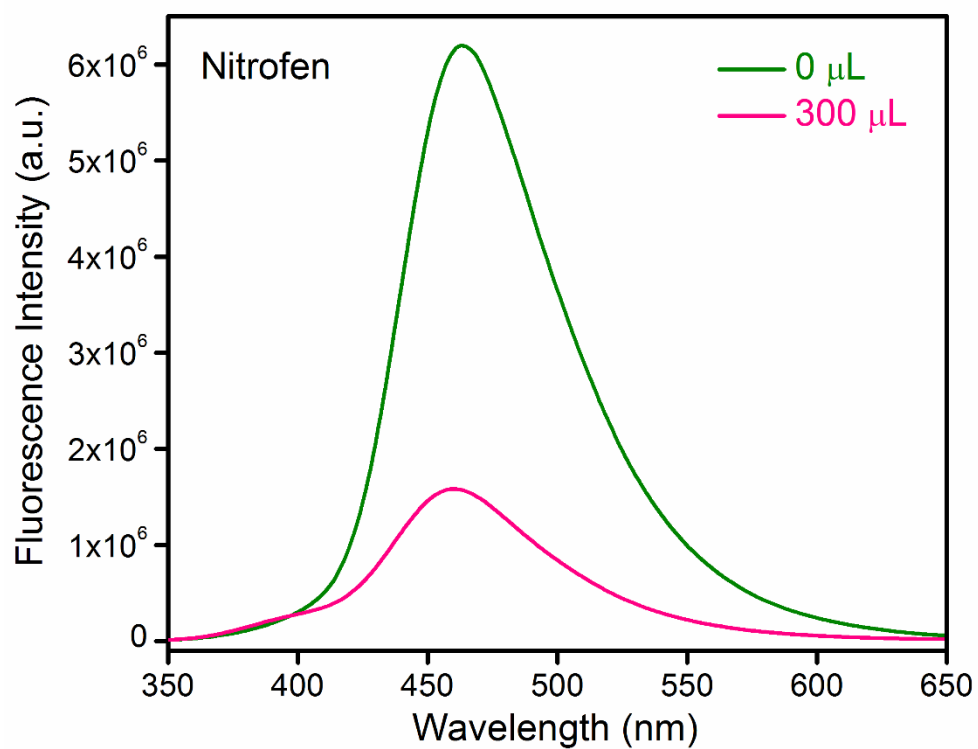
Appendix Figure 3.23: Fluorescence quenching response of IPPOP-1 upon treatment of 300 μL of (a) Ampiciline (AMP), (b) Chloramphenicol (CHMP), (c) Spectinomycin (SPCT), (d) Sulfathiazole (STH), (e) Sulphaguanidine (SGD), (f) Sulphapyridine (SPD), followed by the addition of 300 μL of NFZ in each.



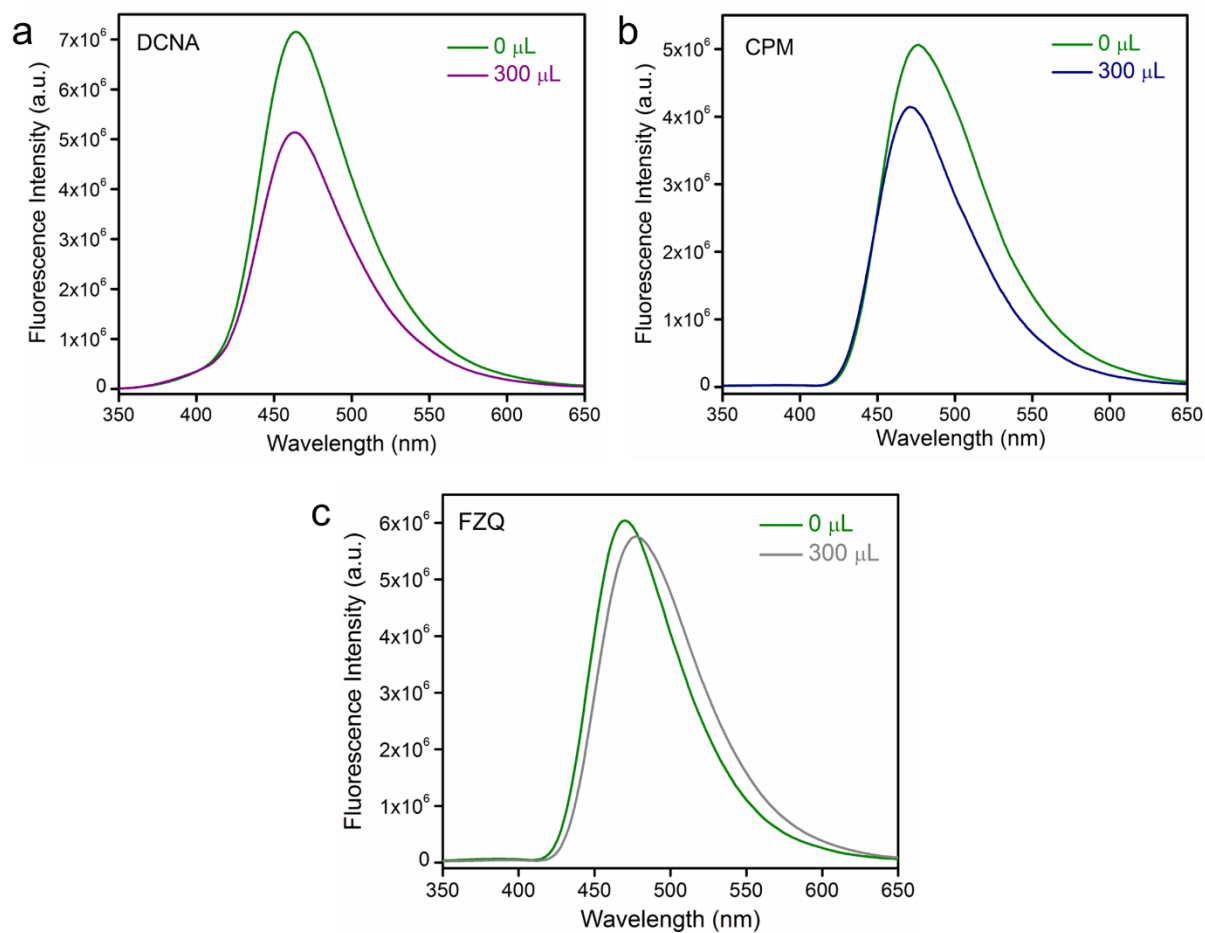
Appendix Figure 3.24: Fluorescence quenching response of IPPOP-1 upon treatment of 300 μL of (a) Ampiciline (AMP), (b) Chloramphenicol (CHMP), (c) Spectinomycin (SPCT), (d) Sulfathiazole (STH), (e) Sulphaguanidine (SGD), (f) Sulphapyridine (SPD), followed by the addition of 300 μL of NFT in each.



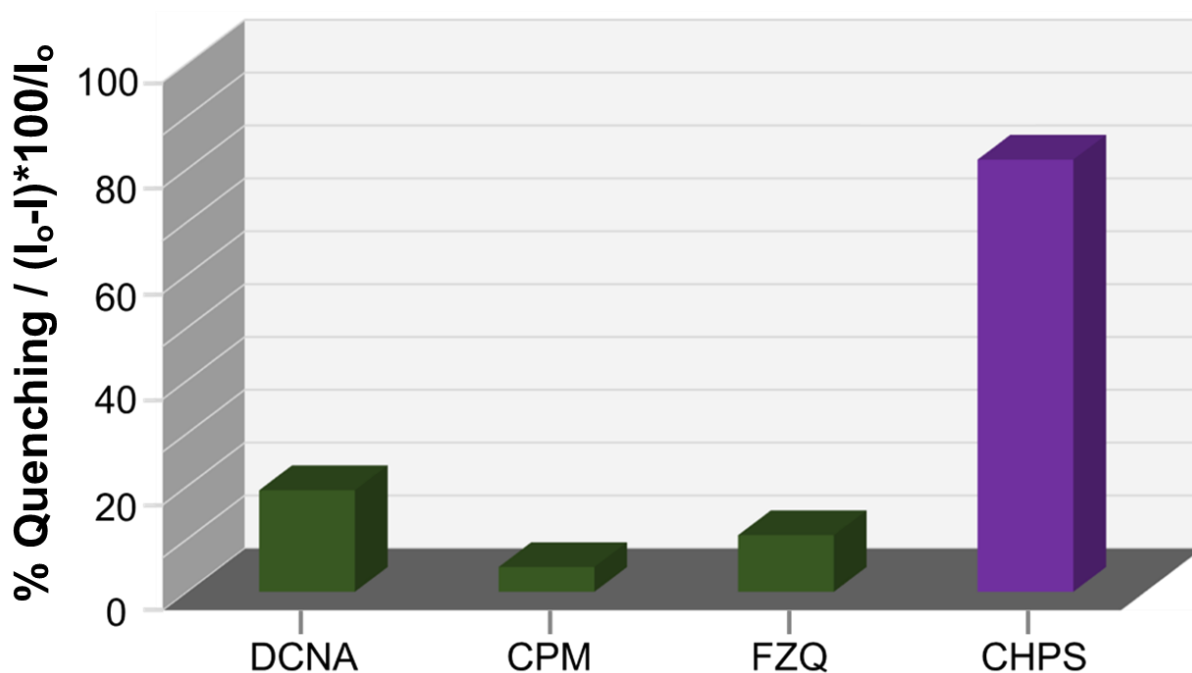
Appendix Figure 3.25: Fluorescence quenching response of IP_{POP}-1 upon treatment of 300 μL of CHPS.



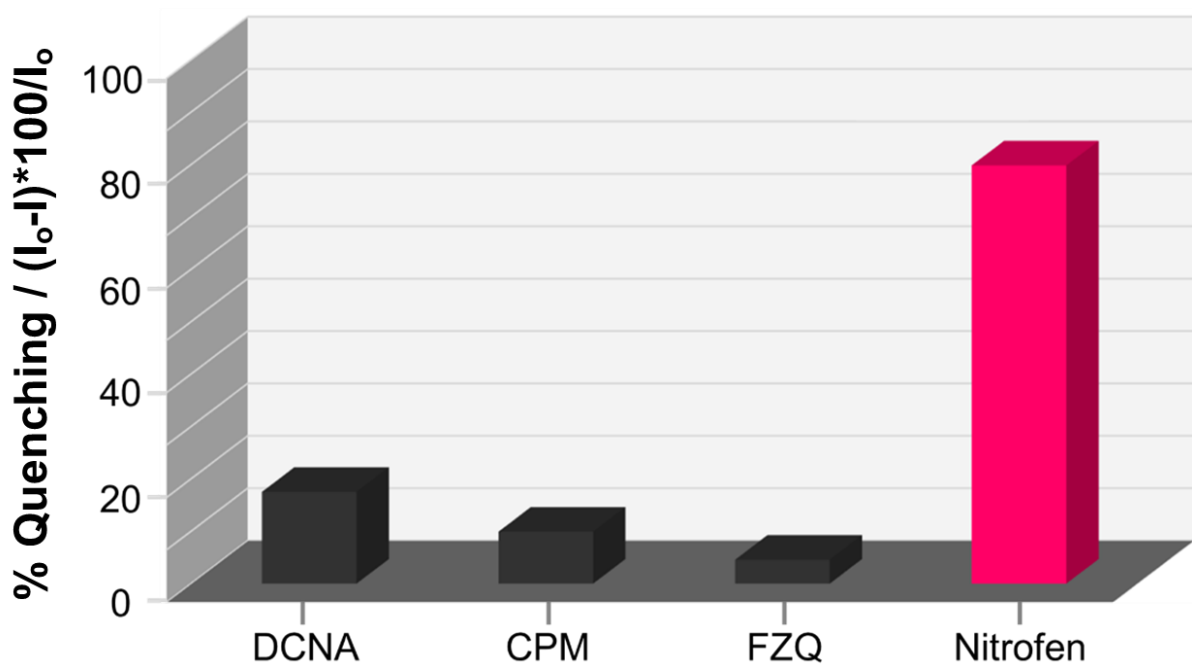
Appendix Figure 3.26 Fluorescence quenching response of IP_{POP}-1 upon treatment of 300 μL of nitrofen.



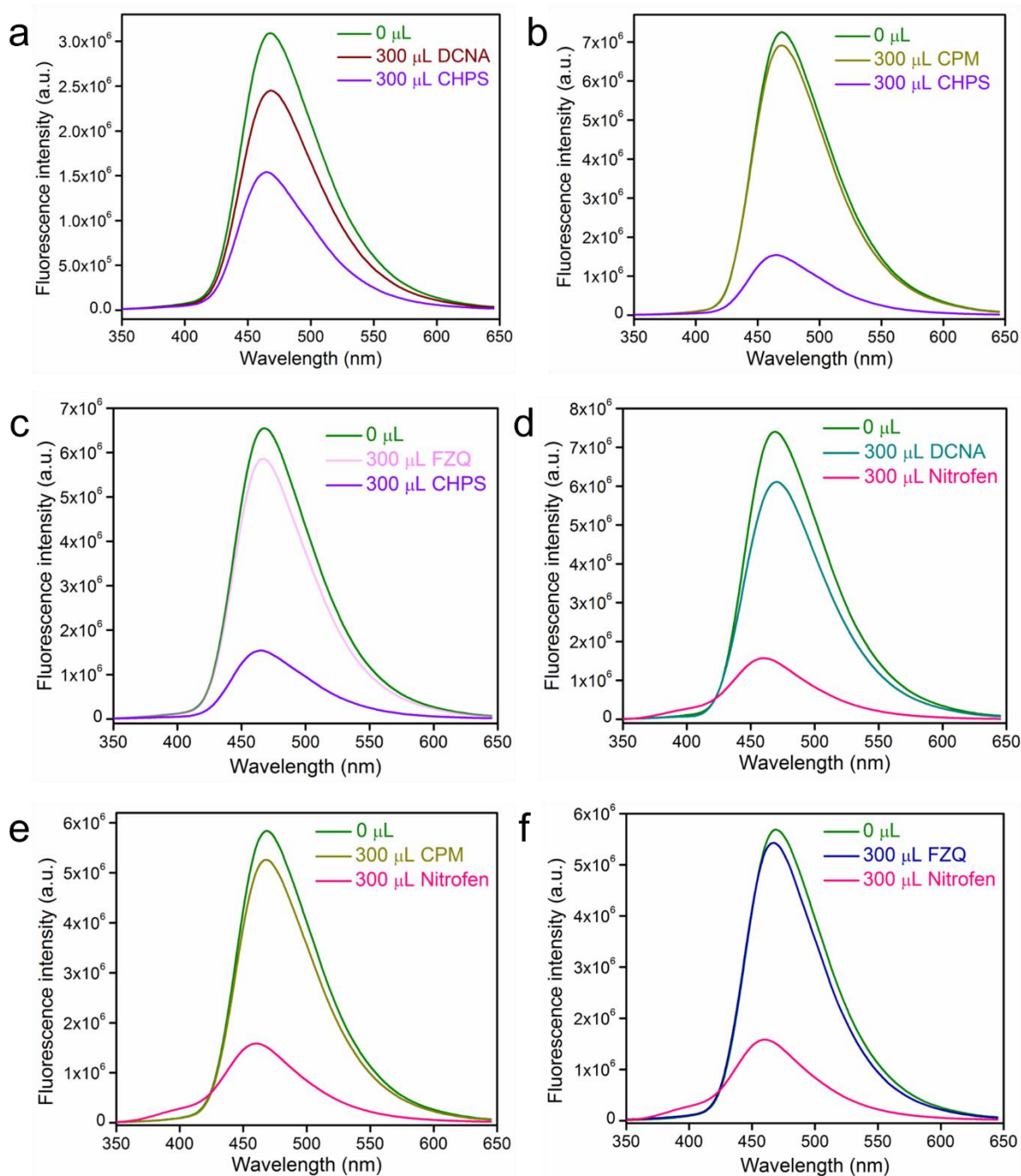
Appendix Figure 3.27: Fluorescence quenching response of IP_{POP}-1 upon treatment of 300 μL of (a) 2,6-Dichloro-4-nitroaniline (DCNA), (b) Cypermethrin (CPM), (c) Fenazaquin (FZQ).



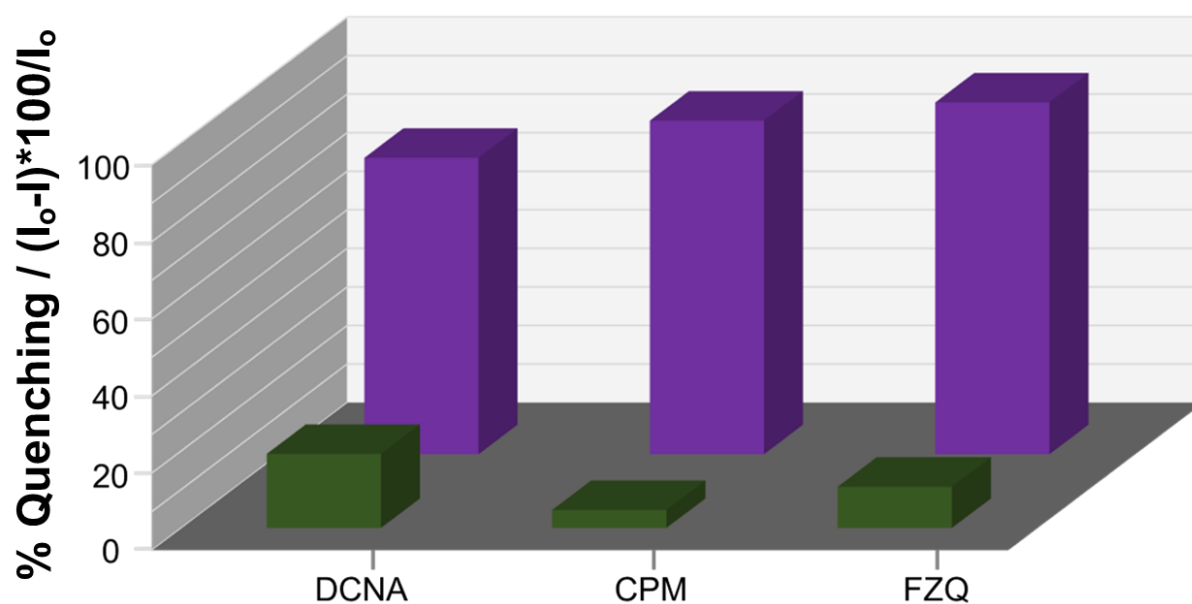
Appendix Figure 3.28: Selective fluorescence quenching response of IP_{POP}-1 by CHPS with compare to other selected pesticides.



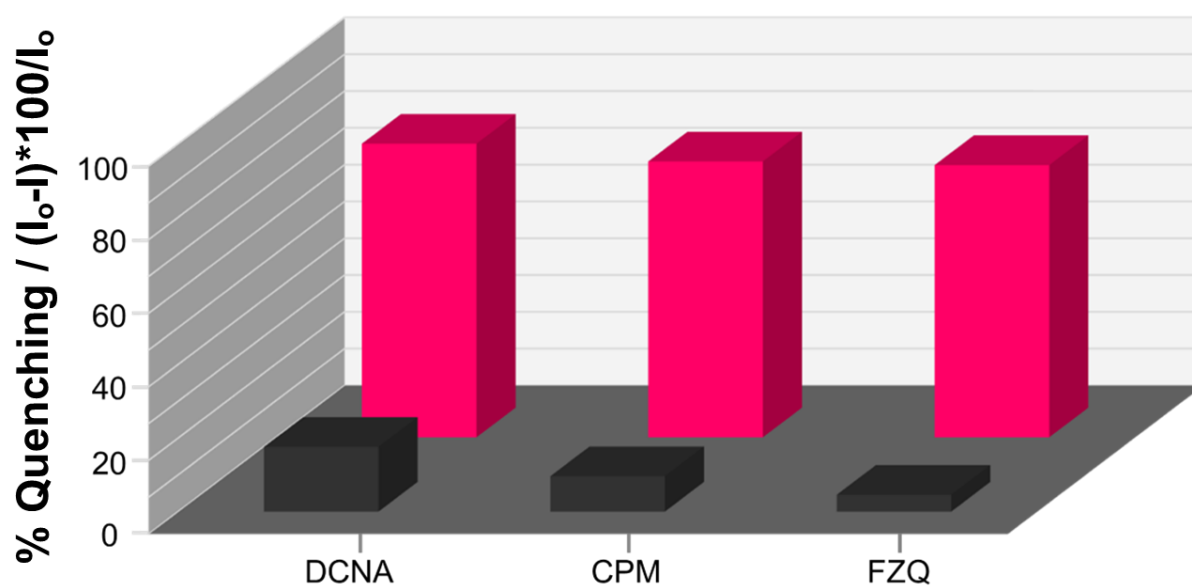
Appendix Figure 3.29: Selective fluorescence quenching response of IP_{POP}-1 by nitrofen, with compare to other selected pesticides.



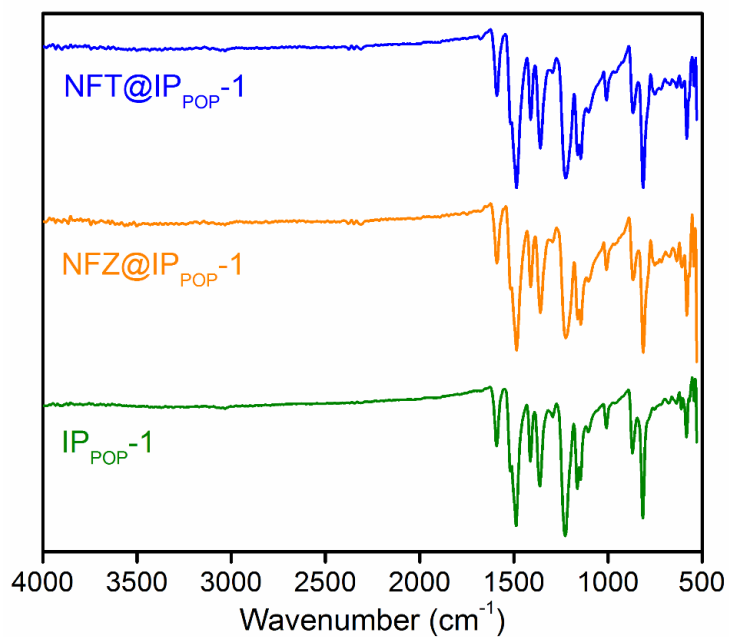
Appendix Figure 3.30: Selective fluorescence quenching response of IP_{POP-1} by (a, d) 2,6-Dichloro-4-nitroaniline (DCNA), (b, e) Cypermethrin (CPM), (c, f) Fenazaquin (FZQ), followed by addition of Chloropyriphos (CHPS) and 2,4-Dichloro-1(4-nitrophenoxy)-benzene (nitrofen), respectively.



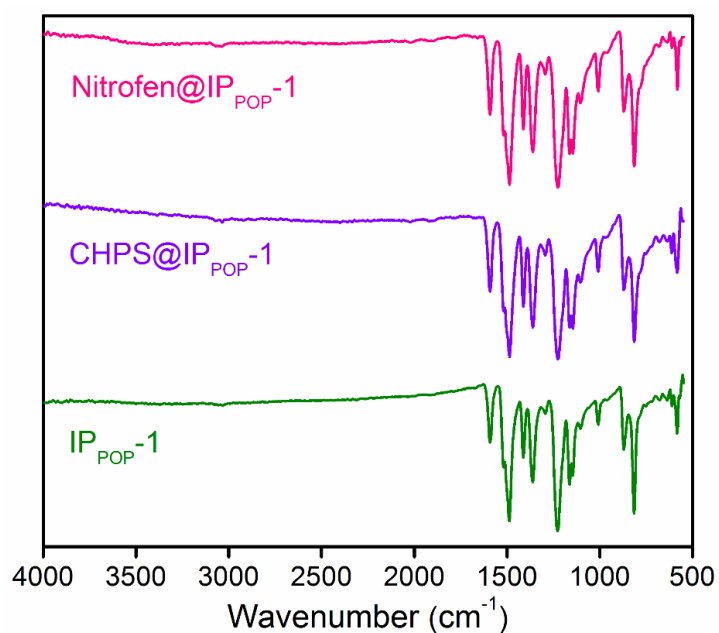
Appendix Figure 3.31: Binary selective quenching response of IP_{POP}-1 by CHPS in the presence of other pesticides.



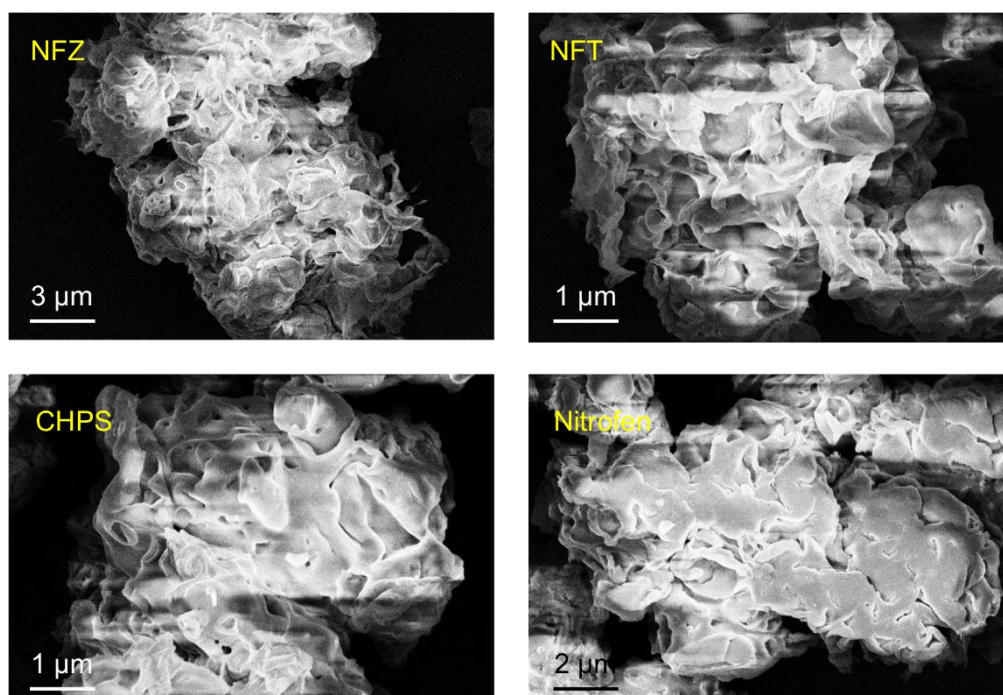
Appendix Figure 3.32 Binary selective quenching response of IP_{POP}-1 by nitrofen, in the presence of other pesticides.

Appendix Section 5: Sensing Mechanism Studies of IP_{POP}-1

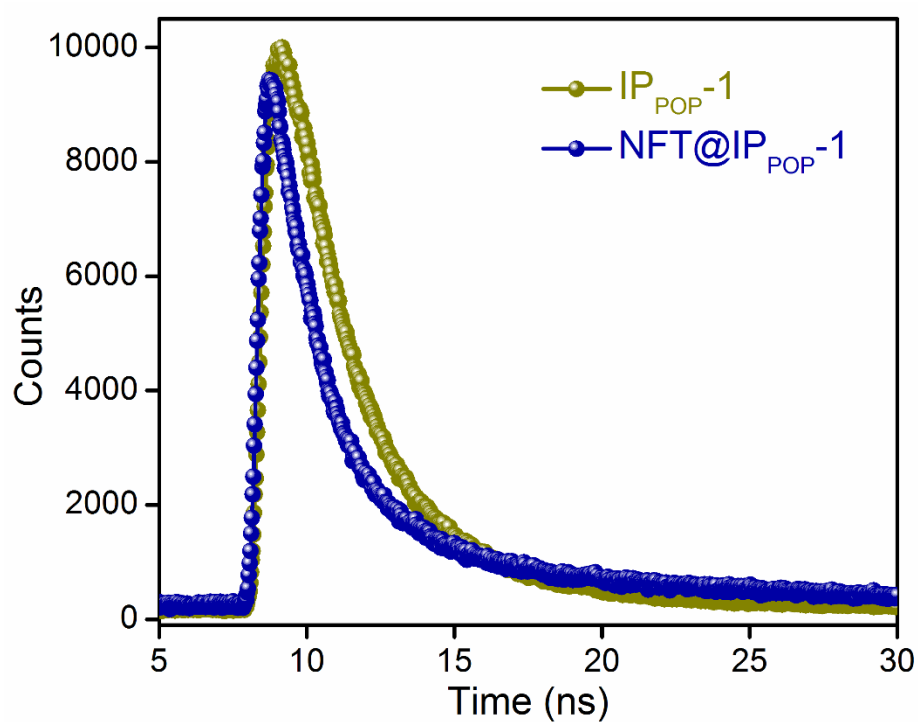
Appendix Figure 3.33 FTIR spectra of IP_{POP}-1 after treatment of antibiotics: NFZ and NFT aqueous solution.



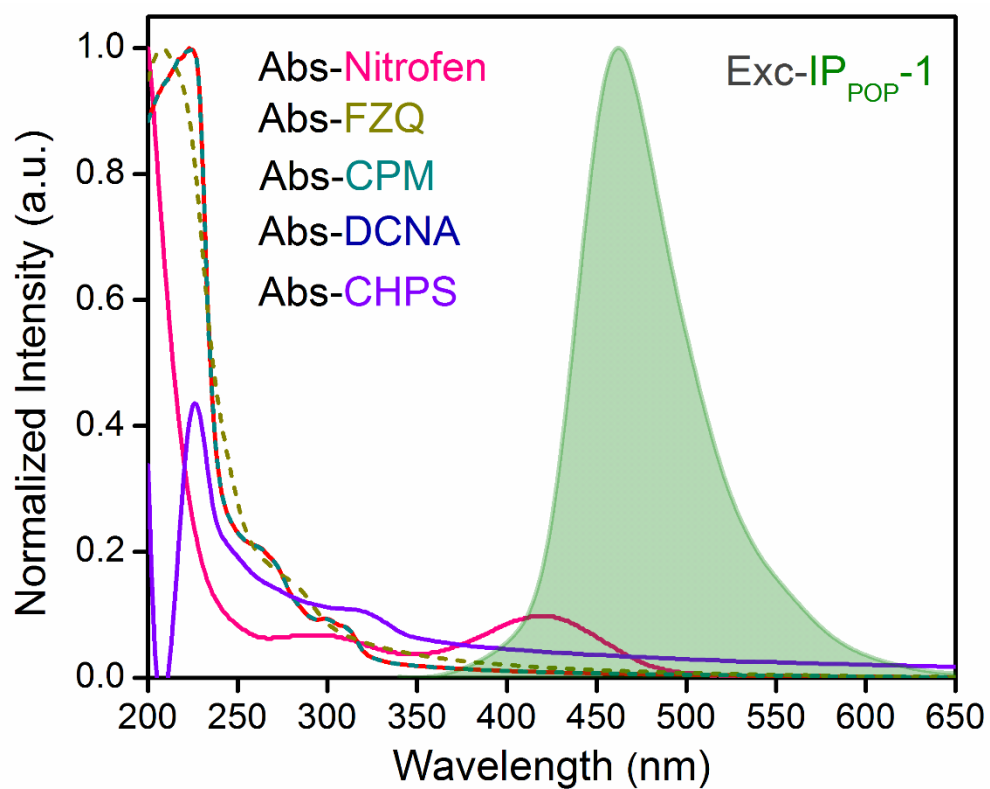
Appendix Figure 3.34: FTIR spectra of IP_{POP}-1 after treatment of pesticides: CHPS and Nitrofen aqueous solution.



Appendix Figure 3.35: FESEM images of IP_{POP}-1 after treatment of antibiotics: NFZ and NFT, and pesticides: CHPS and Nitrofen aqueous solution.

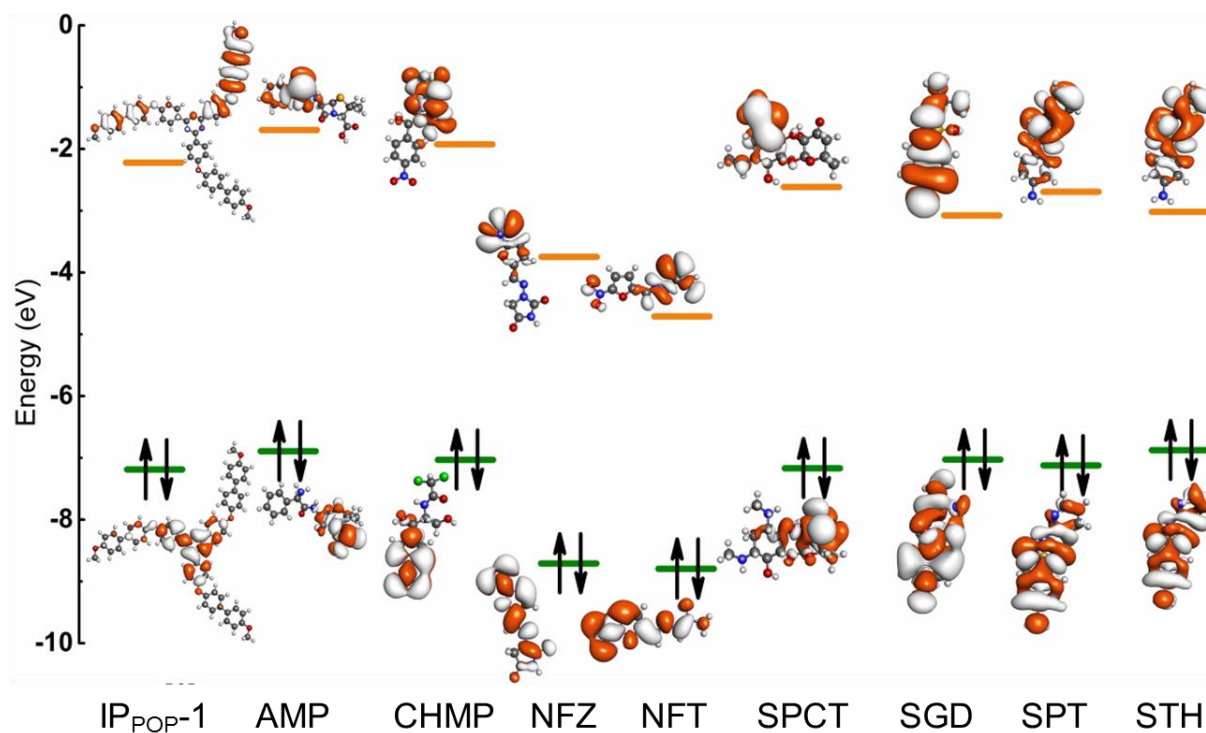


Appendix Figure 3.36: The luminescence lifetime decay profile of IP_{POP}-1 after treatment of high concentration (300 μL) antibiotic: NFT aqueous solution.

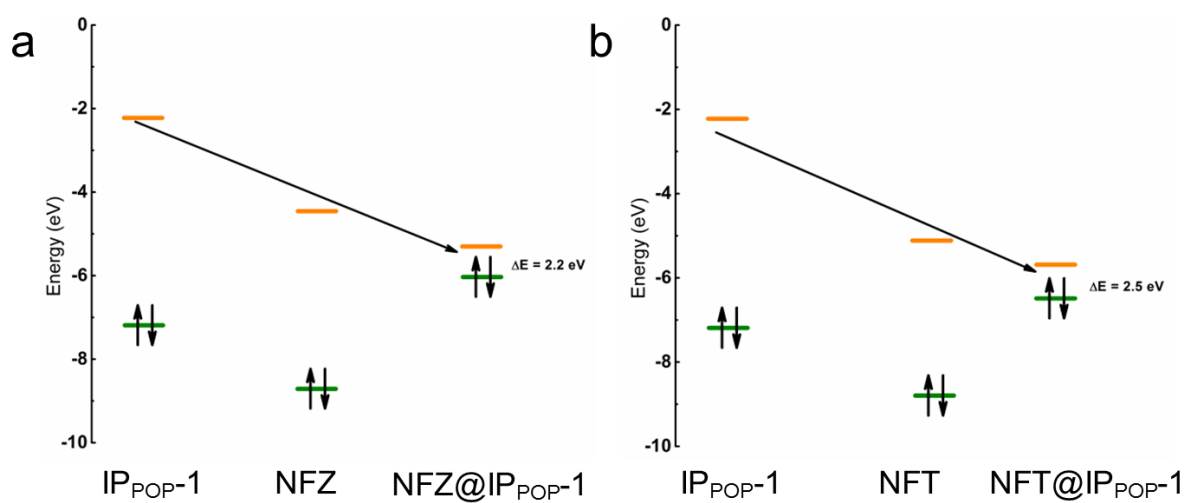


Appendix Figure 3.37: The UV-vis absorption spectra of all pesticides and emission spectra of IP_{POP}-1.

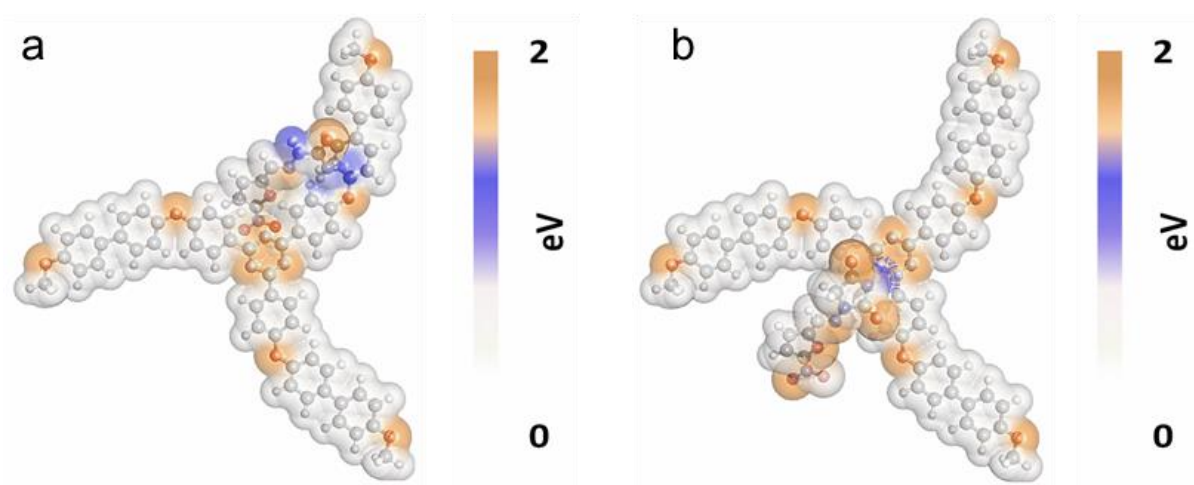
Appendix Section 6: Theoretical Studies



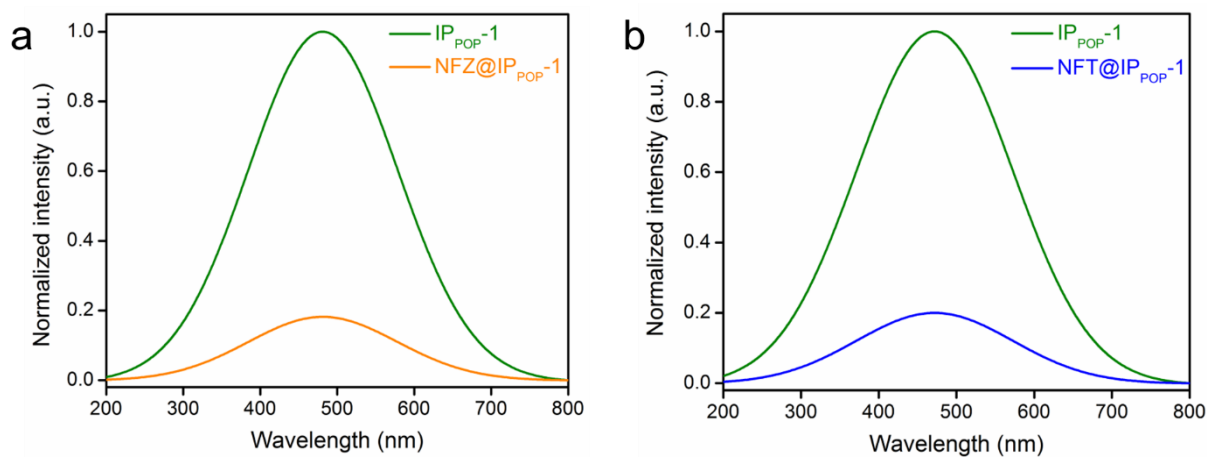
Appendix Figure 3.38: HOMO-LUMO energy gaps of various antibiotics along with units of IP_{POP-1}.



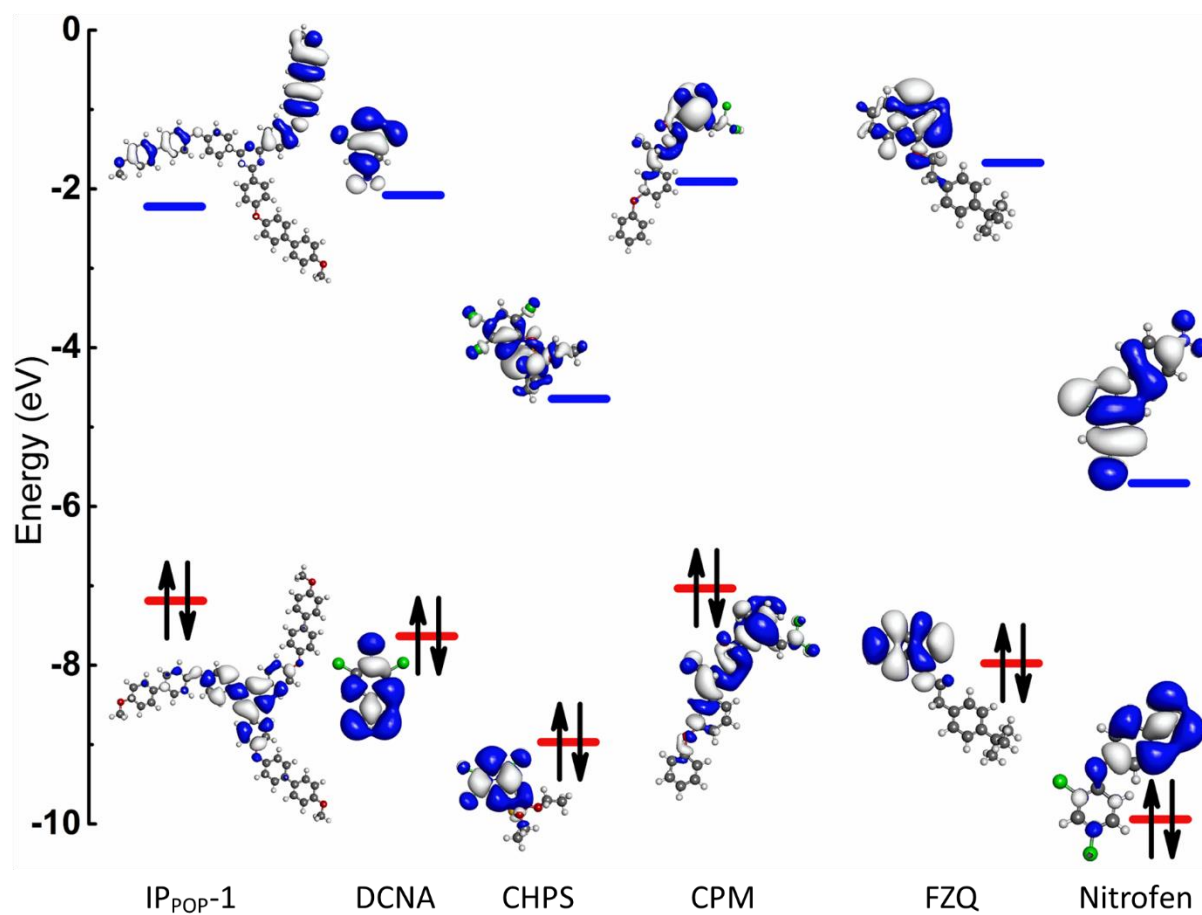
Appendix Figure 3.39: PET process between IP_{POP-1} and complex formation with (a) NFZ antibiotic. (b) NFT antibiotic.



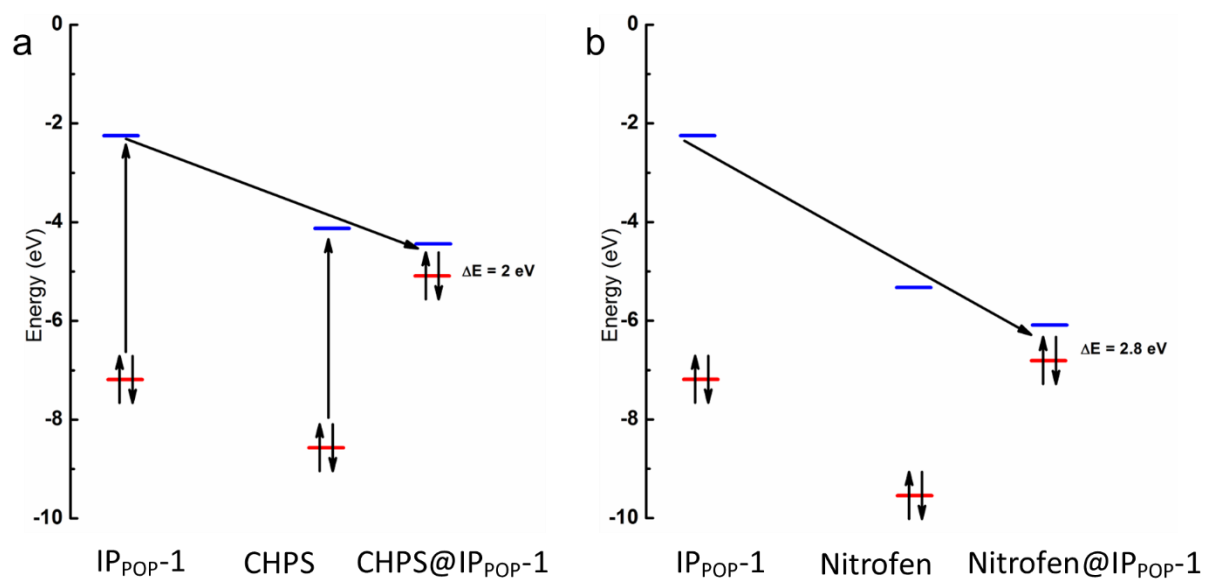
Appendix Figure 3.40: Energy minimized structures of the monomeric unit of IP_{POP}-1 and (a) NFZ complex and (b) NFT complex.



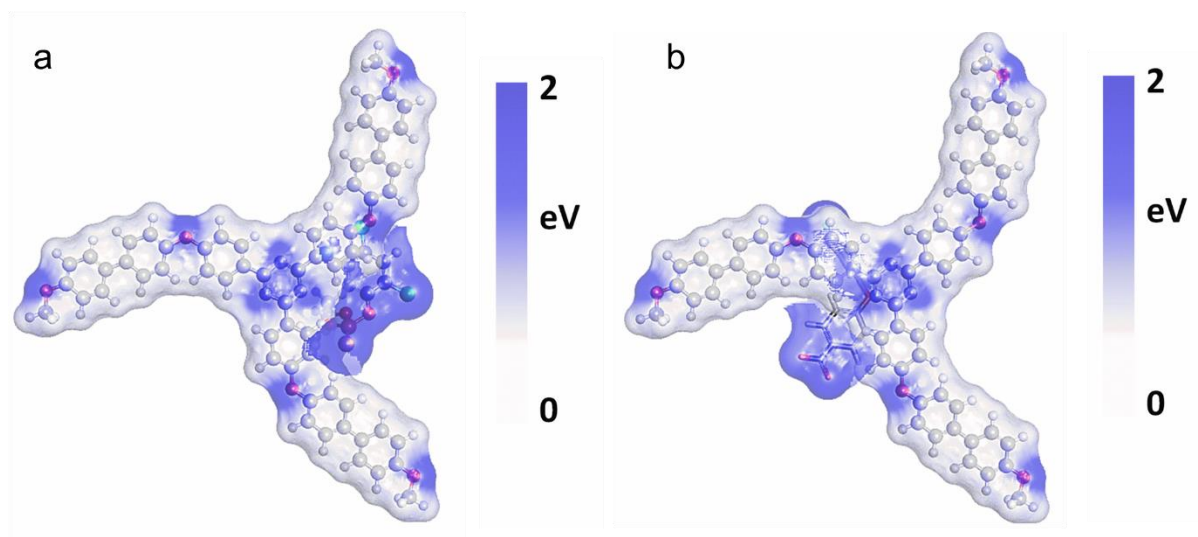
Appendix Figure 3.41: Theoretically predicted emission profiles for IP_{POP}-1 and change in the emission upon interacting with (a) NFZ and (b) NFT, based on DFT calculations on single unit of IP_{POP}-1.



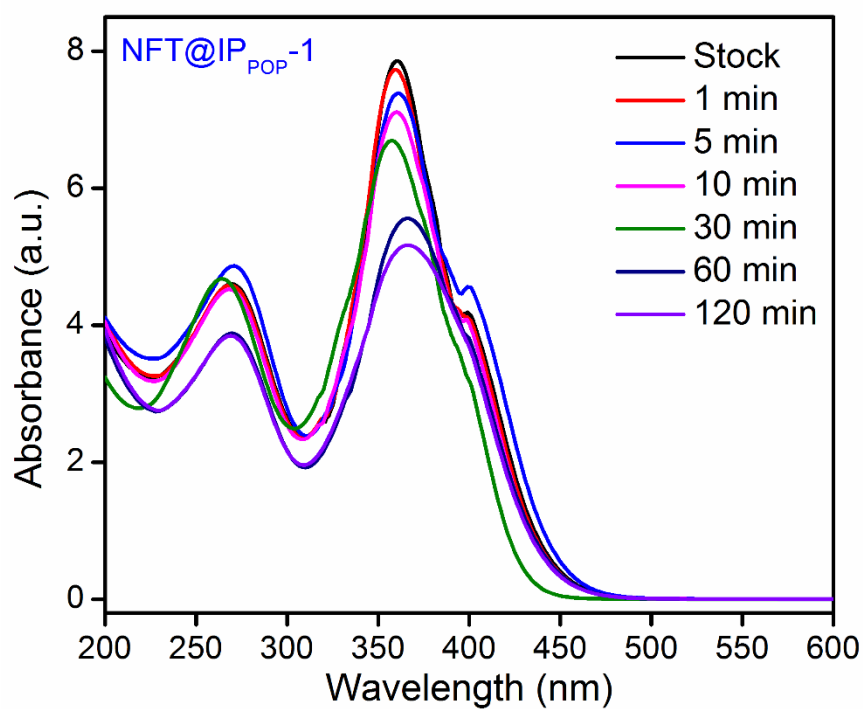
Appendix Figure 3.42: HOMO-LUMO energy gaps of various pesticides along with units of IPPOP-1.



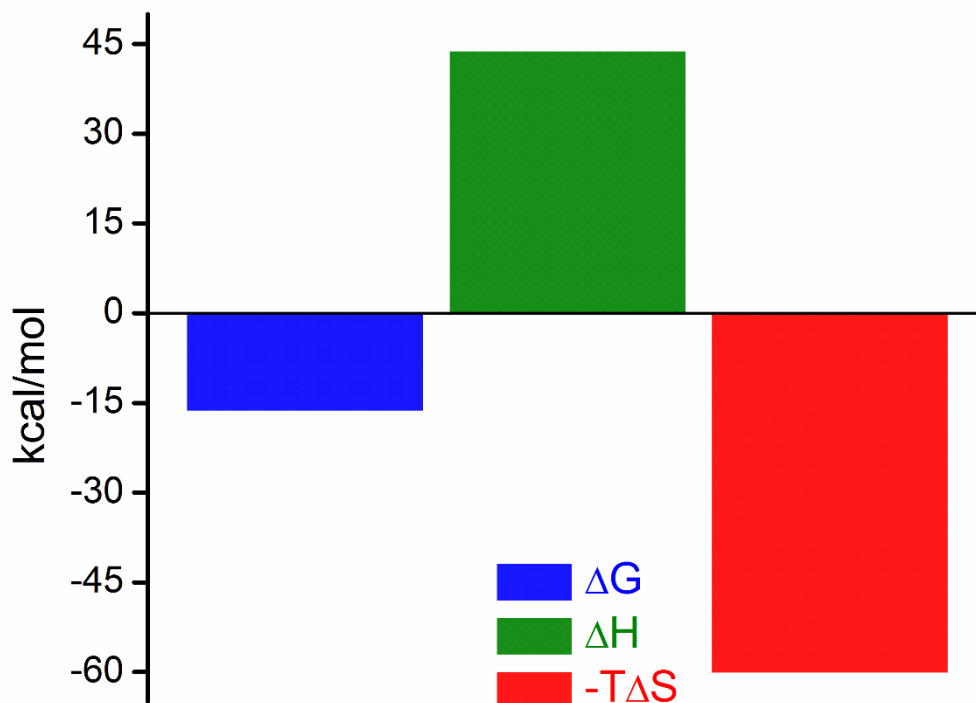
Appendix Figure 3.43: PET process between IP_{POP-1} and complex formation with (a) CHPS pesticide, (b) Nitrofen pesticide.



Appendix Figure 3.44: Energy minimized structures of the monomeric unit of IP_{POP-1} and (a) CHPS complex and (b) Nitrofen complex.

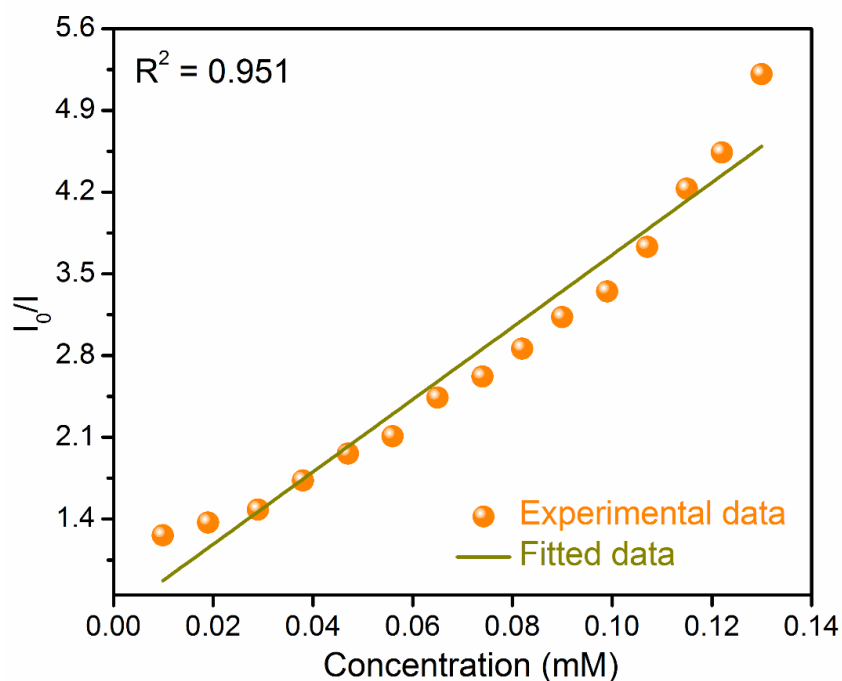


Appendix Figure 3.45: UV-vis spectra of NFT after treated with IP_{POP-1}, showing decreased in the concentration.

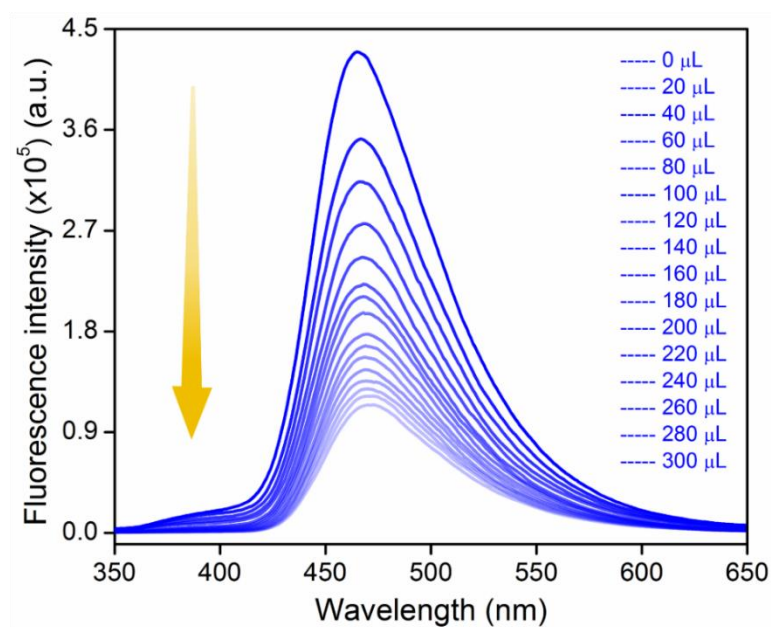


Appendix Figure 3.46: Thermodynamic parameters of interaction between NFT and IP_{POP-1}.

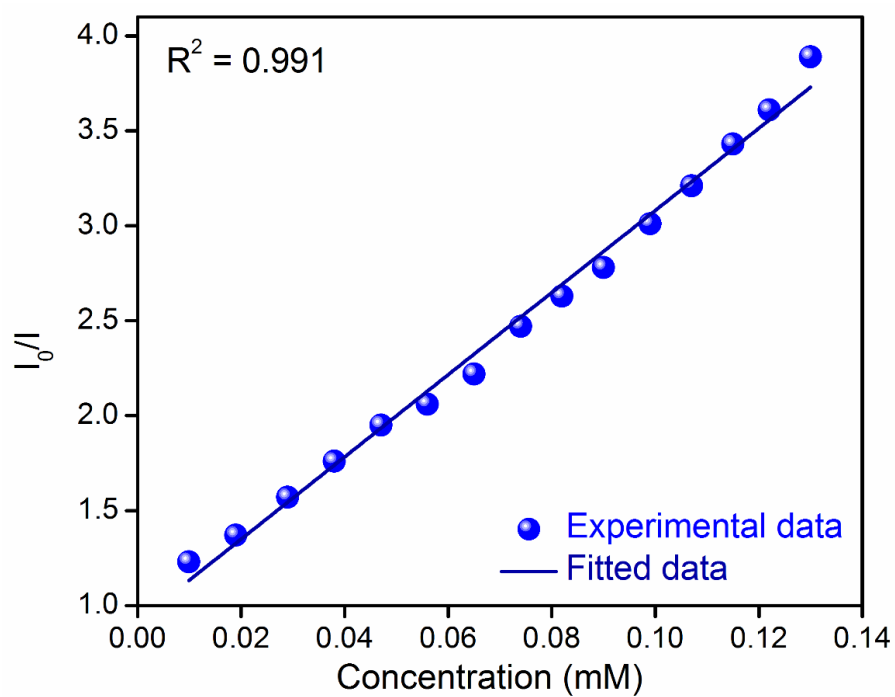
Appendix Section 7: Real-Time Sensing Studies



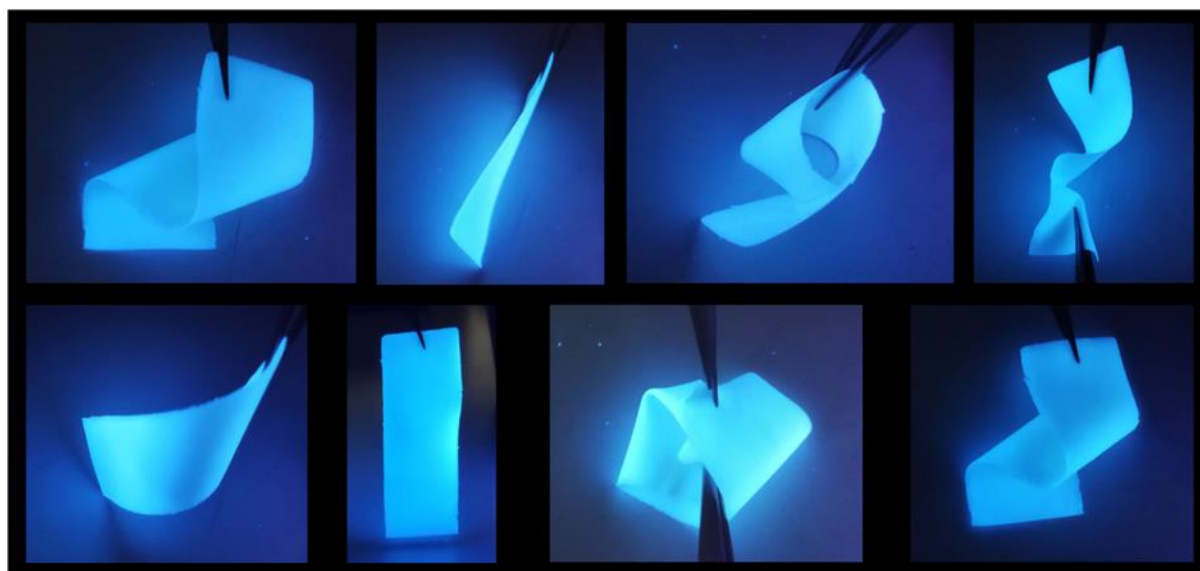
Appendix Figure 3.47: K_{sv} plot of IP_{POP}-1 upon treatment of NFZ in real-water (hospital) system.



Appendix Figure 3.48: Emission profile of IP_{POP}-1 upon treatment of NFT in real-water (hospital) system.



Appendix Figure 3.49: K_{sv} plot of IP_{POP}-1 upon treatment of NFT in real-water (hospital) system.



Appendix Figure 3.50: Digital images of IP_{POP}-1-based self-standing MMMs under UV light.

Appendix Section: Table of comparison

Appendix Table 1: Comparison table for NFT antibiotic sensing studies by various reported start-of-the-art materials.

Compound	K_{sv} (M^{-1})	LOD	Reference
IP_{POP}-1	1.6×10^4	0.046 mM	This Work
BUT-12	3.8×10^4	N.D.	<i>J. Am. Chem. Soc.</i> 2016 , 138, 6204–6216
BUT-13	6.0×10^4	N.D.	<i>J. Am. Chem. Soc.</i> 2016 , 138, 6204–6216
Mg-LMOF	8.82×10^4	126 ppb	<i>Inorg. Chem.</i> 2018 , 57, 13330–13340
Cd-TTPBA-4	6.1×10^4	N.D.	<i>Inorg. Chem. Commun.</i> 2018 , 96, 202–205
RhB@Tb-dcpcpt	6.69×10^4	106 ppb	<i>ACS Appl. Mater. Interfaces</i> 2019 , 11, 21201–21210
CP 1	3.4×10^4	14 ppb	<i>CrystEngComm</i> , 2019 , 21, 6130–6135
CP 2	2.6×10^5	17 ppb	<i>CrystEngComm</i> , 2019 , 21, 6130–6135
{[Zn ₂ (TRZ) ₂ (D BTDC-O ₂)]·DMAc} _n	1.8×10^5	3.53×10^{-7} mol/L	<i>Cryst. Growth Des.</i> 2019 , 19, 694–703

TMPyPE@bio-MOF-1	4.42×10^4	0.134 ppm	<i>J. Mater. Chem. C</i> , 2019 , 7, 8383--8388
IITG-5a	4.30×10^5	96.3 nM	<i>Inorg. Chem. Front.</i> , 2022 , 9, 859–869

N.D.: Not done

Appendix Table 2: Comparison table for NFZ antibiotic sensing studies by various reported start-of-the-art materials.

Compound	$K_{sv} (M^{-1})$	LOD	Reference
IP_{POP}-1	2.75×10^4	0.045 mM	This Work
BUT-12	1.1×10^5	58 ppb	<i>J. Am. Chem. Soc.</i> 2016 , 138, 6204–6216
BUT-13	7.5×10^4	90 ppb	<i>J. Am. Chem. Soc.</i> 2016 , 138, 6204–6216
Mg-LMOF	9.0×10^4	108 ppb	<i>Inorg. Chem.</i> 2018 , 57, 13330–13340
Cd-TTPBA-4	4.8×10^4	N.D.	<i>Inorg. Chem. Commun.</i> 2018 , 96, 202–205
RhB@Tb-dcpcpt	5.98×10^4	99 ppb	<i>ACS Appl. Mater. Interfaces</i> 2019 , 11, 21201–21210
CP 1	4.4×10^4	42 ppb	<i>CrystEngComm</i> , 2019 , 21, 6130-6135
CP 2	2.1×10^5	71 ppb	<i>CrystEngComm</i> , 2019 , 21, 6130-6135

[Zn(L)(BDC)]	1.7×10^4	0.91 μM	<i>Cryst. Growth Des.</i> , 2018 , 18, 7173–7182.
[Cd(L)(BDC)]	4.5×10^4	0.85 μM	<i>Cryst. Growth Des.</i> , 2018 , 18, 7173–7182.
[Cd(L)(NDC)]	1.0×10^5	75 ppb	<i>J. Mater. Chem. A</i> , 2017 , 5, 15797–15807.
[Cd(L)(BPDC)]	1.3×10^5	60 ppb	<i>J. Mater. Chem. A</i> , 2017 , 5, 15797–15807.
[Zn(TRZ)(DBT)]	5.2×10^4	N.D.	<i>Cryst. Growth Des.</i> , 2019 , 19, 694–703.
[Cd(CBCD)]	9.7×10^4	85 ppb	<i>Dalton Trans.</i> , 2019 , 48, 2683–2691.
[Zn(BCTPE)]	N/A	0.1 ppm	<i>J. Mater. Chem. C</i> , 2018 , 6, 2983–2988.
$\{[\text{Zn}_2(\text{TRZ})_2(\text{DBTDC-O}_2)] \cdot \text{DMAc}\}_n$	5.2×10^4	4.04×10^{-7} mol/L	<i>Cryst. Growth Des.</i> , 2019 , 19, 694–703
CSMCRI-2	1.30×10^5	0.7 μM	<i>J. Mater. Chem. A</i> , 2019 , 7, 19471–19484
TMPyPE@bio-MOF-1	4.48×10^4	0.110 ppm	<i>J. Mater. Chem. C</i> , 2019 , 7, 8383–8388
IITG-5a	1.42×10^5	156.7 nM	<i>Inorg. Chem. Front.</i> , 2022 , 9, 859–869

N.D.: Not done

3.6 Reference

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2. I. Ali, *Chem. Rev.*, 2012, **112**, 5073 – 5091.
3. I. Marusic, et. al. *Science.*, 2012, **337**, 681-686.
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Chapter 4

Unveiling the Impact of Diverse Morphology of Ionic Porous Organic Polymers with Mechanistic Insight on the Ultrafast and Selective Removal of Toxic Pollutants from Water

4.1 Introduction

Nowadays, due to rapid industrialization along with widespread urbanization, metal-based toxic oxoanions are ubiquitous species in water that contribute to serious water pollution, a global issue threatening the entire ecosystem.^[1–3] US Environmental Protection Agency (US-EPA) has marked some of the heavy metals which inherently exist as oxoanions in water, such as chromate [Cr(VI)], rhenate [Re(VII)], arsenate [As(V)], selenate [Se(VI)] and so forth, as primary water pollutants.^[4,5] These oxoanions are carcinogenic and mutagenic in nature and cause pernicious consequences, specially toward living organisms and, hence, has been the focus of concern.^[6,7] Among them, Cr(VI) is accounted as one of the most hazardous pollutants in wastewater because of rapid bioaccumulation through food chain, which further causes detrimental effect to human life, even at low concentrations. Toxic hexavalent chromate is widely found in industrial wastewater from chrome plating, tannery, leather, dye, pigment, and steel manufacturing industries. Notably, at least 30 to 35 L of Cr(VI)-contaminated water per each kilogram of leather are generated by the tanning industries.^[7–9] In line, technetium (Tc) is another toxic β -ray emitting radionuclide with long half-life (2.13×10^5 years), which is produced as a nuclear fission product of ^{235}U or ^{239}Pu , that predominantly exists as a pertechnetate anion (TcO_4^-) in the environment as a highly soluble species in water. As a potential low-activity waste material, selective removal of TcO_4^- is challenging owing to its low binding constant and less complexing enthalpy in aqueous medium, originating from the large size and low charge density of the pertechnetate anion.^[10,11] Therefore, considering both the foremost human health risk as well as the emergent scarcity of pure drinking water by water pollution, nowadays, segregation of such hazardous pollutants has received great deal of attention.^[12–14]

In this view, ion-exchange-based chemical separation by various porous materials has been found as an effective technique toward water purification.^[15,16] Therefore, over the past few years, research on ionic porous materials has attracted special attention owing to its energy-intensive, cost-effective, and efficient performance over other conventional materials for adsorption-based chemical separations.^[17–19] Although, considerable endeavours have been paid to sequester various toxic oxoanions by different porous materials,^[20–24] their studies are typically restricted to designing novel materials only, and thus the efficiencies are limited to a great extent due to lack of proper systematic in-depth understanding of the critical role of various physical properties with mechanistic insight of such materials toward improving the adsorption properties such as kinetics, selectivity, and uptake capacity. In this context, unfolding the role of various physical properties to improve the sequestration efficiency of the materials, rather than only synthesizing different new materials, is accounted as a more effective approach. The chemical composition and outer surface morphology are the two most critical parameters that affect the physicochemical properties of the compound.^[25] The surface area, adsorption behaviour,

diffusion kinetics, and catalytic activity can be altered by slight tweaking of morphological configurations of such materials. ^[26–30] Therefore, we envisioned that the morphology engineering at the molecular level of the ionic materials having identical chemical configurations could be an effective way to enhance the efficiency of the adsorbent toward hazardous chemical sorption applications. In this regard, ionic porous organic polymers (iPOPs) is at the forefront due to its virtue of strong electrostatic interaction, facile synthesis, predictable tunable functionality, and high chemical stabilities. Although, iPOPs are well suited for this application, the vital role of fine-tuned morphologies of such polymeric materials toward oxoanion sequestration application has remained unexplored. ^[1,3,11,31]

Keeping this in mind, in this contribution, optimization of oxoanion removal kinetic study with systematic screening of two different morphologies is carried out with a highly efficient imidazolium-based cationic polymer (iPOP-5) containing free exchangeable bromide ions, taking CrO_4^{2-} and ReO_4^- (surrogate anion for TcO_4^-) as model oxoanions in water. The iPOP-5 demonstrated various morphologies, such as spherical, nanotube, and flake depending upon the fine tuning of the reaction duration. The detailed mechanistic investigation revealed the morphological evolution of the flake morphology from self-assembly of nanospheres followed by nanotubes and nanoribbons at different stages of the reaction. Among them, the flake morphology of iPOP-5, [iPOP-5(F)], is seen to exhibit ultrafast capture efficiency toward both the oxoanions in water. Contrarily, the spherical morphology of iPOP-5, [iPOP-5(S)], shows relatively slow removal efficiency for both the oxoanions. The iPOP-5(F) demonstrates significant removal efficiency as it selectively eliminates CrO_4^{2-} and ReO_4^- ions in the presence of excessive (~100-fold) other interfering anions from both high- and low-concentration contaminated water to far below the permitted level of these oxoanions in drinking water. The high capacity, fast separation, recyclability, and capture in a wide range of pH promoted these materials as one of the most comparable with other existing materials in the literature. In addition, highly selective and rapid sequestration efficacy by iPOP-5(F) was observed in various water samples. Moreover, a column exchange-based removal investigation exhibits lowering of concentration to less than 50 ppb, which is the limit in drinking water set by WHO. Investigation of mechanistic insight uncovered that in situ exfoliation of flakes into nanosheets upon oxoanion incorporation is credited with such ultrafast capture efficacy. Again, the efficient selective capture of oxoanions by iPOP-5(F) was further supported by detailed theoretical binding energy calculations with the density functional theory (DFT) method.

4.2 Experimental

4.2.1 Materials: Starting materials, 4-(bromomethyl) benzonitrile, 1,4-dibromobenzene were purchased from Sigma-Aldrich and Alfa-Aesar respectively. Triflic acid, Potassium Carbonate, Copper

sulfate were purchased from local chemicals. All the solvents also purchased locally. The obtained chemicals and solvents were used without any further purification.

4.2.2 General Characterization and Physical Measurements: All infra-red (IR) spectra were recorded using a NICOLET 6700 FT-IR spectrophotometer, using KBr pellets in the range of 400 – 4000 cm^{-1} . Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer STA 6000 TGA analyser under an N_2 atmosphere with a heating rate of 100C min^{-1} . Solid state NMR spectra were recorded on Bruker 400 MHz NMR spectrometer. Carbon chemical shifts are expressed in parts per million (δ scale). The morphology of the materials was recorded with a Zeiss Ultra Plus field-emission scanning electron microscope (FESEM) with an integral charge compensator and embedded EsB and AsB detectors (Oxford X-max instruments 80 mm^2 (Carl Zeiss NTS, GmbH)). The samples were sputter-coated with a 5-10 nm Au film to reduce charging. 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. The scanning electron microscopy (SEM) and energy dispersive X-ray absorption spectroscopy (EDS) analyses were performed using a FEI Quanta 3D dual beam FESEM at 30 kV. UV spectra were acquired on a Shimadzu UV 2600 Spectrophotometer. TEM imaging and STEM-EDS were performed on the HRTEM (JEM-2200FS, JEOL) operating at acceleration voltage of 200 kV. Dynamic light scattering (DLS) and Zeta Potential measurement was performed using Nano ZS-90 setup (Malvern instrument). DLS utilizes a 633 nm laser as the light source, and the detector collects the scattered light at 90° angle. This gives information about the correlation function [$g_2(t)$], from which the diffusion coefficient (D) is calculated using cumulant method and further the diameter of the particle is determined using the Stock Einstein equation. XPS studies was performed using K-Alpha+model (Thermo Fischer Scientific, UK) with Al $\text{K}\alpha$ source. ICP-MS was performed on Quadrupole inductively coupled plasma mass spectrometry (Q-ICP MS; Thermo Scientific iCAP Q) instrument. Multielement standards were purchased from inorganic ventures.

4.2.3 Oxo-pollutant Capture Studies

4.2.3.1 Time dependent study of oxo-anion removal:

In the case of the CrO_4^{2-} removal study, we took 2 mL of an aqueous solution of 0.25 mM CrO_4^{2-} ions in a cuvette and recorded the initial absorbance with UV-Vis spectroscopy. To the cuvette, 2 mg of desolvated compound (iPOP-5) was added, and after several time intervals we recorded the corresponding absorbance spectra of the supernatant solution. In a similar way, we carried out UV-Vis spectroscopy and ReO_4^- ion. But in this case, we took an aqueous solution of 0.5 mM for ReO_4^- ion. Furthermore, from this time dependent study we calculated the % removal and decrease in the concentration of the oxo-anions vs. time using the following equation,

$$D_t = [(C_0 - C_t) / C_0 * 100 \%] = [(A_0 - A_t) / A_0 * 100 \%]$$

$$\text{i.e., } C_t = C_0 - (A_0 - A_t) / A_0 * C_0$$

Where, D_t is the exchange capacity, C_0 and A_0 are the initial concentration and absorbance of the oxo-anion solution respectively, and C_t and A_t , are the concentration and absorbance of the oxo-anion solution at specific times respectively. Furthermore, kinetics data for CrO_4^{2-} and ReO_4^{2-} ions were fitted in a pseudo second-order model with the help of the following equation,

$$Q_t = (k_2 Q_e^2 t) / (1 + k_2 Q_e t)$$

Where, t is the time in minutes, and Q_t and Q_e are the amounts of adsorbate (mg g^{-1}) on the adsorbent at different time intervals and at equilibrium respectively.

4.2.3.2 Adsorption isotherm experiment:

*i*POP-5 (5 mg) was immersed in 5 mL water solution of oxo-anion having different concentration (in case of CrO_4^{2-} ion concentration was taken in the range of 50-500 ppm and for ReO_4^- ion the range of concentration is 50-1500 ppm). After 24 hours UV-Visible spectroscopy was carried out with the supernatant solution and further fitted with following equation,

$$\text{Langmuir model, } Q_e = Q_m C_e / K_d + C_e$$

Where, C_e (ppm) and Q_e (mg gm^{-1}) are the oxo-anion concentration at equilibrium and amount of oxo-anion adsorbed at equilibrium respectively. Q_m (mg gm^{-1}) is the maximum amount of oxo-anion per unit mass of adsorbent to form a complete monolayer. K_d (mg/L) is a constant related to the affinity of the binding sites.

$$\text{Freundlich Model, } Q_e = K_F C_e^{1/n}$$

Where, K_F and $1/n$ are the Freundlich model constants, indicating capacity and intensity of adsorption, respectively.

For the temperature dependent isotherm study, the mixture was stirred at a constant speed of 500 rpm under different temperatures of 298, 313, and 333 K for 24 hours, keeping all the conditions same as the previous.

4.2.3.3 Study of oxoanion trapping in the presence of competing anions

In this study, we took Cl^- , Br^- , NO_3^- , ClO_4^- and SO_4^{2-} ions as the competing anions, which are omnipresent in common water sources and waste water. We took 2.5 mM and 5 mM aqueous solution of targeted oxoanions or Cr and Re, respectively and ~100-fold excess competing anion. To the mixture, 5 mg of desolvated compound (*i*POP-5(F)) was added and stirred for 12 hours. After 12 hours, the

solution was filtered off to separate *i*POP-5(F), and the solution was characterized with UV-Vis spectroscopy. The obtained solution was diluted 10 times to measure the UV-Vis spectroscopy, and furthermore the capture efficiency of *i*POP-5(F) in the presence of other anions was studied by comparison with a blank (Blank: only 2.5 or 5 mM of the respective oxo-anion was taken instead of a mixture). Along with UV-Vis spectroscopy, this study was also affirmed by ICP-AES analyses.

4.2.3.4 Capture study of low-concentration of Cr(VI) and Re(VII):

Stock solution was prepared with effective concentration of Cr(VI) and Re(VII) as ~1 ppm. 5 mg of *i*POP-5(F) was exposed to 5 ml aqueous solution containing mixture of Cr(VI) and Re(VII). The solutions were stirred on vortex to ensure sufficient contact time and after ~2 h, the suspensions were centrifuged for 2 min at 6700 rpm. The solution was taken out and were analyzed further using ICP spectroscopy. Now, the kinetics data at different mentioned time for low-concentration capture has been calculated using the similar previous formula. Also, the selectivity test with ~100-fold other anions at low-concentration has been performed following the similar experiment as in case of high-concentration.

4.2.3.5 pH-dependent capture study:

*i*POP-5(F) (2 mg) was immersed in 2 mL solution of 2.5 mM oxo-anion (in case of CrO_4^{2-} ion pH-1.7, pH-4, pH-9, pH-10 and pH-12.4 were used, whereas for ReO_4^- ion pH-9, pH-10 and pH-12.4 were used) and stirred for 24 hours. After 1 day UV-Vis study was carried out to check the removal efficiency of *i*POP-5(F). Following equation has been used for calculation and compared with the data at pH-7 for relative performance,

$$D_t = (C_0 - C_t)/C_0 * 100\% = (A_0 - A_t)/A_0 * 100\%$$

Where, D_t is the exchange capacity, C_0 and A_0 are initial concentration and absorbance of the oxo-anion solution respectively, C_t and A_t , are concentration and absorbance of the oxo-anion solution at specific times respectively.

4.2.3.6 Recyclability test of *i*POP-5(F)

*i*POP-5(F) (10 mg) was regenerated with a saturated solution of tetrabutylammonium bromide solution by keeping it for 6 hours. Reusability of the regenerated material was checked with 10 mL of the 1 mM oxoanion (CrO_4^{2-} and ReO_4^-) solutions. After ~6 hours, the concentrations of the oxoanion solutions were measured by UV-Vis spectroscopy. These studies were repeated for up to four cycles for each of the cases (CrO_4^{2-} and ReO_4^- ions).

4.2.3.7 Uptake towards oxoanions of Cr(VI) and Re(VII) in real-water system

For real-time analysis, different water system, such as tap, lake, river, sea and tannery water system was spiked with certain (~1 mM) concentration of Cr(VI) and Re(VII). 5 mg of iPOP-5(F) to 5 ml of this spiked solution. The solutions were stirred on vortex for 2 h to ensure sufficient contact time and after 2 h, suspensions were centrifuged for 2 min at 7800 rpm and solution was further analysis by UV-Vis/ICP spectroscopy.

4.2.3.8 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 oxoanions, is given by the equation:

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

Where, V is the volume of the testing solution (mL), m is the amount of solid adsorbent (g), C_o is the initial concentration of As(V), and C_e is the equilibrium concentration of As(V).

4.2.3.9 Column-exchange experiment:

To check the oxoanion removal efficiency by the material (iPOP-5(F)), a column exchange-based sorption experiment was conducted by packing ~100 mg compound with ~5 gm of sand inside a column (bed length ~ 5 cm and diameter ~ 0.75 cm) as bed for oxoanion capture. Then different volume of stock ~25 ppm of aqueous oxoanions (Cr/Re) solution was passed through the column bed with a flow rate of 0.5 mL/min, which was controlled by a water-flow-regulator, and the drops per minute was recorded with the help of a stopwatch. A bed-volume of ~3.5 mL of column eluted solution was collected in a different respective container. The concentration of oxoanions in these solutions were then analyzed through ICP-MS analysis. The recyclability test of the column exchanged-based oxoanions capture study was performed by washing the column with pure water, followed by saturated tetrabutylammonium bromide solution after each cycle. The filtrate of each cycle was collected at the bottom of the column (Figure S32b). Before and after capture studies, the concentration of oxoanions solutions were analyzed through ICP-MS analysis.

4.2.4 Determination of binding energy of interactions, electrostatic – potential surface (ESP) and binding sites

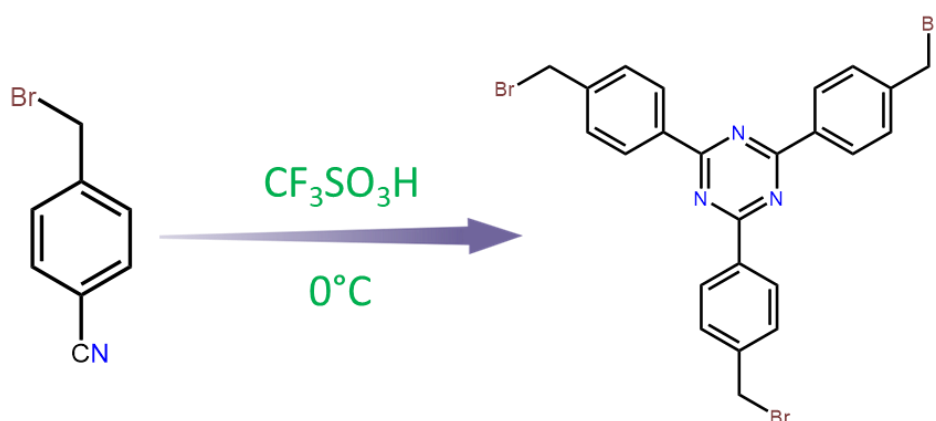
Discovery Studio 2016 (Accelrys) was used to study the interactions between iPOP-5 unit and oxoanions in terms of the binding energy of interactions, electrostatic – potential surface (ESP) and binding sites. All calculations were performed at fine quality calculation level. Firstly, using DMOL3 and B3LYP hybrid function the molecular structure of the iPOP-5 unit was fully relaxed. During

calculations, the Multiplicity factor was kept in Auto mode with double numeric plus polarizing (DNP+) basis set and water as solvent. Successively, structural simulation on the relaxed structure was performed to locate possible interaction site of the anion within the relaxed *i*POP-5 unit was located using simulated annealing technique. The electrostatic potential (ESP) on the van der Waals (VDW) surfaces (isodensity = 0.001 a.u.) of *i*POP-5 unit was derived based on its ground state electron density.

4.2.5. Detail synthetic procedures

4.2.5.1 Synthesis of precursor-1:

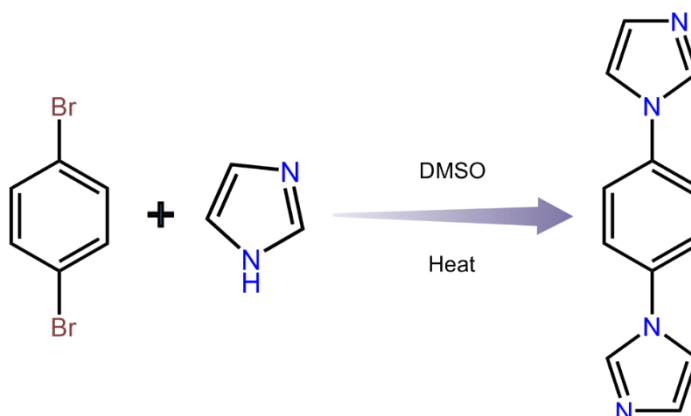
Precursor-1, 2,4,6-tris(4-(bromomethyl) phenyl)-1,3,5-triazine was synthesized according to the previously reported procedure without any modifications.^[32]



Scheme 1: Synthesis scheme of precursor-1.

4.2.5.2 Synthesis of precursor-2:

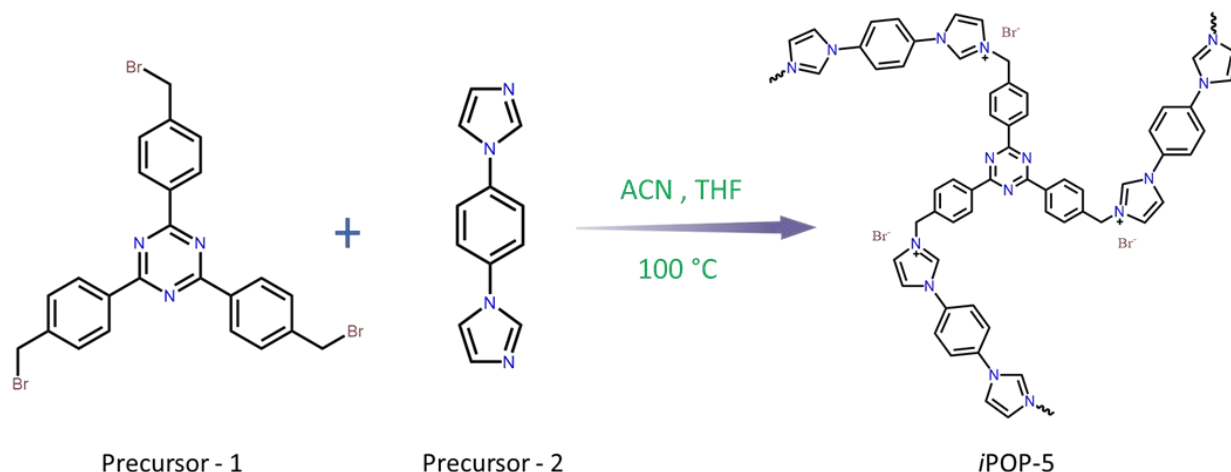
Precursor-2, 1,4-di(1H-imidazol-1-yl) benzene was also synthesized according to the previously reported procedure without any modifications.^[33]



Scheme 2: Synthesis scheme of precursor-2.

4.2.5.3 Synthesis procedure of *i*POP-5:

Precursor 1 and precursor 2 were taken in a 100 ml round bottom flask followed by addition of acetonitrile and THF solvent. Then the mixture was refluxed. After a certain time, a solid product was formed in the flask and it was stuck into the wall. Thereafter, the compound was filtered and washed with various organic solvent followed by acetonitrile and tetrahydrofuran for several times. After drying the compound, it was collected.



Scheme 3: General synthesis scheme of *i*POP-5.

4.3 Results and discussion

The imidazolium-based ionic porous organic polymer (*i*POP- 5) was synthesized by refluxing of 2,4,6-tris(4-bromomethyl) phenyl-1,3,5-triazine (precursor-1) and 1,4-di(1H-imidazol-1- yl) benzene (precursor-2) in a mixture of solvents [acetonitrile and tetrahydrofuran (THF)] (see Appendix part for details, Schemes 1–3) (Figure 4.1). After completion of the reaction, the product was washed extensively with various solvents such as dimethyl formamide, DMAc, acetonitrile, THF, chloroform, ethanol, and so forth several times. Insolubility of the compound in different solvents primarily indicated the formation of the network material. To validate this, the following characterizations, Fourier transform infrared spectroscopy (FT-IR), solid-state NMR (^{13}C), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), were carried out. The signals at ~ 1185 and $\sim 750\text{ cm}^{-1}$ in the FT-IR spectra indicated the formation of quaternary imidazolium linkage (Figure 4.2a). Intense

characteristic absorption peaks at $\sim 1512\text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$) and $\sim 1360\text{ cm}^{-1}$ ($\text{C}-\text{N}$) assured the existence of the triazine ring stretching frequency (Figure 4.2a).^[34, 35]

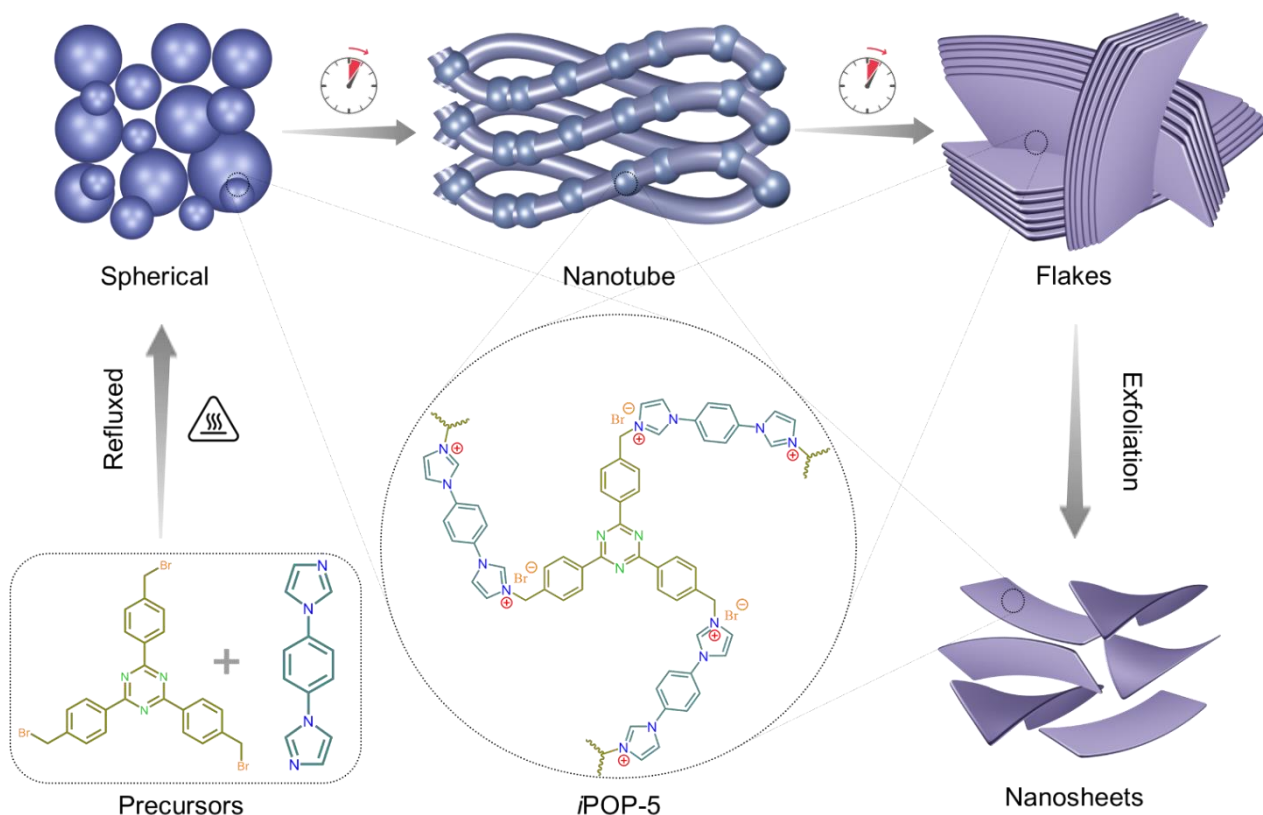


Figure 4.1 Schematic illustration of synthesis of iPOP-5 with different morphologies such as spherical, nanotube and flakes. Also, the scheme representing the formation of nanosheets morphology from flakes of iPOP-5.

Again, molecular level characterization of iPOP-5 was done by employing ^{13}C solid-state NMR. The presence of a peak at 169 ppm in the ^{13}C solid-state NMR spectra of iPOP-5 corresponds to the sp^2 carbon atom of the triazine ring (Figure 4.2b). The peaks from 110 to 140 ppm are ascribed to phenyl and imidazolium carbon atoms, respectively (Figure 4.2b). Moreover, the signal in the spectra at 138 ppm corresponds to the C2 positioned carbon atom of the imidazolium ring, indicating the presence of relevant chemical moieties in the ^{13}C solid-state NMR spectra of iPOP-5.^[36,37] From the TGA profile of iPOP-5, an initial weight loss of 5% was observed at $\sim 90^\circ\text{C}$ which is due to the loss of solvent molecules trapped in the polymeric network (Appendix Figure 4.1). In addition, from the TGA profile of iPOP-5, the polymer exhibited high thermal stability up to $\sim 350^\circ\text{C}$ (Appendix Figure 4.1).

Further, the morphological characterization of the polymer was investigated by FESEM, TEM, and AFM analyses. The flakelike morphology was found from the FESEM analysis of thus synthesized

iPOP-5 (Figure 4.3a).^[38,39] The construction of flakelike morphology by the ordered assembly of sheets was confirmed by FESEM analysis as the images revealed a fine arrangement of several sheets to fabricate a flakelike morphology (Figures 4.3b and Appendix Figure 4.2). Again, a similar observation

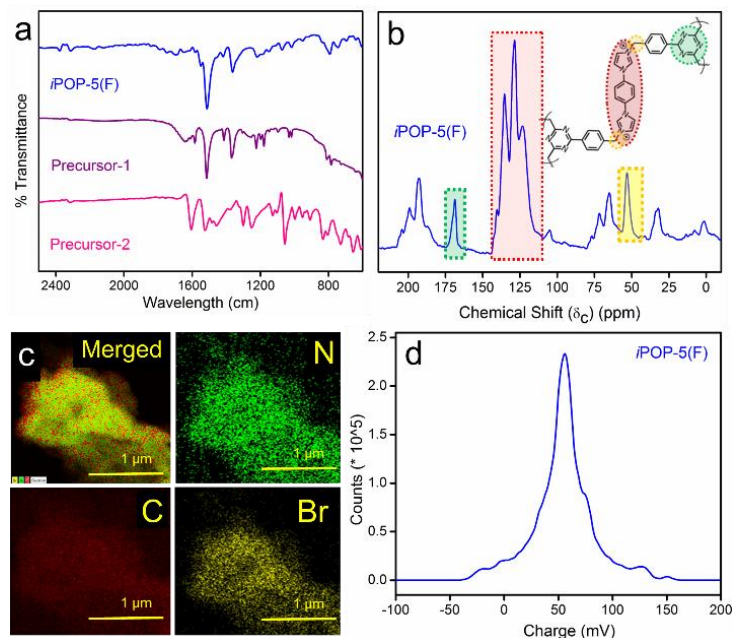


Figure 4.2 (a) FT-IR spectra, (b) Solid-state ¹³C NMR spectra, (c) HAADF-TEM imaging of flake iPOP-5(F), exhibiting homogeneous distribution of elements. (d) Zeta potential profile of iPOP-5(F).

was found from the TEM analysis (Figures 4.3c and Appendix Figure 4.3). To validate this observation, AFM analysis was carried out. AFM images revealed that the surface of the flakes was smooth in nature (Figure 4.3d). The average thickness of flakes obtained from the AFM analysis was found to be ~60 nm (Figure Appendix Figure 4.4). Hereafter, thus-characterized iPOP-5 is further referred as iPOP-5(F). Moreover, the elemental mapping analysis of iPOP-5(F) was examined by high-angle annular dark-field TEM (HAADF-TEM), which demonstrated the existence of all relevant elements (carbon, nitrogen, and bromine) homogeneously distributed throughout the polymeric flake like network (Figure 4.2c). A similar result was observed from energy-dispersive spectroscopy (EDS) and elemental mapping data of the FESEM analysis of iPOP-5(F) (Appendix Figure 4.5). In addition, the presence of corresponding peaks of aforementioned elements in the X-ray photoelectron spectroscopy (XPS) survey profile of iPOP-5(F) also indicated the formation of a charged polymeric network material (Appendix Figure 4.6). The surface charge of iPOP-5(F) was found to be positive with a ζ-potential value +56.3 mV, which indicated its cationic nature originated from the imidazolium backbone of the polymer (Figure 4.2d). The low-temperature (77 K) nitrogen gas adsorption-desorption measurement of the compound does not exhibit a significant uptake of nitrogen, which indicated that the internal pores of

the materials may be blocked due to the existence of counter bromide anions in the cationic skeleton of the material (Appendix Figure 4.7).^[40, 41]

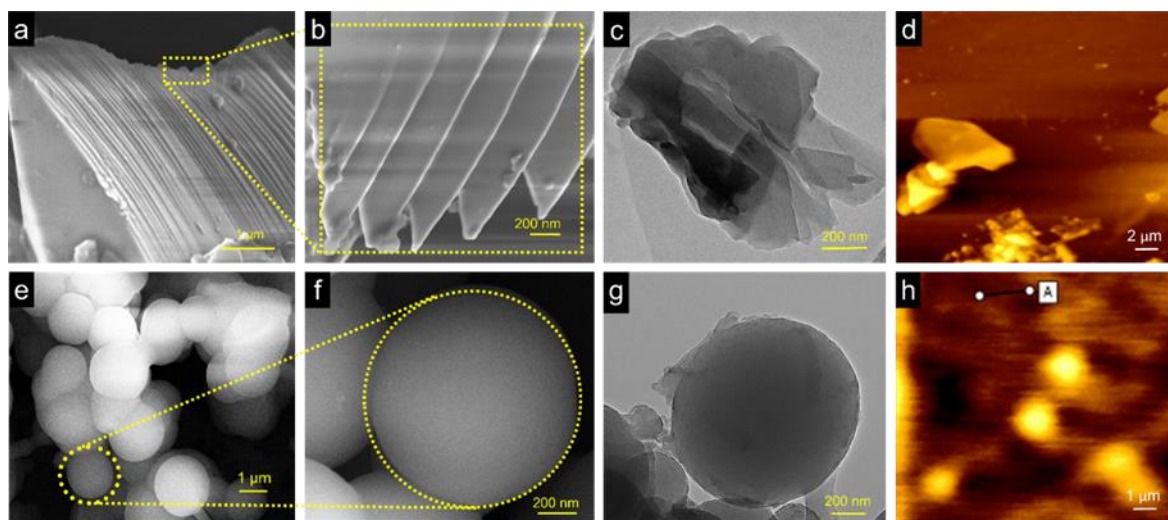


Figure 4.3 (a) FESEM image, (b) high magnification FESEM image, (c) TEM image, (d) AFM image of iPOP-5(F), (e) FESEM image, (f) high magnification FESEM image (g) TEM image, (h) AFM images of iPOP-5(S).

In the literature, ionic polymers, including imidazolium based cationic polymers, are often found to demonstrate diverse morphologies by fine tuning of reaction conditions in terms of solvent combination or by varying the reaction time or temperature or by changing the monomers used for the reaction. Inspired from this, we sought to synthesize other morphologies of iPOP-5 by varying the reaction time. Therefore, initially we collected the reaction product by reacting the respective monomers for only ~8 h (see the Supporting Information for the details) (Figure 4.1). Thus obtained product was again characterized by aforementioned techniques. As for case of iPOP-5(F), both FT-IR and ^{13}C solid-state NMR were employed for structural characterization of these materials, which indicated the formation of an imidazolium-based polymeric network (Appendix Figures 4.8 and 4.9).

The thermal stability up to ~350 °C was observed from the TGA profile of the material (Appendix Figure 4.10). Thereafter, in order to check the morphological nature of the compound, again FESEM, TEM, and AFM analyses were carried out. The FESEM images exhibited a uniform spherical morphology of the materials (Figure 4.3e, f). Identical observation was found in the case of TEM and AFM analyses as both revealed a spherical particle morphology of the compound (Figure 4.3g, h). Thus, the characterized polymer having similar chemical configuration with iPOP-5(F) was further indicated as iPOP-5(S). The average diameter (~800 nm) of the spherical particles of iPOP-5(S) was calculated from dynamic light scattering measurement with polydispersity index 0.172 (Appendix Figure 4.11).

Moreover, like iPOP-5(F), the surface charge of iPOP-5(S) was found to be positive (ζ -potential = +52.3 mV) (Appendix Figure 4.12). The elemental mapping using EDS showed an even distribution of relevant elements (C, N, and Br) throughout the spherical particles (Appendix Figure 4.13).

Motivated from such an observation, that is, the development of two distinct morphologies of a single material by varying the reaction time, we further sought to investigate the time-dependent morphological evolution from spherical to flake morphology of iPOP-5 using both FESEM and TEM analyses (Figure 4.4a-e). Initially, as discussed above, we observed the formation of spherical morphology of the polymer at the early stage (up to ~ 8 h) of the reaction from the FESEM and TEM images (Figure 4f, k). After that, as the reaction time increased (up to ~ 12 h), the spherical particles were found to be fused with each other to form an aggregated spherical morphology of iPOP-5 as indicated from both the SEM and TEM images (Figure 4.4g, l). Further, the aggregated spherical particles were observed to convert into nanotubes upon enhancing the reaction time up to ~ 18 h (Figure 4.4h, m). These nanotubes then assembled to form nanoribbons when the reaction time was increased (~ 24 h) (Figure 4.4i, n). Finally, upon gradual extending the refluxing time up to ~ 36 h, the nanoribbons were observed to combine with each other forming a flakelike morphology, as revealed from the SEM and TEM images (Figure 4.4j, o). Hereafter, the flake like and spherical morphology-based polymers [iPOP-5(F) and iPOP-5(S)] were considered for further study.

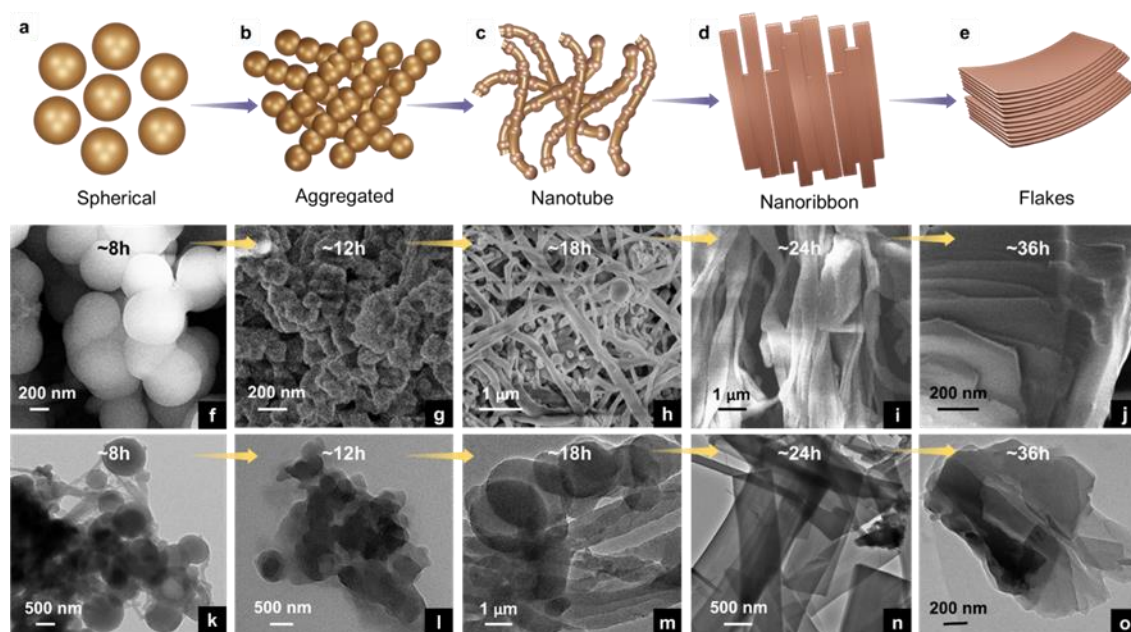


Figure 4.4 (a-e) Schematic representation of morphological evolution of iPOP-5 from spherical to flakes. Corresponding respective FESEM and TEM images of iPOP-5 at various steps of formation: (f,

k) spherical, (g, l) aggregation of spherical, (h, m) nano-tube assembly from spherical, (I, n) nanoribbon, (j, o) flakes formation.

In order to check the chemical stabilities of both the imidazolium-based polymers, the compounds were treated with acidic and basic aqueous solutions. The consistent FT-IR spectra of both iPOP-5(F) and iPOP-5(S) in different pH solutions with pristine phase indicated acid-base stabilities of the polymers (Appendix Figure 4.14). Moreover, identical TGA curves exhibited similar thermal stabilities of both compounds upon acid-base treatment (Appendix Figure 4.15). In addition, the FESEM and TEM images of iPOP-5(F) and iPOP-5(S), treated with various pH solutions, were found to be unchanged, which indicated no morphological changes upon chemical treatment of the compounds (Appendix Figures 4.16 and 4.17). All these results demonstrated high chemical stabilities of both iPOP-5(F) and iPOP-5(S).

4.4 Capture Studies

Propelled by the cationic nature and high hydrothermal and chemical stabilities along with the different morphologies (flake and spherical), we sought to check the availability of free exchangeable bromide ions present in the cationic skeleton of the polymeric network. For this, we performed a small-scale experiment, dipping 2 mg of both iPOP-5(S) and iPOP-5(F) into the visual-colored aqueous solution of CrO_4^{2-} . After a gentle shake, it was observed that the supernatant of iPOP-5(F) underwent decolorization within 1 min, whereas in the case of iPOP-5(S), complete decolorization occurs after 5 min (Appendix Figure 4.18). This observation of rapid decolorization and specifically the difference in the decolorization kinetics between two morphologies spurred their exploration for the detailed anion-exchange studies with chromate (CrO_4^{2-}) and rhenate (ReO_4^-) oxoanions, in addition to exploring the role of two morphologies upon removal kinetics. In situ CrO_4^{2-} removal experiments were initially performed, taking 2 mg of both iPOP-5(F) and iPOP-5(S) individually with 2 mL of 0.25 mM aqueous solution of Cr(VI) anions, and the concentration was monitored by its characteristic absorption maxima at 372 nm through UV-vis spectroscopy (Appendix Figure 4.19 and Appendix Figure 4.20). Remarkably, iPOP-5(F) demonstrated extremely rapid removal rate for CrO_4^{2-} anions in water as the peak at 372 nm disappeared within 1 min (Appendix Figure 4.19), whereas iPOP-5(S) exhibited relatively less removal kinetics as the time taken to complete diminishing of the UV-vis spectra was greater than 5 min (Appendix Figure 4.20). This observation indicated ultrafast and relatively slow entrapment of CrO_4^{2-} by iPOP-5(F) and iPOP-5(S), respectively. In the case of iPOP-5(F), almost 99% removal of CrO_4^{2-} was observed within 1 min as revealed from the % removal with contact time plot, further representing the fastest sequestration of CrO_4^{2-} oxoanion from water (Figure 4.5a). This result

has ever been one of the highest values in the domain of porous materials (Appendix Table 3). In sharp contrast, ~57% removal efficiency was achieved by iPOP-5(S) within 1 min, while ~83% was achieved within 5 min (Figure 4.5a). Furthermore, the absorption kinetics mechanism of both iPOP-5(F) and iPOP-5(S) has been investigated and found to be dependent on the quantity of the adsorbent and adsorbate, demonstrating the pseudo-second-order sorption process with a correlation coefficient value (R^2) of 0.993 [for iPOP-5(F)] and 0.978 [for iPOP-5(S)], respectively (Appendix Figure 4.21). It should be pointed out that the rate constant value of iPOP-5(F) is larger than that of iPOP-5(S). Thereafter, as aforementioned, due to β -emitting-radioactive nature, pertechnetate anion (TcO_4^-) is another hazardous, highly water-soluble oxoanion emerging as a potential toxic pollutant. Due to the rare availability along with high radioactivity, the sorption kinetic experiment of TcO_4^- has been performed taking perrhenate (ReO_4^-) anion as a nonradioactive surrogate for TcO_4^- , having an identical chemical configuration with similar solubility.^[10] The time dependent ReO_4^- removal study has been carried out similar to the CrO_4^{2-} anions capture study, taking KReO_4 solution. The decrease in the concentration of ReO_4^- was found by monitoring the gradual diminishing of UV-vis spectra at maxima (λ_{max}) 208 nm. In a similar line with CrO_4^{2-} capture, again iPOP-5(F) exhibited the fastest decrease in the absorption spectra of ReO_4^- aqueous solution (Appendix Figure 4.22).

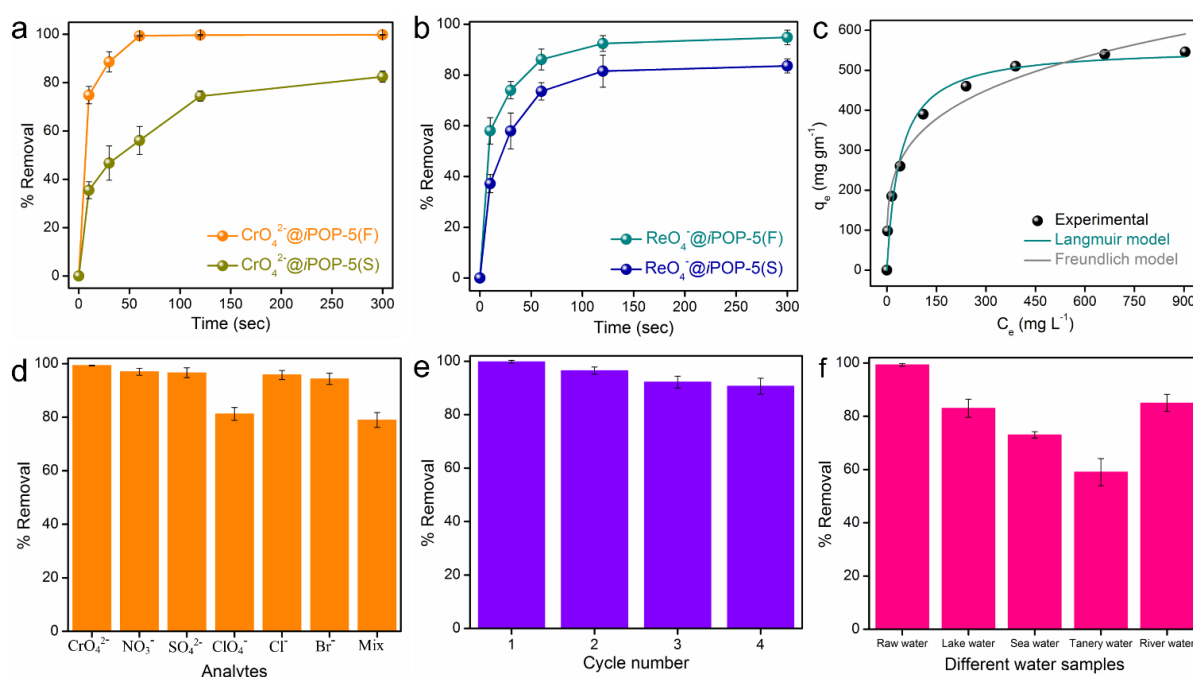
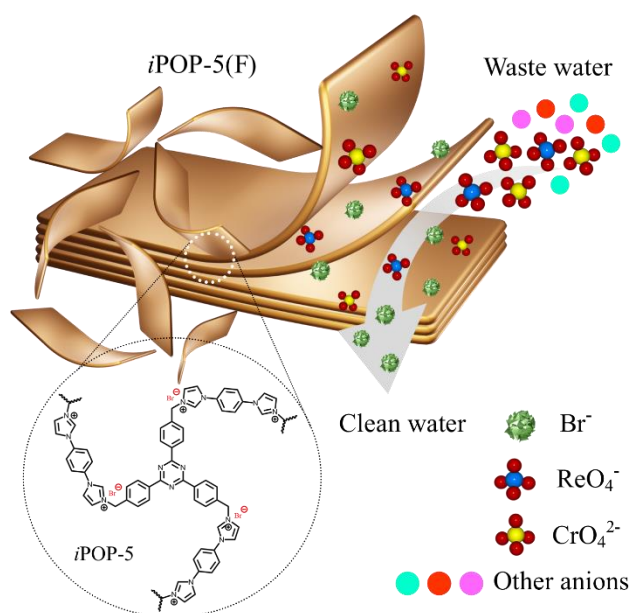


Figure 4.5 Percentage removal of (a) CrO_4^{2-} and (b) ReO_4^- anions in different contact time by iPOP-5(F) and iPOP-5(S). Condition: $[\text{Cr}]_{\text{initial}} = 0.25 \text{ mmol}$, $[\text{Re}]_{\text{initial}} = 0.5 \text{ mmol}$ and $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$. (c) Langmuir isotherm fitting of ReO_4^- anions removal by iPOP-5(F). Condition: $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$

and contact time = 24 h. (d) The removal efficiency of *i*POP-5(F) towards CrO_4^{2-} in presence of other anions. Condition: $[\text{Cr}]_{\text{initial}} = 2.5 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 12 h. (e) Recycle test of *i*POP-5(F) for ReO_4^- ion. Condition: $[\text{Re}]_{\text{initial}} = 1 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 6 h. (f) Relative percentage removal of CrO_4^{2-} in different water system by *i*POP-5(F). Condition: $[\text{Cr}]_{\text{initial}} = 1 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 2 h.

Almost ~82% removal of ReO_4^- was observed within 1 min and ~93% removal within 5 min by *i*POP-5(F) (Appendix Figure 4.5b). On the other hand, *i*POP-5(S) showed relatively slow removal kinetics toward ReO_4^- anions (Appendix Figure 4.23). *i*POP-5(S) exhibited nearly 73% removal within 1 min, while ~86% capture was found within 5 min (Figure 4.4b).



Scheme 4.1: Schematic representation of ultrafast removal of toxic Cr(VI) and Re(VII) oxoanions from water by *i*POP-5(F)

In line with CrO_4^{2-} capture, this result also demonstrated ultrafast sequestration of ReO_4^- oxoanion by *i*POP-5(F) and relatively slow kinetics by *i*POP-5(S). This enhancement in the sorption kinetics by *i*POP-5(F) than *i*POP-5(S) might be attributed to the easily accessible adsorption sites of the sheet like structure of *i*POP-5(F) (Scheme 4.1), resulting in greater electrostatic, H-bonding, and π - π interactions with oxoanions. ^[42] Moreover, with the added advantage of high dispersity with excellent ζ potential

value, iPOP-5(F) exhibited high removal efficiency (Appendix Figure 4.24). In addition, the ReO_4^- capture study with both iPOP-5(F) and iPOP-5(S) was found to be following pseudo second order kinetics with a relatively higher rate constant value for iPOP-5(F) than iPOP-5(S) (Appendix Figure 4.25). Such fast ion-exchange kinetics by iPOP-5(F) promotes this material as a promising oxoanion-exchanger for the continuous treatment of diluted, mild polluted water. Thereafter, inspired from the ultrafast oxoanion removal kinetics by iPOP-5(F), the sorption isotherms of the compound were determined. The plotted results between the capacities of the materials as a function of its concentration at the equilibrium state indicated that both the CrO_4^{2-} and ReO_4^- capture processes by iPOP-5(F) follow the Langmuir isotherm model with correlation coefficient values ($R^2 = 0.99$ for CrO_4^{2-} and $R^2 = 0.97$ for ReO_4^-) (Figures 4.5c and Appendix Figure 4.26). The maximum capacities of iPOP-5(F) for CrO_4^{2-} and ReO_4^- anions were found as ~ 301 and $\sim 610 \text{ mg g}^{-1}$, respectively, which position iPOP-5(F) as the material with high uptake capacity values in the domain of porous adsorbents (Appendix Table 4).

Contaminated industrial wastewater contains various competitive anions, such as NO_3^- , SO_4^{2-} , Cl^- , Br^- , ClO_4^- and so forth, in large excess coexisting with metal-based oxoanions. In the literature, significant attention has been devoted in order to elucidate the working capacities and removal rate to most of the adsorbents. However, the ability of the adsorbent to competitively maintain the efficiencies and fast extraction kinetics in the presence of excessive interfering anions is rarely explored. Keeping this in mind, encouraged by the high uptake capacities and rapid removal performance of iPOP-5(F), we performed the capture study of CrO_4^{2-} and ReO_4^- in the presence of 100-fold excess concentration of various coexisting interfering anions. Interestingly, iPOP-5(F) showed almost identical sequestration efficiency toward both CrO_4^{2-} and ReO_4^- oxoanions in water containing a mixture of large excessive (~ 100 -fold) interfering anions, exhibiting negligible dependency of other competing anions (Figures 4.5d, Appendix Figure 4.27 and Appendix Table 1 and 2).

In addition to this, maintaining excellent removal efficacy in a wide pH range is another important criterion for an efficient adsorbent as the pH of real wastewater can vary in various ranges. Therefore, the capture experiment by iPOP-5(F) in a wide range of pH was performed, and the material exhibited decent removal efficiency toward both CrO_4^{2-} and ReO_4^- in alkaline and acidic mediums (Appendix Figure 4.28 and Appendix Figure 4.29). Further, the recyclability of iPOP-5(F) was evaluated for both oxoanions using a saturated solution of tetrabutylammonium bromide. Notably, it was found that iPOP-5(F) exhibited superior regeneration ability up to four cycles for both respective oxoanions (Figures 4.5e and Appendix Figure 4.30). Moreover, inspired by this unprecedented removal efficiency in terms of both fast kinetics and selective capture of CrO_4^{2-} and ReO_4^- ions, iPOP-5(F) was further employed for the treatment of different water samples [tap, lake, river, sea, and tannery (for CrO_4^{2-} only) water contaminated with respective oxoanions in the presence of 100-times higher concentration of other

anions (NO_3^- , SO_4^{2-} , Cl^- , Br^- , and ClO_4^-). Remarkably, iPOP-5(F) was found to be a potential scavenger in spite of having large excess of competitive anions, and iPOP-5(F) exhibited superior removal efficiency for all different water samples (Figures 4.5f and Appendix Figure 4.31). This result demonstrated the efficacy of iPOP-5(F) for real-life water treatment.

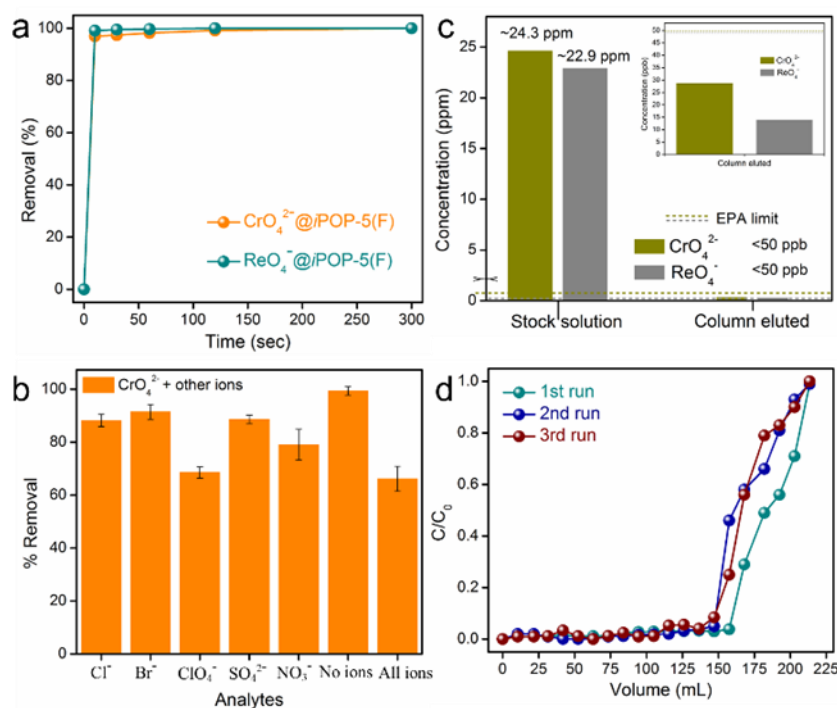


Figure 4.6 (a) Percentage removal of low-concentration (~ 1000 ppb) Cr(VI) and Re(VII) anions at different contact time by iPOP-5(F). Condition: $[\text{Cr}]_{\text{initial}} \sim 983$ ppb, $[\text{Re}]_{\text{initial}} \sim 1017$ ppb and $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L. (b) Selectivity of iPOP-5(F) towards low-concentration (~ 1000 ppb) Cr(VI) capture in presence of other anions. Condition: $[\text{Cr}]_{\text{initial}} \sim 983$ ppb, $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L and contact time = 2 h. (c) ICP-MS analysis of Cr(VI) and Re(VII) before and after passing through the column. Condition: $[\text{Cr}]_{\text{initial}} \sim 24.3$ ppm, $[\text{Re}]_{\text{initial}} \sim 22.9$ ppm $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L. (d) Breakthrough plots for three column exchange runs for Cr(VI) removal experiment. Condition: $[\text{Cr}]_{\text{initial}} \sim 25$ ppm, $m_{\text{sorbent}} = 100$ mg, $m_{\text{sand}} = 5$ gm and flow rate = 0.5 ml/min.

In addition, for practical utilization of an adsorbent, along with high concentration, the material should be able to remove the trace amount of pollutant below the EPA standards for oxoanions in drinking water from a low-concentration, contaminated water sample. To check this, we performed the CrO_4^{2-} and ReO_4^- capture study by iPOP-5(F) with very low concentration (~ 1000 ppb) and monitored through

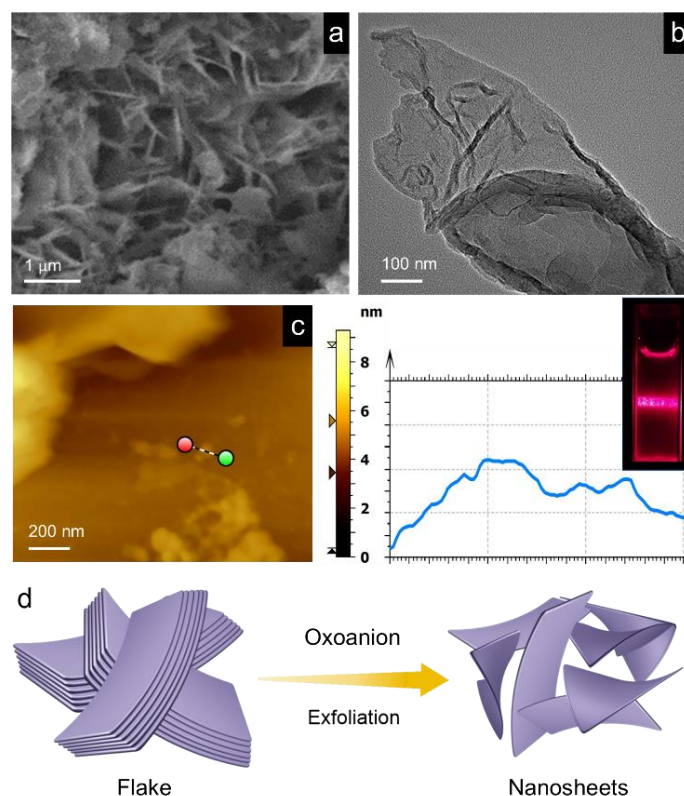


Figure 4.7. (a) FESEM, (b) TEM, (c) AFM image with height profile, of nanosheets (inset: Tyndall effect). (d) Schematic representation of nanosheets formation from flake morphology.

inductively coupled plasma-mass spectrometry (ICP-MS) analysis. From the removal efficiency with the time interval result, it was observed that iPOP-5(F) successfully reduced the concentration of both CrO_4^{2-} and ReO_4^- oxoanions rapidly less than 50 ppb, which is below the EPA standards (Figure 4.6a).^[4, 20] Moreover, the selective removal of trace (~ 1000 ppb) oxoanions in the presence of other aforementioned interfering anions at ~ 100 -fold excess amount was performed. The concentration of both CrO_4^{2-} and ReO_4^- decreased rapidly to much below the WHO permitted level, and it revealed the selectivity of iPOP-5(F) toward oxoanions even at a very low concentration (Figures 4.6b and Appendix Figure 4.32a). Furthermore, encouraged by the fastest sequestration efficiency with superior selectivity toward respective oxoanions by iPOP-5(F) in both high and low concentrations, chromatographic column exchange-based Cr(VI) and Re(VII) contaminated wastewater treatment experiments were performed. Considering the real-time application, the column was packed with iPOP-5(F) and further treated with ~ 25 ppm aqueous solution of Cr(VI) ions along with ~ 100 -fold excess other anions (Appendix Figure 4.32) (see the Experimental part for details). Instantly, while passing through the material, the light yellow color of Cr(VI) solution became colorless, indicating rapid entrapment of

Cr(VI) ions by iPOP-5(F) embedded with the column (Appendix Figure 4.32b). In addition, the results showed that the concentration of Cr(VI) of the column-eluent (calculated from ICP-MS studies) was found to be much below (less than 50 ppb) the permitted drinking water level (Figure 4.6c).^[4, 20] In detail, a ~25 ppm stock solution of Cr(VI) with a bed volume of ~3.5 mL was passing through the column in the first cycle, among which, up to ~154 mL effluent volumes showed negligible Cr(VI) content (Figure 4.6d). Thereafter, for the next two cycles of treatment, the column was regenerated by passing a saturated solution of tetrabutylammonium bromide. Again, both the second and third runs indicated near similar capture performance as the initial Cr(VI) treatment run. Along with this, identical observation was observed in the case of capture of ReO_4^- anion (Figure 4.6d). This excellent iPOP-5(F)-column-based Cr(VI) and Re(VII) capture results indicated the practical utility of the material toward real-time applications. Given the high, ultrafast, and selective oxoanion (Cr and Re) removal kinetics of iPOP-5(F), we sought to investigate the mechanism by both experimental and theoretical insights behind this efficient capture performance. At first, for the experimental understanding, the FT-IR spectra of the solid compound after the oxoanion capture experiment indicated the prominent stretching frequencies of Cr-O (~950 and ~770 cm^{-1}) and Re-O (~902 cm^{-1}) (Appendix Figure 4.33).^[24, 43, 44] Concomitantly, retention of all relevant sharp bands in the FT-IR spectra further demonstrated structural robustness with no deformation of network integrity of iPOP-5(F) (Appendix Figure 4.33). In addition, the TGA profile of oxoanion-treated compounds indicated identical thermal behavior with the pristine compound (Appendix Figure 4.34). Notably, solid-state UV-vis analysis of post capture samples exhibited observable peaks for the oxoanions (Appendix Figure 4.35). The SEM-EDS mapping images of Cr(VI)- and Re(VII)-treated samples revealed the homogeneous distribution of relevant elements throughout the polymeric network of iPOP-5(F) (Appendix Figures 4.36 and 4.37). All these results validated the efficient trapping of both the oxoanions by the compound. Thereafter, in order to investigate the morphological changes of the compound after capture study, FESEM, TEM, and AFM analyses were performed. From the FESEM analysis, it was found that after the oxoanion (Cr and Re) removal experiment, the flakelike morphological compound [iPOP-5(F)] changes into ultrathin nanosheets (Figure 4.7a). Again, TEM images of oxoanion-treated iPOP-5(F) affirmed the ultrathin nanosheet-like uniform morphology in agreement with the SEM data (Figure 4.7b). Moreover, topographic AFM images exhibited nanosheet morphology with an average thickness of ~3.5 nm, which demonstrated the easy, facile, and complete exfoliation of flake compounds to the thin nanosheets (Figure 4.7c). Again, the so-formed compound exhibited Tyndall effect, thereby indicating the colloidal nature of the nanosheets [Figure 4.7c (inset)].^[45] All these observations indicate that iPOP-5(F) undergoes exfoliation to form an ultrathin nanosheet morphology from flake like morphology upon metal-based oxoanion treatment (Figure 4.7d). Such in situ exfoliation of iPOP-5(F) into nanosheets further exposed greater interactive sites for enhanced strong electrostatic interaction between the

cationic host and the anionic metal oxoanions, which are attributed to the ultrafast capture efficiency toward oxoanions in water. [46]

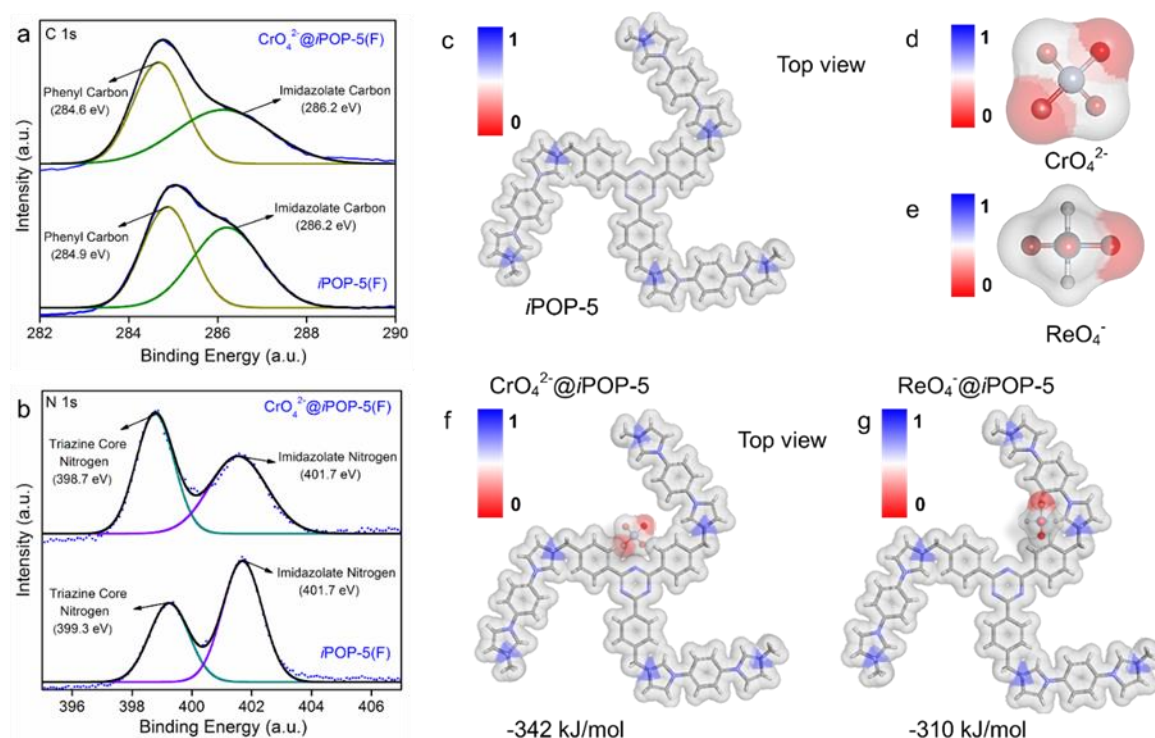


Figure 4.8 XPS and DFT analysis. (a, b) XPS spectra of carbon and nitrogen atom, respectively, of iPOP-5(F) after interaction with Cr(VI). Electrostatic potential (ESP) distributions on the van der Waals surfaces of [(isodensity = 0.001 a.u.) calculated using DFT-DMOL3-B3LYP] (c) fragment of iPOP-5, (d) CrO₄²⁻ and (e) ReO₄⁻, respectively. Optimized complex fragment structure of iPOP-5 with (f) CrO₄²⁻ (g) ReO₄⁻ with corresponding binding energies.

Moreover, in order to elucidate the interaction between the positively charged imidazolium-based backbone and oxoanions, XPS analysis was carried out. The full XPS survey spectra of oxoanion-treated samples consisted of distinctive Cr 2p and Re 4f binding energy peaks, suggesting the presence of Cr and Re on the surface of iPOP-5(F) (Appendix Figure 4.38). [39, 44] The high resolution XPS spectra of Cr 2p and Re 4f confirmed the existence of Cr and Re in their +6 and +7 oxidation states, respectively (Appendix Figure 4.39 and 4.40). Further, Cr(VI) 2p was found to shift from higher to lower binding energy compared to pristine K₂CrO₄, which clearly pointed out the strong electrostatic interaction between the cationic network and these oxoanions. The binding energy peaks of C 1s and N 1s for phenyl groups and the triazine core, respectively, shifted to a lower energy region in the high-magnified XPS spectra, revealing that CrO₄²⁻ exclusively interacts with the hydrophobic triazine core of the

framework (Figure 4.8a, b). This result clearly pointed out that the strong electrostatic interaction between the cationic network and oxoanions was responsible for ultrafast removal efficiency. Furthermore, to explain the selective rapid sequestration, we carried out DFT studies to gain further insights into the experimental observations. The DFT simulation was performed considering a single polymeric network (Figure 4.8c). The geometry-optimized structures for a minimized unit of iPOP-5 with CrO_4^{2-} and ReO_4^- revealed crucial insights regarding the binding sites (Figure 4.8d-g). The electrostatic potential (ESP) distribution of iPOP-5 shows the presence of energy maxima and minima sites favourable for interaction with other iPOP-5 units and analytes. The simulation reveals key supramolecular noncovalent interactions comprising hydrogen bonding interactions and van der Waals interactions that afforded stabilization of CrO_4^{2-} and ReO_4^- analytes. Interestingly, the binding energies for CrO_4^{2-} and ReO_4^- analytes within the geometry-optimized unit of iPOP-5 were quite significant, which elucidates the exceptional affinity and uptake competency. The binding energy value for iPOP-5 with CrO_4^{2-} and ReO_4^- was observed to be - 4.37 and - 3.72 eV, respectively. Further, we also assessed the binding energy of interaction between iPOP-5 and different competing ions such as NO_3^- , SO_4^{2-} , ClO_4^- , and Br^- (Appendix Figures 4.41-4.43). Remarkably, the binding energy for the interaction between iPOP-5 and CrO_4^{2-} and ReO_4^- was at a relatively higher end as compared to other competing ions, thereby corroborating the experimental selectivity. Overall, simulation data endorse our experimental findings and support our understanding about the observed selective and competent capture performance by iPOP-5 toward CrO_4^{2-} and ReO_4^- .

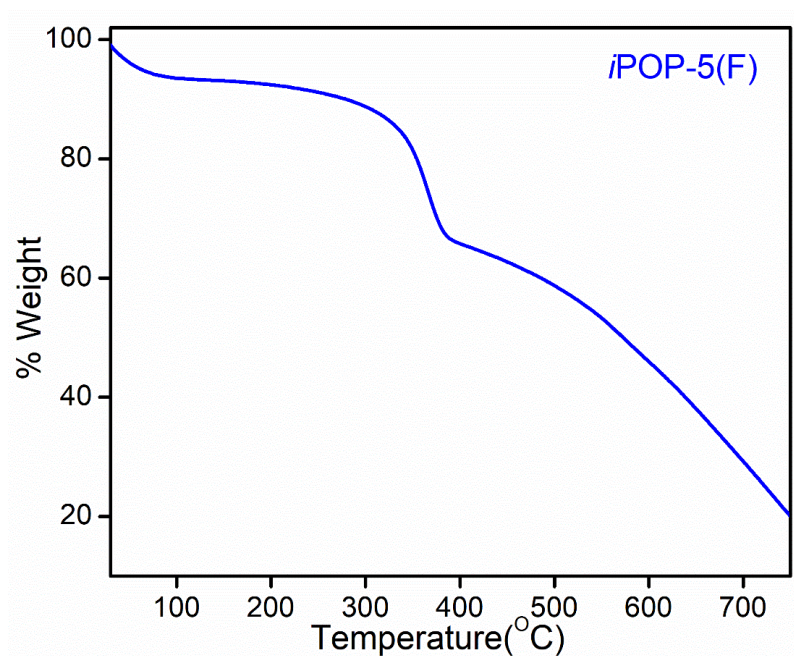
4.5 Conclusion

In conclusion, various morphologies of an imidazolium-based cationic polymer (iPOP-5) were strategically synthesized by finely controlling the duration of the reaction. Detailed morphological investigation of iPOP-5 demonstrated the time-dependent evolution of flake morphology from the spherical one. Further, owing to the highly stable cationic surface with the presence of free exchangeable Br^- ions, a comparative morphology-based study for detoxification of Cr(VI) and Re(VII) oxoanion-contaminated water was performed by both the flake- and spherical-shaped polymers. Among them, flakelike polymer, iPOP-5(F), exhibited ultrafast removal efficiency toward both Cr(VI) and Re(VII) with high exchange capacities, whereas spherical morphology-based polymer [iPOP-5(S)] exhibited relatively slow removal efficiencies. This finding demonstrated the critical role of morphologies upon the sequestration kinetics of oxoanions in water. Notably, iPOP-5(F) exhibited highly selective capture of CrO_4^{2-} and ReO_4^- in the presence of 100-fold other interfering anions from both high and low concentrations. Moreover, removal of respective oxoanions with high efficiencies

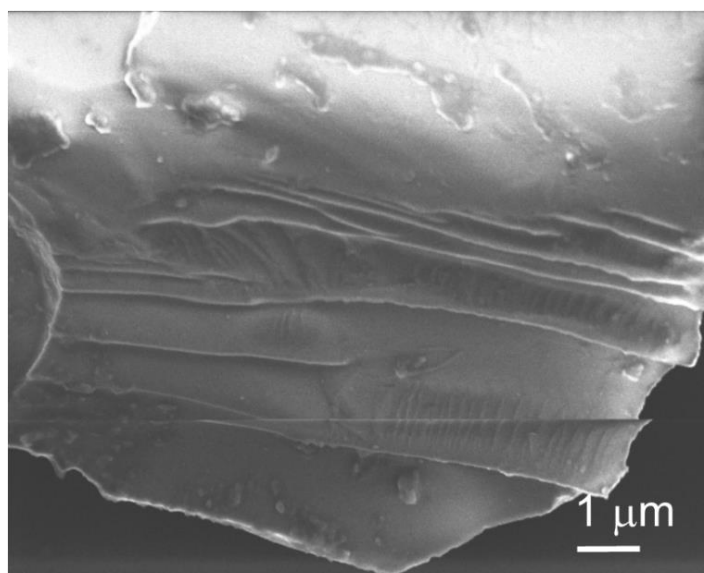
from different water systems, pH medium, being column exchange-based, and reusability manifested iPOP-5(F) as a propitious candidate for the remediation of wastewater. Mechanistic identification revealed in situ exfoliation of flakes into thin nanosheets of iPOP-5(F) upon oxoanion treatment, unveiling greater interactive sites for fastest sequestration of oxoanions in water. Further, theoretical insights validated the strong interaction between selective recognition moieties of iPOP-5 with oxoanions.

Appendix Section

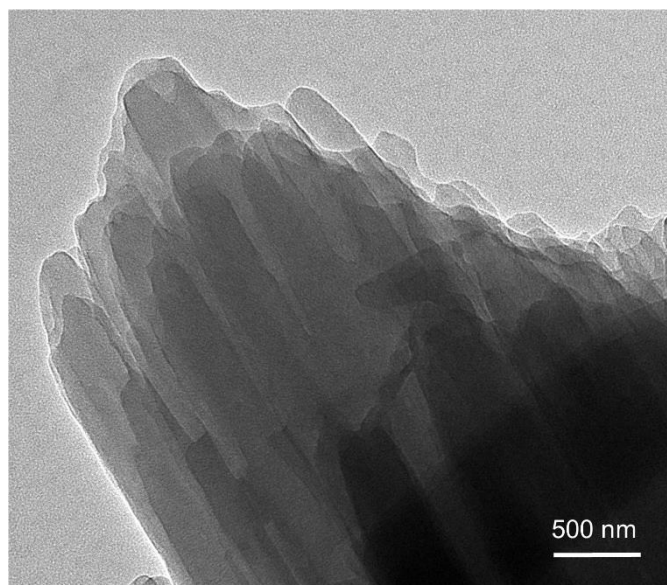
Appendix Section 1: Characterization of *i*POP-5(F) and *i*POP-5(S)



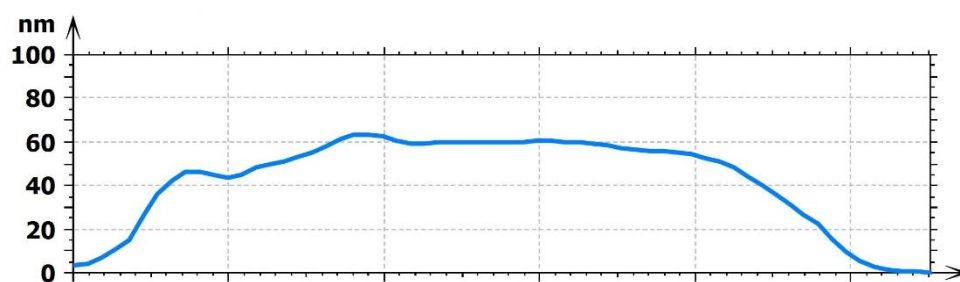
Appendix Figure 4.1: Thermogravimetric analysis of *i*POP-5(F).



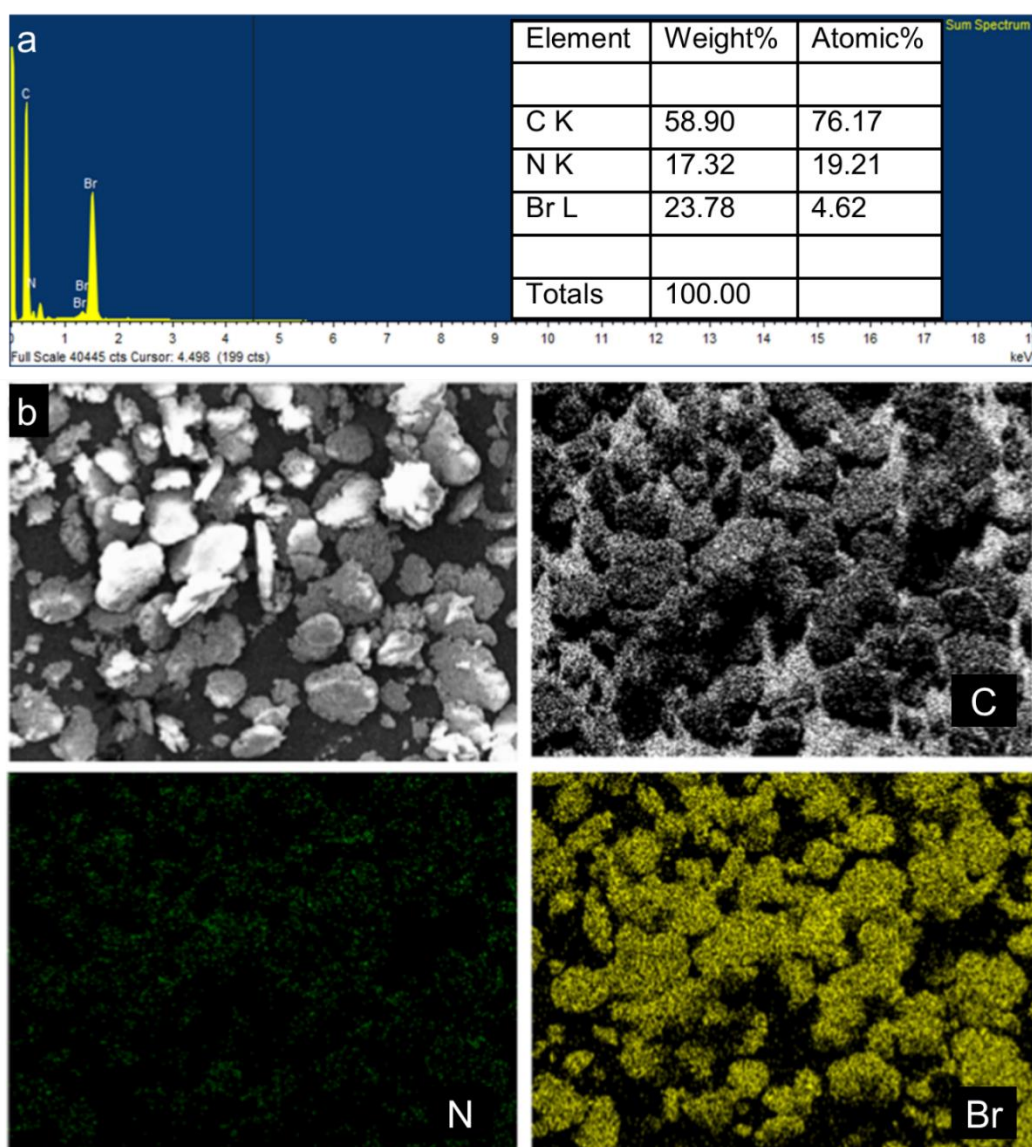
Appendix Figure 4.2: Additional FESEM image of *i*POP-5(F).



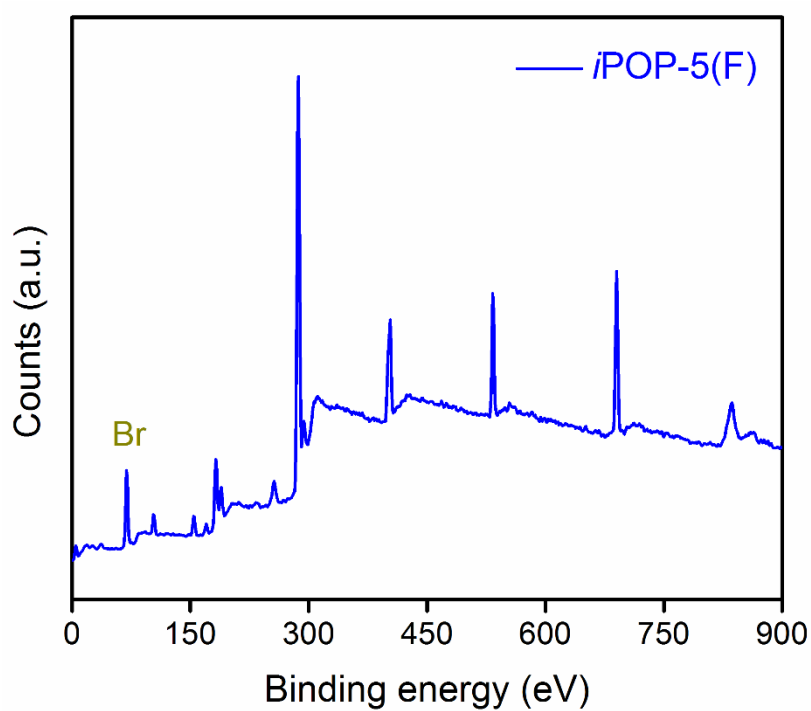
Appendix Figure 4.3: Additional TEM image of *iPOP-5(F)*.



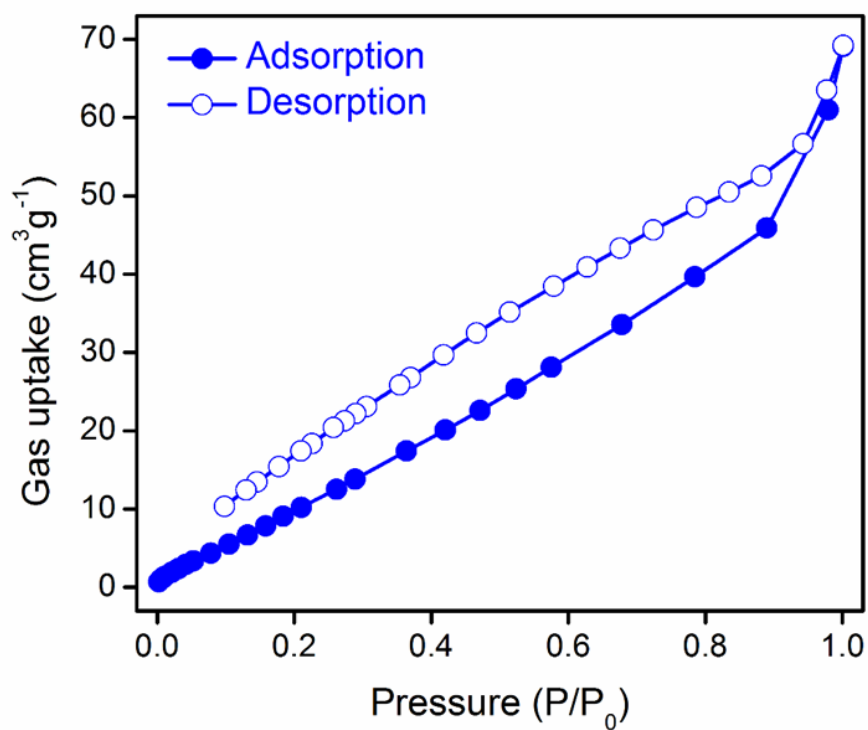
Appendix Figure 4.4: AFM height profile diagram of *iPOP-5(F)*.



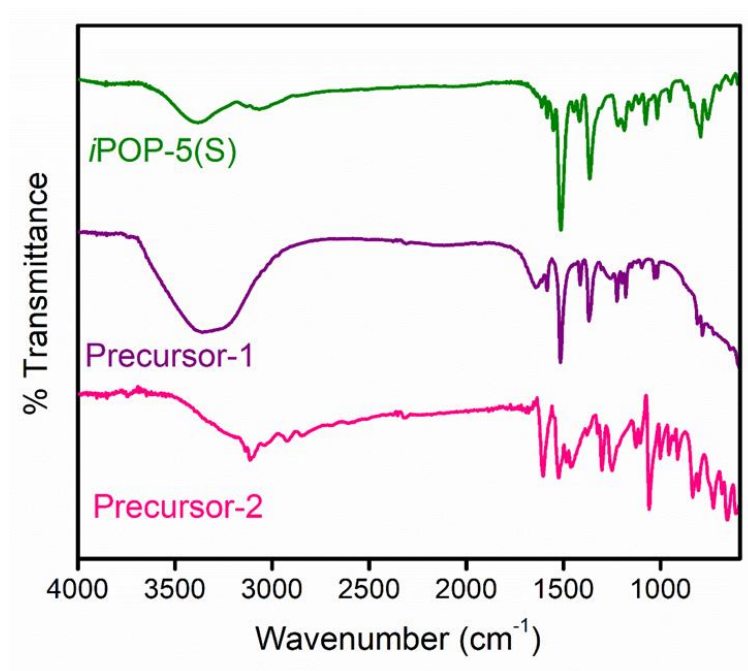
Appendix Figure 4.5: (a) FESEM-EDS data and (b) elemental mapping of *iPOP-5(F)*.



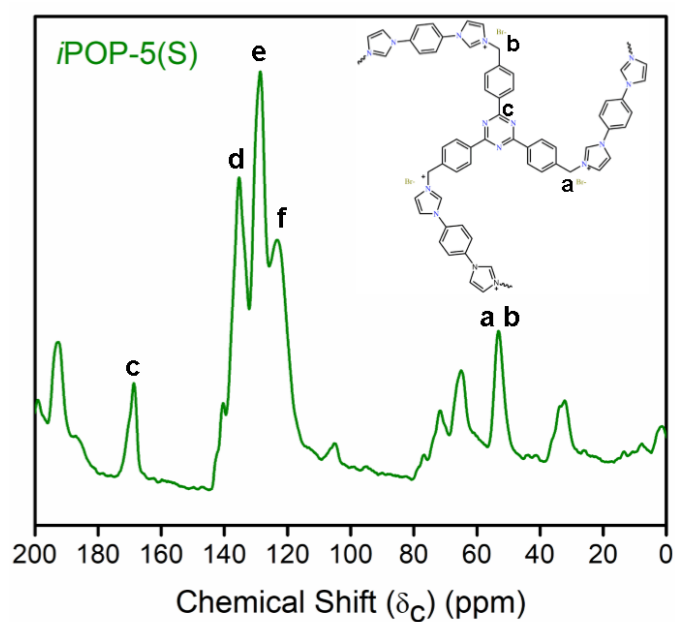
Appendix Figure 4.6: XPS Survey Spectra of iPOP-5(F)



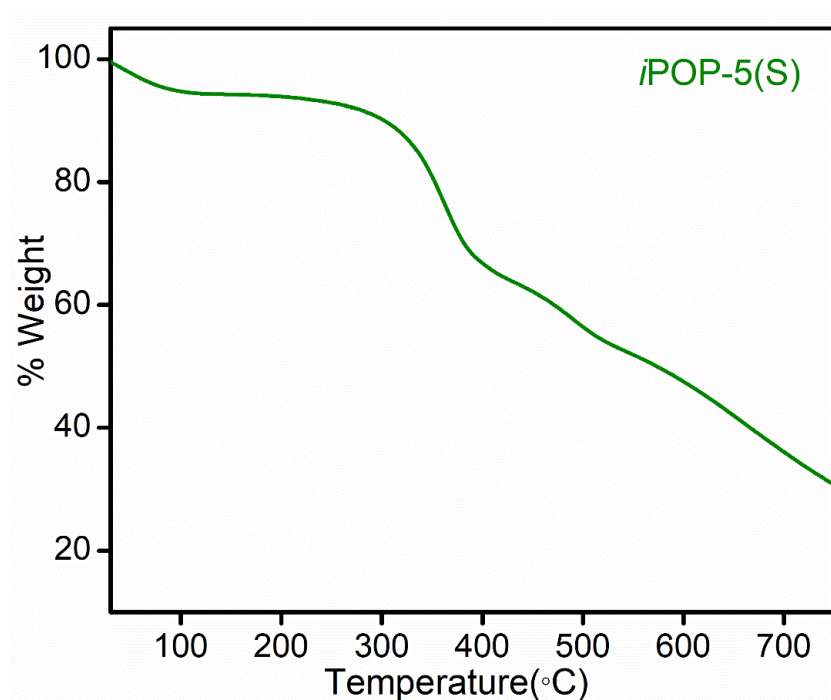
Appendix Figure 4.7: Nitrogen gas adsorption-desorption data at 77 K.



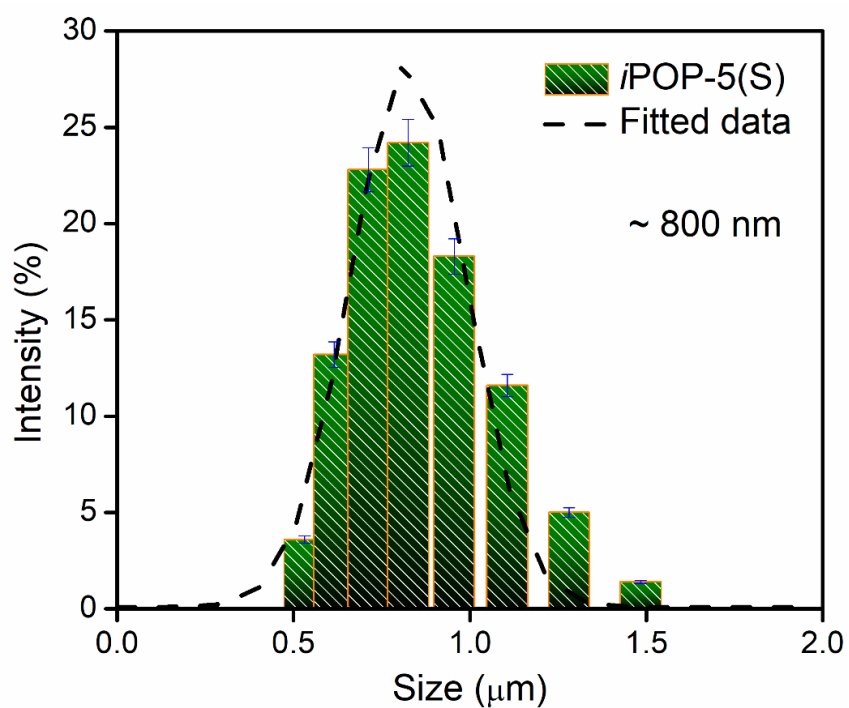
Appendix Figure 4.8: FTIR Spectra of *iPOP-5(S)*.



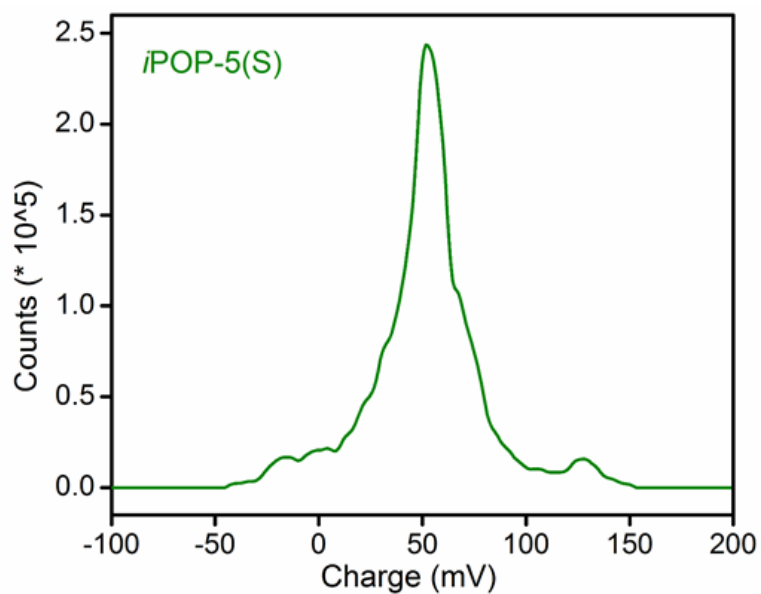
Appendix Figure 4.9: ¹³C solid-state NMR Spectra of *iPOP-5(S)*.



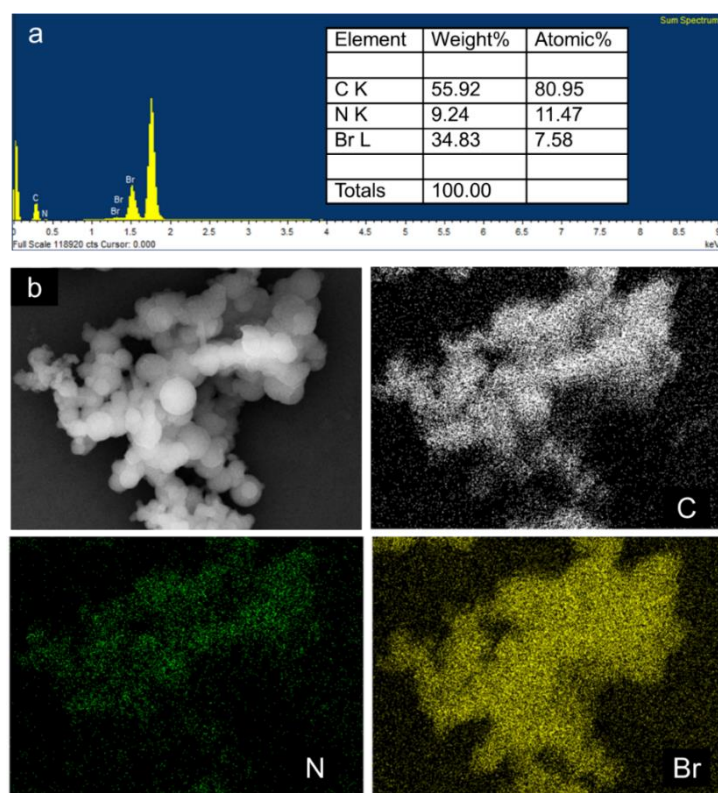
Appendix Figure 4.10: Thermogravimetric analysis of *iPOP-5(S)*.



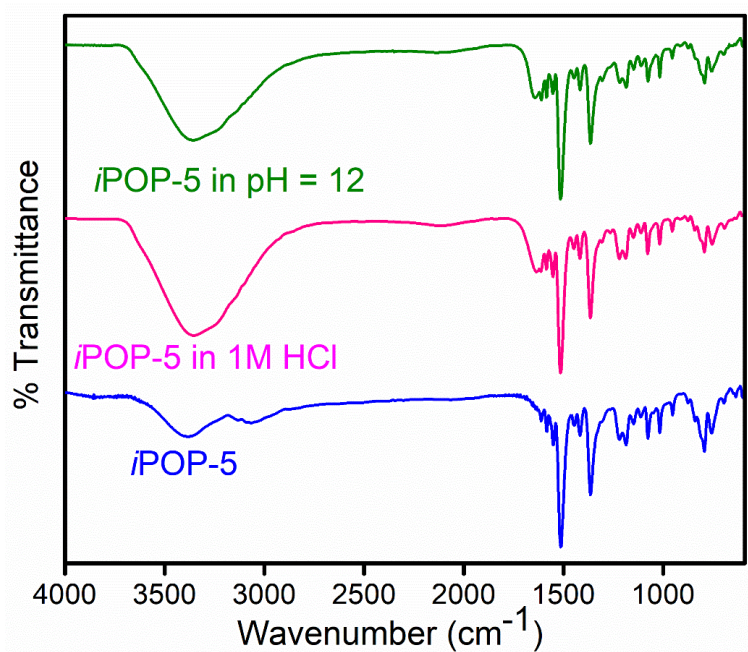
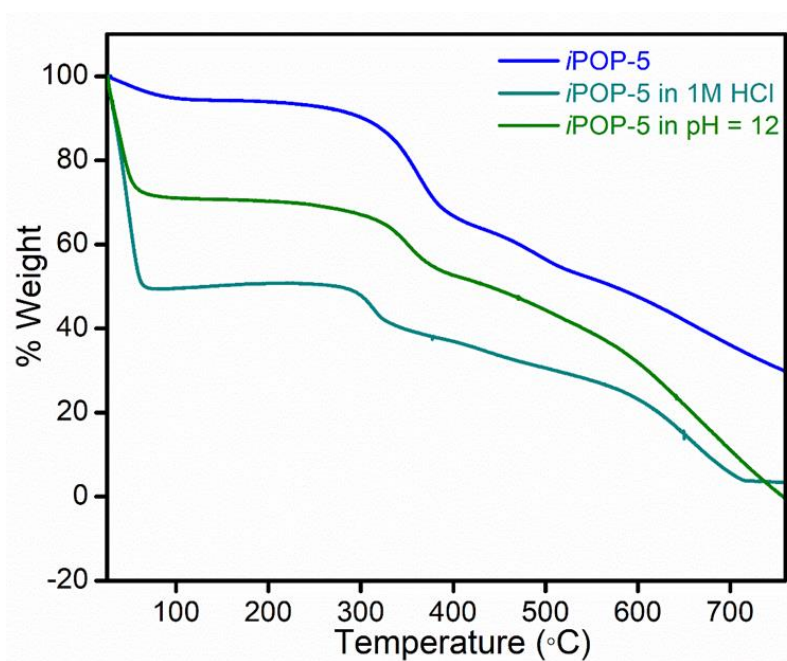
Appendix Figure 4.11: DLS analysis of *iPOP-5(S)*.

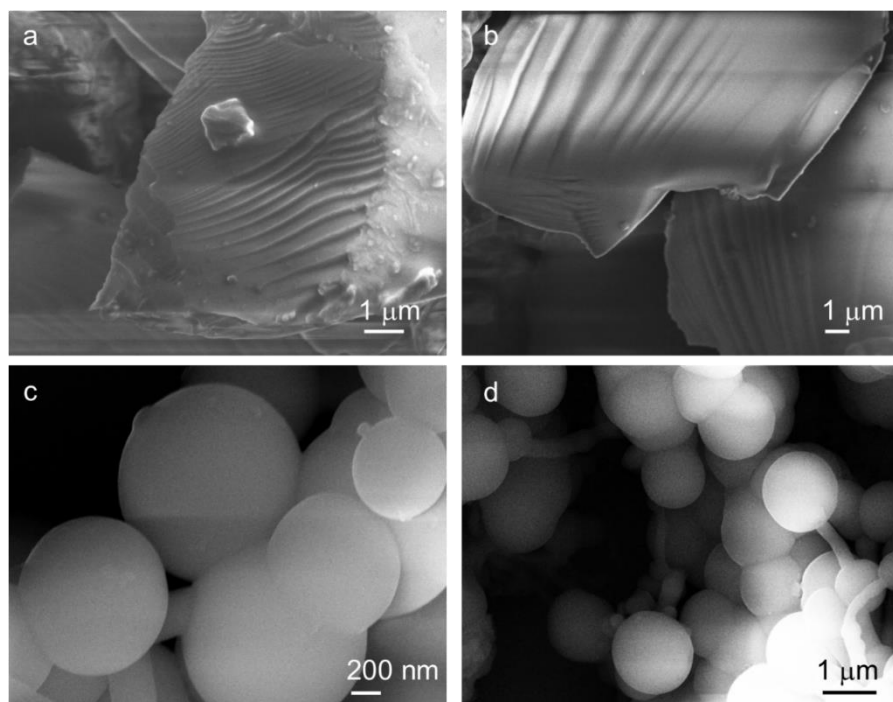


Appendix Figure 4.12: Zeta potential profile of iPOP-5(S)

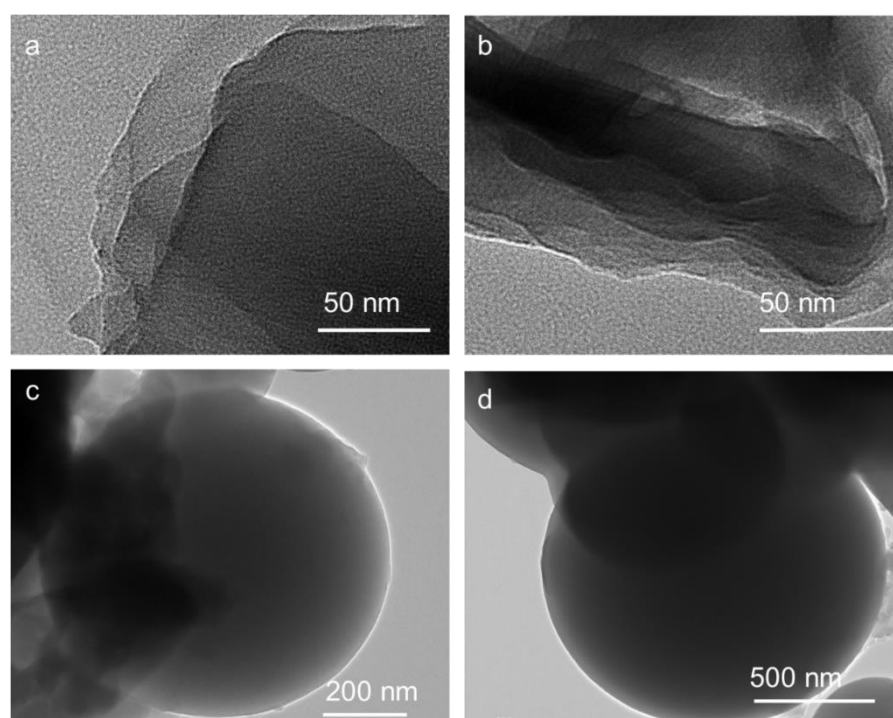


Appendix Figure 4.13: (a) FESEM-EDS data and (b) Elemental mapping of iPOP-5(S).

Appendix Section 2: Characterization of *i*POP-5(F) and *i*POP-5(S)Appendix Figure 4.14: FTIR spectra of *i*POP-5 in different pH solutionAppendix Figure 4.15: Thermogravimetric analysis of *i*POP-5 at different pH solution

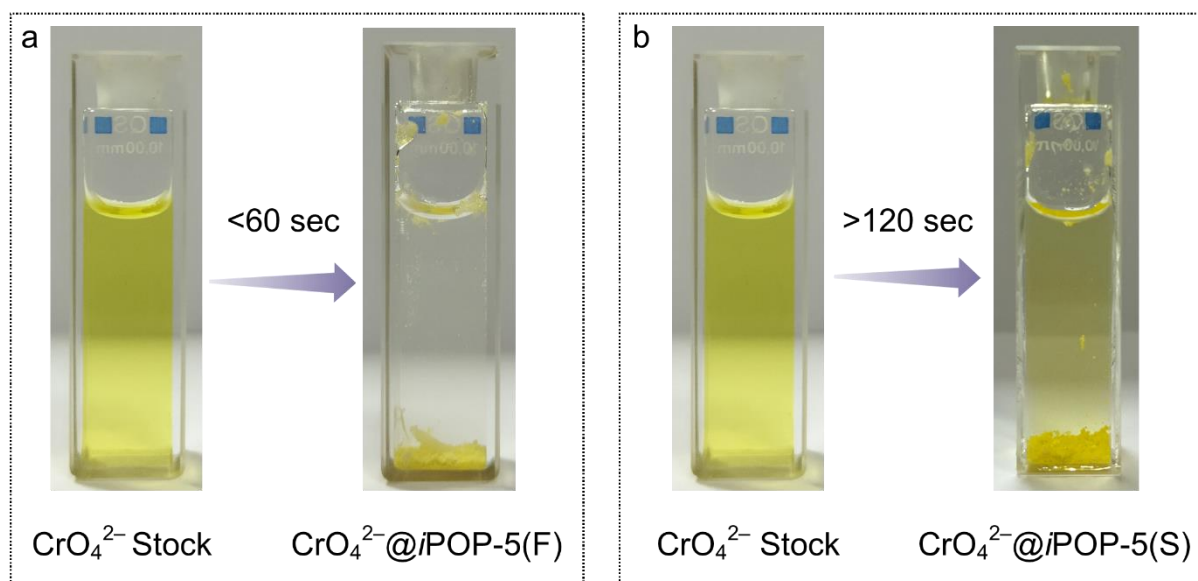


Appendix Figure 4.16: FESEM image of (a, c) acid and (b, d) base treated *iPOP-5(F)* and *iPOP-5(S)*, respectively.

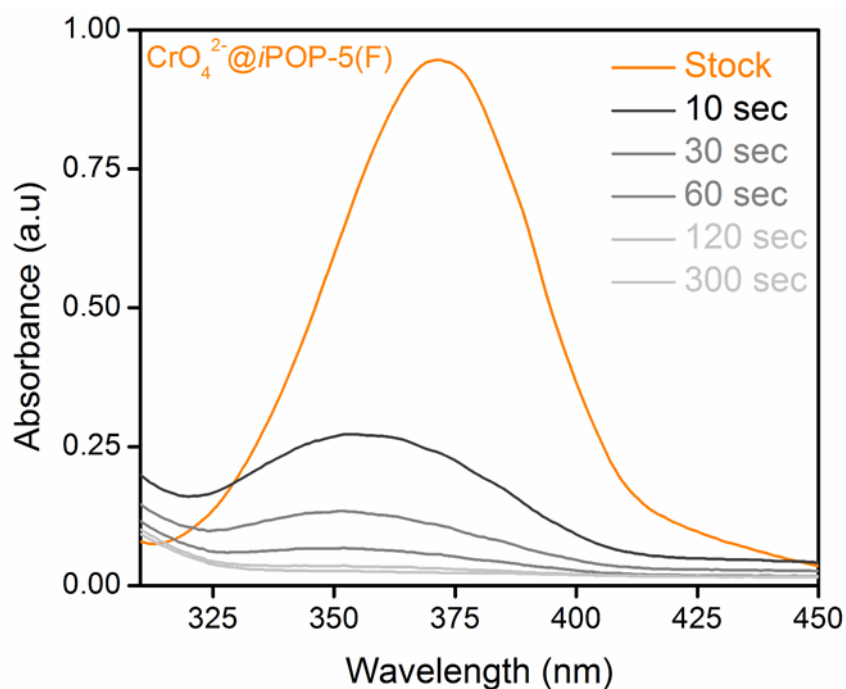


Appendix Figure 4.17: TEM image of (a, c) acid and (b, d) base treated *iPOP-5(F)* and *iPOP-5(S)*, respectively.

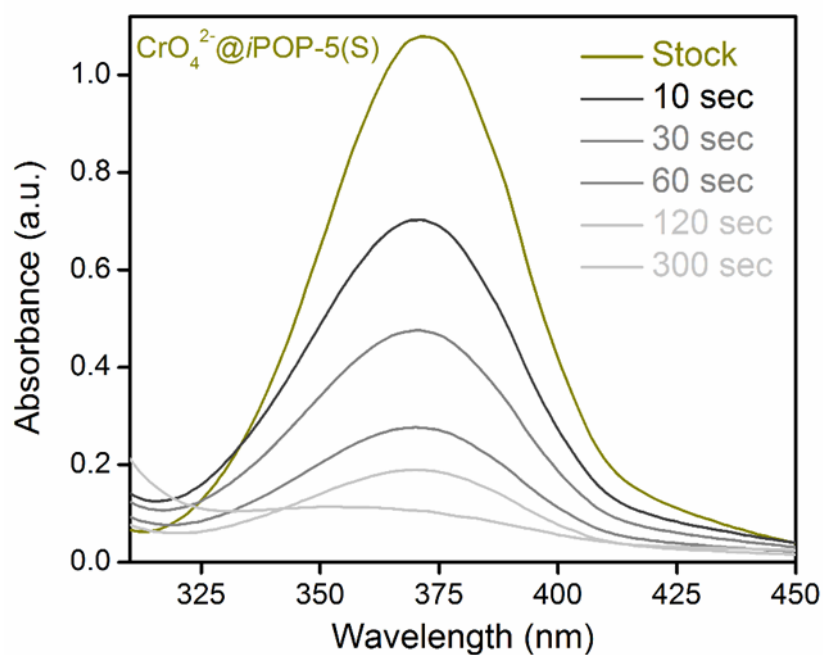
Appendix Section 3: Capture studies



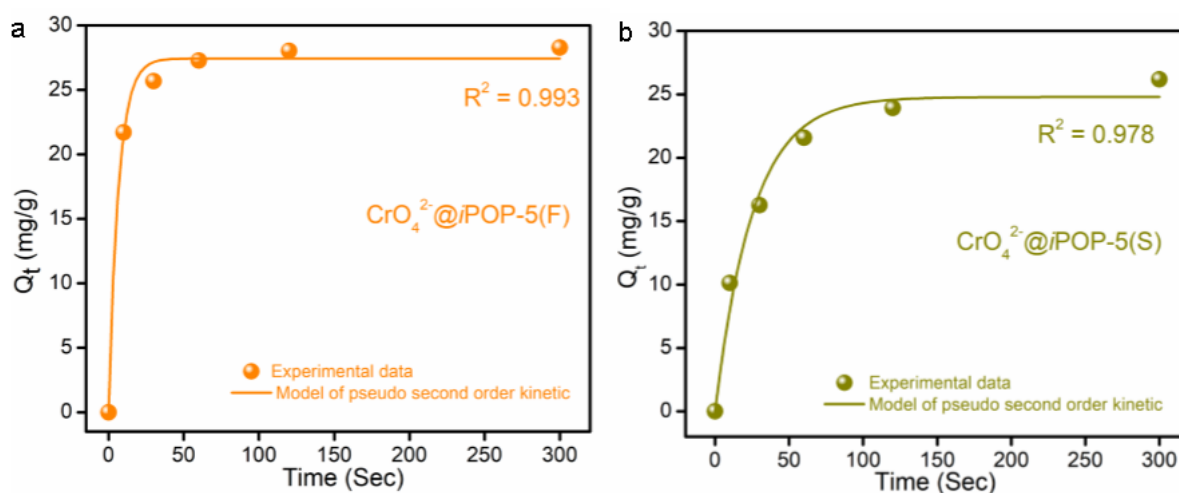
Appendix Figure 4.18: Digital images of decolorization of Cr(VI) aqueous solution by (a) iPOP-5(F) and (b) iPOP-5(S) .



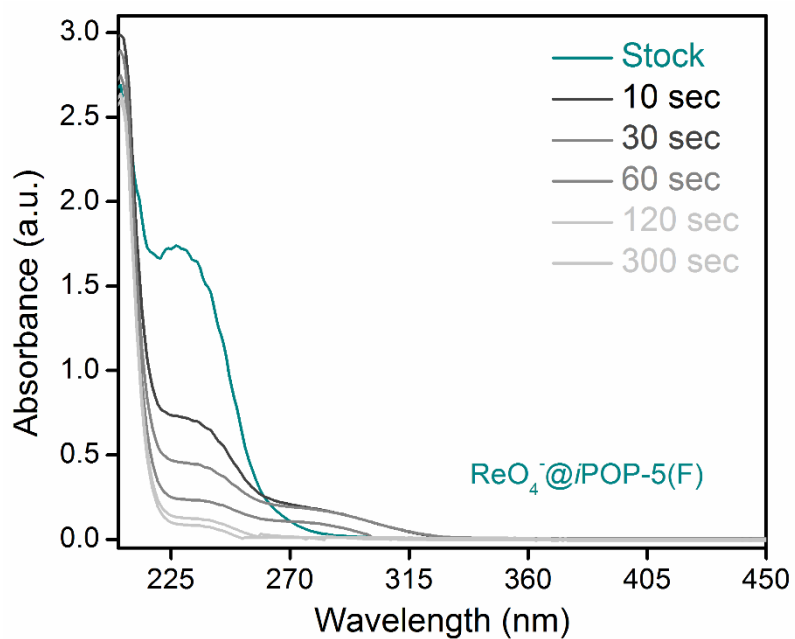
Appendix Figure 4.19: Decrease in UV-vis intensity of Cr(VI) aqueous solution by iPOP-5(F) .



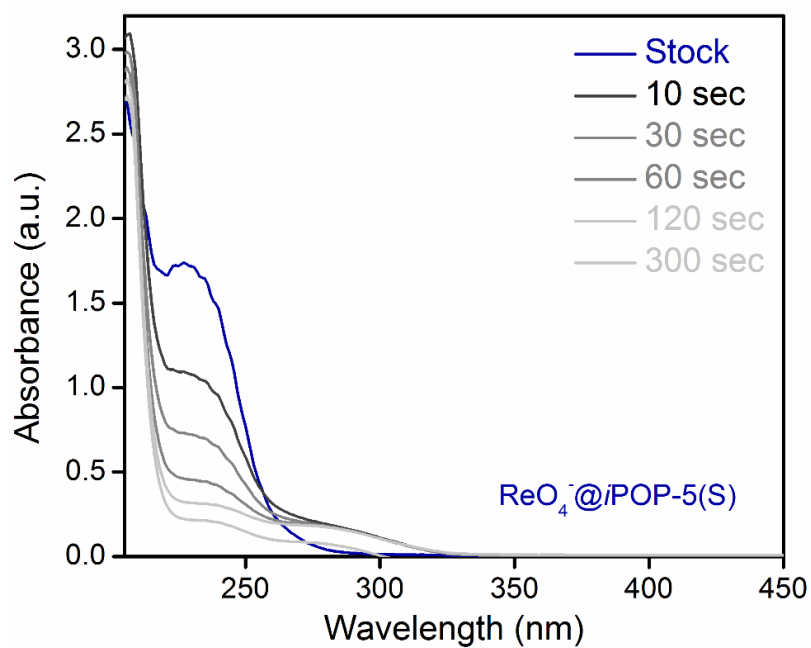
Appendix Figure 4.20: Decrease in UV-vis intensity of Cr(VI) aqueous solution by iPOP-5(S).



Appendix Figure 4.21: Pseudo-second order fitting curve of Cr(VI) aqueous solution by (a) iPOP-5(F) and (b) iPOP-5(S).



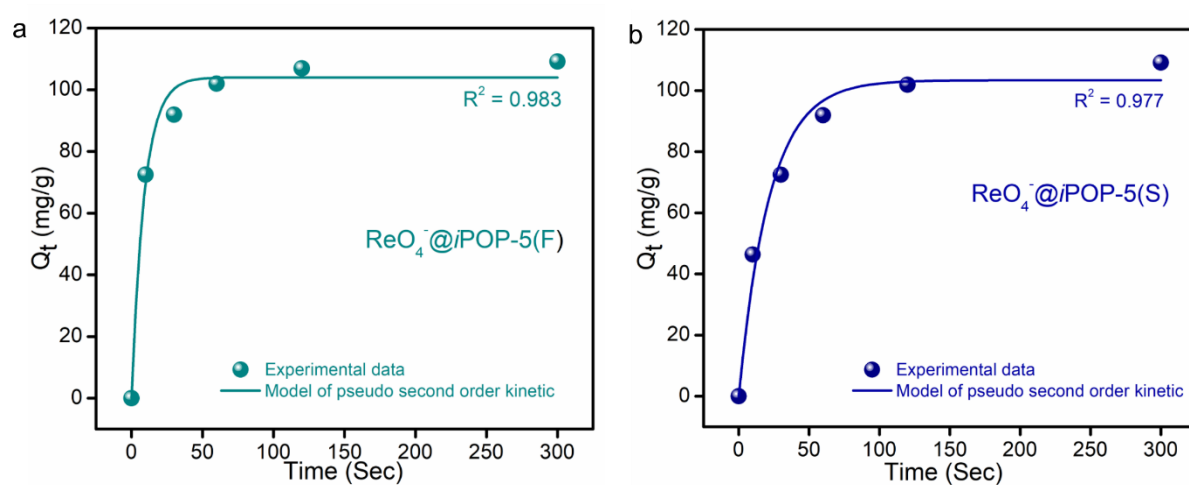
Appendix Figure 4.22: Decrease in UV-vis intensity of Re(VII) aqueous solution by *i*POP-5(F).



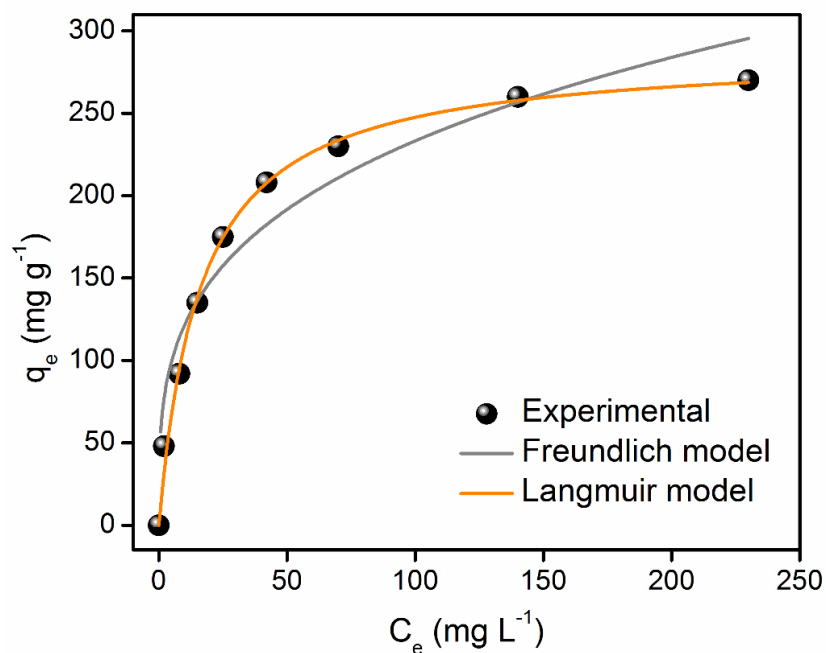
Appendix Figure 4.23: Decrease in UV-vis intensity of Re(VII) aqueous solution by *i*POP-5(S).



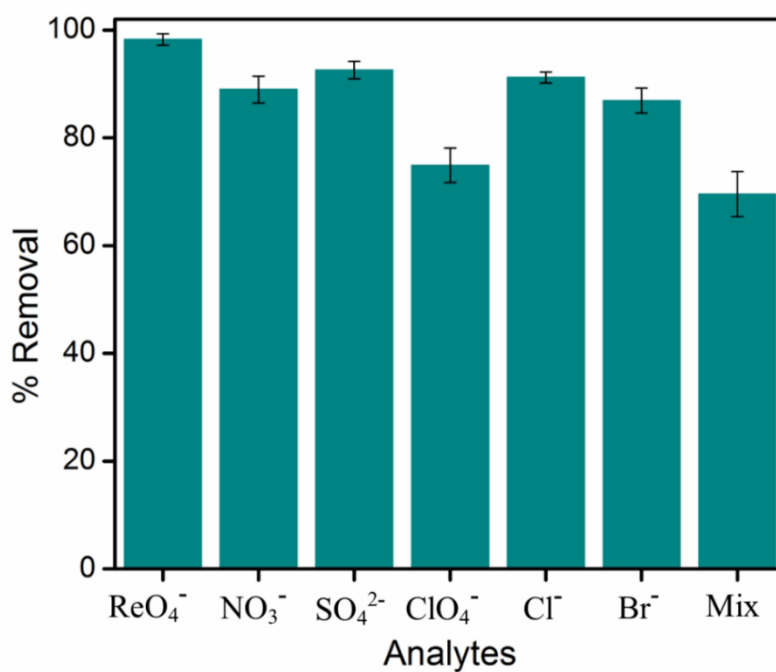
Appendix Figure 4.24: Dispersity of iPOP-5(F) in aqueous solution.



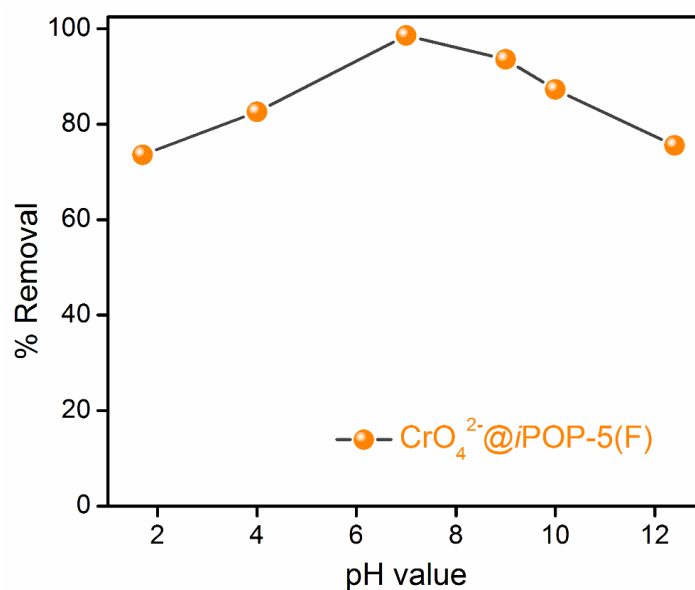
Appendix Figure 4.25: Pseudo-second order fitting curve of Re(VII) aqueous solution by (a) iPOP-5(F) and (b) iPOP-5(S).



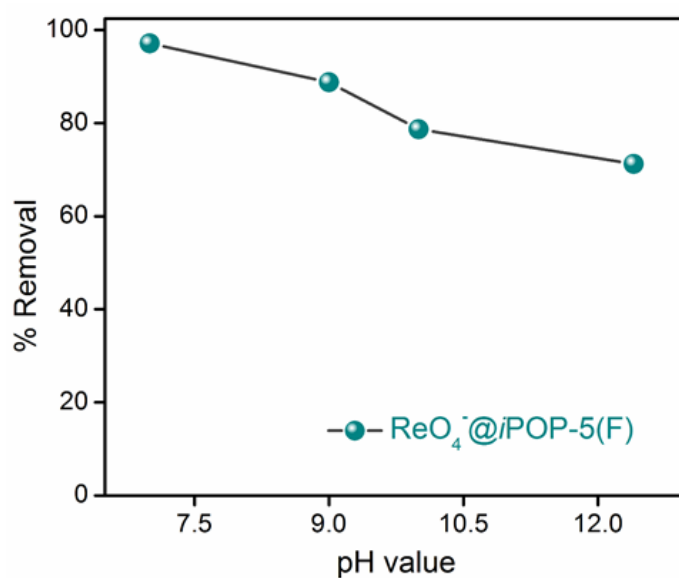
Appendix Figure 4.26: Isotherm fitting of Cr(VI) by iPOP-5(F). Condition: $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L and contact time = 24 h.



Appendix Figure 4.27: Removal efficiency of iPOP-5(F) towards ReO₄⁻ in presence of other anions. Condition: $[\text{Re}]_{\text{initial}} = 5$ mmol, $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L and contact time = 12 h.



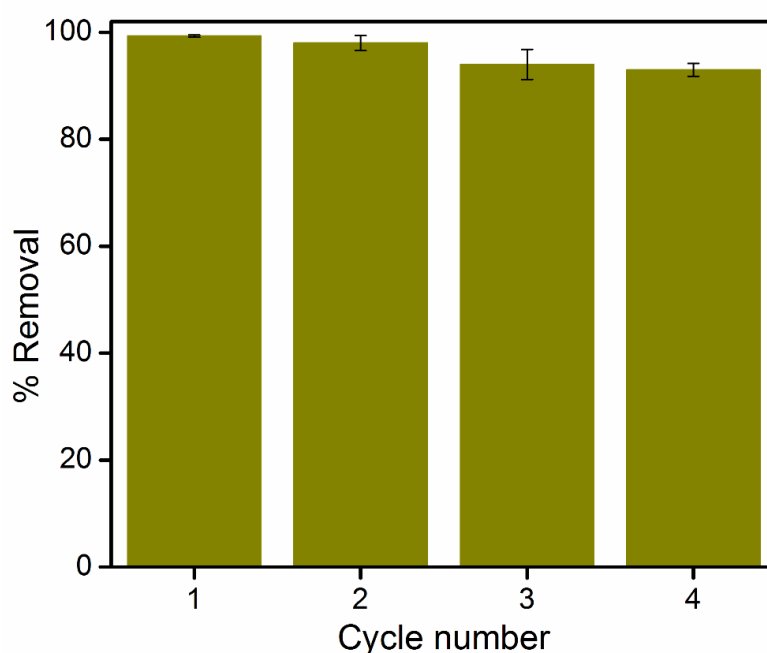
Appendix Figure 4.28: Removal efficiency of *iPOP-5(F)* towards CrO_4^{2-} in different pH



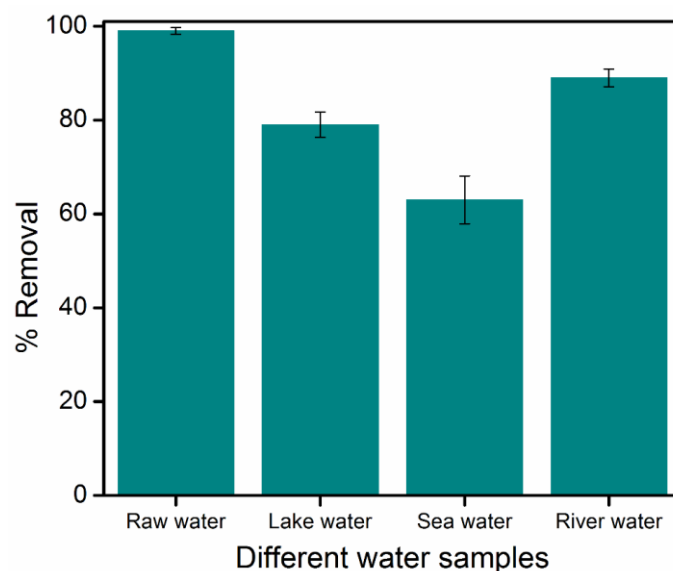
Appendix Figure 4.29: Removal efficiency of *iPOP-5(F)* towards ReO_4^- in different pH.

In the figure S28 and S29 the removal efficiency of the compound towards Cr/Re oxoanions capture in basic pH (from >8 to 12) was decreased from the maximum (99%). The probable reason behind such diminution in the capture performance might be cause of the presence of excess hydroxy (OH^-) group

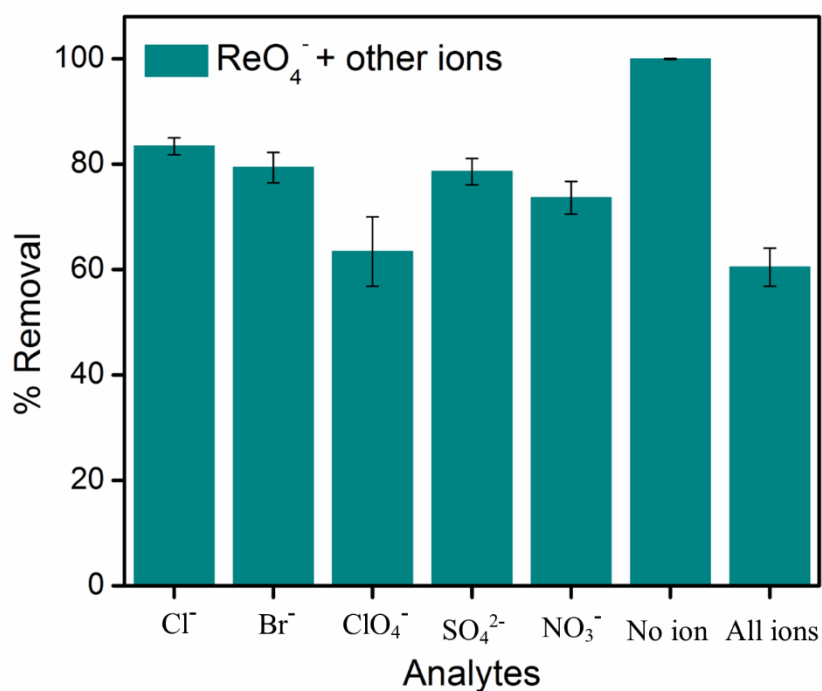
in basic pH, which act as a competing anion in aqueous medium towards target oxoanions of Cr(VI) and Re(VII). Similarly, in case of acidic pH (<6 to 2), the removal percentage of the compound was again decreased. This deduction in the capture efficiency might be due to the excess Cl^- ions in the solution, which generated strong competition with the CrO_4^{2-} anions in water. Therefore, due to the enhancement of the concentration of competing anions, either OH^- or Cl^- ions in the solution of respective pH, the capture performance was decreased by boosting the desorption process.



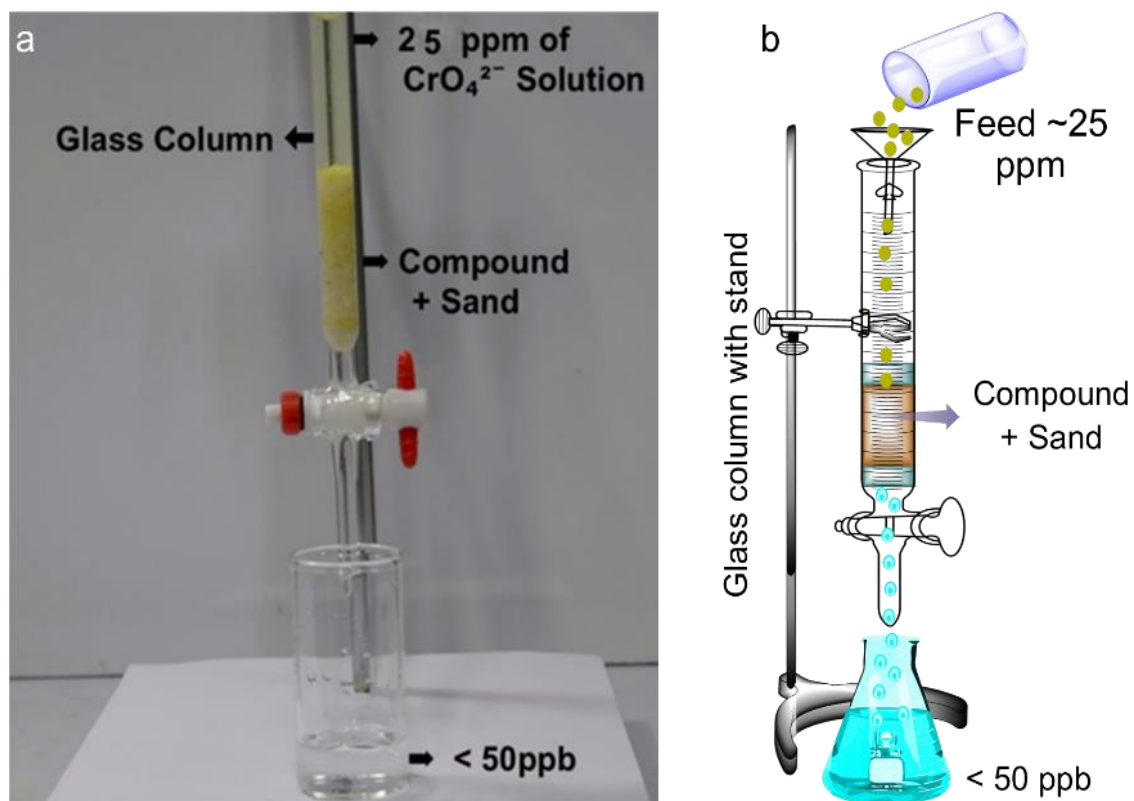
Appendix Figure 4.30: Recycle test of *iPOP-5(F)* for CrO_4^{2-} ion. Condition: $[\text{Cr}]_{\text{initial}} = 1 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 6 h.



Appendix Figure 4.31: Re(VII) removal efficiency by *iPOP-5(F)* in various water system. Condition: $[\text{Re}]_{\text{initial}} = 0.5 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 1 h.

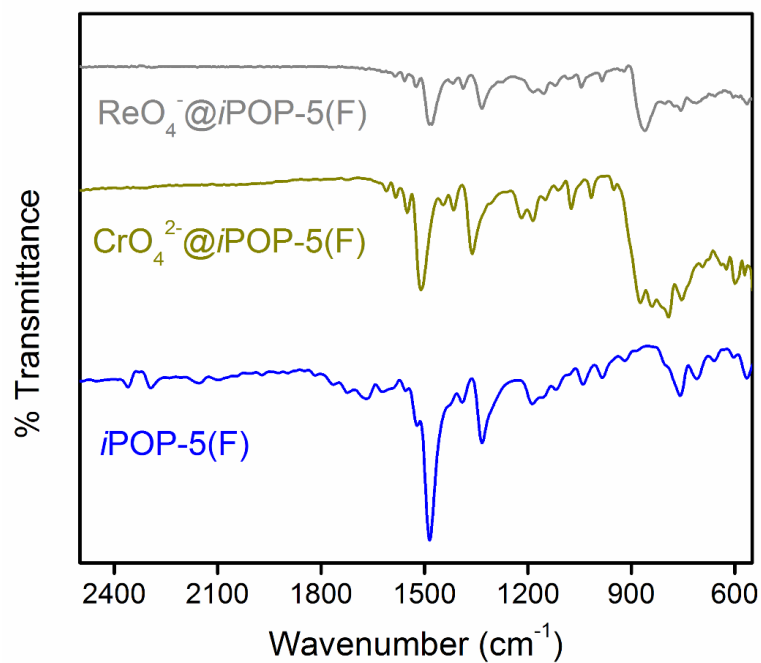
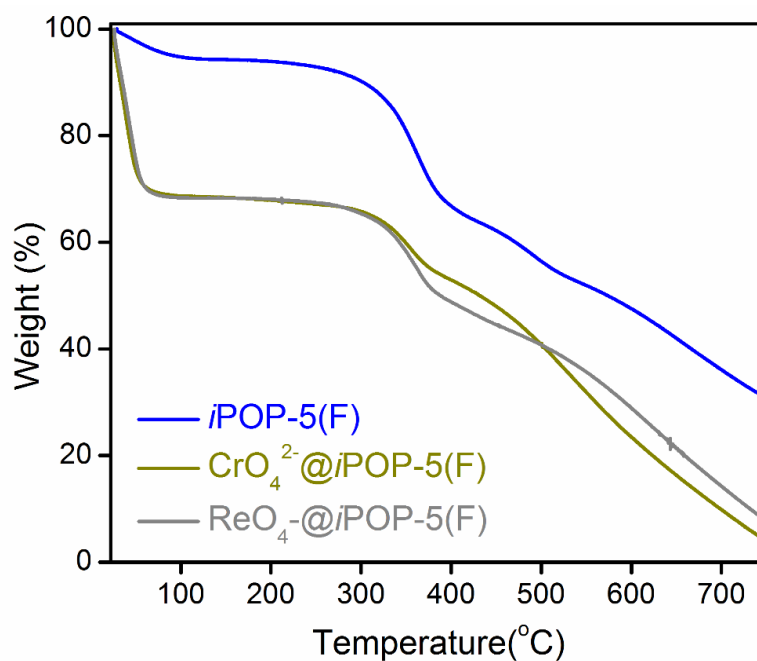


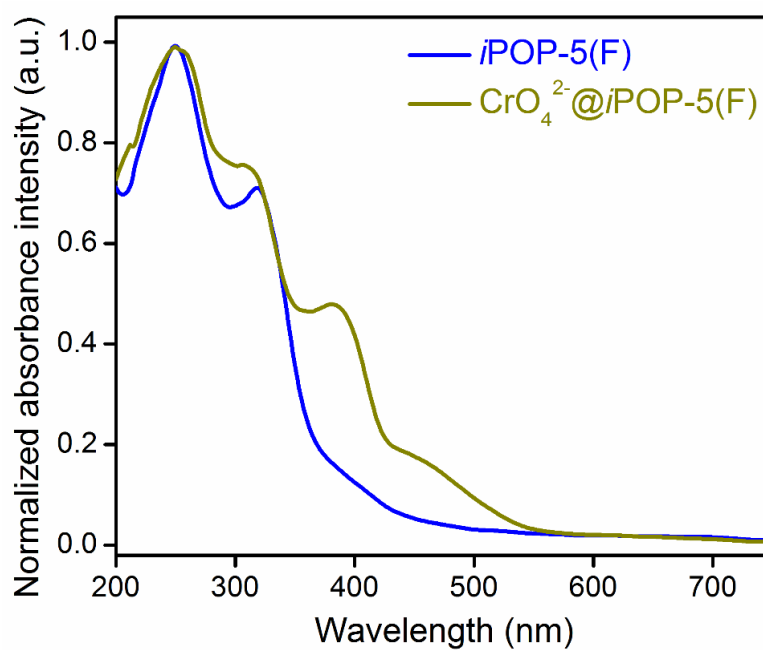
Appendix Figure 4.32a: Selectivity of *iPOP-5(F)* towards low-concentration ($\sim 1000 \text{ ppb}$) Re(VII) capture in presence of other anions. Condition: $[\text{Re}]_{\text{initial}} \sim 1017 \text{ ppb}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 2 h.



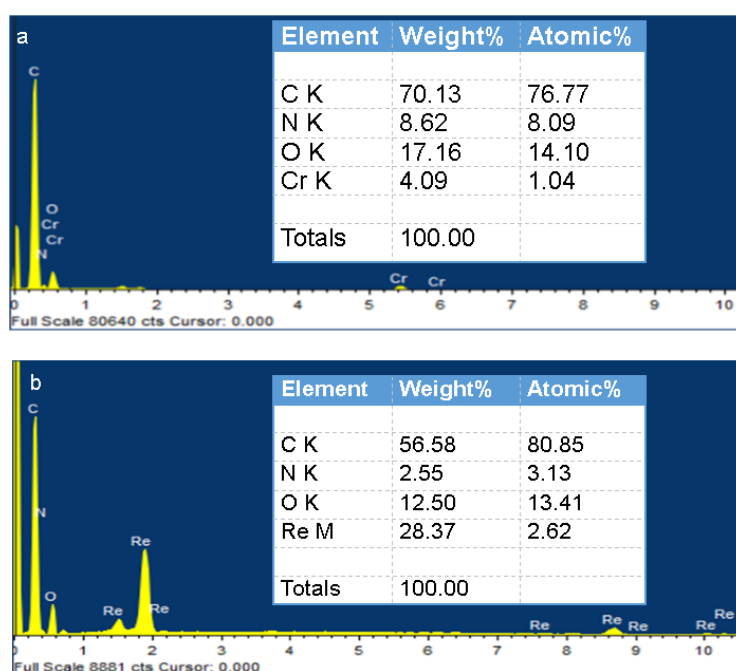
Appendix Figure 4.32b: (a) Digital image, (b) schematic representation of compound loaded column for Cr(VI) removal experiment.

Appendix Section 4: Post Capture Characterization & Stability

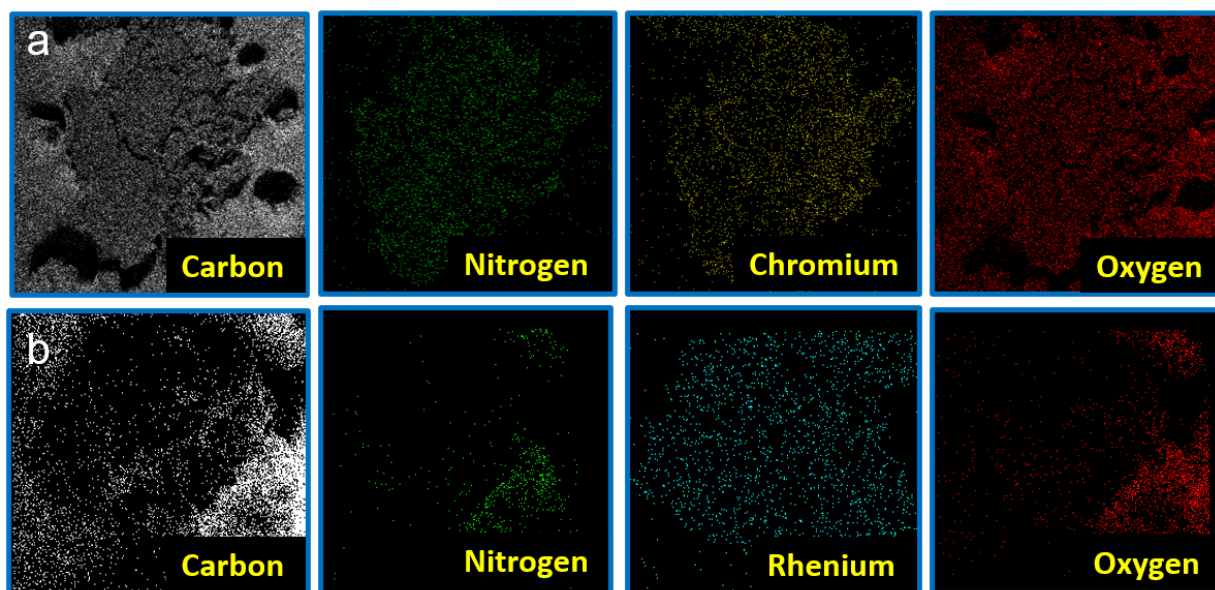
**Appendix Figure 4.33:** FT-IR spectra of Cr(VI) and Re(VII) treated iPOP-5(F) .**Appendix Figure 4.34:** TGA profile of Cr(VI) and Re(VII) treated iPOP-5(F) along with the pristine compound.



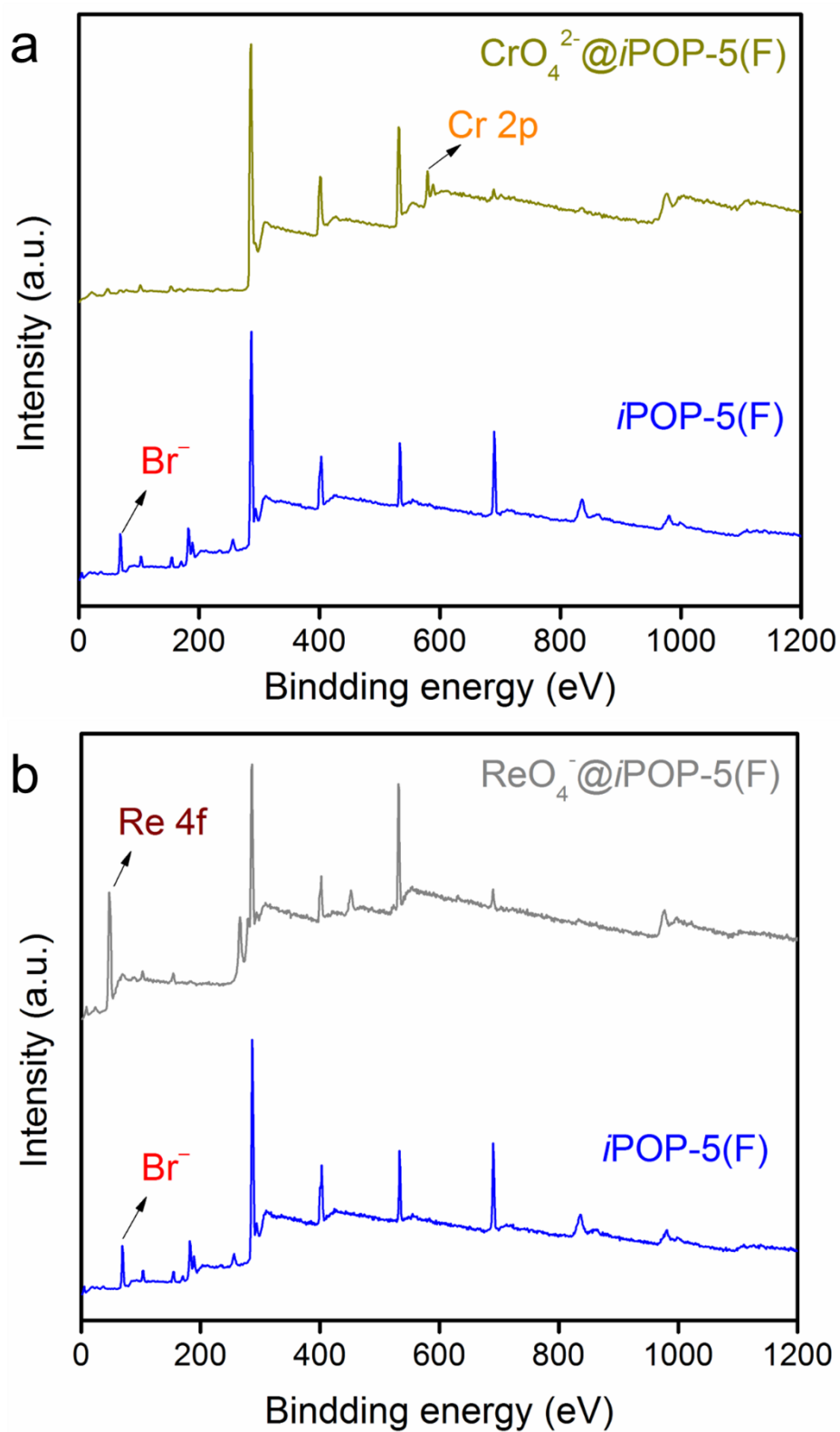
Appendix Figure 4.35: Solid-state UV profile of Cr(VI) treated *iPOP-5(F)*.



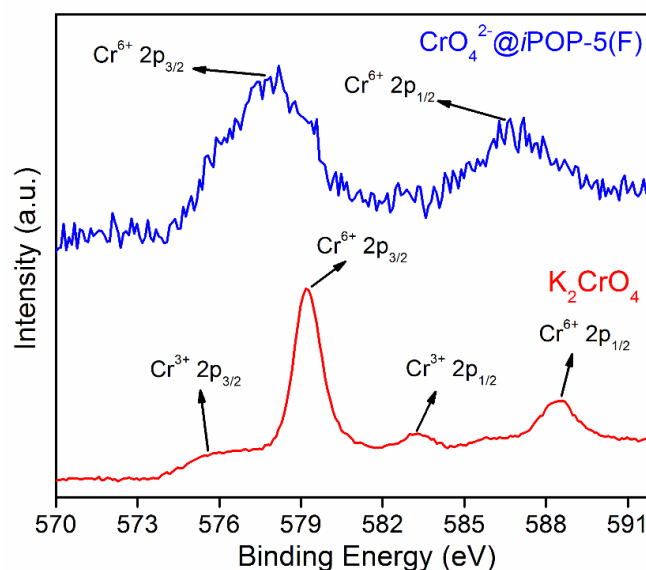
Appendix Figure 4.36: SEM-EDS data of (a) Cr(VI) and (b) Re(VII) treated *iPOP-5(F)*.



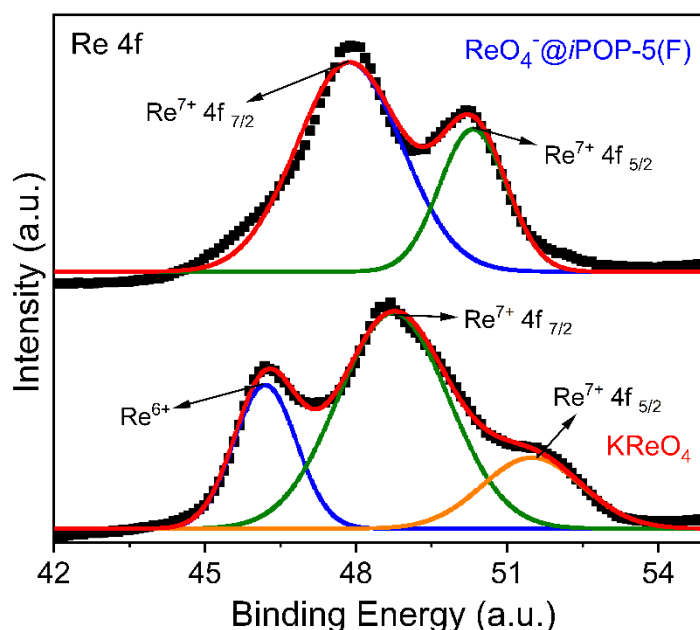
Appendix Figure 4.37: Elemental mapping data of (a) Cr(VI) and (b) Re(VII) treated *iPOP-5(F)*.



Appendix Figure 4.38: XPS spectra of (a) Cr(VI) and (b) Re(VII) treated iPOP-5(F).

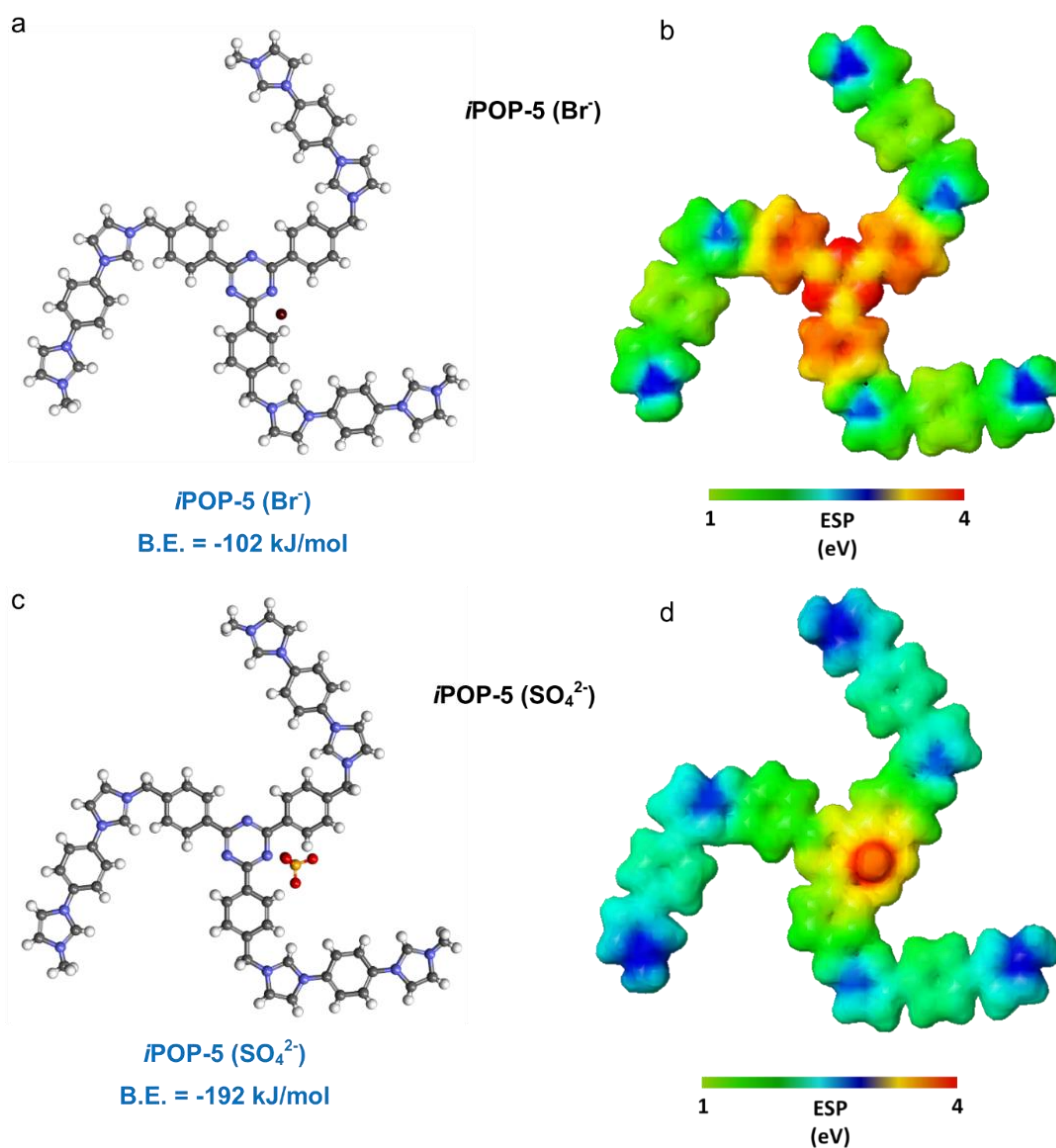


Appendix Figure 4.39: High resolution XPS spectra of Cr 2p. The CrO_4^{2-} treated *i*POP-5(F) contained characteristics binding energy peaks for only Cr^{6+} 2p, confirming *i*POP-5(F) act as Cr(VI) adsorbent. The characteristic binding energy of Cr^{6+} shifted to lower energy region, confirming the strong interaction between framework and CrO_4^{2-} oxoanion.

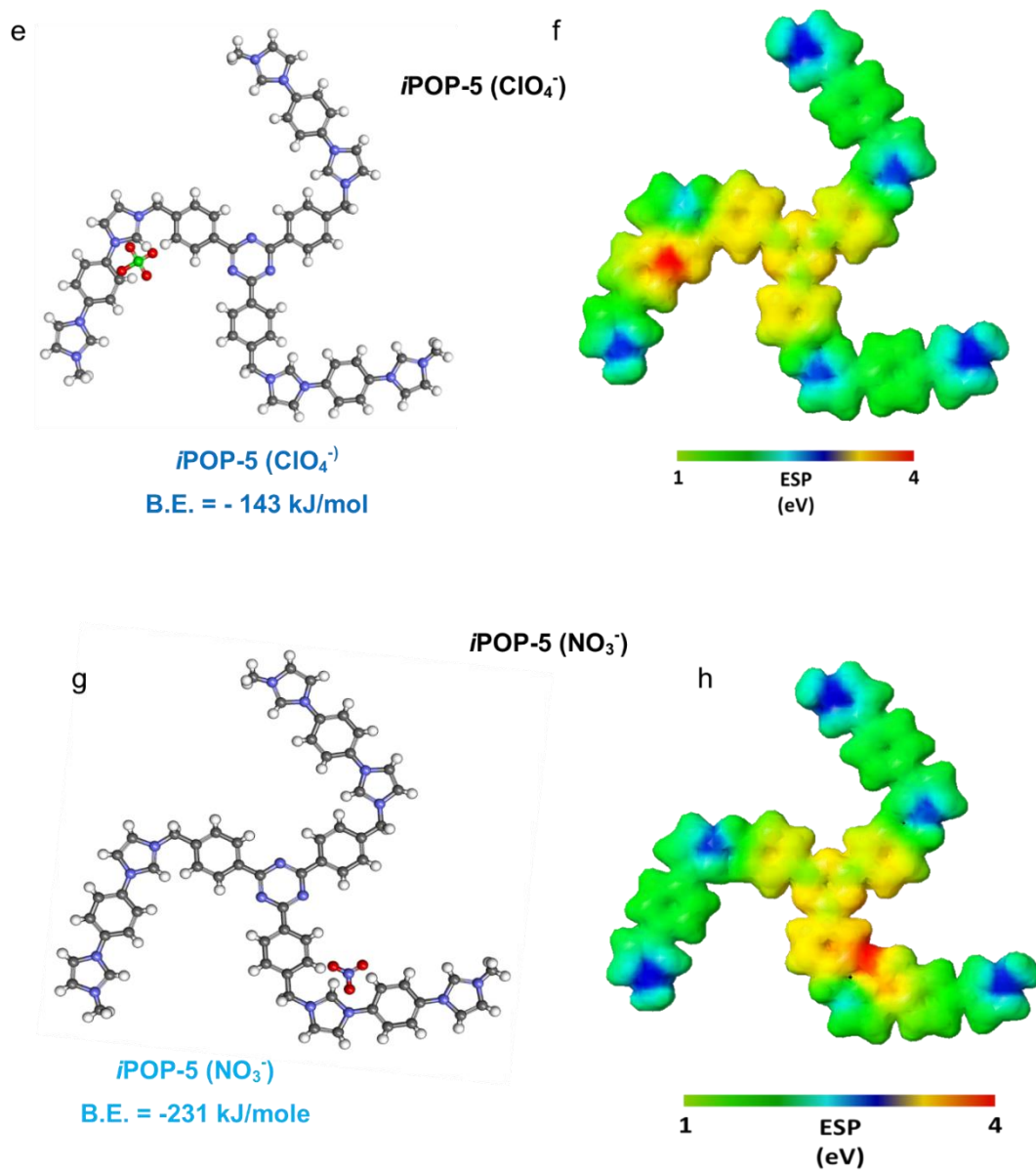


Appendix Figure 4.40: High resolution XPS spectra of Re 4f. The ReO_4^- treated *i*POP-5(F) contained characteristics binding energy peaks for only Re^{7+} 4f, confirming *i*POP-5(F) act as Re(VII) adsorbent. The characteristic binding energy of Re^{7+} shifted to lower energy region, confirming the strong interaction between framework and ReO_4^- oxoanion.

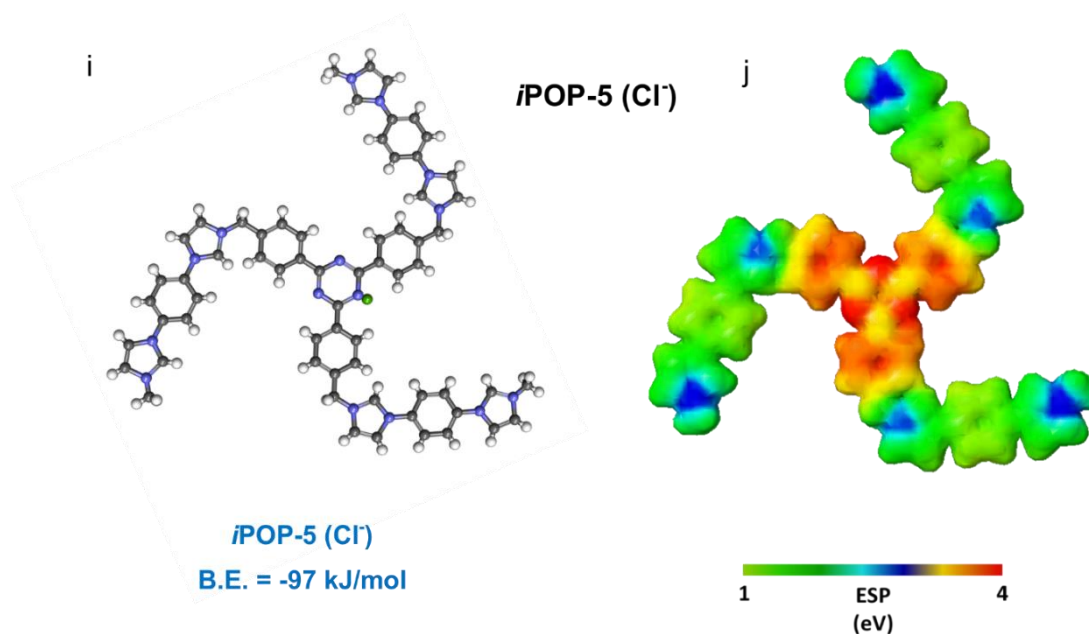
Appendix Section 5: Theoretical studies



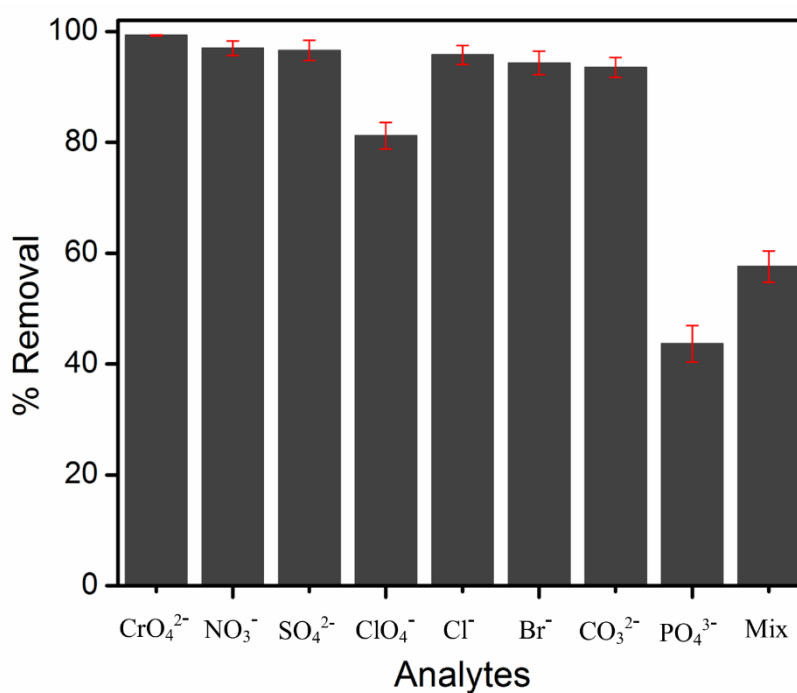
Appendix Figure 4.41: Optimized structures of monomeric unit of *i*POP-5 with different binding anions and the corresponding binding energies calculated based on DFT-DMOL3-B3LYP method, (a, b) *i*POP-5_ Br^- (c, d) *i*POP-5_ SO_4^{2-} .



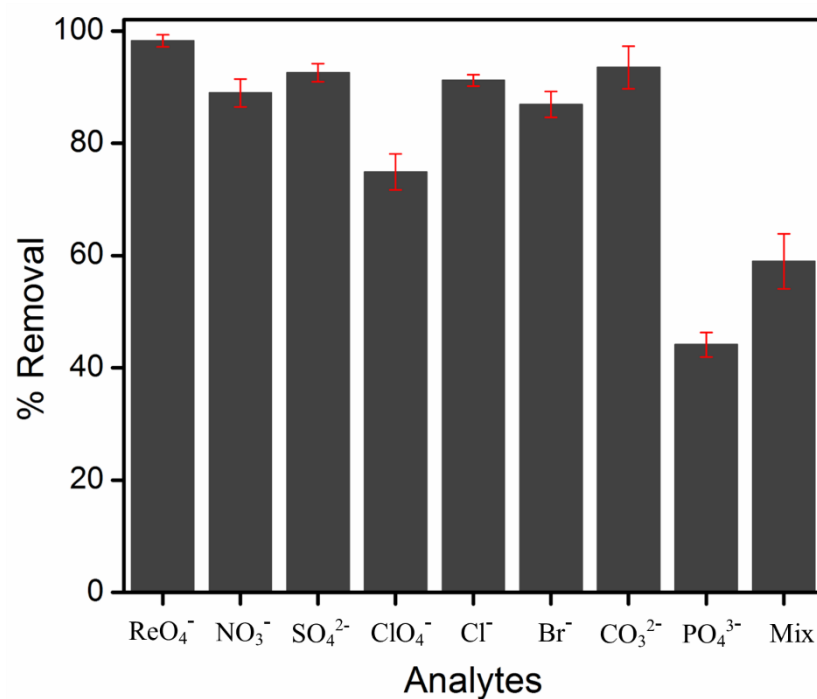
Appendix Figure 4.42: Optimized structures of monomeric unit of *iPOP-5* with different binding anions and the corresponding binding energies calculated based on DFT-DMOL3-B3LYP method, (e, f) *iPOP-5*_ClO₄⁻ (g, h) *iPOP-5*_NO₃⁻



Appendix Figure 4.43: Optimized structures of monomeric unit of *i*POP-5 with different binding anions and the corresponding binding energies calculated based on DFT-DMOL3-B3LYP method (i ,j) *i*POP-5_ Cl^-



Appendix Figure 4.44: Removal efficiency of *i*POP-5(F) towards CrO_4^{2-} in presence of other anions. Condition: $[\text{Cr}]_{\text{initial}} = 2.5 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 12 h.



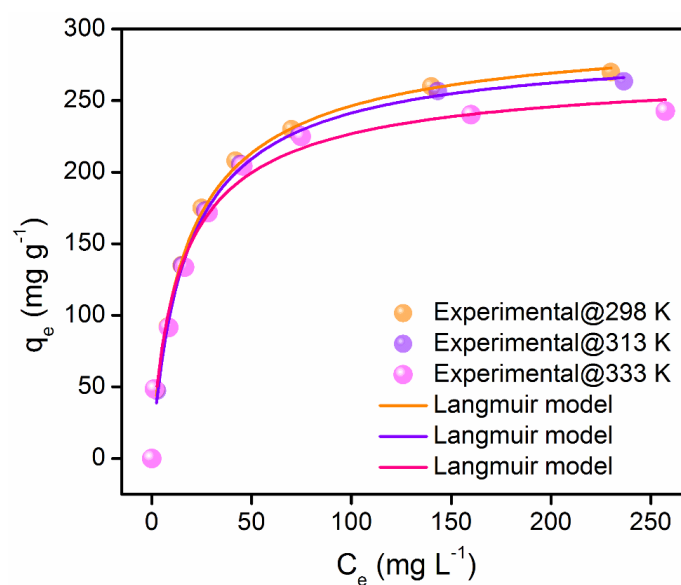
Appendix Figure 4.45: Removal efficiency of *iPOP*-5(F) towards ReO_4^- in presence of other anions. Condition: $[\text{Re}]_{\text{initial}} = 5 \text{ mmol}$, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 12 h.

Appendix Table 4.1: Distribution coefficient (K_d) value for Cr(VI) in presence of following other anions by *iPOP*-5(F).

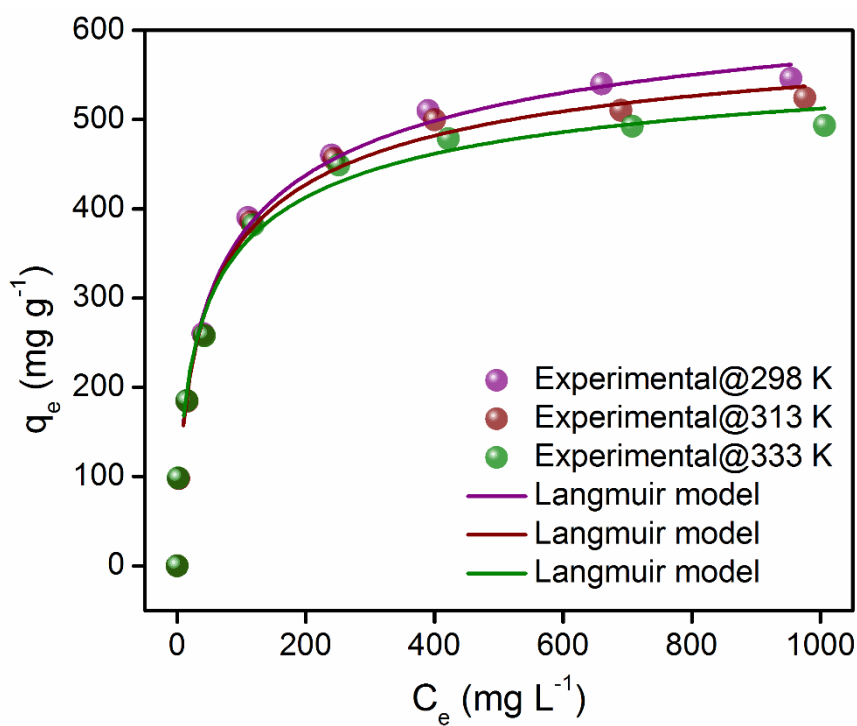
Anions	K_d value
Only CrO_4^{2-}	1.41×10^5
$\text{CrO}_4^{2-} + \text{NO}_3^-$	0.32×10^5
$\text{CrO}_4^{2-} + \text{SO}_4^{2-}$	0.28×10^5
$\text{CrO}_4^{2-} + \text{ClO}_4^-$	0.43×10^4
$\text{CrO}_4^{2-} + \text{Cl}^-$	0.22×10^5
$\text{CrO}_4^{2-} + \text{Br}^-$	0.16×10^5

Appendix Table 4.2: Distribution coefficient (K_d) value for Re(VII) in presence of following other anions by *i*POP-5(F).

Anions	K_d value
Only ReO_4^-	0.56×10^5
$\text{ReO}_4^- + \text{NO}_3^-$	0.80×10^4
$\text{ReO}_4^- + \text{SO}_4^{2-}$	0.12×10^5
$\text{ReO}_4^- + \text{ClO}_4^-$	0.29×10^4
$\text{ReO}_4^- + \text{Cl}^-$	0.10×10^5
$\text{ReO}_4^- + \text{Br}^-$	0.66×10^4



Appendix Figure 4.46: Isotherm fitting of Cr(VI) by *i*POP-5(F) at different temperature viz. 298 K, 313 K and 333 K. Condition: $m_{\text{sorbent}}/V_{\text{solution}} = 1$ g/L and contact time = 24 h.



Appendix Figure 4.47: Isotherm fitting of Re(VII) by iPOP-5(F) at different temperature viz. 298 K, 313 K and 333 K. Condition: $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ g/L}$ and contact time = 24 h.

Appendix Table 4.3: A comparison table of CrO_4^{2-} and/or $\text{Cr}_2\text{O}_7^{2-}$ capture with some well-studied examples in the literature (N.D. Not done).

Compound	Contact Time	Capacity	Selectivity		Ref
			Presence of other interfering ions		
			Binary mixture of ions	Mixture of ions	
iPOP-5	1 min	301 mg/g	Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-, Br^-	Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-, Br^- (100-fold)	This Work
MOR-2	1 min	194 mg/g	Cl^- , NO_3^- , HCO_3^-	ND	47
IPcomp-3(200)	<2 min	274.4 mg/g	Cl^- , SO_4^{2-} , NO_3^- , ClO_4^- , Br^-	Cl^- , SO_4^{2-} , NO_3^- , ClO_4^- , Br^- (1000-fold)	48
POP-Ims ($\text{Cr}_2\text{O}_7^{2-}$)	5 min	171.99 mg/g	Cl^- , NO_3^- , SO_4^{2-}	ND	49
MGNC	50 min	-	ND	ND	50
Zn-Co-SLUG-35	4 h	68.5 mg/g	NO_3^- , SO_4^{2-}	NO_3^- , SO_4^{2-} (50-fold)	51
IMIP-Br($\text{Cr}_2\text{O}_7^{2-}$)	30 min	318 mg/g	NO_3^- , SO_4^{2-} , Cl^- , BF_4^-	ND	52
Compound-1	30 min	133 mg/g	Cl^- , NO_3^- , Br^- , SO_4^{2-}	ND	53
FIR-53 FIR-54	4 h	74.2 mg/g 103 mg/g	Cl^- , Br^- , NO_3^- , CO_3^{2-} , ClO_4^- , SO_4^{2-}	ND	54
CON-1($\text{Cr}_2\text{O}_7^{2-}$)	1 h	293 mg/g	ND	ND	55
1- ClO_4	8 h	62.88 mg/g	Halide anions	ND	56
ZJU-101	10 min	245 mg/g	Cl^- , F^- , I^- , Br^- , NO_3^- , SO_4^{2-}	Cl^- , F^- , I^- , Br^- , NO_3^- , SO_4^{2-} (12 fold)	57
aMOC-1 aMOC-2	6 min 6 min	157.4 mg/g , 242.0 mg/g	Cl^- , Br^- , NO_3^- , SO_4^{2-} , CO_3^{2-}	ND	58
1- SO_4 ($\text{Cr}_2\text{O}_7^{2-}$)	24 h	166 mg/g	CF_3SO_3^- , BF_4^- , NO_3^- , ClO_4^-	ND	59
ED-rGO	24 h	-	ND	ND	60
TJU-1	24 h	279 mg/g	Cl^- , HCO_3^- , NO_3^- , SO_4^{2-}	ND	61
ABT.2 ClO_4 ($\text{Cr}_2\text{O}_7^{2-}$)	48 h	0.73 mol/mol	CF_3SO_3^- , BF_4^- , NO_3^-	CF_3SO_3^- , BF_4^- , NO_3^- (2-fold)	62
iPOP-3 iPOP-4	60 min 30 min	170 mg/g 141 mg/g	SO_4^{2-} , Br^- , Cl^- , NO_3^-	ND	63

Appendix Table 4.4: A comparison table of ReO_4^- capture with some well-studied examples in the literature (N.D. Not done).

Compounds	Contact Time	Capacity	Selectivity Presence of Other Interfering Ions		Ref
			Binary Mixture of Ions	Mixture of Ions	
SCU-COF-1	1 min	702.4 mg/g	CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , NO_3^-	CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , NO_3^- (100 fold)	64
iPOP-5	5 min	610 mg/g	SO_4^{2-}, Cl^-, Br^-, ClO_4^-, NO_3^-	100-fold SO_4^{2-}, Cl^-, Br^-, ClO_4^-, NO_3^-	This Work
IPcomp3(200)	<2 min	600.1 mg/g	Cl^- , NO_3^- , Br^- , SO_4^{2-} , ClO_4^-	Cl^- , NO_3^- , Br^- , Cl^- , NO_3^- , Br^- , (1000-fold)	48
α -MOC-1 α -MOC-2	10 min	350 mg/g 583.9 mg/g	Cl^- , NO_3^- , Br^- , SO_4^{2-} , CO_3^{2-}	ND	58
SCU-100 ($\text{ReO}_4^-/\text{TcO}_4^-$)	30 min (TcO_4^-)	541 mg/g (ReO_4^-)	CO_3^{2-} , NO_3^- , SO_4^{2-} , PO_4^{3-}	NO_3^- (100 fold) SO_4^{2-} (1000 fold)	65
SBN	10 min	786 mg/g	CO_3^{2-} , Cl^- , NO_3^- , SO_4^{2-} , ClO_4^- , H_2PO_4^-	NO_3^- (100 fold)	66
SCU-101 ($\text{ReO}_4^-/\text{TcO}_4^-$)	10 min (TcO_4^-)	217 mg/g (ReO_4^-)	CO_3^{2-} , NO_3^- , SO_4^{2-} , ClO_4^- , PO_4^{3-}	6000 fold SO_4^{2-} 20 fold NO_3^-	67
SLUG-21	60 min	602 mg/g	ND	ND	68
Compound-1	60 min	517 mg/g	Cl^- , NO_3^- , Br^- , SO_4^{2-}	ND	53
PAF-1-F	24 h	420 mg/g	SO_4^{2-} , PO_4^{3-}	ND	69
iPOP-3 iPOP-4	25 min 30 min	515.5 mg/g 350.3 mg/g	SO_4^{2-} , Cl^- , Br^- , NO_3^-	ND	63
TbDa-COF	2 min	952 mg/g	Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}	NO_3^- (100 fold) SO_4^{2-} (1000 fold)	70
bis- $\text{PC}_2(\text{Cl})@\text{MIL}-101$	30 sec	362 mg/g	NO_3^-	ND	71
SCU-CPN-1	30 sec	876 mg/g	NO_3^- , SO_4^{2-}	100 fold NO_3^- & SO_4^{2-}	72
CPN-tpm	20 min	1133 mg/g	NO_3^- , SO_4^{2-} , AsO_4^{3-}	NO_3^- (100 fold) SO_4^{2-} (10 fold)	73

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Chapter 5

Nanotrap Infused Ultrathin Hybrid Composite Material for Highly Selective Entrapment of Radioactive TcO_4^-

5.1 Introduction

^{99}Tc is one of the most hazardous fission product in the nuclear fuel cycle owing to its long half-life ($t_{1/2} = 2.13 \times 10^5 \text{ a}$), potential radiation threat, high environmental mobility and elevated redox-active nature. ^{99}Tc is a long lived ($t_{1/2} = 2.13 \times 10^5 \text{ a}$) β^- -emitting radionuclide ($E = 294 \text{ keV}$) that is both chemically toxic and hazardous. ^[2, 4] Inhaling ^{99}Tc -contaminated vapour or dust poses a significant cancer risk ^[5], and ^{99}Tc can accumulate in breast tissue and the thyroid after digestion. ^[6] Additionally, ^{99}Tc is mostly found in aquatic conditions and in the nuclear fuel cycle as pertechnetate oxy-anion ($^{99}\text{TcO}_4^-$). $^{99}\text{TcO}_4^-$ is not a strong oxidant like its congener MnO_4^- , as a result this contributes to its remarkable stability under challenging environmental circumstances. Low charge density and the high symmetry (T_d) of $^{99}\text{TcO}_4^-$ results in its extremely high solubility (11.3 M at 20 °C) in water ^[7] As a result, $^{99}\text{TcO}_4^-$ can go through the natural water system without any difficulty, and the bulk of plentiful natural elements have no effect on it. The only practical solution for dealing with the significant amounts of nuclear waste is now Vitrification followed by geological disposal in a number of countries. ^[8, 9] Solid sorbents have displayed significant promise for established TcO_4^- remediation technologies due to their easy, safe, and low-cost processes and better performances towards anion removal at low concentration levels and point-of-use applications. ^[10-16] Till now, there have been only few materials, including inorganic cationic framework materials, ^[17] anion exchange resin and polymeric networks, ^[18] and also cationic metal-organic framework (MOFs), ^[19] reported to showcase $^{99}\text{TcO}_4^-$ sequestration ability from toxic nuclear waste. Out of these materials, inorganic crystalline ionic materials such as layered double hydroxides (LDHs), NDTB-1 and $\text{Y}_2(\text{OH})_5\text{Cl}$ feature serious limitations of less selectivity, low saturation capacity and slow uptake/removal kinetics. Since various anions (NO_3^- , Cl^- , SO_4^{2-} , Br^- , CO_3^{2-} , ClO_4^- and PO_4^{3-}) can be found in both natural water systems and nuclear waste system, those with low selectivity are unable to serve as viable candidates are coexisting in 100 to 10000 fold of excess with the $^{99}\text{TcO}_4^-$ which can act as an interfering analytes. ^[20] This fundamental issue is magnified by the fact that $^{99}\text{TcO}_4^-$ absorption kinetics of these materials are very sluggish, resulting in a significantly greater dosage received during the anion-exchange process. Recently reported cationic metal-organic frameworks (MOFs) built from neutral soft ligand and transition metal cations with free exchangeable anions inside the void are potential candidates to extract $^{99}\text{TcO}_4^-$ from aqueous solution ^[21-24], as they show fast adsorption kinetics, high uptake capacity, outstanding selectivity and great radiation resistance capability. However, these materials have major drawback as they don't survive in highly acidic conditions that is required for used fuel reprocessing.

Therefore, considering the importance of selective separation of targeted analytes i.e.; TcO_4^- from a complex mixture of other coexisting interfering anions with high concentrations, there has been a considerable focus on the development of effective regenerable materials with augmented segregation

capabilities. That being said, to find effective adsorbents for the removal of TcO_4^- from contaminated water, innovative efforts have been put forward. However, as an enduring bottleneck, advancement in terms of high selectivity, swift kinetics, and capacities at trace concentration are still needed from nuclear waste water sources to point-of-use, which is unexplored due to the lack of appropriate synthetic techniques. In this regard, by virtue of controlled engineering at the molecular level has enabled infusing advanced functionality in diverse porous materials to flourish in recent years.^[25] The synthesis of composite materials results in the combined benefits and maximised performance of several functional materials.^[26-30] Because of the development of innovative and multipurpose platforms to achieve desired applications, hybrid composite materials have come to the forefront and garnered a lot of attention.^[31-33] Although, composite materials have advanced significantly in recent years,^[34] hybrid composite materials have not been fully investigated. Accordingly, due to the combined qualities of the host and guest, host-guest-based hybrid composite materials can serve as the best adsorbents. In this context, metal-organic polyhedral (MOP), a zero-dimensional crystalline material, made up from metal ions (or metal clusters) and organic linker, and covalent organic frameworks (COFs), a crystalline porous material which are assembled from covalent linking of pure organic linkers, could be an ideal platform as guest and host materials, respectively. These two are widely known porous materials for variety of applications such as gas storage, sensing, catalysis, photoelectric conversion, energy storage and biological activities etc.^[35-38] However, MOPs are typically unable to reach their full potential in the aforementioned applications because of unavoidable aggregation-induced active site occlusion upon guest removal in the solid-state.^[39] Only a few approaches (such as enclosing MOPs in porous materials like silica or metal-organic frameworks, MOFs) have been used to address this crucial issue, but it has remained difficult to combine MOP with other porous materials.

Considering all the above facts, herein an efficient anion exchangeable ultrathin host-guest hybrid composite material (IPcomp-8, (where “IP” stands for IISER Pune, and “comp” stands for composite)) has been synthesized through covalent grafting of amino-functionalized cationic Zr-MOP (Zr-iMOP) with a chemically stable positively charged COF (iCOF) (Figure-5.1). We have strategically designed and grafted the NH_2 -functionalized cationic MOP molecules into the ionic COF matrix, where the abundance of excess exchangeable Cl^- anions both from host-iCOF and guest-Zr-iMOP, free $-\text{NH}_2$ functional groups of the MOP, and charged triammoniumguanidine (TAG) moiety of the iCOF can accelerate the anion exchange process on account of electrostatic and hydrogen-bonding interactions with the radioactive oxoanions (TcO_4^-). Most importantly, the $\text{Cp}_3\text{Zr}_3\text{O}(\text{OH})_3$ SBU of the MOP molecule can selectively interact with TcO_4^- through exchange with its labile hydroxyl groups.^[42-44] Also, the iCOF matrix can tightly anchor the MOP molecules achieving most of the active sites well exposed (Figure-5.1). In addition to this, the covalent tethering of the cationic MOP into the cationic COF architecture results in easy and self-exfoliation into ultrathin hybrid nanosheets, owing to the

strong interlayer electrostatic repulsion. This results in full exposure of all the multifunctional active sites originating from both guest-Zr-iMOP and host-iCOF matrix, further triggering the rapid mass diffusion and high selectivity towards the targeted TcO_4^- anions in water. , IPcomp-8 was found to exhibit ultrafast and highly selective separation of radioactive $\text{TcO}_4^-/\text{ReO}_4^-$ anions from the contaminated water samples in the presence of large excess (~ 10 , ~ 100 , and ~ 1000 fold) of other competing anions in both high (~ 50 ppm) and ultralow (~ 1000 ppb) concentration. The compound demonstrated TcO_4^- entrapment from a wide range of pH medium with fast adsorption kinetics and the sorption was found to be easily regenerable. Consequently, ReO_4^- was successfully eliminated from various waste water samples using IPcomp-8. It significantly lowered the concentration of ReO_4^- to below the WHO-set permissible level for drinking water (10 ppb). Numerous experimental along with theoretical calculation studies also backed up this quick and efficient adsorption performance provided by the cooperative synergistic multifunctionalities of IPcomp-8.

5.2 Experimental

5.2.1. Materials: The starting materials, solvents, reaction precursors and reagents were acquired from TCI chemicals, Sigma-Aldrich and Alfa Aesar chemicals, and used as received unless noted otherwise.

5.2.2 General Characterization and Physical Measurements:

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

5.2.2.2 Infrared spectroscopy (IR): A Bruker Optics ALPHA-E spectrometer equipped with a common Zn-Se ATR (attenuated total reflection) accessory was used to collect the IR spectra. The wave number (cm^{-1}) scale for AIR data ranges from 500 to 4000 cm^{-1} .

5.2.2.3 Thermogravimetric analysis (TGA): By heating the samples from 40°C to 800°C under a N_2 environment with a heating rate of $10^\circ \text{C min}^{-1}$, the samples' thermogravimetric analyses were recorded on a Perkin-Elmer STA 6000 TGA analyzer.

5.2.2.4 Field emission scanning electron microscopy (FESEM): A Zeiss Ultra Plus field-emission scanning electron microscope (FESEM) with an integrated charge compensator and embedded EsB and AsB detectors (Oxford X-max instruments 80 mm^2 ; Carl Zeiss NTS, GmbH) was used to capture the morphology of the materials. To lessen charge, a 5–10 nm Au coating was sputtered onto the samples.

An EDX detector and a voltage of 15 KV were used for the elemental analysis. An accumulation time of 600s was used for data collection.

5.2.2.5 Transmission electron microscopy (TEM): On the HRTEM (JEM-2200FS, JEOL) operating at an acceleration voltage of 200 kV, TEM imaging and STEM-EDS were carried out. All of the materials were dissolved in isopropanol and sonicated for TEM examination. The samples were then left for 2 minutes, and the upper portion of the solution was collected to prepare TEM samples on a copper grid that had been coated in lacey carbon (200 mesh; Electron Microscopy Science).

5.2.2.6 Nitrogen adsorption-desorption isotherm measurements: The BelSorp-Max equipment (Bel Japan) was used to measure the adsorption of N₂ gas. The activated samples were heated at 120 °C under vacuum for 12 hours prior to adsorption measurements using BelPrepvacII..

5.2.2.7 X-ray photoelectron spectroscopy (XPS): 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.

5.2.2.8 Nuclear magnetic resonance (NMR): On a Bruker 400 MHz NMR spectrometer, ¹H and ¹³C NMR spectra were captured. Parts per million (scale) are used to express the chemical changes.

5.2.2.9 High-resolution mass spectroscopy (HRMS): High-resolution mass spectrometry (HRMS-ESI-Q-TOF) and an Applied Biosystems 4800 PLUS matrix-assisted laser desorption/ionization (MALDI) TOF/TOF analyzer were used to perform the mass analysis of the MOPs.

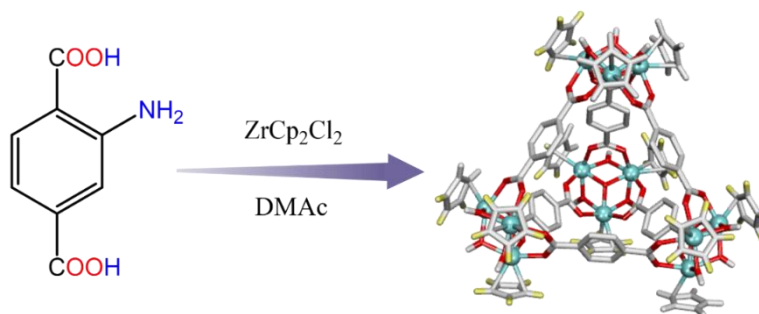
5.2.2.10 UV-visible absorption spectra: Over the whole range of 200-800 nm, UV-vis absorption tests were carried out using a Shimadzu UV 3600 UV / Vis spectrophotometer in an optical quartz cuvette (10 mm path length).

5.2.2.11 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS): Thermo Scientific's iCE 3000 Series underwent ICP-AES examination. Simultaneous ICP Spectrometer ARCOS underwent ICP-AES investigation. Thermo Scientific's iCAP Q quadrupole inductively coupled plasma mass spectrometry apparatus was used to carry out the ICP-MS. Inorganic ventures were used to purchase multi-element standards.

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

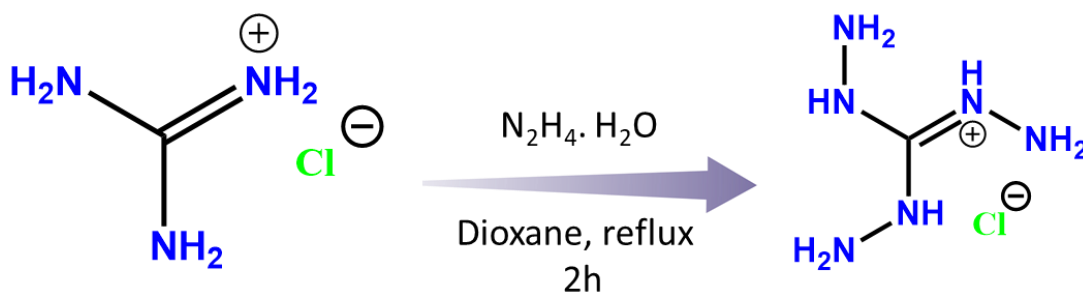
5.2.3 Detailed procedures for synthetic preparation

Synthesis of Metal-organic Polyhedra (MOP): The MOP was synthesized accordance with literature report with slight modification. ^[45] 2-aminoterephthalic acid (50 mg, 0.3 mM) and Zirconocene dichloride (150 mg, 0.5 mM) were dissolved in N, N-dimethylacetamide (DMA, 10 mL) with a trace amount of water (40 drops) and kept it at room temperature and left undisturbed state for 72 hours. The yellow cubic block crystals were collected by filtration and dried under vacuum at room temperature.



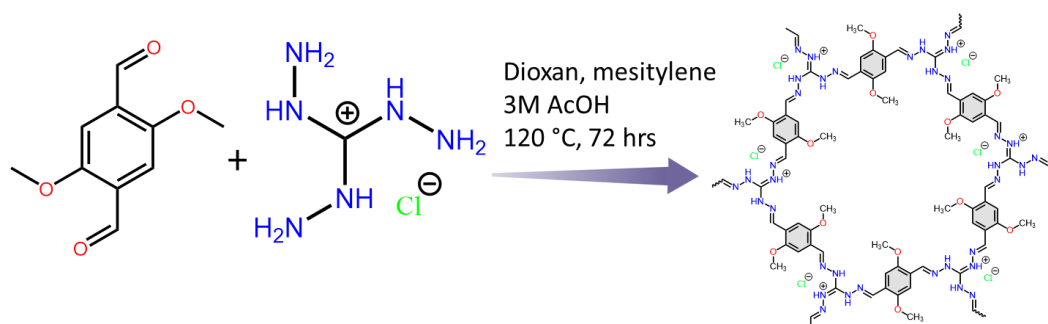
Scheme 1: Synthesis scheme of the Metal-Organic Polyhedra (MOP).

Synthesis of triaminoguanidine hydrochloride (TG_{Cl}): Triguanidine hydrochloride (TG_{Cl}) was synthesized following a reported protocol without any further modifications. ^[46] First, guanidinium hydrochloride was suspended in 1,4-dioxane (260 mL). After the addition of hydrazine monohydrate (86.6 mL, 1.782 mol), the mixture was heated at $\sim 105^\circ\text{C}$ for 2-3 hours. The reaction solution was filtered and continually rinsed with 1, 4-dioxane after cooling to room temperature. To get TG_{Cl} (yield: 74.2%), the resultant white precipitate was dried in a high vacuum atmosphere.



Scheme 2: Synthesis scheme of triaminoguanidine hydrochloride (TG_{Cl}).

Synthesis of iCOF: The iCOF was synthesized accordance with literature report with slight modification.^[46] A glass tube was loaded with TG_{Cl} (0.11 mM, 14.8 mg) and 2,5-dimethoxyterephthalaldehyde (29.1 mg, 0.15 mM) in a solution mixture of deionized water/mesitylene/EtOH/3 M acetic acid (0.3/0.1/0.5/0.2 mL). The glass tube was frozen by liquid nitrogen at 77 K. After that, the tube was sealed with gas flame (the length of the tube was about 13.0 cm). The reaction mixture was heated at 123 °C for 3 days and the obtained orange powder, which was further washed with DMF (3 times with 15 mL), water (3 times with 15 mL) and EtOH (3 times with 15 mL) in turn. After removing the solvent under vacuum iCOF was afforded as orange powder.



Scheme 3: Synthesis scheme of pristine iCOF.

Synthesis of hybrid composite (IPcomp-8): In a typical synthesis protocol, firstly 15 mg of NH_2 functionalized MOP was charged with TG_{Cl} (14.8 mg, 0.11 mM) and 2,5-dimethoxyterephthalaldehyde (29.1 mg, 0.15 mM) in a solution of deionized water/mesitylene/EtOH/3 M acetic acid (0.3/0.1/0.5/0.2 mL). The tube was flash frozen by liquid nitrogen at 77 K. After that the tube was sealed with flame (the length of the tube was about 13.0 cm). The reaction mixture was heated at 123 °C for 3 days and the obtained orange powder was washed with DMF (3 times with 15 mL), water (3 times with 15 mL) and EtOH (3 times with 15 mL), DMAc (3 times with 15 mL) and methanol (3 times with 15 mL). After that compound was dipped in the DMSO, water and methanol accordingly for 24 h respectively. After that it was filtered off and dried.

5.2.4 Oxoanion Capture Study

5.2.4.1. General Consideration: Unless otherwise stated, the different concentrations were achieved by diluting the stock solution with the appropriate amount of distilled water. The aqueous solution of oxoanion was prepared by dissolving a specific amount of potassium salt of Re into deionized water.

HNO₃ aqueous solution was used to change the pH values of the solutions. ICP-AES and ICP-MS (for ultra-low concentrations) analyses were used to find the oxoanions' concentrations throughout all of the tests. The ambient conditions were used for all of the adsorption trials. All the data has been collected three times through ICP analysis to plot the final adsorption results.

5.2.4.2. TcO₄⁻ adsorption kinetics studies: For the sorption, 25 mg of MOF was taken as solid phase, while 5 mL of aqueous phase containing TcO₄⁻ in specified pH (~5.4) made using nitric acid. The biphasic system was allowed to equilibrate for 3 hours followed by centrifugation for phase separation for a duration of 10 min. In case of pH variation experiments, the pH of the aqueous phase was varied from pH 1-9 and the temperature was kept constant 303 K. The aqueous phase before extraction and after extraction were collected and estimated (C_i and C_e) for Tc. The % removal values were estimated based on the equation below:

$$\% \text{ Sorption} = (C_i - C_e) / C_i \times 100 \% \quad (1)$$

Where, *v* is the volume of aqueous phase taken and *m* is the mass of MOF used for sorption experiments. The Tc-tetraphenyl arsonium chloride (TPAC) complex technique was used to determine the pertechnetate ion concentration in an aqueous solution. To determine the ⁹⁹Tc concentration in waste streams, ⁹⁹Tc radionuclide was analyzed by precipitating with the TPAC complex and then measuring beta activity with a GM counter. Self-absorption of low energy beta particles through the precipitate introduces inaccuracy during beta activity counting. By employing its gross beta cut-off (95%) and an Al-absorber with a thickness of 100 mg cm², the concentration of ⁹⁹Tc was verified. To optimize the time of equilibration, the contact time between solid-liquid phase was varied from 5 min to 2 hours, while keeping the other experimental parameters same. The aqueous phase pH was kept pH ~5.4 for the experiments. In a similar fashion for understanding the sorption capacity, the experiments were performed at pH 5.4. The amount of TcO₄⁻ was varied in concentration range 25-250 mg L⁻¹. For all the experiments involving pH variation and capacity determination, the same solid to liquid ratio was kept and the time of biphasic equilibration was kept as 2 hours, while 10 min was employed for centrifugation to achieve complete phase separation. The experiments were carried out at 300 K in a thermostated water bath with ±0.1 °C precision, procured from Lab Enterprise, Mumbai, Maharashtra. The centrifugation machine was also procured from Lab India.

5.2.4.3. Adsorption kinetics studies: The standard procedure that we adopted for the adsorption kinetics experiments was as follows. In a 17 mL glass vial fitted with magnetic stir bars, the capture investigation of the oxoanion ReO₄⁻ was carried out at a constant 350 rpm. In the beginning, 5 mg of the substance was dissolved in 5 mL of a 25 ppm stock solution of oxoanion. After continuous stirring for different time at room temperature the solution was collected by a syringe with having 0.22 μm

nylon membrane filter. The concentration of this filtrate was analysed through ICP-AES and the kinetic adsorption study were measured at different time intervals. We used the following formulae to compute the removal percentage and decreasing concentration of the oxoanions over time based on the time-dependent study:

$D_t = (C_o - C_t) \times 100 / C_o = (A_o - A_t) \times 100 / A_o$, Where, D_t = oxoanions removal efficiency (%), C_o = initial concentration, A_o = initial absorbance, C_t = final concentration, A_t = final absorbance at specific time.

5.2.4.4. Re (VII) adsorption isotherm experiment: 5 mg of material was immersed in 5 mL aqueous solution of perrhenate having different concentrations. After about 24 hours, the filtrate was collected using a syringe filter (0.22 μ m), the concentration was determined using ICP-AES, and the following equations were then fitted.

Langmuir model, $Q_t = Q_i \cdot C_t / (K_d + C_t)$; Where C_t (ppm) and Q_t (mg g⁻¹) stand for the equilibrium Tc/Re(VII) concentration and equilibrium Tc/ReO₄⁻ adsorbed quantity, respectively. The maximum quantity of Tc/Re(VII) per mass of adsorbent required to generate an entire monolayer is Q_i (mg g⁻¹). The constant for the binding sites' affinities is K_d (mg L⁻¹).

Freundlich model, $Q_t = K_1 \cdot C_e^{1/n}$; Where the Freundlich model constants K_1 and $1/n$, which represent the capacity and intensity of adsorption, respectively, are used.

5.2.4.5. Pseudo-second-order kinetic model equation: This is how the pseudo-second-order equation is written: $t/q_t = 1/K_2 q_e^2 + t/q_e$ Where k_2 is the pseudo-second-order rate constant of adsorption (g mg⁻¹ min⁻¹) and q_t and q_e are the adsorbed amounts (mg g⁻¹) at time and equilibrium, respectively. With the use of a pseudo-second-order kinetic model, the experimental data was fitted.

5.2.4.6. Distribution coefficient value (K_d): The equation provides the distribution coefficient (K_d) value that is used to assess the affinity and selectivity of sorbents for oxoanions is: $K_d = [V \{ (C_o - C_e) / C_e \}] / m$; Where C_o is the starting concentration of Re(VII), C_e is the equilibrium concentration of Re(VII), and V is the volume of the testing solution (mL), m is the weight of the solid adsorbent (g), and so forth.

5.2.4.7. Oxoanions capture capacity: The amount of oxoanions adsorbed per gram of material was determined by treating 5 mg of material to 10 mL of ~500/1000 ppm concentrated solution of respective oxoanions salts for ~24 hours under stirring conditions at room temperature. After 24 hours, the composite material was filtered off and the filtrate was characterized through ICP-AES/UV-vis by diluting the solution. The adsorption capacity per gm was calculated using following equation:

$$Q_t = (C_o - C_t) * V / m;$$

In this case, Q_t , C_0 , C_t , V and m are the capacity of adsorbent, initial concentration of the oxoanions solution, final concentration of oxoanions at a specific time, volumes of the solution and mass of the material used for the adsorption study respectively.

5.2.4.8. Oxoanions capture study in the presence of interfering ions: To test the influence of interfering ions, binary selectivity of salts such as, NaCl, NaBr, NaNO₃, NaClO₄, Na₂SO₄ and large excess of competing salt NaNO₃ and Na₂SO₄ were added to the different aforementioned oxoanions aqueous solution and carried out the capture studies by following the aforementioned method. The capture studies were monitored through ICP-AES.

5.2.4.9. pH-dependent Tc(VII) extraction study: The effect of pH on Tc(VII) removal performance was recorded in a wide range of pH and compared with the data at pH-7 to check the relative performance. The variation of pH values was realized by the addition of either acid (HCl) or base (NaOH). We adopted the similar adsorption experiment for this study.

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

5.2.4.11. Recyclability test: The first cycle of Re(VII) uptake in the recyclable experiment was performed according to the aforementioned adsorption protocol. After the first run of adsorption, the Re(VII) containing material was regenerated by treatment with a saturated Na₂SO₄ aqueous solution. The resulting solid was dried and washed three times with pure deionized water. After being finally dried under vacuum, the resultant material was used for the next cycle adsorption experiments.

5.2.4.12. ICP Calibration: The calibration curve was recorded before each ICP measurement using various standard samples prepared by dilution of respective oxoanion salts aqueous solution of a known concentration with 2% w/w HNO₃. The calibration curves indicated the regression line with high correlation coefficient ($R^2 = 0.999$, $R^2 = 0.998$). Most of the ICP data were conducted triplicate. Whereas, few critical ICP data (such as kinetics of oxoanions capture, capacities of oxoanions removal) has been collected and verified from three different instruments.

5.3 Results and Discussion

Following earlier literature findings, a discrete, hydrolytically stable, amino-group functionalized, nanosized (2 nm) cationic MOP ($\{[\text{Cp}_3\text{Zr}_3\text{O}(\text{OH})_3]_4(\text{NH}_2\text{-BDC})_6\}\cdot\text{Cl}_4$) was synthesized and then characterized (Appendix Figure 5.1, 5.2).^[45] The cationic COF (iCOF) was also synthesized and thoroughly characterized following previously reported literature (Appendix Figure 5.3).^[46] (see the appendix section for detail synthetic methods). The cationic MOP/COF hybrid material was developed in a single step process by reacting the Zr-MOP with the COF precursors in a solvothermal method, and is known as IPcomp-8, where IP stands for IISER Pune and comp for composite material, (Figure 5.1) (See the appendix for detail synthetic method).^[46] After the synthesis, thorough characterizations of the composite material have been performed in order to understand the structural properties of the composite before performing the capture studies. The structural analysis of the composite material was deduced through a combination of powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), x-ray photoelectron spectroscopy (XPS), nitrogen gas sorption studies, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and others. The formation of the crystalline structure of the composite material was corroborated through PXRD studies (Figure 5.2a).^[47] This data also indicated the formation of the crystalline COF structure in the composite keeping the structural integrity of the iCOF. The FTIR spectra were recorded to illustrate the successful covalent threading of the MOP molecules into the iCOF matrix. From the FT-IR spectrum of the composite material, it the presence of the new imine bonds ($\sim 1665\text{ cm}^{-1}$) and metal-carboxylate bonds ($\sim 1112\text{ cm}^{-1}$, 1498 cm^{-1}), indicated successful covalent grafting joining of the Zr-MOPs into iCOF matrix. (Figure 5.2b, Appendix Figure 5.4).^[47] Also, the peak of N-H stretching in the IPcomp-8 confirms the presence of free NH_2 functional group in the composite material. The XPS survey spectra of the composite clearly indicated the presence of all relevant elements, including C, N, O, Zr, and Cl, as compared to pristine iCOF, validating the grafting of Zr-MOP in the porous structure of the iCOF (Figure 5.2c). Moreover, the deconvoluted XPS spectra of Zr 3d energy level of IPcomp-8 was found to be shifted towards lower binding energy compared to pristine Zr-MOP, indicating a significant interaction between the guest MOP and host iCOF matrix (Figure 5.2d, and Appendix Figure 5.5). Next, the nitrogen sorption isotherm at low temperature (77 K) showed lower uptake for IPcomp-8 than the pristine iCOF material which imply the successful incorporation of Zr-MOP inside the iCOF matrix (Figure 5.2e).^[39]

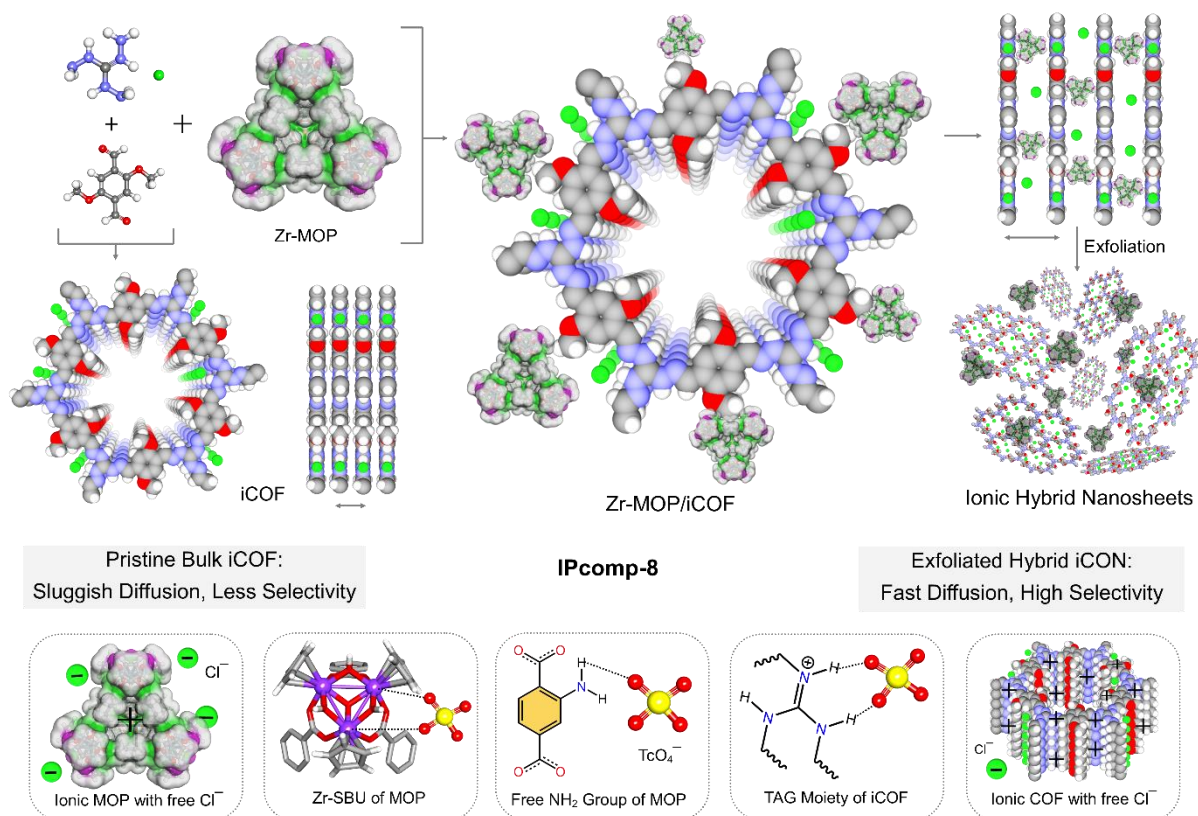


Figure-5.1: Schematic representation of synthesis of ultrathin hybrid composite material (IPcomp-8) by covalently embedding Zr-iMOP with iCOF, and pristine iCOF. Various multifunctional features of IPcomp-8 showing electrostatic and functional group mediated interactions with radioactive oxoanions.

However, IPcomp-8 feature typical microporous nature, as revealed from the $\text{N}_2@77\text{K}$ measurement. Further, in order to evaluate the ionic property of the composite material, Zeta potential measurement has been carried out. The surface charge of IPcomp-8 was found to be positive with Zeta potential value $+49.3 \pm 2.1$ mV, which inferred its cationic nature (Figure 5.2f). Importantly, the surface charge of the pristine cationic MOP and iCOF was found to be lower than the composite. The thermogravimetric analysis (TGA) illustrated an improved thermal stability of MOP molecules when anchored into the COF matrix with no disintegration of the structure up to 400°C . (Appendix Figure 5.6).^[39] The presence of featured signals of both MOP and iCOF in the ^{13}C solid-state CP-MAS NMR spectrum of the composite material denoted that the composite material consisted of both MOP and iCOF structures (Appendix Figure 5.7). The MOP molecules' covalent bonding to the iCOF matrix was confirmed by the emergence of a new peak at 151 ppm in the spectrum of IPcomp-8, which was caused by the development of a new imine bond between MOP (amine) and iCOF (aldehyde).^[32] The morphology of IPcomp-8 was examined by the FESEM, TEM and AFM analysis. The high resolution FESEM images

of IPcomp-8 showed robust sheet like morphology with small thin layers (Figure 5.2g). While the pristine MOP and iCOF showed cube like and bulk-flake like morphology, respectively (Appendix Figure 5.8). The image from HRTEM experiment also confirms the similar type morphology with clear lattice fringes and selected area electron diffraction (SAED) pattern of IPcomp-8 structure (Figure 5.2h). In addition, the Zr/Cl ratio of the composite material found in the energy dispersive X-ray (EDX) analysis as ~ 2.9 , which confirms the presence of stable cationic MOP molecules in the iCOF matrix (Appendix Table 1).^[47] The EDX elemental mapping from TEM experiment of the composite materials proved the even distribution of MOPs throughout the composite along with all the relevant elements (Appendix Figure 5.9). Moreover, the AFM experiment has been performed to explore the surface morphology with greater details. The AFM images of IPcomp-8 demonstrated the ultrathin sheet like morphology with the average height of ~ 4 -8 nm (Figure 5.2i). However, the average height of the pristine iCOF was found as ~ 40 nm (Appendix Figure 5.10). This data clearly indicated the ultrathin nature of the composite (nanosheets), which formed due to self-exfoliation of the iCOF 2D layers in the composite induced by intermolecular ionic repulsion by the cationic MOP.

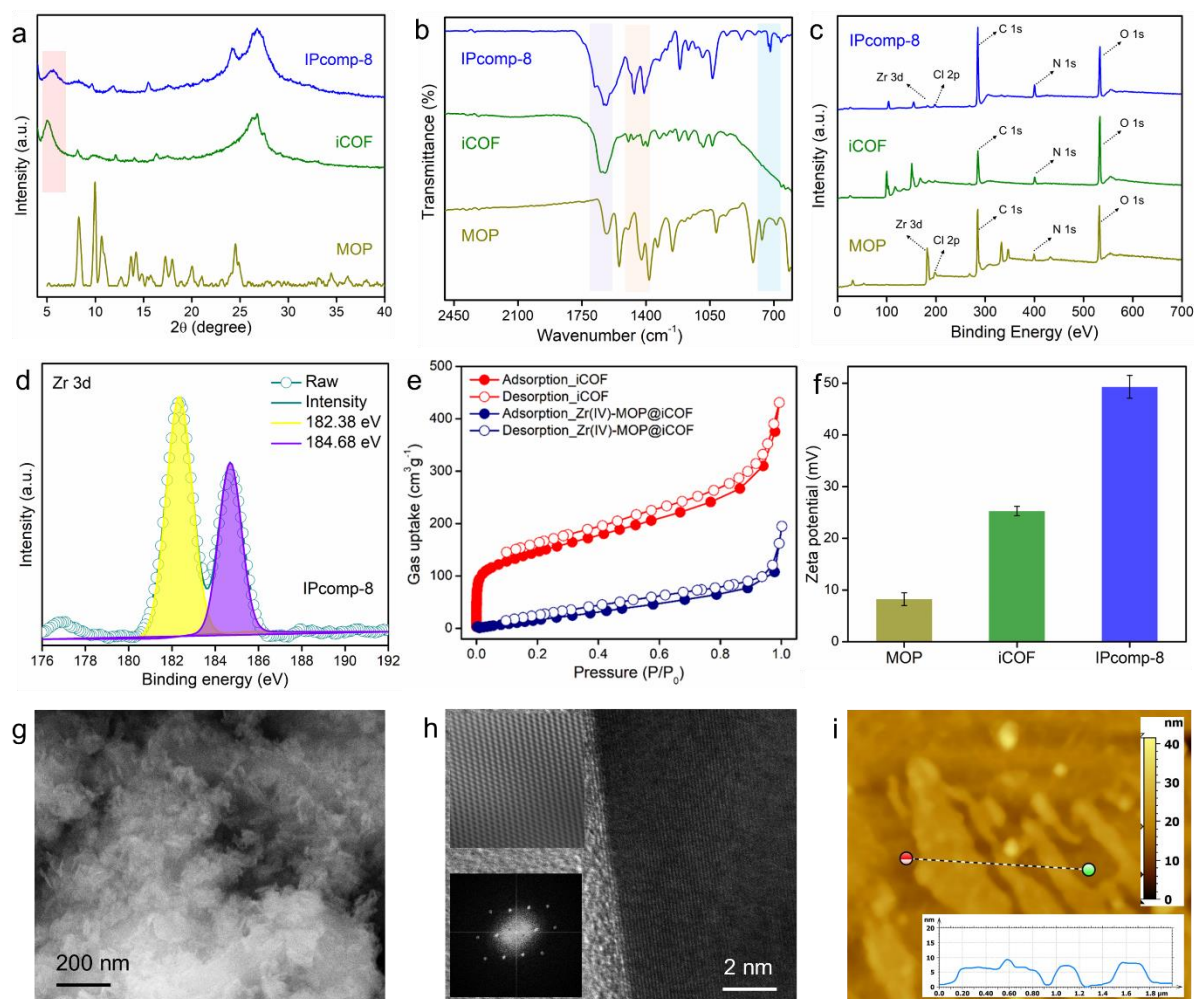


Figure 5.2 (a) PXRD profile, (b) FTIR spectra, (c) XPS survey spectra of the IPcomp-8 along with the pristine materials, (d) deconvoluted Zr 3d XPS spectra of IPcomp-8, (e) N₂ sorption profile of iCOF and IPcomp-8 at 77 K, (f) Comparison of Zeta potential values of MOP, iCOF and IPcomp-8, (g) FESEM, (h) HRTEM image of IPcomp-8, (inset: lattice fringes and SAED images), (i) AFM image and the corresponding height profile of IPcomp-8.

The optical characteristics of the hybrid composite material also helped to clarify how the MOP/iCOF hybrid material was created. The hybrid composite's UV-vis diffuse reflectance spectroscopy (DRS) revealed distinct absorption peaks for both MOP and iCOF, demonstrating the presence of both components in the hybrid composite. (Appendix Figure 5.11).^[48] All these characterizations indicated successful formation of the Zr-MOP/iCOF hybrid composite materials.

5.4 Oxoanion Capture Studies

The presence of excess free exchangeable Cl⁻ anions and multiple interactions sites, including the Zr(IV) SBU and amine functional group of the MOP, and cationic TAG moiety of the iCOF in the hybrid composite material enthused us to examine its sequestration capability toward toxic/hazardous oxoanions in water.^[49-56] Metal derived radioactive oxoanion TcO₄⁻ and its surrogate oxoanion ReO₄⁻ have chosen for the sequestration study. Initially, to optimize the performance, we performed the capture study with a series of compounds (composites synthesized with different amount of MOPs) in ReO₄⁻ solution (~50 ppm) for 2 hours. From the result of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis it was found that the composite made by taking ~15 mg of MOP (IPcomp-8) showed the best ReO₄⁻ sequestration performance (Appendix Figure 5.12). Thereafter, all the following capture studies have been performed with IPcomp-8 only. At first, the kinetics study of TcO₄⁻ capture was conducted with radiometry method where IPcomp-8 exhibited ultrafast sequestration performance as within less than 10 seconds almost >93% removal was observed (Figure 5.3a). This result motivated us to perform the detail sequestration studies of TcO₄⁻/ReO₄⁻ in water. For this, the kinetic experiment was performed by taking 5 mg of IPcomp-8 in 25 ppm of ReO₄⁻ solution. After a certain time, the compound was filtered and the residual concentration was measured. The result from ICP-AES data indicated the significant lowering of Re(VII) concentration in very less time, as almost 99% ReO₄⁻ removal efficiency was observed in case of IPcomp-8 (Figure 5.3b and Appendix Figure 5.13). Further, the sorption kinetics towards ReO₄⁻ was found to follow pseudo second order kinetics model with high correlation coefficient of R²>0.98. The rate constant value of IPcomp-8 showed an ultrafast sorption rate (mention value) (Appendix Figure 5.14). The pH of the industrial

wastewater or any real wastewater system may vary drastically from acidic to alkaline depending upon the environment of the discharge system. Therefore, it is important to check the sequestration efficiency of a sorbent material in a wide pH range. Interestingly, IPcomp-8 was found to eliminate TcO_4^- across a wide range of pH without losing its actual efficiency (Figure 5.3.c). Next, the adsorption capacity of an adsorbent is a fundamental parameter in order to understand its full efficiency. The saturation capacity of TcO_4^- by IPcomp-8 was calculated and it demonstrated very high uptake capacity (~ 576 mg/g) (Appendix Figure 5.15). We also estimated the maximum uptake capacity of IPcomp-8 for ReO_4^- . In a typical test, 5 mg of IPcomp-8 was taken in 5 mL of various range of concentration (20 ppm - 800 ppm) of ReO_4^- aqueous solution for a contact period of 24 h to reach sorption equilibrium. The uptake of ReO_4^- by IPcomp-8 follows the Langmuir isotherm model with the high correlation coefficient value (Figure 5.3d). The maximum uptake capacity of ReO_4^- by IPcomp-8 was found as ~ 632 mg/g.

It should be mentioned that apart from the kinetics and capacity, selectivity of an adsorbent is another highly important parameter to realize its potential towards real-time application. Therefore, the efficacy of an adsorbent towards a specific analyte in the presence of excess of other interfering analytes should be tested. According to the previous literatures, it has been seen that most of the work mainly focused on the storage capacity or uptake performance, but very little attention has been paid to the selectivity aspect in the presence of other interfering analytes anions which is very necessary toward sequestration from the real wastewater system.^[57] Industrial wastewater contains anions like Cl^- , NO_3^- , Br^- , SO_4^{2-} , ClO_4^- , etc., in enormous excess amounts, which interfere in this adsorption process.^[54-56] Initially, to check the influence of these aforementioned interfering anions in this adsorption process, a similar ReO_4^- capture experiment has been performed by taking a binary mixture of ReO_4^- as target anion along with these anions individually in similar concentration. To our delight, it was found that the ReO_4^- sorption efficiency by IPcomp-8 remained intact (almost 97%) in the presence of other competing anions (Figure 5.3e). Inspired by this result, we were motivated further to further test the efficiency of IPcomp-8 towards ReO_4^- in the presence of surplus concentration (~ 10 , ~ 100 , ~ 1000 , and ~ 5000 -fold) of two specific interfering analytes such as NO_3^- and SO_4^{2-} , which are generally omnipresent with ReO_4^- in wastewater. By performing similar sorption test, we observed no significant effect of both NO_3^- and SO_4^{2-} competing ions on the sequestration efficiency of IPcomp-8 up to ~ 100 -fold (Figure 5.3f and 5.3g). However, in case of excessive concentration (~ 1000 and ~ 5000 -fold) the ReO_4^- removal efficiency of IPcomp-8 was found to diminish a little. However, IPcomp-8 exhibited $\sim 83\%$ and $\sim 75\%$ ReO_4^- removal efficiency in the presence of ~ 1000 and ~ 5000 -fold NO_3^- , respectively (Figure 5.3g) which is very impressive. All these results validate the highly selective nature of IPcomp-8 towards TcO_4^- or ReO_4^- radioactive anions, making it a suitable material potential for practical application. Next, to be an ideal adsorbent, the recyclability is another imperative requirement. The hybrid material loaded with ReO_4^- anions was regenerated using saturated Na_2SO_4 solution by stirring it for ~ 10 hours.

Even after four cycles, it was discovered that IPcomp-8 could be easily recycled without losing any of its sorption effectiveness, demonstrating exceptional regeneration capacity. (Figure 5.3h). Overall, IPcomp-8 hybrid material is superior to conventional adsorbents due to its rapid capture efficiency and unparalleled selectivity toward $\text{ReO}_4^-/\text{TcO}_4^-$.

That being said, in real wastewater system the concentration of the toxic analyte exists in very low concentration ($<1\text{ppm}$). Therefore, it is important to explore the ability of the adsorbent to sequester the target analyte at trace concentrations. By the virtue of rapid and efficient $\text{TcO}_4^-/\text{ReO}_4^-$ oxo-anion adsorbing behaviour of IPcomp-8, treatment of Re(VII) contaminated wastewater was performed, by mimicking the real time scenario. Moreover, a ultralow-concentration ($\sim 1000\text{ ppb}$) sequestration experiment in the presence of an abundance of other competing ions was also carried out and monitored using ICP-MS analysis to show the material's effectiveness towards segregation from drinking water.

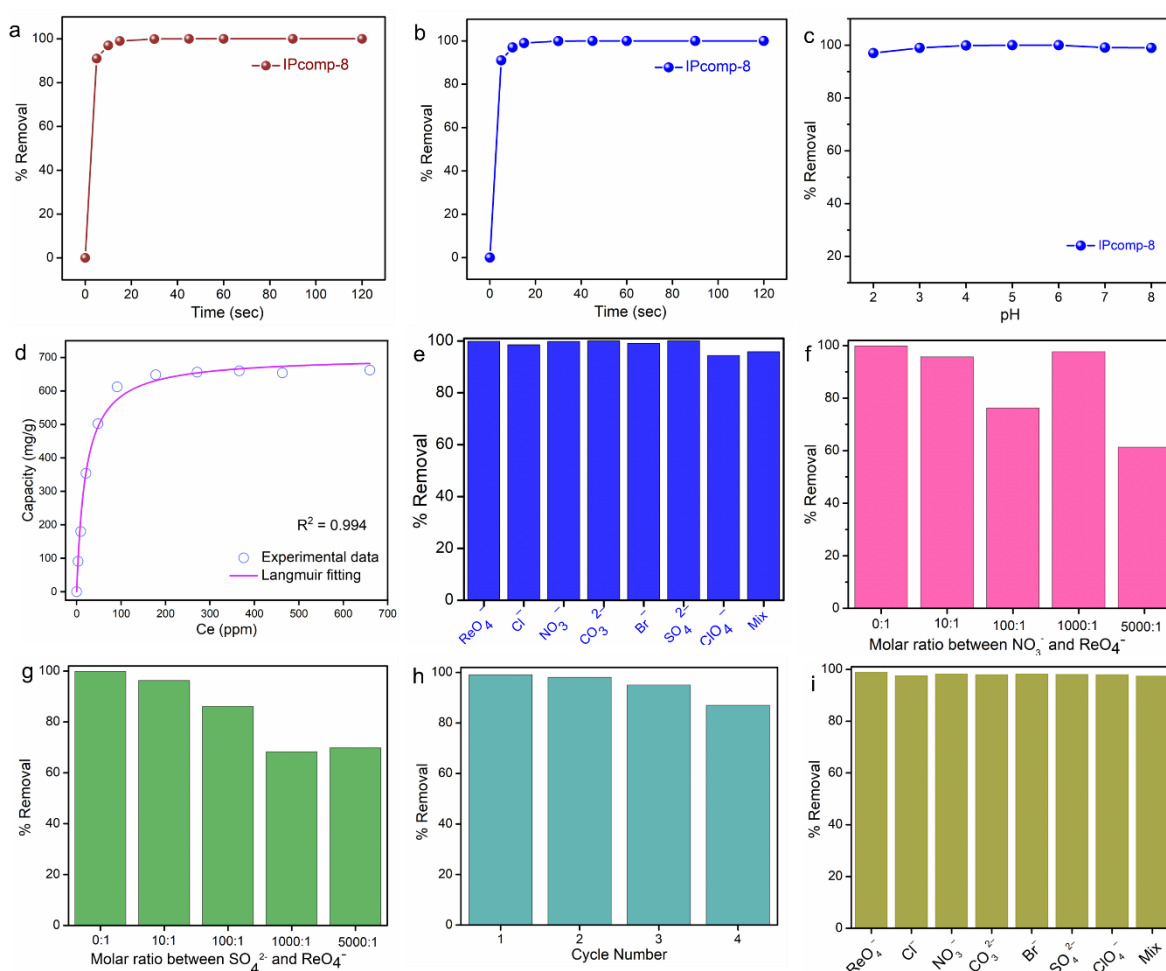


Figure 5.3: % Removal of (a) TcO_4^- and (b) ReO_4^- anion in different contact times by IPcomp-8, (c) Removal efficiency of IPcomp-8 towards TcO_4^- at different pH, (d) Langmuir isotherm fitting model for ReO_4^- capture, (e) Result of selectivity for ReO_4^- removal efficiency in the presence of different anions,

(f, g) Selectivity result for ReO_4^- in the presence of excess NO_3^- and SO_4^{2-} anions, respectively, (h) Recycle test result of IPcomp-8 for ReO_4^- ion, (i) Selectivity of IPcomp-8 towards ReO_4^- capture at ultralow concentration

Initially, in the kinetics study, IPcomp-8 was found to exhibit ultrafast sequestration efficiency towards ReO_4^- achieving ~99% removal efficiency within less than 2 min. (Appendix Figure 5.16). Consequently, the concentration of ReO_4^- was found to decrease rapidly, and the final concentration was found to be much below the WHO permitted level of drinking water (Appendix Figure 5.16).^[58] Further, the kinetic study was found to follow pseudo-second order kinetic with high rate constant value (Appendix Figure 5.17 and 5.18). Moreover, the selectivity of IPcomp-8 in low concentration was also investigated taking all the aforementioned coexisting anions. From the selectivity test it was found that IPcomp-8 exhibit superior ReO_4^- capture efficiency even in the presence of all other anions in equal as well as highly excess concentration (Figure 5.3i and Appendix Figure 5.19 and 5.20). All these results of efficient and selective entrapment of radioactive TcO_4^- or ReO_4^- oxo-anions indicated the potential of IPcomp-8 towards real-time nuclear waste water treatment application.

5.5 Mechanism Studies

After evaluating the capture performance, the underlying mechanistic insight was further explored in order to understand the multiple interactions that are responsible behind such efficient TcO_4^- sequestration performance by IPcomp-8. For this, following post capture characterizations have been performed. At first the FTIR analysis of Re(VII) loaded IPcomp-8 displayed appearance of a sharp peak ($\sim 901\text{ cm}^{-1}$) corresponding to ReO_4^- anions, which support the selective binding of ReO_4^- with IPcomp-8 (Appendix Figure 5.21).^[59] The thermogravimetric analysis of ReO_4^- loaded material showed weight losses related to absorbed ReO_4^- anions, however, similar thermal stability was observed in both the cases (Appendix Figure 5.22).^[59] Furthermore, the EDX elemental mapping analysis from the TEM experiment of ReO_4^- @IPcomp-8 was performed, which indicated the appearance of homogeneous distribution of Re metal ions along with other relevant elements throughout the structure of the composite (Figure 5.4a, 5.4b and Appendix Figure 5.23). Next, XPS analysis was performed to understand the interaction between the positively charged backbone of the composite material and the oxo-anion in depth. Re 4f binding energy peak was clearly visible in the XPS survey spectra of samples that had undergone oxo-anion treatment, indicating that Re was present on the surface of IPcomp-8 (Figure 5.4c).

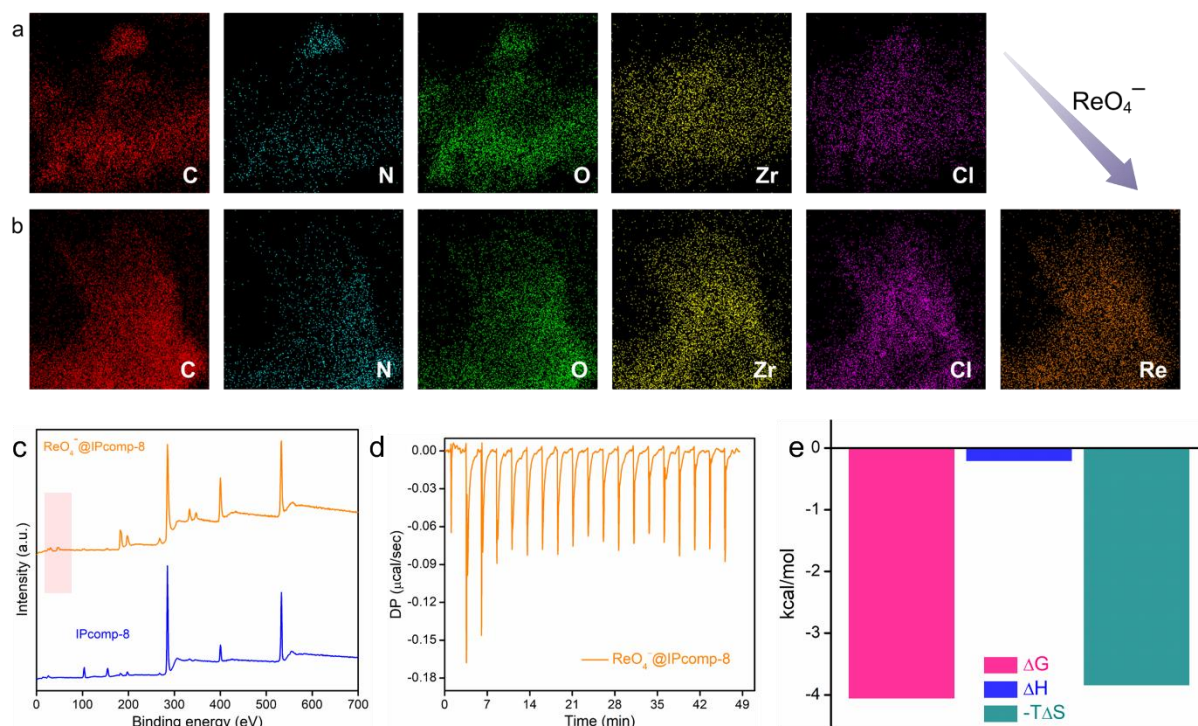


Figure 5.4: (a, b) TEM EDX elemental mapping of IPcomp-8 and ReO_4^- @IPcomp-8, respectively, (c) XPS survey spectra of IPcomp-8 and ReO_4^- @IPcomp-8, (d, e) ITC thermogram with its corresponding parameters.

The deconvoluted XPS spectra of Re 4f confirmed the existence of Re in their +7 oxidation state. Re 4f was also discovered to transition from having a greater binding energy to having a lower one when compared to pure KReO_4 , which amply demonstrated the strong interaction between the cationic network and the oxo-anion. (Appendix Figure 5.24).^[59] This finding demonstrated unequivocally that the strong electrostatic interactions between the cationic network and the oxoanions was responsible for the rapid removal efficiency. Thereafter, apart from the XPS and other experimental investigations, we have also performed isothermal titration calorimetry (ITC) experiment to evaluate thermodynamic feasibility of the favourable interactions between the compound and the analyte in aqueous medium. ITC experiment quantitatively provides the change in enthalpy, entropy and Gibbs free energy associated with the adsorption driven by the ion-exchange process between adsorbent and adsorbate. The recorded thermogram depicted a high association constant with exothermic binding event along with the parameter (see appendix section for this). This result indicated the adsorption of ReO_4^- by IPcomp-8 was favourable as the Gibbs free energy of the process is found to be negative with positive association constant and positive entropy (Figure 5.4d, 5.4e and Appendix Figure 5.25). Thus the ITC data clearly demonstrated the similarities between the thermodynamic parameters and the experimental findings of strong interaction of IPcomp-8 and ReO_4^- .

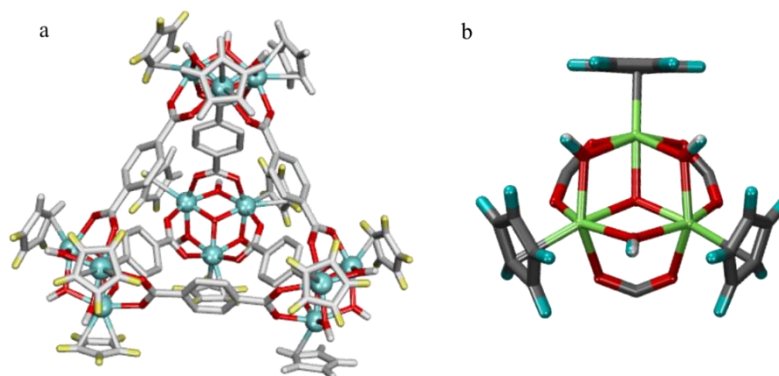
All these above investigations and characterizations were carried out to support the possible TcO_4^- binding mechanism with IPcomp-8. Previously in the literature it is well established that Zr(IV) SBU and amino functional groups can act as active sites for selective oxoanion binding.^[60, 61, 62] As a result, the composite material's cationic guest (NH_2 -MOPs) has a significant impact on the selective trapping of $\text{ReO}_4^-/\text{TcO}_4^-$. Having said that, pristine MOP molecules undergo self-aggregation^[63] which inhibits the functional groups from interacting with the incoming oxo-anions, hence this results in the reduction of the capture efficiency. In IPcomp-8 hybrid composite material nanosized MOP are covalently tethered with the layers of the iCOF that restricts the self-aggregation process. When the MOP molecules binds to the iCOF it gets exfoliated driven by electrostatic repulsions and forms ultrathin nanosheets. This nanosheets bear greater number of exposed interactive sites for the amplified strong electrostatic interactions between cationic host matrix and anionic metal based oxo-anions ($\text{ReO}_4^-/\text{TcO}_4^-$) which enhances ultrafast and selective capture efficiency.

5.6 Conclusion

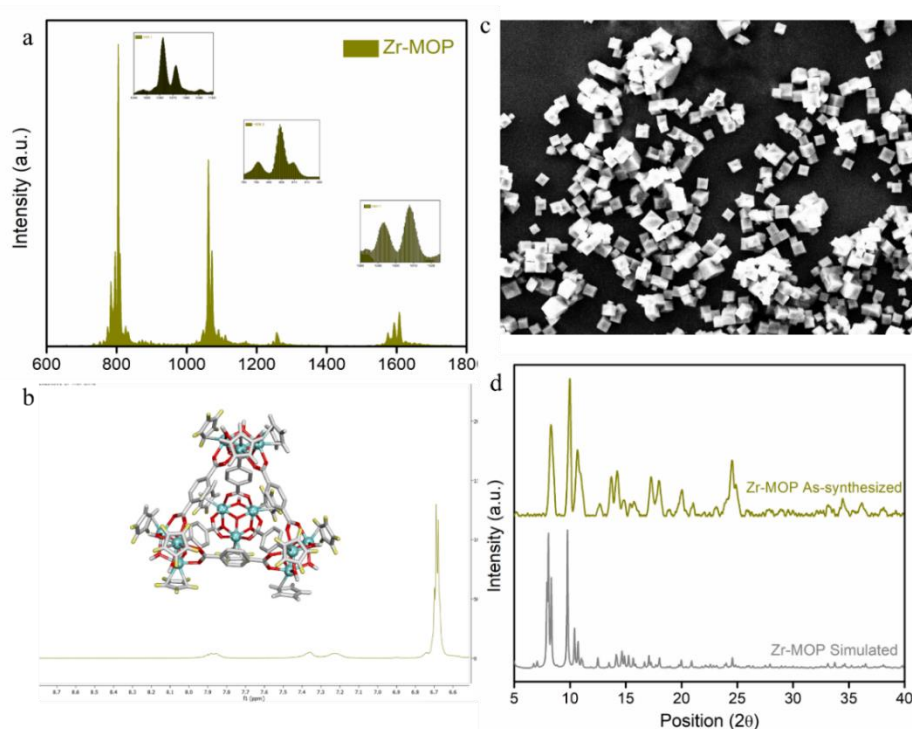
In conclusion, we have strategically designed and successfully synthesized a covalently linked MOP@iCOF hybrid composite material (IPcomp-8). This work demonstrates an optimization strategy to greatly enhance the stability of the compound along with enhanced selectivity towards pertechnetate sequestration. Structural and optical characterisations have been thoroughly carried out to gain detailed insights into the composite material. The major targeted criterion being the selective entrapment of $\text{TcO}_4^-/\text{ReO}_4^-$, careful anchoring of nanosized discrete cationic MOP molecules based on $\text{Cp}_3\text{Zr}_3\text{O}(\text{OH})_3$ SBU into the highly stable iCOF matrix produces the best selectivity and ultrafast kinetics for $\text{TcO}_4^-/\text{ReO}_4^-$ capture. This newly discovered hybrid cationic nanotrap material is a possible contender for wastewater treatment due to its rapid uptake capability, excellent selectivity, and satisfactory recyclability. We think that the current discoveries will pave the way for the creation of a range of effective improved sorbent materials for use in other environmentally important separation applications.

Appendix Section

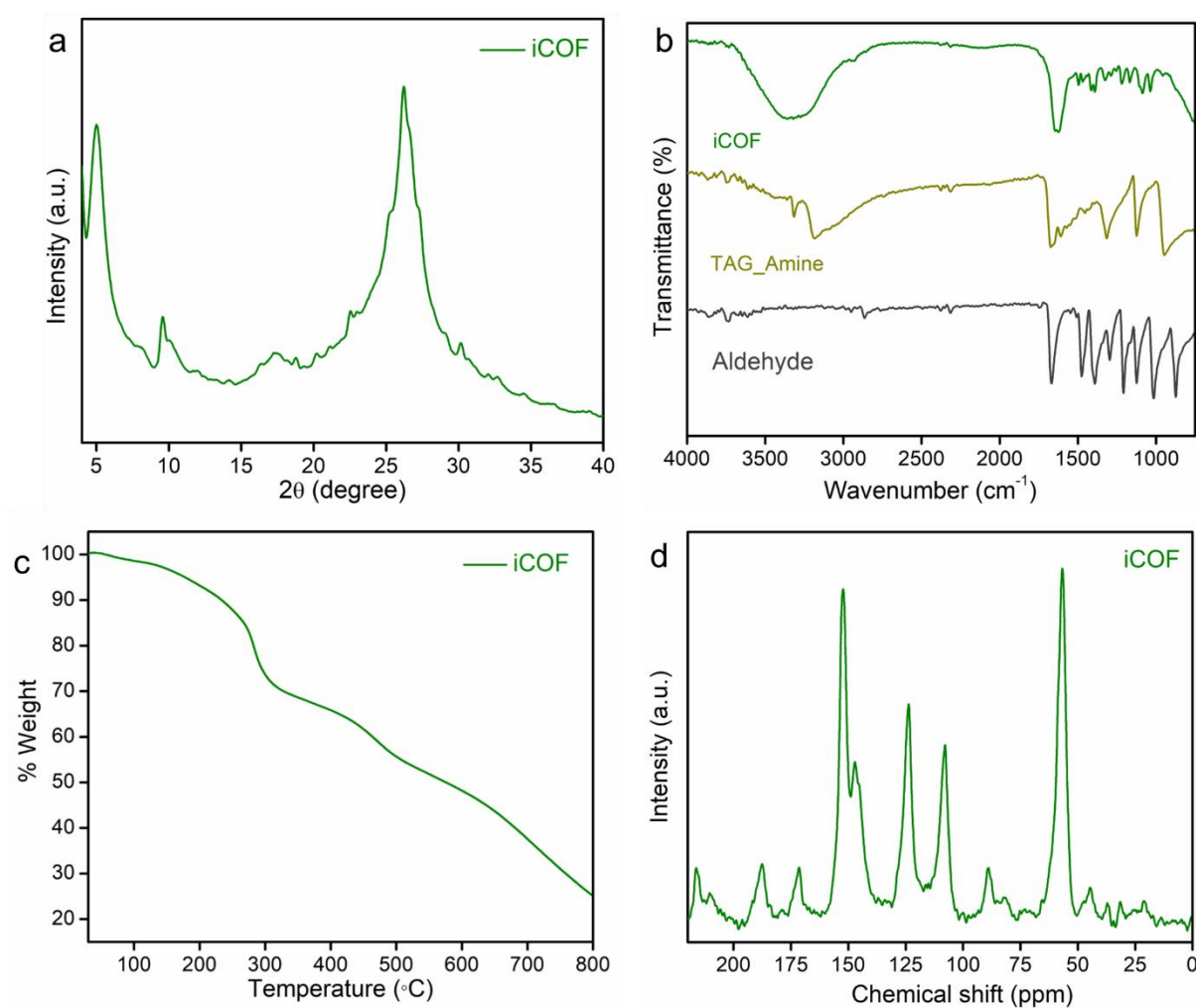
Appendix Section 1: Structural characterization of the material



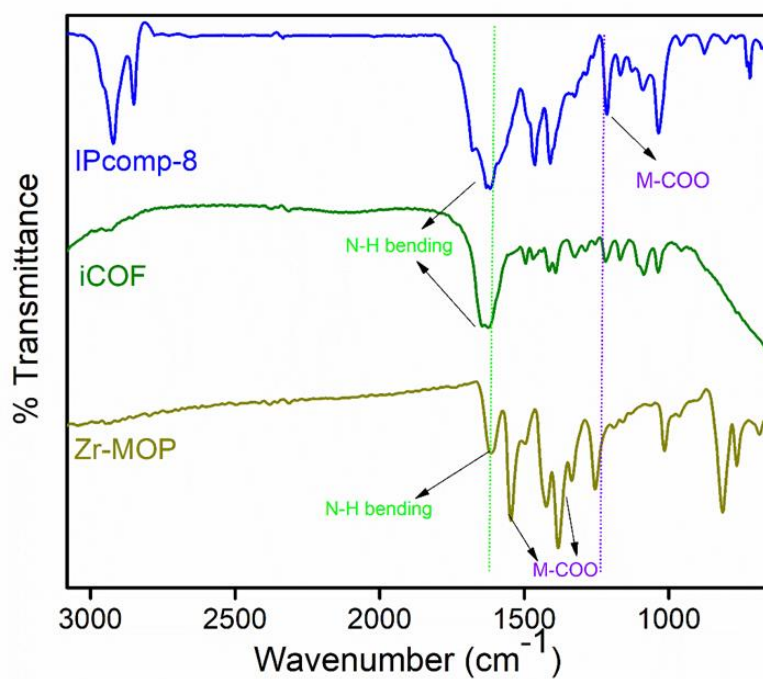
Appendix Figure 5.1. Structural features of the (a) amino functionalized metal organic polyhedral (Zr-MOP), (b) Zr(IV)-based secondary building unit (SBU) of the MOP.



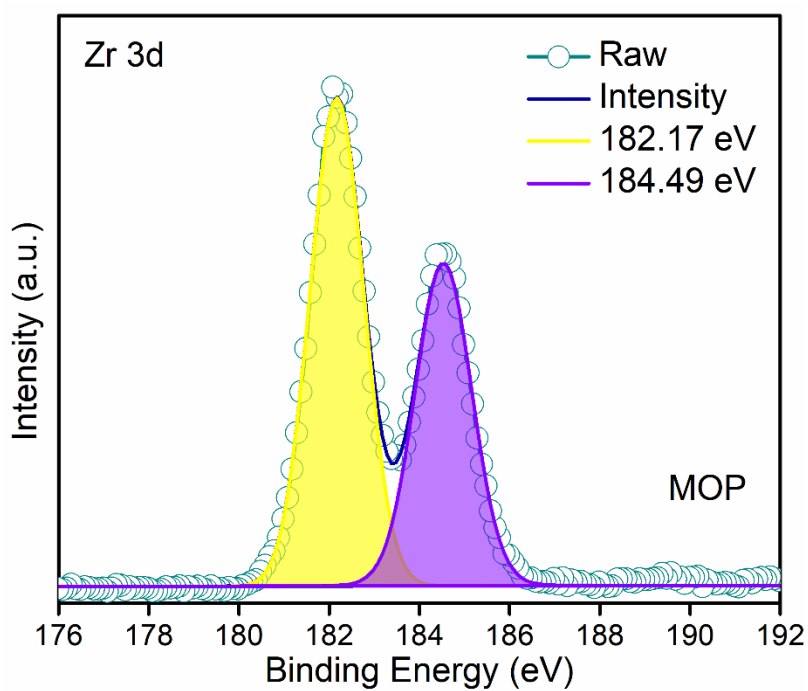
Appendix Figure 5.2. (a) ESI-TOF-MS analysis of as-synthesized NH_2 -MOP; (b) ^1H NMR spectra of the NH_2 -MOPs in MeOD and D_2O ; (c) FESEM image of the MOPs, indicated highly cubic microcrystalline morphology; (d) PXRD analysis of the NH_2 -MOP indicated formation of bulk phase purity of the MOP in as-synthesized phase.



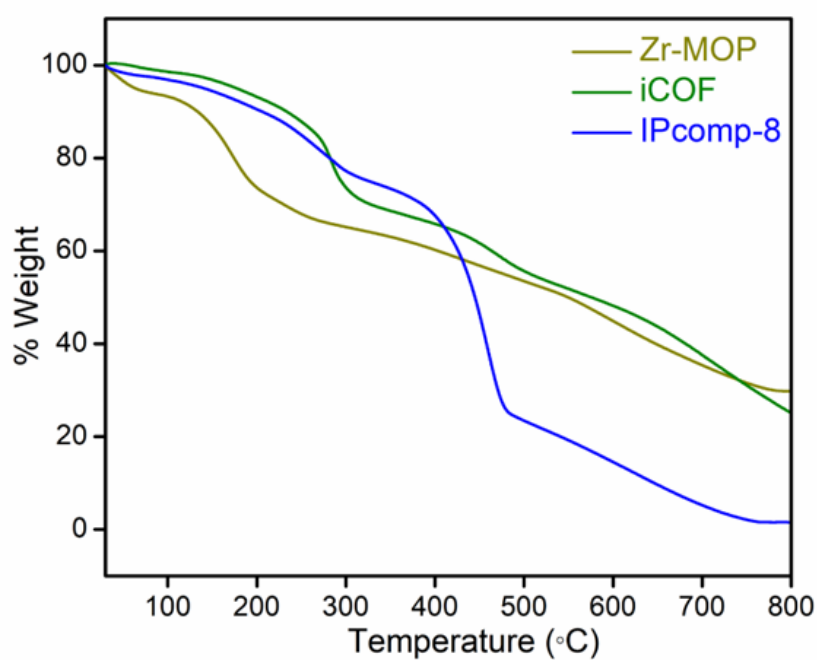
Appendix Figure 5.3. (a) PXRD patterns, (b) FTIR spectra, (c) TGA profile, (d) Solid-state ^{13}C CP-MAS NMR spectra of the iCOF.



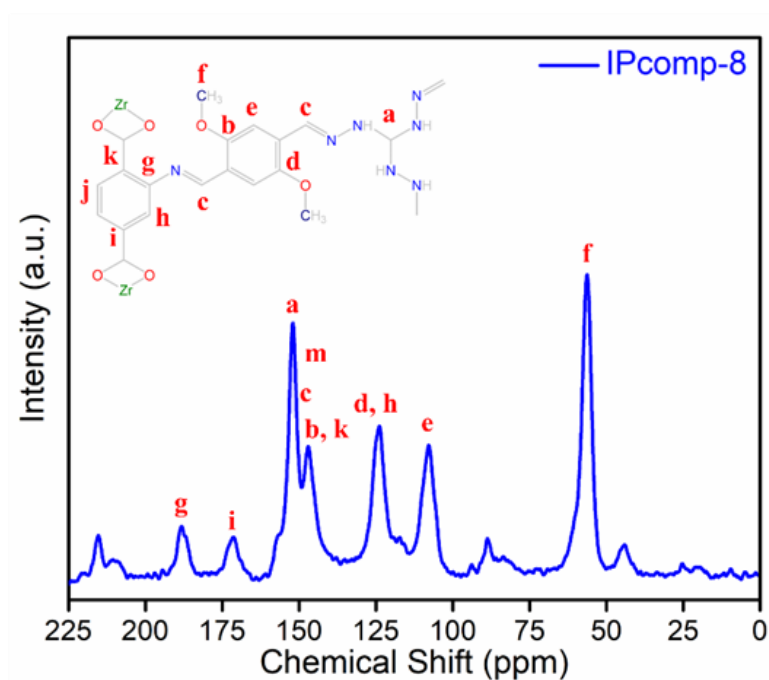
Appendix Figure 5.4. FTIR spectra of IPcomp-8 along with pristine MOP and iCOF.



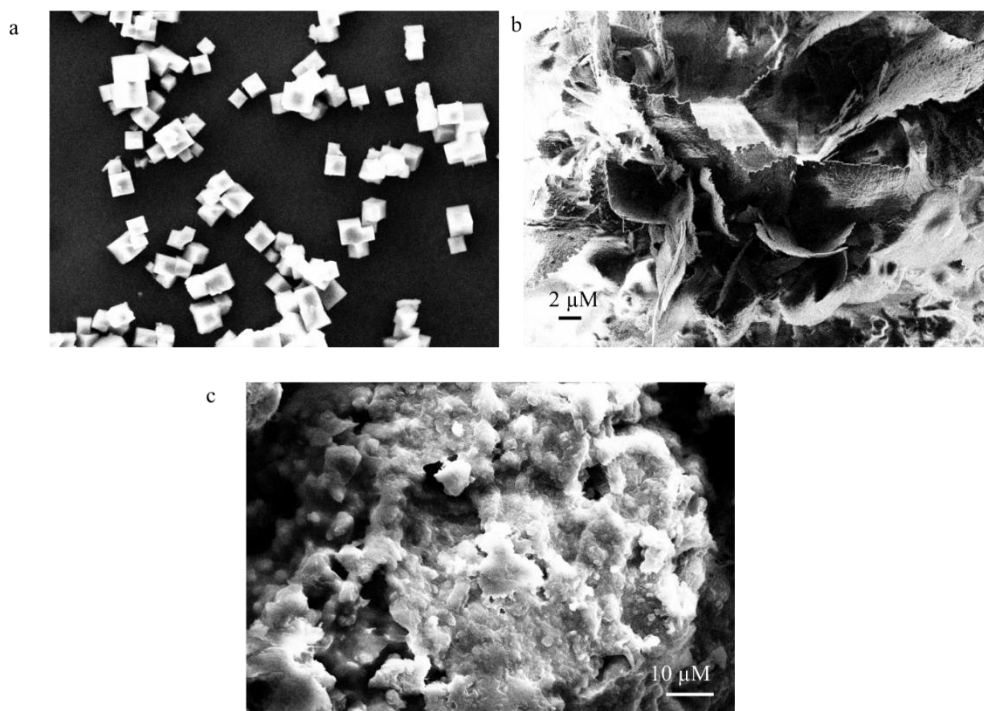
Appendix Figure 5.5. Deconvoluted XPS spectra of Zr 3d orbital of pristine MOP.



Appendix Figure 5.6. TGA profile of the Zr-MOP, iCOF and IPcomp-8 composite.



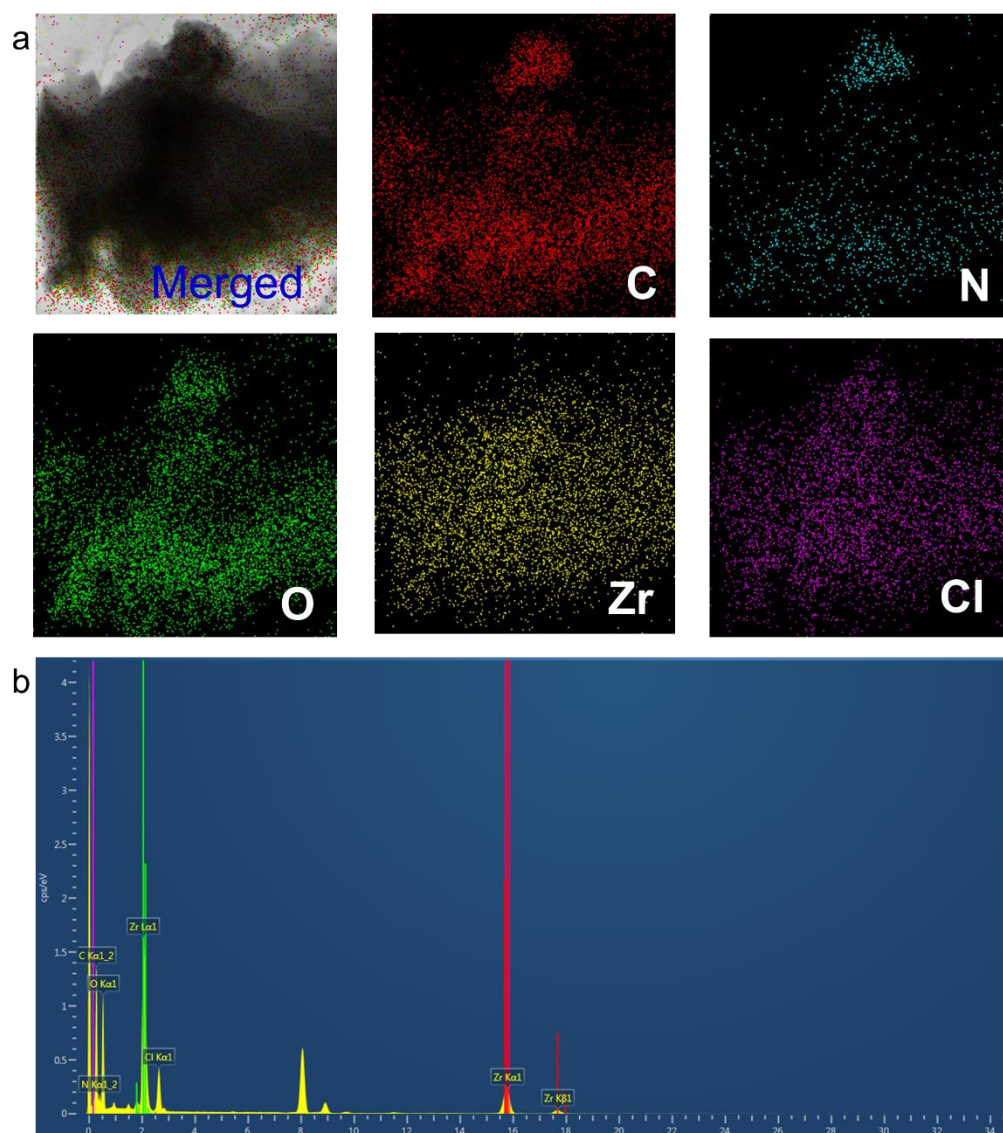
Appendix Figure 5.7. ¹³C solid-state CP-MAS NMR spectrum of IPcomp-8.



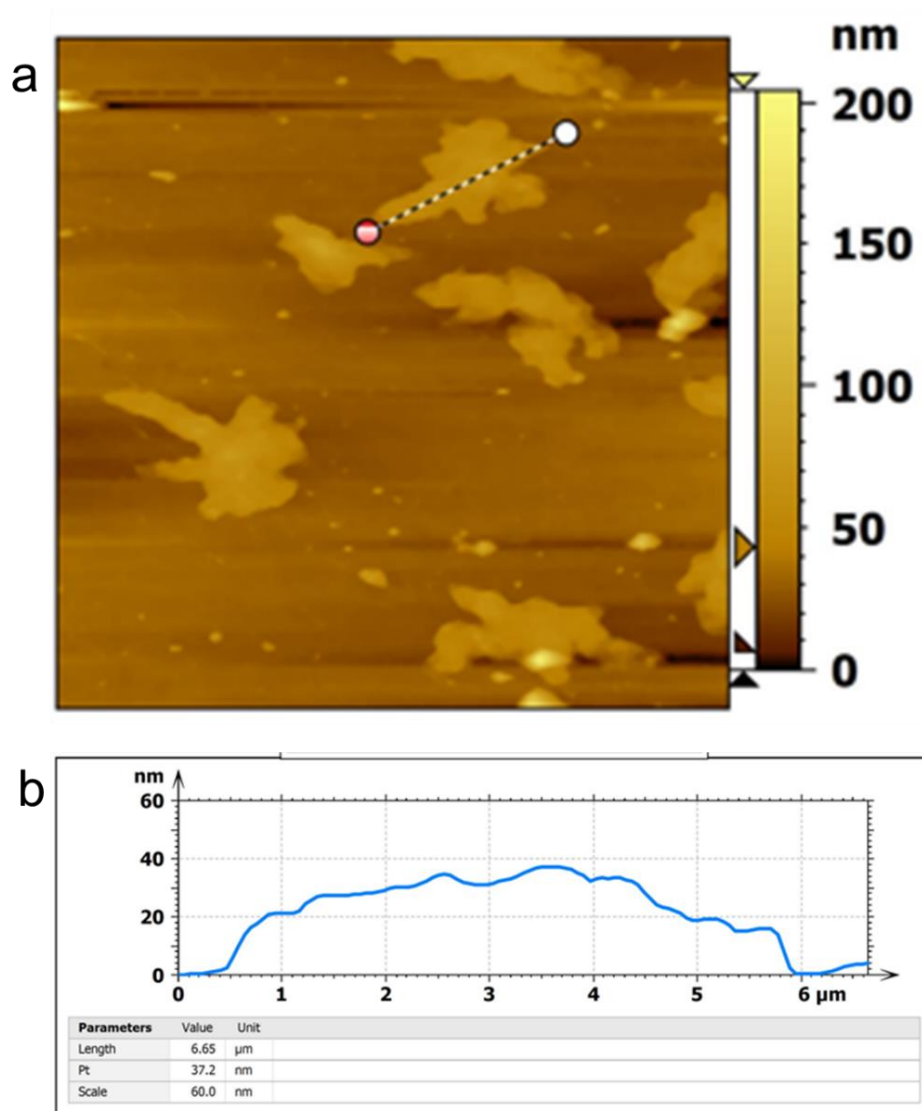
Appendix Figure 5.8. FESEM images of (a) Zr-MOP; (b) iCOF; (c) IPcomp-8 composite.

Element	Weight %	Atomic%
C K	46.66	67.09
N K	3.88	4.79
O K	19.86	21.44
Cl K	3.64	1.77
Zr L	25.95	4.91
Totals	100	100

Appendix Table 1: EDX data from FESEM experiment of IPcomp-8.

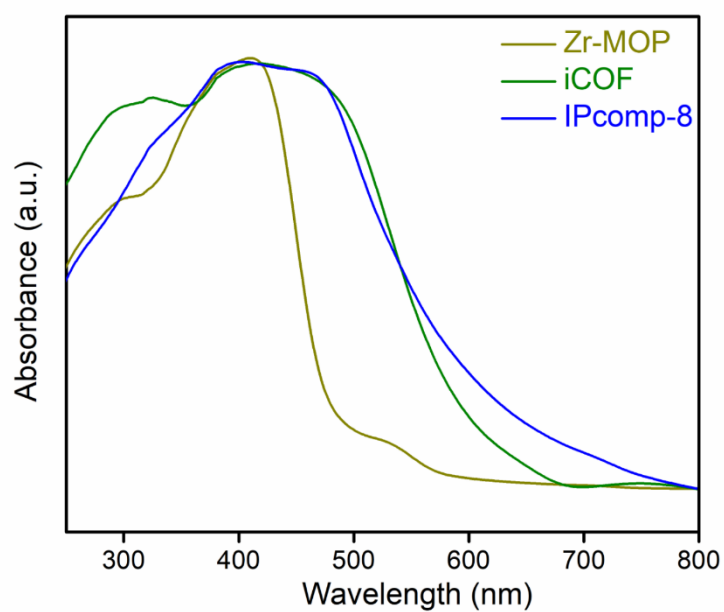


Appendix Figure 5.9. (a) Elemental mapping image and (b) EDX profile of IPcomp-8.



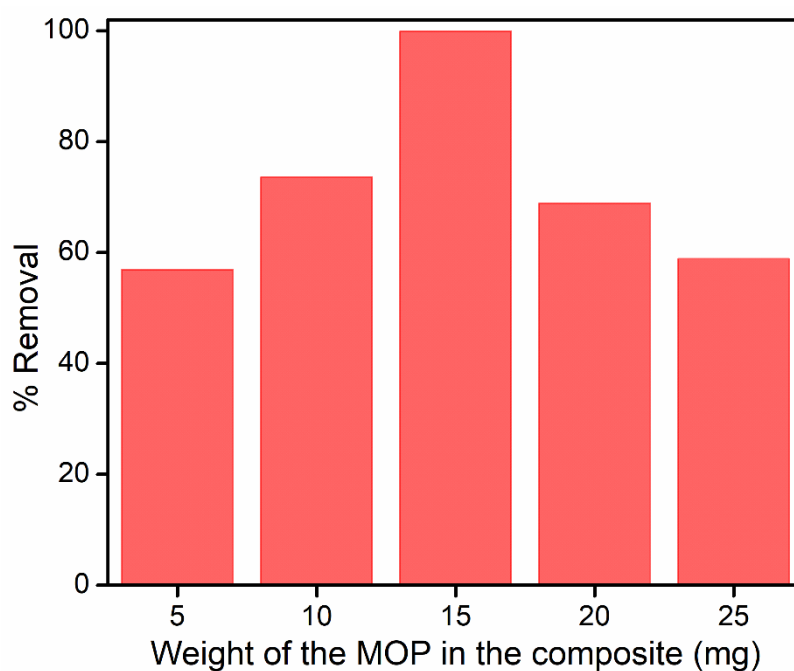
Appendix Figure 5.10. (a) AFM image and (b) height profile of pristine iCOF.

Appendix Section 2: Optical Characterisation of Synthesized Materials

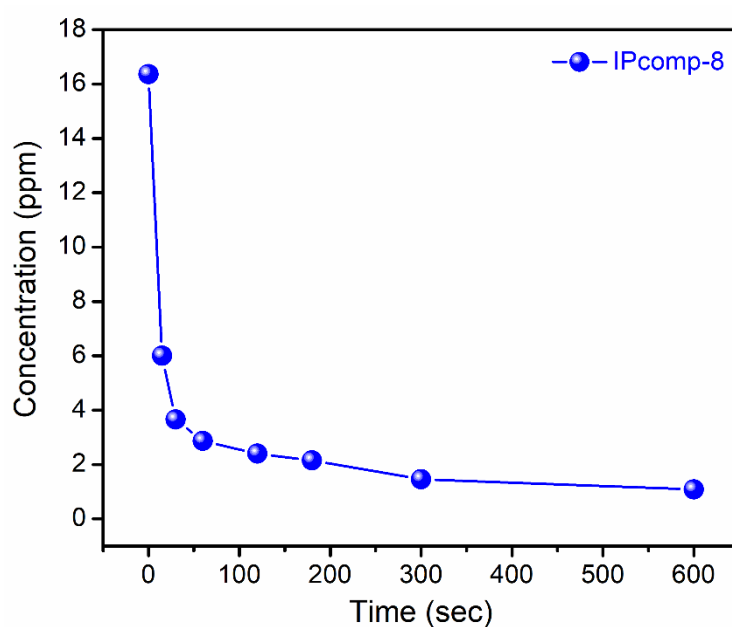


Appendix Figure 5.11. UV-vis diffuse reflectance spectroscopy (DRS) of the Zr-MOP, iCOF and IPcomp-8.

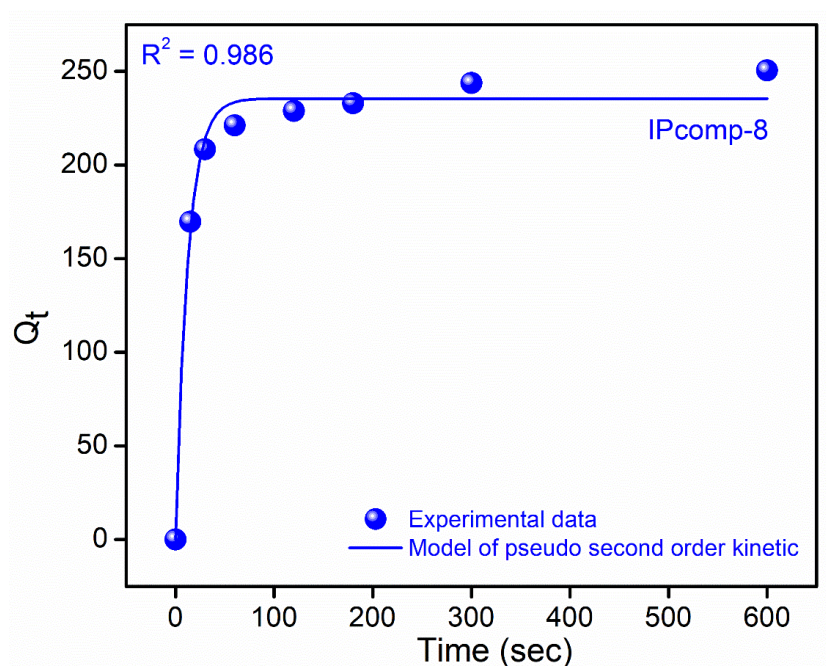
Appendix Section 3: Capture Studies



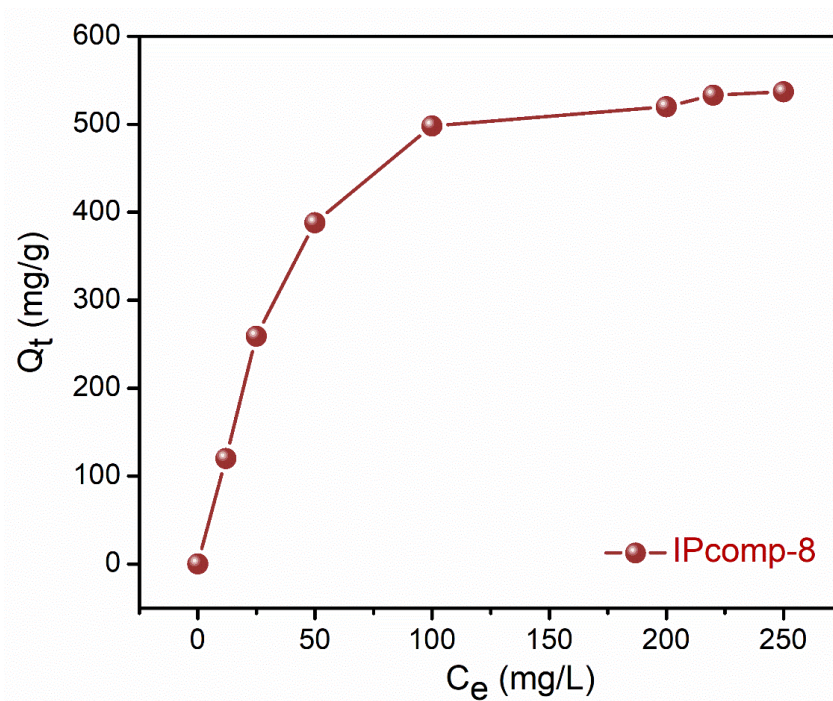
Appendix Figure 5.12. Optimization result of ReO_4^- capture study with various compounds.



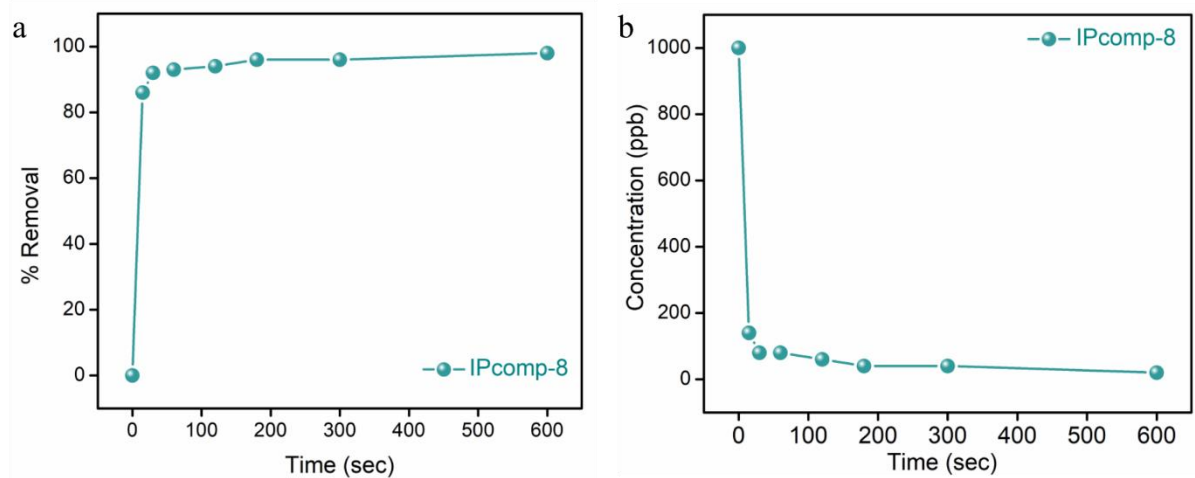
Appendix Figure 5.13. Decrease in the concentration of ReO_4^- anion in different contact times by IPcomp-8.



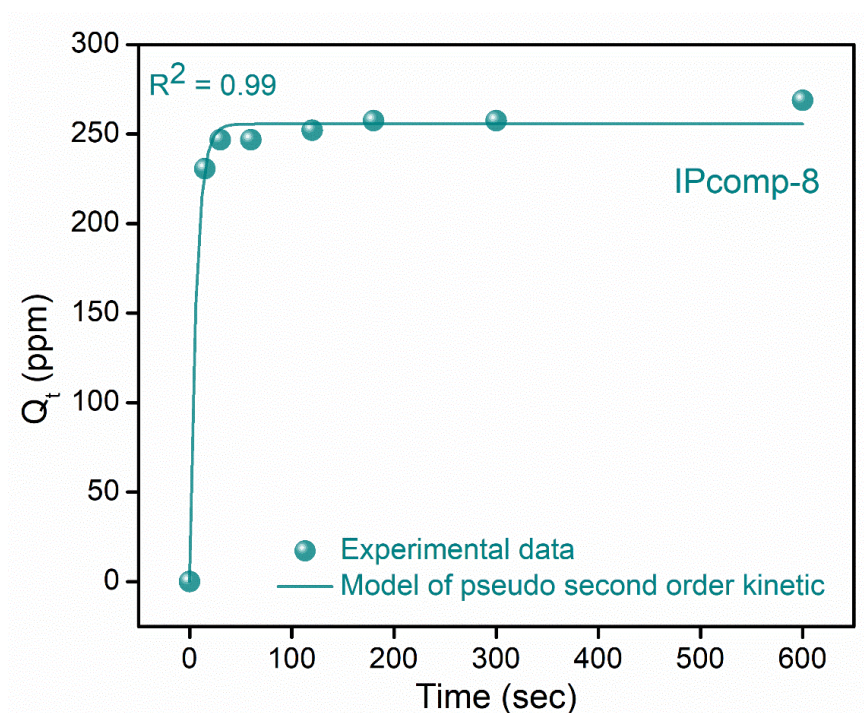
Appendix Figure 5.14. Pseudo-second order model fitting curve of ReO_4^- aqueous solution by IPcomp-8.



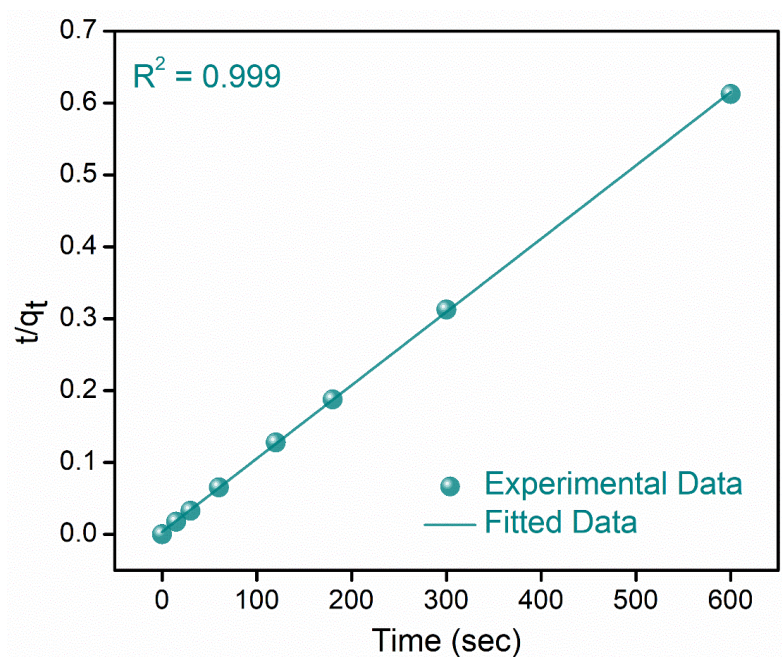
Appendix Figure 5.15. Adsorption capacity of TcO_4^- by IPcomp-8.



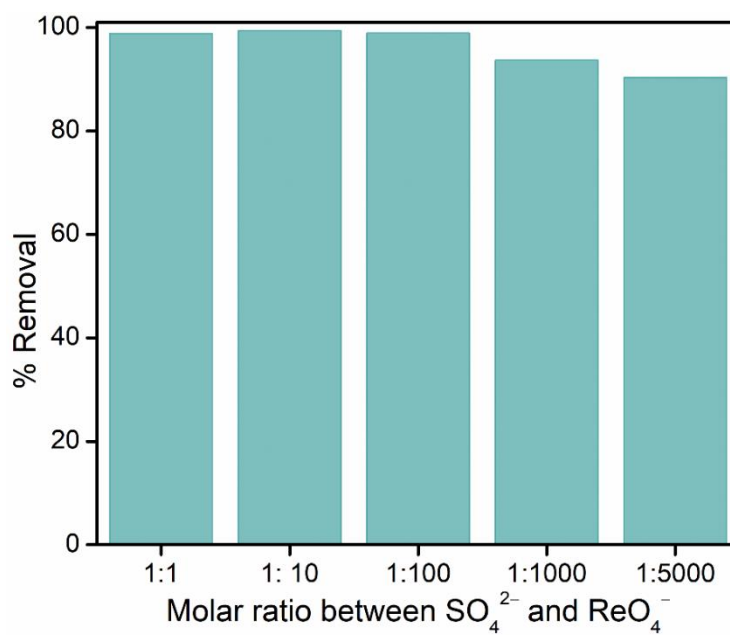
Appendix figure 5.16. Low concentration kinetics (a) % Removal vs time (b) Concentration decrease vs time.



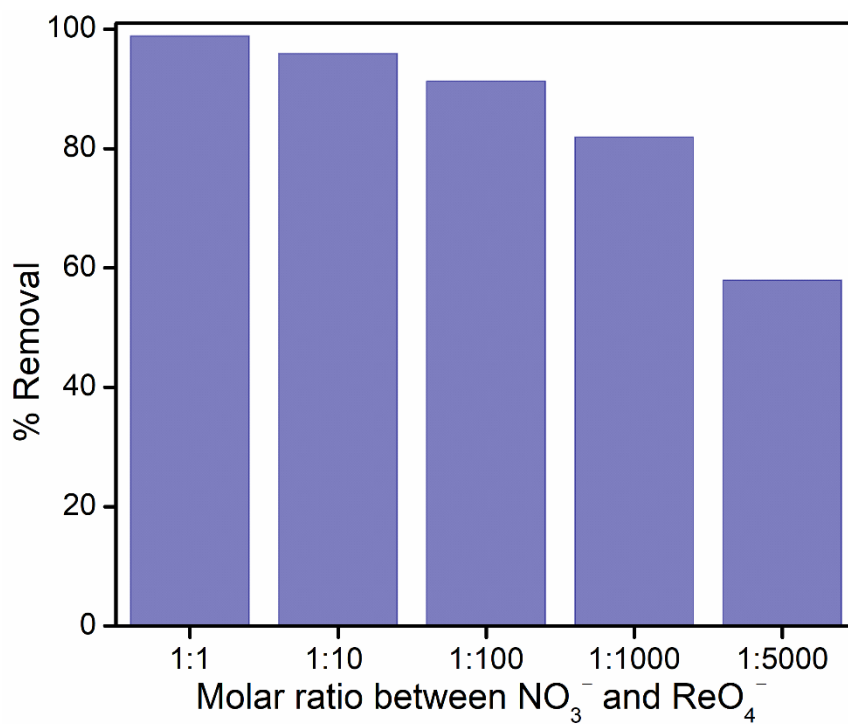
Appendix figure 5.17. Pseudo-second order non-linear model fitting curve of Re(VII) aqueous solution by IPcomp-8 at low concentration.



Appendix figure 5.18. Pseudo-second order linear model fitting curve of Re(VII) aqueous solution by IPcomp-8 at low concentration.

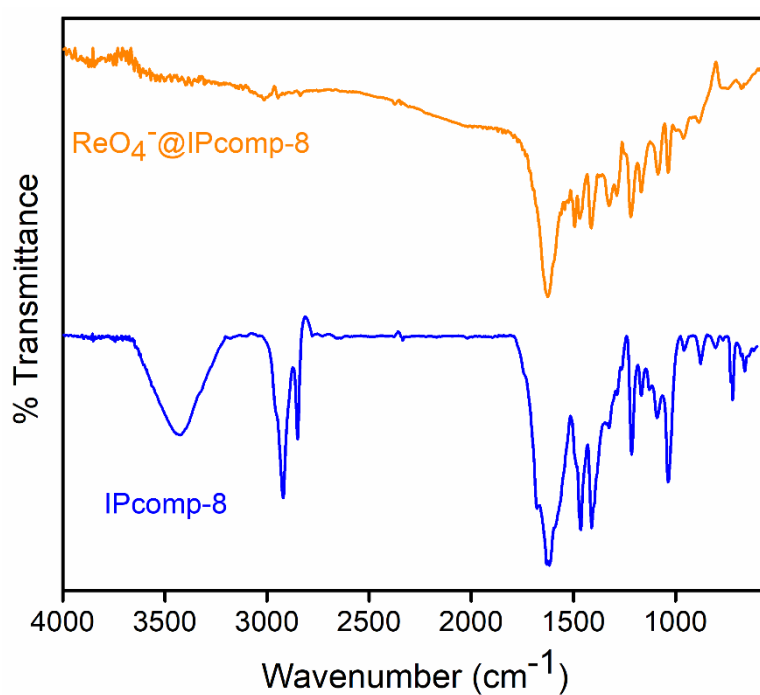


Appendix figure 5.19. Removal efficiency of IPcomp-8 towards ReO_4^- in the presence of excess SO_4^{2-} anions at low concentration.

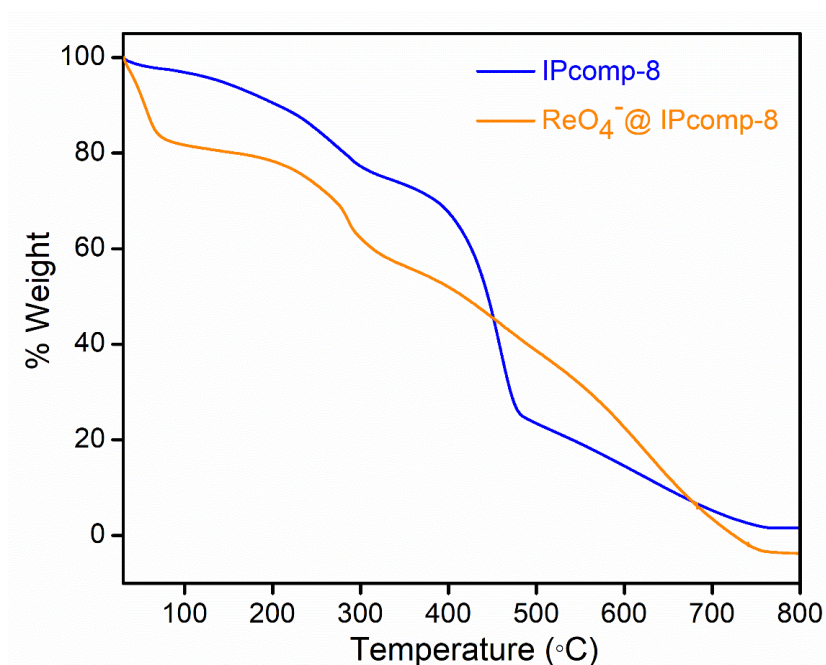


Appendix figure 5.20. Removal efficiency of IPcomp-8 towards ReO_4^- in the presence of excess NO_3^- anions at low concentration.

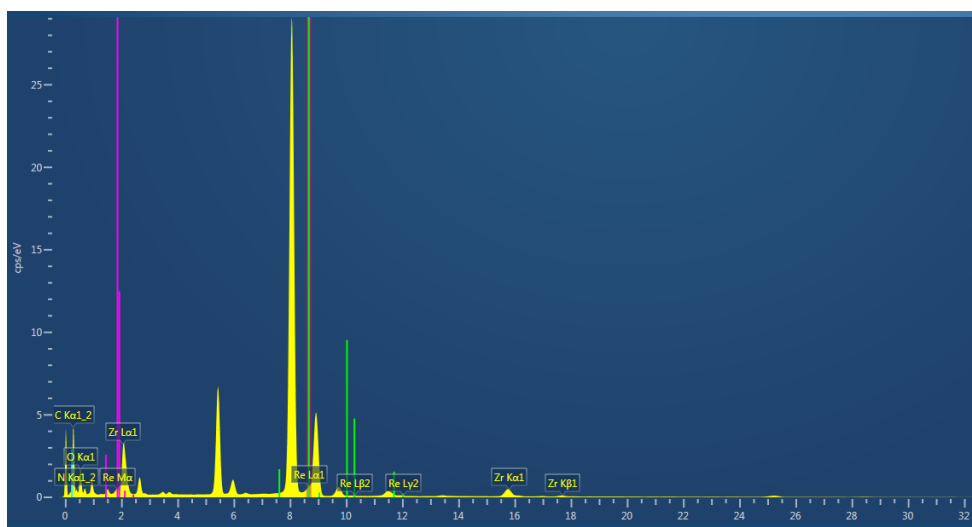
Appendix Section 4: Post Capture Characterization



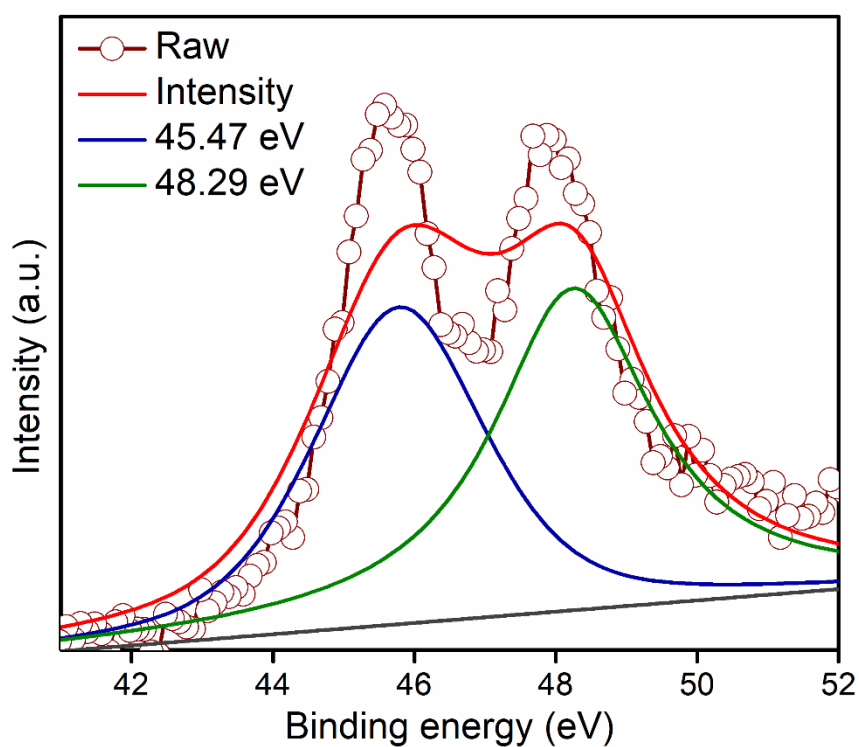
Appendix figure 5.21. FTIR spectra of IPcomp-8 and Re(VII) treated IPcomp-8.



Appendix figure 5.22. TGA profile of Re(VII) treated IPcomp-8 along with the pristine compound.



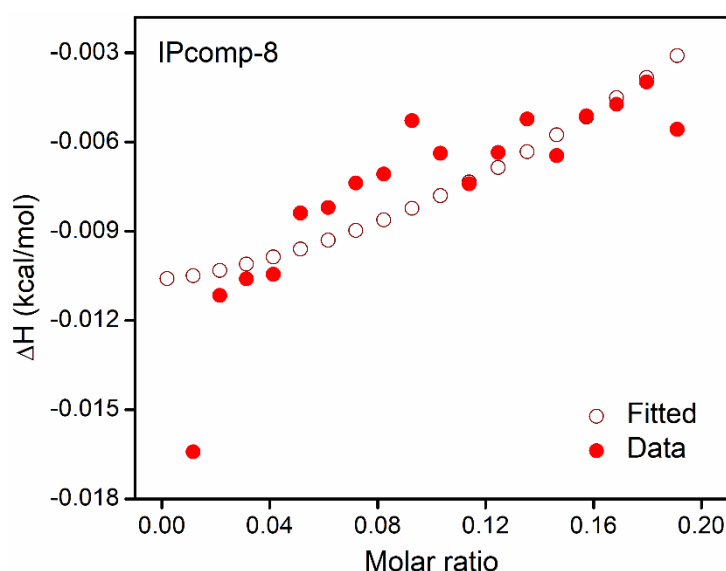
Appendix figure 5.23. TEM-EDX profile of Re(VII) treated IPcomp-8.



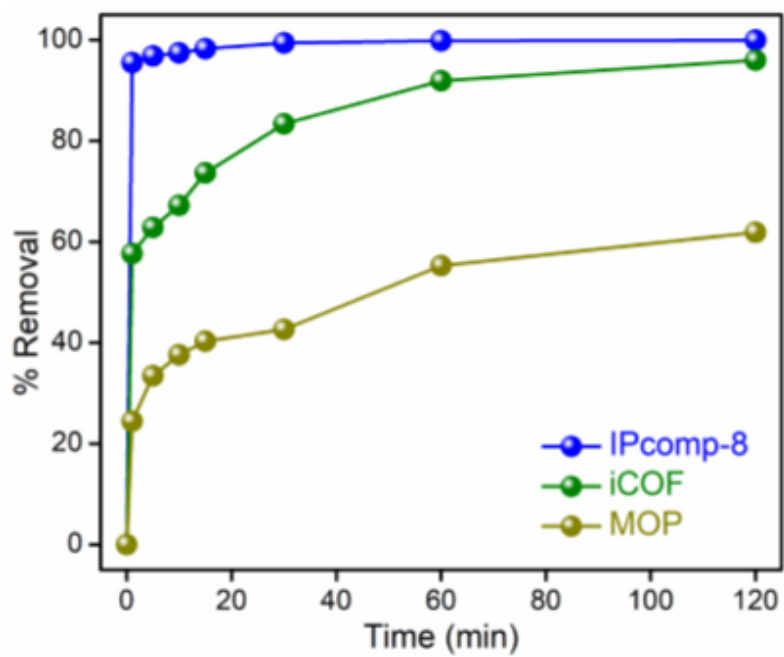
Appendix figure 5.24. Deconvoluted XPS spectra of Re 4f orbital of ReO_4^{2-} @IPcomp-8.

Appendix Section 5: Isothermal titration calorimetry (ITC) studies

Further, beyond the XPS and other experimental investigations, we have also performed isothermal titration calorimetry (ITC) for the thermodynamic validation of such favourable interactions between the targeted oxoanion (ReO_4^-) and the hybrid composite material (IPcomp-8) in aqueous medium. ITC experiment quantitatively provides the change in enthalpy, entropy and Gibbs free energy associated with the adsorption followed by the ion-exchange process between adsorbent and adsorbate. In this typical experiment, first, the reference cell was filled with deionized water, and a homogeneous aqueous suspension of 1 mmol adsorbate (IPcomp-8) (which was grounded into fine powder) was poured into the sample cell and the 100 ppm concentration of adsorbent (Re(VII)) aqueous solution was placed into the syringe, while the complete mixture was stirring at 750 rpm. The first injection of each titration was fixed at 0.4 μL . The analyte concentration was determined by ICP-MS. At least two titrations for each analyte-compound pair were collected. Data analysis was performed in y. MicroCal PEAQ-ITC analysis software. The heats of injection for blank titrations (analyte [Re(VII)] into blank) were subtracted from the heats of injection into compound suspensions. The recorded thermogram (in the main text, Figure 5.4d,e), (Appendix Figure 5.25) demonstrated a high association constant with the endothermic binding event along with the thermodynamic parameters. This result indicated the adsorption of ReO_4^- by IPcomp-8 was thermodynamically favourable as the Gibbs free energy of the process was found to be negative with positive association constant (K_a) and negative entropy. Thus, these ITC data clearly indicated the similarities between the thermodynamic parameters and the bulk-scale experimental data of strong interactions of ReO_4^- with IPcomp-8 in water.



Appendix figure 5.25. Heat of injection of ReO_4^- sorption in IPcomp-8.



Appendix figure 5.26. Control experiment of pristine MOP and iCOF towards ReO_4^- capture along with IPcomp-8.

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Chapter 6

Summary and Perspectives

6.1 Summary and Perspective

Advanced functional porous materials (AFPMs) have grown in popularity in recent decades due to its use in a range of disciplines such as clean energy, molecular recognition, and environmental applications. The scientific study done in this thesis was to create task-specific AFPMs to address global environmental pollution challenges. In the first part of the work MOF has been utilised for recognition of toxic pollutant in water by using fluorescence based detection methods. In this regard, a functional luminescent MOF has been synthesized. Primarily, MOF-808 has been synthesized after that it has been post synthetically modified by para-amino benzoic acid (PABA). Further this MOF recognises nitric oxide (NO) via chemodosimetric approach. This PABA@MOF-808 shows high selectivity in presence of other interfering analytes. Furthermore, a flexible mixed matrix membrane (MMM) has been fabricated with PABA@MOF-808 which can detect NO both in aqueous medium as well as in gaseous medium. However, MOF have some stability issues, like it is often unstable in water medium as well as at varied pH-ranges. For this reason, in the next work we have synthesized a highly luminescent porous organic polymer (IP_{POP-1}) for detection of micro pollutant in water. IP_{POP-1} selectively detects electron deficient antibiotics as well as electron deficient pesticides from water with a very good quenching constant (K_{sv}) and a good limit of detection (LOD) value. There are charge transfer happens from electron dense probe (IP_{POP-1}) to electron deficient analytes (antibiotic and pesticides). IP_{POP-1} could be recycled after the detection test with no obvious loss of function. Finally, IP_{POP-1} based mixed matrix membrane was fabricated for real time antibiotic detection in water. Also the detection test has been performed by using the hospital waste water.

Detection of harmful elements in water is not the end goal; extraction of those toxic contaminants from water is critical. For the later part of this thesis work, effective sequestration of toxic pollutant by ionic porous organic polymer and inorganic-organic hybrid composite materials have been discussed respectively.

In the fourth chapter, a chemically stable ionic porous organic polymer (iPOP-5) has been synthesized for the extraction of toxic pollutant CrO_4^{2-} and ReO_4^- from water. The efficiency of the compound has been increased in this work by modifying the morphologies of the compound. Among different morphologies flake morphology [iPOP-5(F)] shows ultrafast kinetics over spherical [iPOP-5(S)] ones. Notably, in the presence of excessive other anions, iPOP-5(F) selectively removed Cr(VI) and Re(VII). Furthermore, the chemical separated these oxoanions efficiently throughout a wide pH range and in a variety of water systems (including potable, lake, river, sea, and tannery water). Mechanistic analysis revealed that rare in situ exfoliation of flakes into thin nanosheets aids in rapid sequestration efficiency.

In the last chapter a hybrid composite material has been synthesized for selective entrapment of radioactive TcO_4^- . To address the inadequacies of a single material in the sequestration process, we investigated a composite material in this work. $\text{MOP}@i\text{COF}$ is a hybrid composite material that was created by combining MOP and $i\text{COF}$ as a single component first. Because of the presence of its Zr-SBU, which is well known for its interaction with the oxoanion, Zr-MOP was chosen as a guest. Aside from this, Zr-MOP contains some free NH_2 groups that are oriented along the pore and can interact with the oxoanions via H-bonding, as well as free Cl^- anions that are exchangeable with the ReO_4^- anions. Furthermore, we picked $i\text{COF}$ because of its excellent chemical stability and abundance of free exchangeable Cl^- anions. $\text{MOP}@i\text{COF}$ rapidly entraps TcO_4^- and selectively catches ReO_4^- in the presence of other interfering analytes. This material is extremely recyclable and has a high removal effectiveness in various water systems (lake water, river water, and sea water).

These studies demonstrated that porous materials with tuneable architecture are highly suited for environmental contaminant clean-up. The design flexibility, high surface area, and chemical stability of such porous organic materials have allowed their use in the removal of ecologically noxious and hazardous substances. Although porous organic materials have not been widely used in this type of application until now, they may be well suited for water pollution remediation in the near future.



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Post engineering of a chemically stable MOF for selective and sensitive sensing of nitric oxide†



Writakshi Mandal,^a Dipanjan Majumder,^a Sahel Fajal,^b Sumanta Let,^a Mandar M. Shirolkar^b and Sujit K. Ghosh^b *^{ac}

Author affiliations

Abstract

A hydrolytically stable luminous metal–organic framework (MOF) sensor was strategically designed for precise dual phase recognition of biologically relevant yet toxic nitric oxide (NO). Judicious utilization of the enabling post-synthetic modification (PSM) technology in chemically robust MOF-808 yielded amine decorated and highly luminescent PABA@MOF-808. The thus-prepared functionalized sensory probe was employed for sensitive detection of NO in both aqueous and gaseous phases in a selective manner. An exclusive fluorogenic “turn-off” response was

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W. Mandal, D. Majumder, S. Fajal, S. Let, M. M. Shirolkar and S. K. Ghosh, *Mol. Syst. Des. Eng.*, 2023, **8**, 756 DOI: 10.1039/D2ME00278G

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Selective and Sensitive Recognition of Specific Types of Toxic Organic Pollutants with a Chemically Stable Highly Luminescent Porous Organic Polymer (POP)

Author: Writakshi Mandal, Sahel Fajal, Partha Samanta, et al

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Unveiling the Impact of Diverse Morphology of Ionic Porous Organic Polymers with Mechanistic Insight on the Ultrafast and Selective Removal of Toxic Pollutants from Water

**Author:** Writakshi Mandal, Sahel Fajal, Samraj Mollick, et al**Publication:** Applied Materials**Publisher:** American Chemical Society**Date:** May 1, 2022*Copyright © 2022, American Chemical Society*

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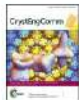
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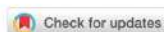
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Metal-organic frameworks as hosts for nanoparticles



[Christoph Rösler](#)^a and [Roland A. Fischer](#)^a

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Abstract

The fabrication of metal nanoparticles (NP) in porous host matrices, especially metal-organic frameworks (MOFs) has become of great interest in recent years, due to the broad field of applications. In this article we summarize the progress in the field of NP@MOF materials and illustrate the different preparation methods as well as suitable characterisation techniques. Furthermore, practical applications in the fields of hydrogen storage and heterogeneous catalysis are briefly discussed.

Metal-organic frameworks as hosts for nanoparticles

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ARTICLE

Post Engineering of a Chemically Stable MOF for Selective and Sensitive Sensing of Nitric Oxide

Writakshi Mandal,^a Dipanjan Majumder,^a Sahel Fajal,^a Sumanta Let,^a Mandar M. Shirolkar,^b and Sujit K. Ghosh^{*a,c}Received 00th January 20xx,
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A hydrolytically stable luminous metal-organic framework (MOF) sensor was strategically designed for precise dual phase recognition of biologically relevant yet toxic nitric oxide (NO). Judicious utilization of the enabling post-synthetic modification (PSM) technology in chemically robust MOF-808 yielded amine decorated and highly luminescent PABA@MOF-808. Thus prepared functionalized sensory probe was employed for sensitive detection of NO in both aqueous and gaseous phase in a selective manner. An exclusive fluoregenic “turn-off” response was observed for NO over other relevant reactive nitrogen and oxygen species (RNS and ROS) with high quenching efficiency via deamination reaction as the *modus operandi*. The potency of PABA@MOF-808 toward accurate detection of NO was further punctuated by high K_{sv} value ($6.10 \times 10^3 \text{ M}^{-1}$) and exception limit of detection (LOD) value of $0.715 \mu\text{M}$ (21.45 ppb). Additionally, the underlying sensing mechanism was disseminated with the help of experimental data as well as theoretical insights. Pertaining to processability toward practical implementation, a flexible self-standing mixed-matrix membrane (MMM) of PABA@MOF-808 was further devised for efficient sensing of NO both in water medium and vapor phase.

Introduction

Nitric oxide is produced naturally by oxidation of amino acid (L-arginine to L-citrulline) with a heme-containing enzyme known as nitric oxide synthase (NOS).¹ Nitric oxide (NO) works as a retrograde neurotransmitter, allows the blood flow in brain and also has significant roles in intercellular signaling.^{1,2} It can act as a regulatory agent in various physiological and pathological process e.g., leukocyte adhesion inhibition, bronchodilation, renal functioning etc.^{1,3} Owing to the immense importance of NO in various biological signalling process it has attracted much attention to the biologists, chemists, and medical researchers.⁴ On the other hand, excess concentration of NO in aqueous medium and air causes deleterious consequences to the living systems, especially for human being.^{5,6} Therefore, considering both the importance and adverse impacts of nitric oxide selective and sensitive monitoring of NO from water medium as well as vapour phase has become an imperative research topic, which is highly relevant to practical environmental surveillance. Moreover, in perspective of various biological and pathological process the selective identification of NO is also vital. However,

owing to its very brief lifetime along with high diffusivity and volatility it is extremely difficult to precisely recognize NO.^{1,7} In this view, up until now, several efforts have been attempted to develop effective sensory materials for the specific recognition of nitric oxide from different medium. Also, various methods like calorimetry, electron paramagnetic resonance, electrochemical and chemiluminescence have been applied for the detection of NO.^{1,7} However, all these methods exhibited several limitations such as time consuming, less efficiency, expensive, complex technique etc.⁷ In regard with this, recently, fluorescence based detection methods have been considered as promising over other due to its unique properties including quick response time, easy simple economical operation, large Stokes shifts, high sensitivity towards real-time monitoring and non-invasive nature.^{8,9} Moreover, the optimal fluorescence probe should show a notable variation in fluorescence intensity along with high selectivity even in the presence of interfering analytes.¹⁰ Owing to these advantages, numerous small organic molecules and metal based fluorescent probes have been developed and further utilized for the detection of various environmentally relevant toxic species. Importantly, to our particular interest, ortho-diamine based fluorescent probes and metal based complexes are widely been used for NO sensing.¹¹⁻¹⁶ However, in spite of substantial progress in the development of in vivo targeted synthetic probes, there are several intrinsic limitations including the water solubility and hydrolytic instability of the organic molecules based probes, which

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Selective and Sensitive Recognition of Specific Types of Toxic Organic Pollutants with a Chemically Stable Highly Luminescent Porous Organic Polymer (POP)

Writakshi Mandal, Sahel Fajal,^{||} Partha Samanta,^{||} Subhajit Dutta, Mandar M. Shirolkar, Yogeshwar D. More, and Sujit K. Ghosh*



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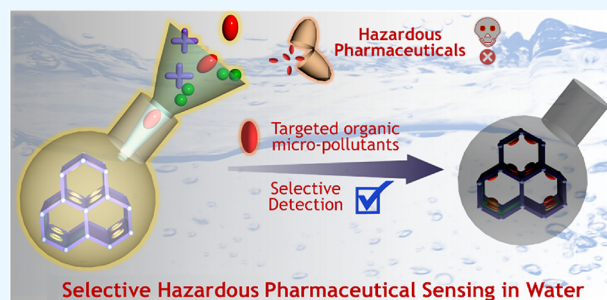
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ABSTRACT: The excessive use of anthropogenic wastes, such as emerging antibiotics and pesticides, has led to serious water pollution. Therefore, selective identification of those specific types of pollutants in wastewater is of significance owing to their direct detrimental impact upon human health. For practical requirements, a potential sensory material is highly desirable for detection of antibiotics and pesticides in water. As an advanced class of porous materials, porous organic polymers (POPs) are considered a potential candidate for the detection of micropollutants. Herein, we investigated the selective fluorescence quenching mechanism of a highly luminescent, electronically rich chemically stable POP (IP_{POP}-1) toward detection of antibiotics and pesticides in an aqueous medium. IP_{POP}-1 exhibited a selective strong quenching response in the presence of electron-deficient antibiotics (such as nitrofurantoin [NFT] and nitrofurazone [NFZ]) and pesticides like chlorpyrifos (CHPS) and nitrofen, among others. IP_{POP}-1 was found to be highly sensitive to NFT and NFZ at trace levels, and the detection limits were found as 0.046 and 0.045 mM, respectively. On the other hand, in the case of the pesticides, CHPS and nitrofen, the detection limits were 0.470 and 0.471 mM, respectively. After the detection test, IP_{POP}-1 could be regenerated for further use without any apparent loss of function. Moreover, detailed mechanism of the detection ability of IP_{POP}-1 were elucidated with the help of a time-resolved photoluminescence lifetime decay study and the density functional theory (DFT). All of these studies suggested that both the fluorescence resonance energy transfer (FRET) and photoinduced electron transfer (PET) processes are responsible behind such selective emission quenching. Furthermore, isothermal titration calorimetry (ITC) experiment was carried out in addition to demonstrate IP_{POP}-1 being able to detect electron-deficient antibiotics in trace amounts in simulated hospital wastewater. Finally, IP_{POP}-1-based mixed-matrix membranes (MMMs) were fabricated and employed to mimic real-time antibiotic detection in water.

KEYWORDS: antibiotic, pesticide, porous covalent framework, sensing, luminescent, selective detection, chemically stable



INTRODUCTION

In the 21st century, the drinking water crisis has emerged as a serious issue across many regions of the world.^{1,2} With ever-increasing populations and urbanization, water pollution is becoming a great threat to the entire ecosystem.³ Anthropogenic water pollutants, such as emerging organic contaminants, contribute a major portion to water pollution.⁴ The Safe Drinking Water Act (SDWA) defines the term “contaminant” as any foreign physical, chemical, radiological, or biological substance in water.⁵ Among anthropogenic wastes, antibiotics and pesticides are considered two major pollutants that cause severe water pollution.⁶ Since the discovery of penicillin, a well-known antibiotic used as an antimicrobial substance active against bacteria, it has been used widely as a medicine in hospitals for humans and also as veterinary medicine owing to its ability to inhibit the growth of various pathogens.^{7,8} Apart from this, with the development of

agricultural production, it is also used in agricultural fields for food production, aquaculture, beekeeping, etc.^{6,9,10} However, the excessive use of antibiotics causes bacterial drug resistance and antibiotic resistance. In line with this, the abuse or misuse of such species also further results in severe environmental pollution.^{11–13} On the other hand, pesticides, another class of potential organic contaminants, have become a “matter of concern” in recent times. Pesticides have been extensively used in modern agriculture to raise production.^{6,14,15} Not only are pesticides extremely toxic in nature to agricultural pests, but

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Unveiling the Impact of Diverse Morphology of Ionic Porous Organic Polymers with Mechanistic Insight on the Ultrafast and Selective Removal of Toxic Pollutants from Water

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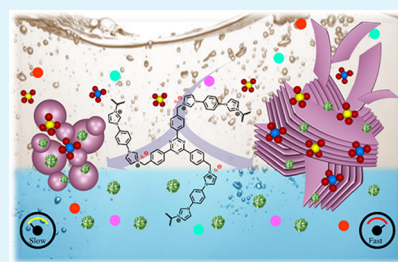


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ABSTRACT: In recent years, detoxification of contaminated water by different types of materials has received a great deal of attention. However, lack of methodical in-depth understanding of the role of various physical properties of such materials toward improved sorption performance limits their applicable efficiencies. In perspective, decontamination of oxoanion-polluted water by porous materials with different morphologies are unexplored due to a shortfall of proper synthetic strategies. Herein, systematic optimization of sequestration performance toward efficient decontamination of toxic oxoanion-polluted water has been demonstrated by varying the morphologies of an imidazolium-based cationic polymeric network [ionic porous organic polymers (iPOP-5)]. Detailed morphological evolution showed that the chemically stable ionic polymer exhibited several morphologies such as spherical, nanotube, and flakes. Among them, the flakelike material [iPOP-5(F)] showed ultrafast capture efficiency (up to ~99 and >85% removal within less than 1 min) with high saturation capacities (301 and 610 mg g⁻¹) toward chromate [Cr(VI)] and perrhenate [Re(VII)] oxoanions, respectively, in water. On the other hand, the spherical-shaped polymer [iPOP-5(S)] exhibited relatively slow removal kinetics (>5 min for complete removal) toward both Cr(VI) and Re(VII) oxoanions. Notably, iPOP-5(F) eliminated Cr(VI) and Re(VII) selectively even in the presence of excessive (~100-fold) competing anions from both high- and low-concentration contaminated water. Further, the compound demonstrated efficient separation of those oxoanions in a wide pH range as well as in various water systems (such as potable, lake, river, sea, and tannery water) with superior regeneration ability. Moreover, as a proof of concept, a column exchange-based water treatment experiment by iPOP-5(F) has been performed to reduce the concentration of Cr(VI) and Re(VII) below the WHO permitted level. Mechanistic investigation suggested that the rare in situ exfoliation of flakes into thin nanosheets helps to achieve ultrafast capture efficiency. In addition, detailed theoretical binding energy calculations were executed in order to understand such rapid, selective binding of chromate and perrhenate oxoanions with iPOP-5(F) over other nonmetal-based anions.



KEYWORDS: porous organic polymer, oxoanions, morphology, selective capture, toxic chemical adsorption, column exchange, cationic network

INTRODUCTION

Nowadays, due to rapid industrialization along with widespread urbanization, metal-based toxic oxoanions are ubiquitous species in water that contribute to serious water pollution, a global issue threatening the entire ecosystem.^{1–3} US Environmental Protection Agency (US-EPA) has marked some of the heavy metals which inherently exist as oxoanions in water, such as chromate [Cr(VI)], rhenate [Re(VII)], arsenate [As(V)], selenate [Se(VI)] and so forth, as primary water pollutants.^{4,5} These oxoanions are carcinogenic and mutagenic in nature and cause pernicious consequences, specially toward living organisms and, hence, has been the focus of concern.^{6,7} Among them, Cr(VI) is accounted as one of the most hazardous pollutants in wastewater because of rapid bioaccumulation through food chain, which further causes detrimental effect to human life, even at low

concentrations. Toxic hexavalent chromate is widely found in industrial wastewater from chrome plating, tannery, leather, dye, pigment, and steel manufacturing industries. Notably, at least 30 to 35 L of Cr(VI)-contaminated water per each kilogram of leather are generated by the tanning industries.^{7–9}

In line, technetium (Tc) is another toxic β -ray emitting radionuclide with long half-life (2.13×10^5 years), which is produced as a nuclear fission product of ²³⁵U or ²³⁹Pu, that predominantly exists as a pertechnetate anion (TcO₄⁻) in the

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