# Design and Synthesis of Ionic Porous Organic Polymers (iPOPs) towards a Sustainable Environment

Ph.D. Thesis

By Sayantan Sarkar



# DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE July 2024

# Design and Synthesis of Ionic Porous Organic Polymers (iPOPs) towards a Sustainable Environment

# A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> *by* Sayantan Sarkar



# DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE July 2024



# **INDIAN INSTITUTE OF TECHNOLOGY INDORE**

# **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **'Design and Synthesis of Ionic Porous Organic Polymers (iPOPs) towards a Sustainable Environment'** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the period from **July 2019** to **July 2024** under the supervision of Dr. Suman Mukhopadhyay, Professor, Department of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Sayawlay Sarkar. 30.07.2024 Signature of the student with date Sayantan Sarkar

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Sayantan

Dedicated to

Dada and Didan

## **SYNOPSIS**

#### **1. Introduction**

With rapid globalization and rapid industrialization, environmental sustainability is being affected significantly [1]. On the path of restoring it, several new materials have evolved, and porous materials are one such material that finds their applications in various fields directly related to environmental hazards and their solutions [2]. Ionic porous organic polymers (iPOPs) are one of the newest additions to the porous material family that continue to give exciting results directly related to the sustainable environment [3,4]. This thesis explored some of such iPOPs in environmental remediation, biomedical application, toxic gas sensing, electrochromic device fabrication, and electrocatalysis.

#### 2. Summary of the Thesis Work

The contents of each chapter included in the thesis are discussed as follows:

#### **1.1. General Introduction and Background (Chapter 1)**

This chapter briefly introduces the background of porous materials and the origin of ionic porous organic polymers, one of the newest members in the porous materials family. Further, it addresses the classification of iPOPs, potential building blocks, and the synthesis and characterization of these materials. It also summarizes some of the current environmental problems and their probable remediation and how iPOPs could be the potential material for addressing ecological issues.

## 2.2 A Bifunctional Imidazolium Functionalized Ionic Porous Organic Polymer in Water Remediation (Chapter 2)

This chapter presents a thermally and chemically robust imidazolium-based ionic porous organic polymer **iPOP-ANT** with exchangeable counter anion Cl-. The polymer was synthesized via a one-step condensation reaction between 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine and

9,10 bis(chloromethyl)anthracene under inert atmosphere. The chemical structure of the material was thoroughly characterized by <sup>13</sup>C-CPMAS NMR, FTIR spectroscopy, FESEM, EDX, XPS, and TGA. Owing to the presence of exchangeable counter anion Cl<sup>-</sup> in the polymeric skeleton, the polymer was used as a potential polymeric adsorbent in capturing toxic oxoanions ( $Cr_2O_7^{2-}$ ,  $MnO_4^{-}$ ) and anionic dyes (methyl orange, amaranth, congo red). The material shows high uptake capacity, fast kinetics, and selectivity toward capturing the anionic pollutants. The low optical band gap of the material (2.58 eV) makes it an ideal photocatalyst for the degradation of cationic dyes (rhodamine B, rhodamine 6G, and methylene blue) under solar irradiation.



Figure 1. Schematic representation of wastewater remediation by iPOP-ANT

# 2.3 Investigation of the Role of Charge Density and Surface Area of High-Performance Ionic Porous Organic Polymer Adsorbents and their Antibacterial Actions (Chapter 3)

This chapter addresses an efficient strategy for designing highly efficient polymeric adsorbents. Developing high-performance adsorbents for environmental remediation is a current need, and ionic porous organic polymers have already established themselves as better adsorbents. However, research on the structural design of high-performance iPOP- based adsorbents is still developing. This chapter explores the role of building blocks to optimize the charge density and surface area in the polymers to develop better polymeric adsorbents. Three cationic polymers, iPOP-ZN1, iPOP-ZN2, and iPOP-ZN3, were designed, synthesized, and characterized using standard characterization techniques. Among the three polymers, **iPOP-ZN1**, having the highest surface area and larger charge density, comes up as the best adsorbent for anionic inorganic and organic pollutants in an aqueous medium. The polymers also reveal excellent adsorption capability in the presence of higher concentrations of competing ions and highly acidic and basic solutions. The polymers show excellent reusability up to several cycles. The polymers further show excellent adsorption capacity of iodine vapor at room temperature and at 75 °C. Among them, the adsorption of iodine by iPOP-ZN1 at 75 °C is one of the highest reported values in reported literature. The iodine-loaded polymers show impressive antibacterial properties against E. coli, B. subtilis, and H. pylori. This study not only presents a strategy for designing polymeric adsorbents with high performance but also shows a glimpse of how contaminant-loaded polymeric matrices could be used for further applications.



The closer the building blocks better the adsorption

**Figure 2.** Schematic representation of the role of charge density in the polymeric skeleton to develop better polymeric adsorbent.

# 2.4. Exploring Redox-Active Ionic Porous Organic Polymer in Environmental Remediation & Electrochromic Application (Chapter 4)

This chapter presents a multifunctional ionic porous organic polymer (iPOP-Bpy) containing redox-active viologen sites. The material shows excellent iodine uptake capacity in vapor (540 wt%), organic (1009.77 mg/g), and aqueous phases (3921.47 mg/g), along with fast kinetics and multiple-time reusability. Due to the presence of redox-active viologen sites in the polymer, it also shows its utility in being used as a solid-state NH<sub>3</sub> vapor sensor as it shows ultrafast color switching from yellow to blue in the presence of electron-rich ammonia vapor and shows excellent efficiency as solid-state ammonia vapor sensor. Further, the material found application as a n-type complementary electrochromic electrode and was fabricated into a bilayer device. Bias-dependent in-situ transmission and electrochemical measurements of a solid-state ECD fabricated using iPOP-Bpy reveal its capability to be the best choice from the viologen family in fabricating an organic ECD. The above conclusion can be drawn from the excellent electrochromic performance parameter values of switching times (~0.5 s), color contrast (~50%), and coloration efficiencies (up to  $800 \text{ cm}^2/\text{C}$ ). In addition, the device shows color switching for multiple wavelengths with a low applied bias of 2V while showing the above-mentioned performance parameters.



**Figure 3.** Schematic representation of the multifunctional application of **iPOP-Bpy** 

# 2.5. Exploring Counter Anions in a Redox-Active Viologen-Based Ionic Porous Organic Polymer (iPOP) for Selective Reduction of Oxygen to H<sub>2</sub>O<sub>2</sub>

This chapter explores another viologen-based ionic porous organic polymer (iPOP-TAPA-Cl) as an efficient electrocatalyst for selective 2e<sup>-</sup> reduction of oxygen to hydrogen peroxide. Hydrogen peroxide, an environmentfriendly oxidant, is in high demand in various industrial sectors. Electrochemical  $H_2O_2$  production by  $2e^-$  reduction of  $O_2$  is a greener alternative to the traditional anthraquinone process. However, developing metal-free electrocatalysts that predominantly follow the 2e<sup>-</sup> reduction process over the more favorable 4e<sup>-</sup> reduction is challenging. iPOP-TAPA-Cl shows its efficiency as a metal-free electrocatalyst for the selective production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from oxygen in an alkaline medium. The H<sub>2</sub>O<sub>2</sub> production ability of the catalyst was further tuned by exchanging the  $Cl^-$  counter anion with other halide ions (F<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>). Among these catalysts, **iPOP-TAPA-F** shows exceptional catalytic activity towards the selective production of  $H_2O_2$  (98.5 %) with a significant current efficiency of 99 %. This type of viologen-based polymeric system could open a new avenue toward designing a metal-free electrocatalyst with controllable catalytic performance for the electrocatalytic production of  $H_2O_2$ .



**Figure 4.** Schematic representation of **iPOP-TAPA-X** (X= F, Cl, Br, and I) in selective  $2e^{-}$  reduction of oxygen to hydrogen peroxide.

#### 3. References

- Nahar N., Mahiuddin S., Hossain Z. (2021), The Severity of Environmental Pollution in the Developing Countries and Its Remedial Measures, Earth, 2, 124–139 (DOI:10.3390/earth2010008)
- Al-Jubouri S. M., Al-Batty S., Al-Hamd R. Kh. S., Sims R., Hakami M. W., Sk M. H. (2023), Sustainable Environment through Using Porous Materials: A Review on Wastewater Treatment, Asia-Pacific Journal of Chemical Engineering, 18, e2941 (DOI: 10.1002/apj.2941)
- Xu D., Guo J., Yan F. (2018), Porous Ionic Polymers: Design, Synthesis, and Applications, Progress in Polymer Science, 79, 121–143 (DOI: 10.1016/j.progpolymsci.2017.11.005)
- Sun J.-K., Antonietti, M., Yuan J. (2016), Nanoporous Ionic Organic Networks: From Synthesis to Materials Applications, Chem. Soc. Rev., 45, 6627–6656 (DOI: 10.1039/C6CS00597G)

## LIST OF PUBLICATIONS

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2. Chanchal Sonkar, **Sayantan Sarkar**, Novina Malviya, Maxim L Kuznetsov, Suman Mukhopadhyay, Recognition and Mechanistic Investigation of Anion Sensing by Ruthenium(II) Arene Complexes and Bio-imaging Application, Dalton Trans., 2022, 51, 13071-13084 (DOI: 10.1039/D2DT01726A)

3. Argha Chakraborty, **Sayantan Sarkar**, Reena Kyarikwal, Probal Nag, Sivaranjana Reddy Vennapusa, Suman Mukhopadhyay, Piperazine-Linked Covalent Triazine Polymer as an Efficient Platform for the Removal of Toxic Mercury (II) Ions from Wastewater, ACS Appl. Polym. Mater. 2022, 4, 11, 8118–8126 (DOI: 10.1021/acsapm.2c01085) 4. Argha Chakraborty, **Sayantan Sarkar**, Probal Nag, Rishi Ranjan, Sivaranjana Reddy Vennapusa, Suman Mukhopadhyay, Exploring Multifunctional Applications of a Luminescent Covalent Triazine Polymer in Acid Vapour Sensing, CO<sub>2</sub> Capture, Dye Removal, and Turn-off Fluorescence Sensing of Dichromate Ions, Mater. Chem. Front., 2023, 7, 1831-1840 (DOI: 10.1039/D2QM01329K) (Impact factor 7.0)

5. Pragti, Bidyut Kumar Kundu, Satyam Singh, Wilson Alphonse Carlton Ranjith, **Sayantan Sarkar**, Avinash Sonawane, Suman Mukhopadhyay, Chitosan–Biotin-Conjugated pH-Responsive Ru (II) Glucose Nanogel: A Dual Pathway of Targeting Cancer Cells and Self-Drug Delivery, ACS Appl. Mater. Interfaces 2023, 15, 37, 43345–43358 (DOI: 10.1021/acsami.3c07157)

6. **Sayantan Sarkar**, Snehanjali Behera, Ritika Munjal, Argha Chakraborty, Biswajit Mondal, Suman Mukhopadhyay (= Equal contribution), Non-Noble Metal-Based Porphyrin Covalent Organic Polymers as Additive/Annealing Free Electrocatalysts for Water Splitting and Biomass Oxidation, Energy and Fuels, 2024, 38, 6, 5183 (DOI: 10.1021/acs.energyfuels.4c00029)

7. Ritika Munjal, Reena Kyarikwal, **Sayantan Sarkar**, Probal Nag, Sivaranjana Reddy Vennapusa, Suman Mukhopadhyay, A Siderophore Mimicking Gelation Component for Capturing and Self-Separation of Fe(III) from an Aqueous Solution of Mixture of Metal Ions, Inorg. Chem. 2024, 63, 15, 7089–7103 (DOI: 10.1021/acs.inorgchem.4c01177)

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8. <sup>¶</sup>Ritik, <sup>¶</sup>Sayantan Sarkar, Pragti, Nidhi Varshney, Amardeep Kumar, Maxim L Kuznetsov, Hem Chandra Jha, Suman Mukhopadhyay (<sup>¶</sup>= Equal contribution), Exploring a Nano-Structured Gel Material in Environmental Remediation and Biomedical Application (Under revision)

9. Argha Chakraborty, Saraswati Roy, Pragti, **Sayantan Sarkar**, Sounak Roy, Suman Mukhopadhyay, A Conjugated Porous Organic Polymers as

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10. Argha Chakraborty, **Sayantan Sarkar**, Ritika Munjal, Jagannath Majhi, Anasuya Bandyopadhyay, Suman Mukhopadhyay, Catalyzing Knoevenagel Condensation and Sequestration of Nuclear Waste by Porous Organic Polymers with Tuned Surface Area and Pore Volume (Manuscript submitted)

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# LIST OF CONFERENCES

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# NOMENCLATURE

θ	Angle
λ	Wavelength
α	Alfa
β	Beta
δ	Chemical shift
Å	Angstrom
μm	Micrometer
π	Pi
σ	Sigma
γ	Gamma
μΜ	Micromolar
ppm	Parts per million
mL	Milliliter
μL	Microliter
a.u.	Arbitrary unit
°C	Degree centigrade
Κ	Kelvin

## ACRONYMS

Abbreviations used for chemicals, polymers, and reagents largely follow the recommendations of the IUPAC-IUB commission on Biochemical Nomenclature, 1974, Pure and Applied Chemistry, 40, 315-331. Additional abbreviations used in this thesis are listed below

ACN	Acetonitrile
CDCl <sub>3</sub>	Chloroform-d
COF	Covalent organic framework
COP	Covalent organic polymer
CP-MAS	Cross polarization magnetic angle spinning
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide

DMF	Dimethylformamide
EDX	Energy Dispersive X-Ray analysis
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
HCl	Hydrochloric acid
HRTEM	High-Resolution Transmission Electron Microscopy
iPOP	Ionic porous organic polymer
MeOH	Methanol
Me	Methyl
Μ	Molar
nm	Nanometer
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
pН	The negative logarithm hydrogen-ion activity
POP	Porous organic polymer
PXRD	Powder X-ray Diffraction
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UV-Vis	UV-Visible Spectroscopy
UV-DRS	UV-Visible-Diffuse reflectance Spectroscopy

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Introduction

#### 1. Introduction

#### 1.1. Background

Earth is home to around 8.1 billion people, with an expected population increase of around 2 billion in the next 30 years [1]. This rapid increase in the human population has led to exponential growth in industrialization that directly impacts the environment [2]. Excessive consumption of natural resources, huge waste generation, and uncontrolled release of harmful toxins directly pollute the environment, leading to severe consequences like fatal diseases and climate change. Depending on the types of pollutants, environmental pollution can be categorized into two subclasses: Primary pollution, where the contaminants are harmful in their original form, and secondary pollution, where the pollutants are produced from the chemical reactions of seemingly harmless natural elements [3]. Generating high amounts of such pollutants can negatively impact every sphere of our environment. Consequently, we encounter several types of pollution, like water, air, soil, noise, thermal, light, radiation, etc., having natural or anthropogenic causes [4]. Around nine million annual early mortalities are recorded worldwide because of environmental pollution [5].

Among the mentioned pollutions, air and water pollution are the most concerning in the current era, and they have common sources most of the time. Particulate matter has been recognized as one of the primary sources of air pollution which contains toxic components like sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO), several nitrogen oxides, volatile organic compounds (VOCs) like several alcohols and amines, volatile radioactive substances like radio iodides, etc [6,7]. The water can be polluted from several sources, like chemical pollutants (fertilizers, pesticides, heavy metal-based pollutants, organic components, microplastics, etc.), biological pollutants like bacteria and viruses, thermal pollution (release of hot industrial water), and waste discharge. Though some of these pollutants are generated by naturally occurring incidents like wildfire or volcanic

eruptions, the anthropogenic pollution caused by the industries has become a worldwide issue[8-11]. These pollutants have a direct environmental impact as they can alter the atmospheric composition, ultimately hampering ecological sustainability. The contaminants in the air can interact with the clouds and alter the cloud formation and precipitation patterns, causing hydrological imbalance [12-14]. On the other hand, water pollution severely impacts the survival of animals and plants, ultimately creating ecological imbalance [15]. Moreover, the pollutants can cause several health issues like headaches, nausea, respiratory problems, heart disease, gene mutation, damage to reproductivity, cancer, etc. [16-20]. As a universal solvent, water can also be a source of several infectious waterborne diseases like cholera, diarrhea, hepatitis A, dysentery, etc. [21].

Soil pollution is directly linked with water and air pollution. The increasing level of air and water pollution leads to the deposition of several toxins in the soil, directly impacting its acidity, inhibiting the fertility of the soil, and affecting the growth of fruits and vegetables [22,23]. Heavily dumped industrial and urban wastes to empty lands, use of excessive fertilizers and pesticides, and related chemicals in cultivation are other major causes of soil pollution [24-27]. On the other hand, the leaching of pollutants from the soil to the groundwater and released VOCs from the soil can cause secondary water and air pollution [28-31].

Thermal pollution is another global concern that refers to the abnormal change in the average global temperature. The average global temperature has been increasing at an alarming rate of 0.06 °C per decade since 1850 [32], and the current decade is probably the hottest decade recorded. One of the major reasons for thermal pollution is industrial processes and excessive use of cooling systems that release several toxic gases, which leads to global warming [33,34]. Excessive use of fossil fuel-based energy affects natural resources, and the poisonous gases released from burning carbon-based fuels create significant air pollution and elevate the average

global temperature [35-37]. This elevating temperature affects human health and harms aquatic life by causing hypoxic conditions in water due to the reduced solubility of oxygen in water [38].

Noise pollution is the amplification of noise levels by natural or anthropogenic causes with adverse side effects like sleep disruption, hypertension, cardiovascular problems, etc. [39-41]. Other than that, human-caused over-illumination also causes several adverse effects, like depression, sleep disorders, etc. [42,43]. At the same time, these highly energy-consuming processes passively put a burden on natural resources, creating an environmental imbalance.

Environmental pollution and environmental sustainability are two related concepts that go hand-in-hand [44]. Environmental sustainability refers to the reasonable interaction of the environment to the conservation of natural resources and ecological balance while meeting the needs of current and future generations [45]. In contrast, environmental pollution refers to the infiltration of unwanted natural or artificial substances into the environment that directly threaten life and ecological balance [46]. Therefore, addressing these various types of current environmental challenges is crucial for maintaining environmental sustainability. In this situation, the major solutions could be the adaptation of cleaner technologies, effective waste management, promotion of renewable and energy-efficient technologies, and use of renewable and sustainable materials.

#### 1.2. Materials towards sustainability

Material research has greatly impacted the development of a sustainable environment. Though several conventional materials are being developed to aid the mentioned problems, most suffer disadvantages like smaller selflife, high preparation cost, low product selectivity, compromised stability in harsh conditions, etc. [47]. At the same time, the compromised reusability and poor recyclability of these materials make them unsuitable

for use for a longer period [48]. In this situation, developing materials that are easy to handle, have low preparation costs, and have substantial reusability and recyclability is one of the main priorities of the current research community.

In this regard, sustainable material is one of the newly emerging concepts that refers to materials that can be reused or recycled without hampering environmental sustainability [49]. There are several factors that make a material sustainable [50,51] (**Figure 1.1**):



Figure 1.1. Factors that make a material sustainable.

**1. Source:** The source of the material production significantly impacts material sustainability. The material can be termed sustainable if the source is sustainable or renewable.

**2. Impact:** Depending on the environmental impact of synthesizing and using the material, a material is classified as sustainable.

**3. Durability:** Durability is another crucial factor that makes a material sustainable. The durability of the materials makes them work for a longer time and lowers their replaceability over time.

**4. Life cycle:** Reusability is an essential factor for material sustainability. If a material can be used for multiple cycles by simply reactivating it, its durability improves, which is an advantage in ecological and material sustainability.

**5.** Usage: Usage is a crucial factor in sustainable development. Regardless of the source, if a material can be reused and recycled, it qualifies as sustainable.

Porous materials such as zeolites, metal-organic frameworks, coordination polymers, several oxides, etc., are the materials of the current era that have found their applications in various fields directly related to environmental sustainability. They are used for environmental remediation, sensing toxic pollutants, adsorption and storage of gases, green energy generation, and energy storage [52-55]. However, these materials face several challenges regarding stability, reusability, and activity impose restriction in their use at the industrial level. For example, metal-based porous materials suffer significant disadvantages in terms of stability in water and extreme pH conditions. MOFs and coordination polymers are mostly unstable in water, and their disintegration in water and extreme pH conditions makes them inappropriate for use at the industrial level for water remediation [56]. Additionally, the leaching of metals from the metal-based electrocatalysts further increased the chances of secondary metal pollution [57]. In this scenario, the specific development of metal-free systems could be an efficient strategy. Porous organic polymers are a class of porous material made of organic covalent bonds and could help in the development of the next generation of sustainable material [58].

#### **1.3.** Porous organic polymers as sustainable materials

Modern concepts of polymer chemistry started to evolve after the legendary macromolecular hypothesis proposed by Hermann Staudinger in 1920, in his work 'On polymerization' where he stated, "*not very different structures* 

can be obtained from a few building blocks; but if 10,000 or 100,000 blocks are at hand, the most varied structures become possible" [59]. Since this discovery, polymer research has grown significantly, and researchers have synthesized polymers combining various building blocks to develop polymers of different morphologies [60,61]. The field of porous organic material has evolved since the historic discovery of covalent organic framework by Professor Omar M. Yaghi in 2005 [62] (**Figure 1.2**).



**Figure 1.2.** Representative timeline of the development of various porous organic polymers. Reproduced with the permission of the Elsevier Publishing Company [60].

Porous organic polymers are one of the unique classes of porous materials as they consist of the properties of both porous materials and polymers [63]. These are primarily pure organic materials with strong covalent bonds between organic build blocks. Being made of light elements like boron, carbon, nitrogen, sulfur, etc., they are generally lightweight. As shown in **Figure 1.2.**, hypercrosslinked polymers (HCPs), polymers of intrinsic microporosity (PIMs), covalent organic frameworks (COFs), covalent microporous polymers (CMPs), and porous organic frameworks (PAFs) are some of the known classes of porous organic polymers [60]. Being constructed by assembling 2D or 3D organic building blocks, they develop

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permanent voids that make them porous. Another unique feature of porous organic polymers is the choice of a wide range of chemical reactions and synthetic methods [64]. The flexibility to design task-specific monomers at the atomic level gives these materials an added advantage in optimizing their properties. As they are mostly made of pure organic building blocks, the porosity of the polymers could be tuned by simple post-synthetic modifications [65]. The very high thermal and chemical stability of the materials due to strong covalent bonds, high surface area, specific pore structure, and reusability make them usable in various applications directly related to environmental sustainability, like heterogeneous catalysis [66-69], gas adsorption and storage [70-73], chemical separation [74,75], green energy generation [76,77], energy storage [78-80], water purification [81-86], optoelectronic [87-90], biology [58,91,92], etc. The development of task-specific porous organic polymers for environmental applications is one of the current challenges to the research community. Constant efforts are being made worldwide to make these materials more efficient for various environmental-related applications.

# **1.4.** Ionic porous organic polymers (iPOPs): a potential porous material for sustainability

Neutral polymers have played a crucial role in various fields directly related to environmental sustainability. Incorporating ionic functionality in the polymeric backbone will diversify the porous materials and broaden their applicability. In this regard, as a subgroup of porous organic polymers, ionic porous organic polymers (iPOPs) have emerged as a new type of porous material, first reported by Cho et al. as a tubular microporous organic network in 2010 [93]. This type of material consists of all the unique features of conventional porous organic polymers with an extra feature: a charged skeleton. The presence of ionic moieties in the pores and the polymeric skeleton provides the facility to tune the electronic and physiochemical properties of the polymers by simple counter-ion exchange

[94]. These exciting features, like high charge density, high surface area, and facile tunability of the polymer's electrotonic and physiochemical properties, make iPOPs one of the rising stars in the porous material family [95].

#### 1.5. Classification of ionic porous organic polymers (iPOPs)

Depending on the charge of the polymeric skeleton, iPOPs can be broadly classified into two subclasses: cationic and anionic porous organic polymers. A third class of iPOPs is called zwitterionic porous organic polymer, where the cationic and anionic sites coincide in the polymeric skeleton [95] (**Figure 1.3**). This thesis mainly focused on developing noble cationic porous organic polymers and their application towards environmental sustainability.





#### 1.6. Synthesis strategy of cationic porous organic polymers

Cationic porous organic polymers contain positively charged sites in the polymeric skeleton, with changeable counteranions such as halides and pseudohalides. Three major synthetic strategies exist in synthesizing cationic porous organic polymers: 1. Ionization and polymerization using neutral building blocks (Type I) 2. Direct synthesis using ionic building

blocks (Type II) and 3. post-synthetic modification (Type III) [95,96] (**Figure 1.4**). In all cases, the choice of suitable building blocks plays a significant role in determining the properties and functionalities of the polymers.



**Figure 1.4.** Classification of cationic porous organic polymers depending on their synthesis.

#### 1.6.1. Ionization and polymerization using neutral building blocks

The ionization and polymerization method are one of the simplest methods of fabricating ionic porous organic polymers. Unlike neutral polymers, it requires no catalyst or harsh conditions and is relatively simple to operate. Most of the polymers synthesized by this method have either quaternary imidazolium or viologen units as the cationic center. **Table 1.1** represents some standard building blocks fabricating cationic imidazolium centers in the polymer.

iPOPs	Building blocks	Synthesis	Reference
IM-POP	$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ &$	S <sub>N</sub> 2 nucleophilic substitution	97,98
pDPA		ARS <sub>N</sub> 2 nucleophilic substitution	99
CalCOP-1		S <sub>N</sub> 2 nucleophilic substitution	100
SCU- CPN-1-Br	$\left(\begin{array}{c} N \\ N $	S <sub>N</sub> 2 nucleophilic substitution	101
IOP	$Br \xrightarrow{H} Br \xrightarrow{N} N$	S <sub>N</sub> 2 nucleophilic substitution	102

**Table 1.1.** Some standard building blocks are used to fabricateimidazolium-based ionic porous organic polymers.

Most of the reactions go via simple  $S_N 2$  substitution reactions. For example, Gong et al. synthesized an imidazolium-based ionic porous organic polymer (**IOP**) by reacting 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (TBPT) and 1,3,5-tri(1H-imidazol-1-yl)benzene (TImB) in MeCN [102] (**Scheme 1.1a**). A similar reaction was reported by Li at el. for the fabrication of a very robust ionic polymeric material **SCU-CPN-1-Br** by reacting 1,1,2,2-tetrakis(4-(imidazolyl-4-yl)phenyl)ethene (TIPE) and 1,4-

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bis(bromomethyl)benzene (BBB) in a  $S_N2$  quaternization reaction [101] (Scheme 1.1b).



Scheme 1.1. Synthesis of imidazolium-based iPOPs (a) **IOP** and (b) **SCU-CPN-1-Br** [101,102].

Using pyridine-based building blocks is another smart choice to fabricate a cationic building center in the polymeric skeleton. In this regard, the Menshutkin reaction, a form of  $S_N2$  reaction, has been used extensively. This reaction proceeds faster in polar solvents than in solvents of lower polarity [96]. Alkyl halides containing (chloride or bromide) building blocks are used as a substrate. A nucleophilic attack by the pyridine-based nucleophile (4,4'-bipyridine, for example) replaces the halide from the substrate, creating a quaternary N-positive center. Some of the well-reported substrate and pyridine-based building blocks are presented in **Table 1.2**.

Table 1.2. List of some well-reported building blocks used in the Mensutki	n
reaction	

iPOPs	Building blocks	Synthesis	Reference
CATN	Br	Menshutkin reaction	103
PION1		Menshutkin	104
PION2		reaction	
PION3	B1 B2 B3		
IM-IPOP	N Br	Menshutkin	105
	Br Br	reaction	
COP1 <sup>++</sup>	CI CI	Menshutkin	106
		reaction	
CON-	N Br	Menshutkin	107
LDU5		reaction	
TP-iPOP-		Menshutkin	108
2	N S N N NH NH HN HN N Br	reaction	

Friedel-Crafts alkylation is another reaction that is being extensively used to fabricate ionic and neutral hypercrosslink polymers. This reaction generally uses aliphatic or aromatic alkyl halide as a substrate and dry FeCl<sub>3</sub> as a catalyst in chlorinated solvents like DCM or DCE. For example, Shang et al. synthesized two cationic polymers, **ID-PIP** and **IB-PIP**, through Friedel-Crafts reaction followed by quaternization in solvothermal condition, reacting 1-(dichloromethyl)-4-methylbenzene (DMB) and 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMB) separately with 2-phenyl imidazoline (PI) in the presence of anhydrous FeCl<sub>3</sub> [109] (**Scheme 1.2**).



Scheme 1.2. Synthesis of **ID-PIP** and **IB-PIP** by Friedel-Crafts alkylation [109].

#### 1.6.2. Direct polymerization using ionic building blocks

Another widely used protocol is directly synthesizing ionic porous organic polymers using cationic monomers. This strategy has the flexibility to use a wide range of organic transformations to produce various types of polymers using different linkages. The building blocks can be connected by

-C-C-, -C=C-, hydrazine, triazine, and imine linkages. Some of the widely used cationic building blocks are listed in **Scheme 1.3**.



Scheme1.3. Some well-used cationic building blocks.

#### 1.6.2.1. Imine linkage

The Schiff-base reaction to make imine linkage is widely used in synthesizing ionic porous organic polymers with high thermal stability and surface area [110]. Using either a cationic aldehyde or amine group as a building block leads to the formation of a cationic polymer. The critical selection of suitable solvent systems is one of the crucial features of this type of reaction. Generally, a combination of solvents like mesitylene/dioxane or n-butanol/ortho-DCB is used along with different concentrations of acetic acid as a catalyst, which plays a vital role in the polymerization reaction. For example, Fu et al. synthesized a series of cationic polymers by using a unique cationic building block 4,4',4"-(1-Methyl-1H-imidazole-2,4,5-triyl)tribenzaldehyde (MITT). Among the polymers, **IMP-4** and **IMP-5** were made of the same building blocks in
different solvents, as depicted in **Scheme 1.4**. As can be seen from the figure, **IMP-4** has a higher

surface area than **IMP-5**, which shows the effect of solvent systems in imine condensation reactions, which ultimately determines the properties of the polymers *[111]*.



Scheme 1.4. Schematic representation of the synthesis of imine-linked polymer IMP-1 to IMP-5. Reproduced with the permission of the American Chemical Society [111].

Huang et al. reported the synthesis of another ionic covalent organic framework (iCOF) by the Schiff base condensation reaction of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline (PyTTA) and 5,6-bis(4-formylbenzyl)-1,3-dimethyl-benzimidazolium bromide (BFBIm) (**Scheme 1.5a**). The material shows excellent thermal and chemical stability and an exceptionally high surface area of 1532 m<sup>2</sup>/g, which is probably the highest reported surface area among ionic porous organic polymers (**Scheme 1.5b-1.5e**) [*112*].



Scheme 1.5. (a) Synthesis of **PyTTa-BFBIm-iCOF** (b)  $N_2$  adsorptiondesorption and (c) pore size distribution of the iCOF. (d) and (e) represents the PXRD data, and the  $N_2$ -adsorption-desorption analysis of the iCOF after treatment with different solvents represents its chemical stability. Reproduced with the permission of John Wiley and Sons [112].

Ethidium bromide is another widely used cationic amine to synthesize different cationic polymers for various applications. Ma et al. reported the synthesis of a cationic covalent organic framework using ethidium bromide as a building block (**EB-CON-Br**). The electrostatically connected counter anions exchange facile counter anions in the polymeric skeleton. By introducing  $PW_{12}O_{40}^{3-}$  in the porous framework, they obtained enhanced conductivity [113].

Though most of the cationic porous organic polymers synthesized by Schiff base reaction consider either a cationic aldehyde or cationic amine as the charged building block, Luo et al. reported the synthesis of a bi-cationic covalent organic framework (**DC-COF**), using both the cationic aldehyde (**Am1**) and cationic amine (**Vio-NH2**) incorporating both the imidazolium and viologen center in the same polymeric skeleton [114] (**Scheme 1.6**).



Scheme 1.6. Synthesis of DC-COF [114].

#### 1.6.2.2. Hydrazine linkage

Hydrazone linkage is another widely used linkage in fabricating ionic porous organic polymer material. Unlike imine linkage, hydrazone linkage provides extra thermodynamic stability and is less prone to hydrolysis, providing iPOPs with an added robust nature. Guanidium halide-based building blocks are widely used in hydrazone-based iPOPs. Mitra et al. synthesized a series of ionic covalent organic nanosheets using guanidium halide as a cationic building block. The materials show excellent self-exfoliation properties due to the interlayer repulsion. Guanidium halide has biological activity, and the polymers were further used for antibacterial actions (**Scheme 1.7**) *[115]*.



**Scheme 1.7**. Schematic representation of the self-exfoliation of iCONs and their antibacterial actions. Reproduced with the permission of the American Chemical Society [115].

In another study, Ding et al. reported the synthesis of an ionic liquiddecorated covalent organic framework and a composite aerogel out of it for selective CO<sub>2</sub> adsorption and their catalytic conversion using an imidazole functionalized hydrazine building block (**Scheme 1.8**) *[116]*.



**Scheme 1.8.** Synthesis of hydrazine-based cationic building bock IL-ADH and cationic hydrazone **COF-IL**. Reproduced with the permission of the Royal Society of Chemistry [116].

#### 1.6.2.3. -C=C- linkage

-C=C- linkage is another common way to assemble ionic porous organic polymers, and olefin linkage is one of the efficient ways to produce fully conjugated cationic porous organic networks. Acid/Base-assisted activation of the methyl groups followed by the nucleophilic addition of the aldehyde groups in an Aldol-type polycondensation reaction results in a highly stable conjugated porous organic polymeric network. For example, Lin et al. reported the base-assisted synthesis of a series of fully conjugated porous organic polymers with high yield by reacting a cationic building block 1,1',6,6'-tetramethyl-[3,3'-bipyridine]-1,1'-diium iodide (TMBPI) a series conjugated aldehydes (**Scheme 1.9**) *[117]*. All the polymers show high BET surface area with excellent thermal and chemical stability.



**Scheme 1.9**. Synthesis of olefin-linked conjugated porous organic polymers by base-catalyzed Aldol condensation reaction. Reproduced with the permission of the Royal Society of Chemistry [117].

In another study, a couple of 3D ionic covalent organic for wastewater remediation was reported by Zhang et al. by using two tetrahedral building blocks, TAPM and TFPM, in an acid-catalyzed Aldol condensation reaction, where trifluoroacetic acid was used as a catalyst (**Scheme 1.10**) *[118]*.



Scheme 1.10. Synthesis of 3D iCOFs TAPM-PZI and TFPM-PZI in an acid-catalyzed polycondensation reaction [118].

Besides the Aldol condensation reaction, the Knoevenagel reaction is another way to obtain ionic vinyl-containing conjugated ionic porous organic polymer with -C=C- linkage. Liu et al. reported the synthesis of **PyiPOP-1** using a Knoevenagel condensation reaction between benzene 1,3,5tricarbaldehyde (TFB) and acetonitrile-functionalized ionic liquid IL-ACN [119] (Scheme 1.11).



Scheme 1.11. Synthesis of **Py-iPOP-1** by Knoevenagel condensation reaction [119].

#### 1.6.2.4. Ionothermal reaction

Metal salt-assisted trimerization is another reaction mainly used to synthesize cationic triazine polymers. Though this method produces polymers with higher thermal and chemical stability and high surface area, it requires a relatively longer time and higher temperature. These polymers show excellent activity in the selective capture and conversion of CO<sub>2</sub>. **Scheme 1.12** shows the synthesis of two such cationic triazine polymers [120,121].



**Scheme 1.12.** Ionothermal synthesis of cationic covalent triazine polymers. Reproduced with the permission of John Wiley and Sons *[120]* and the American Chemical Society *[121]*.

### 1.6.2.5. Coupling reaction

-C-C- bond formation by coupling reaction is a widespread polymerization reaction in constructing porous organic polymer. Suzuki coupling is a commonly used coupling reaction in synthesizing ionic porous organic polymers. Cationic porous organic polymers, **EOF-15** and **EOF-16**, were synthesized by Suzuki reaction by Rose et al. (Scheme 1.13) [122].



Scheme 1.13. Synthesis of EOF-15 (E=Si) and EOF-16 (E=C) by Suzuki coupling reaction [122].

In another study, a series of imidazolium-linked tetraphenylethene-based cationic conjugated microporous polymers were prepared by Mousa et al. by Sonogashira–Hagihara cross-coupling reaction (**Scheme 1.14**) [123].

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**Scheme 1.14.** Synthesis of imidazolium-linked cationic conjugated porous organic polymers using Sonogashira–Hagihara cross-coupling reaction. Reproduced with the permission of the Royal Society of Chemistry *[123]*.

Yamamoto coupling reaction is another cheaper alternative for constructing highly conjugated ionic porous organic polymers as a comparatively cheaper catalyst Ni(COD)<sub>2</sub> is used in this reaction instead of expensive Pd-based catalysts. Su et al. reported an imidazolium-based porous organic polymer for nitroaromatic reduction using the Yamamoto coupling reaction (Scheme 1.15) [124].



**Scheme 1.15.** Construction of imidazolium-based cation porous organic polymers by Yamamoto coupling reaction *[124]*.

#### 1.6.2.6. Zincke reaction

Zincke reaction is widely used to synthesize viologen-based ionic porous organic polymer. In this reaction, a primary amine is reacted to the pyridinium salt of 2,4-dinitro-chlorobenzene to construct the polymeric skeleton. Ali Trabolsi and co-workers first reported synthesizing viologen-based ionic conjugated polymeric network reacting using Zincke reaction under microwave irradiation (**Scheme 1.20**) *[125]*.



Scheme 1.16. Synthesis of viologen-based ionic porous organic polymer using Zincke reaction [125].

#### 1.6.3. Post-synthetic modification of neutral porous organic polymers

Along with the strategies mentioned above to construct ionic porous organic polymers, post-synthetic modification is another alternative to introduce cationic units in the polymeric skeleton. As shown in **Scheme 1.17**, the quaternization reaction in the saturated pyridine centers to generate positive pyridinium salt is an alternative to generating cationic centers in the polymeric skeleton.



**Scheme 1.17**. The strategy of generating a positive center in the pyridine center by post-synthetic modification

Based on the strategy mentioned above, Mi et al. reported the synthesis of **Py-Bpy<sup>2+</sup>-COF** from a neutral COF, **Py-Bpy-COF** (Scheme 1.18) [126].



**Scheme 1.18.** Generation of cationic center in **Py-Bpy-COF** by postsynthetic modification. Reproduced with the permission of the American Chemical Society [126].

The attachment of a cationic building block on the skeleton of porous organic polymer is another alternative to produce a cationic center in the polymeric skeleton, as can be seen in **Scheme 1.19** *[127]*.



**Scheme 1.19.** Installation of a cationic unit in a neutral porous organic polymer skeleton. Reproduced with the permission of the American Chemical Society [127].

#### 1.7. Synthesis methods of iPOPs

Being one of the subclasses of conventional porous organic polymers, ionic porous organic polymers can be synthesized by following the same synthetic protocol of neutral porous organic polymers. **Figure 1.5** depicts various synthetic protocols and their advantages in synthesizing porous organic polymers [128].



**Figure 1.5.** Various synthetic protocols and their advantages in the synthesis of porous organic polymers. Reproduced with the permission of the Royal Society of Chemistry [128].

Solvothermal is the most widely used protocol for synthesizing crystalline porous organic polymers. However, it takes more time and produces less product yield than the other methods. Choice of reactions, like Schiff base or Aldol condensation reactions, which are reversible in nature, helps to produce crystalline polymers. Microwave reactions are another method that is becoming popular among researchers as it requires less reaction time and produces a high yield. The ionothermal or molten salt method is another

method that uses molten salt as a solvent/catalyst, and triazine-based polymers are majorly synthesized by this method [129].

#### 1.8. Aim and objective of the project

Based on the synthetic strategies discussed above, this thesis presents a few noble ionic porous organic polymers fabricated using imidazolium and viologen linkages with similar protocols discussed above. The intended structures were chosen with specific strategies to utilize the synthesized iPOPs for various applications like wastewater remediation, volatile iodine adsorption, amine sensing, electrochromic device fabrication, and electrocatalytic hydrogen peroxide production. The synthetic strategies are further discussed in individual chapters. The following is a brief account of the applications and status of polymers for different applications, which are mostly explored in the current thesis.

#### 1.8.1. Wastewater remediation

There is a huge increase in water demand with the rapid growth in the industrial and agricultural sectors. As per the AQUASTAT report, yearly, 3928 km<sup>3</sup> of water from various freshwater sources is used for human consumption, and around 22% of this is consumed by the industrial sectors *[130]*. These vast amounts of water are ultimately released as wastewater to various water resources without proper treatment, causing severe water pollution that causes adverse effects on animal health and damages aquatic life *[131]*. As per a recent report, industrial discharge is a major contributor to the multiple causes of water pollution, contributing around 41% (**Figure 1.6**) *[132-134]*.



Figure 1.6. Different sources of water pollutants

Among the various industrial contaminants, metal-based oxoanions like  $Cr_2O7^{2-}$ ,  $TcO4^-$ ,  $SeO4^-$ ,  $AsO4^-$ , etc., are some of the significant threats as their bioaccumulation to the living organism causes several toxic effects [135]. Cr (VI) based ions are carcinogenic and mutagenic and are listed as 'priority pollutants' by the US Environmental Protection Agency (US EPA) considering the poisonous impacts of Cr (VI) oxoanions [136]. Chromate is used mainly in industries like wood preservation, leather, textile, steel, dyes, pigments, etc. Among these industries, only the leather tanning industry takes around 30-35 liters of chromate for tanning 1 kg of leather [137]. This chromate-containing water ultimately gets released to various freshwater sources, causing chromate pollution in water. Hinkey groundwater contamination is one of the known incidents where Pacific Gas and Electric Company (PG&E) dumped about 370 million gallons of Cr-containing wastewater into freshwater sources [138].

TcO<sub>4</sub><sup>-</sup> is another toxic oxoanion that evolved from various atomic power plants as a secondary nuclear waste [139]. It is a form of radioactive <sup>99</sup>Tc, which is  $\beta$  emitting in nature, and has a half-life of around 2.1×10<sup>5</sup> years [140]. As per recent reports, until 2010, nuclear power industries and atomic weapon testing produce around 305 metric tons of <sup>99</sup>Tc-containing pollutants [140]. Selective removal of TcO<sub>4</sub><sup>-</sup> from aqueous solution is a big challenge due to its high solubility, low binding constant, and low binding enthalpy in aqueous medium [141].

Organic dyes are one of the major water pollutants. Several printing, textile, and painting industries use around 10000 organic dyes. These organic dyes are highly water soluble, carcinogenic, and mutagenic [142]. During their production and use at the industrial level, a massive amount of dye-containing wastewater is generated and ultimately released into several waste resources [143]. Due to the complex organic structure of these dyes, it can be challenging to process them by simple bioprocessing. Therefore, their accumulation in the living organism might cause severe fetal disease [144].

Considering the water stability and toxic effects of these pollutants, it is one of the recent challenges to remove these pollutants from water resources. Significant technologies have been developed recently, like adsorption, photocatalytic and electrocatalytic degradation, chemical precipitation, etc. [145-148]. Among them, adsorption and photocatalysis have proved to be a user-friendly, cost-efficient, safe, and greener approach. Several porous materials, like zeolites and metal-organic frameworks, coordination polymers, activated carbons, etc., are active in adsorbing several organic and inorganic pollutants from water [149-153]. However, their lower uptake capacity and reusability make them inefficient for use at the industrial level. In the case of metal-organic materials, their compromised stability in water and chances of metal leaching make them an improper choice. Photocatalysis is another green technique that has proved its efficiency in degrading organic dyes. Developing photocatalysts that show efficiency under solar irradiation instead of artificial light sources will be an added advantage, making the system more environmentally sustainable [154]. Though several metal oxides show excellent photocatalytic activity, they show compromised activity under visible light [155]. Additionally, using these catalysts for multiple cycles might increase the risk of metal leaching, leading to secondary metal pollution in water [156]. In this scenario, the development of metal-free sustainable materials is one of the current challenges.

Ionic porous organic polymers, owing to their charged skeleton, robust nature, and high surface area, proved to be an efficient metal-free adsorbent for removing several anionic pollutants from wastewater and showed their efficiency as metal-free adsorbents [158-161]. Based on the previous reports, it has been well established that imidazolium and viologen-based ionic porous organic polymers are proven to be excellent adsorbents for selectively capturing anionic pollutants with high uptake capacity and excellent reusability [157]. Though there are sufficient reports, these reports lack an efficient strategy for designing high-performing iPOPs for wastewater remediation. Though several factors can be tuned to develop efficient iPOP-based adsorbents, charge density in the polymeric skeleton is a very important parameter that is often overlooked. Higher charge density in the polymeric skeleton can access higher affinity towards various anionic pollutants if manipulated tactically. This thesis addresses an efficient strategy for tuning the positive charge density in the polymeric skeleton of viologen-based ionic porous organic polymers by simply replacing a larger secondary building block with a smaller one.

Another major gap in using cationic porous organic polymer-based adsorbents is their selectivity only towards anionic pollutants. Along with anionic dyes, several cationic dyes are also being used at the industrial level, which also has several ill effects. Cationic porous organic polymers, owing to their cationic nature, proved to be inactive in capturing these cationic dyes [108,158,162,163]. In this scenario, though there are reports of the degradation of these dyes photo-catalytically, there are hardly any reports of cationic porous organic polymers working as an efficient photocatalyst for the degradation of these cationic dyes. Strategic incorporation of organic photosensitizers as an active building block in the polymeric skeleton can serve as a bifunctional material that could be useful in the remediation of both anionic and cationic pollutants [164]. This thesis presents one of its first kinds of bifunctional imidazolium-functionalized ionic porous organic polymer containing an anthracene moiety, which is one of the building

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blocks of the polymer. The polymer shows excellent adsorption of anionic pollutants and photocatalytic degradation of cationic dyes under solar irradiation.

#### **1.8.2.** Iodine as a potential threat

Besides other utilization, iodine is essential to the thyroid gland's functionality [165]. It is a well-known reactant with several uses, as it is an integral part of various chemical reactions, a known disinfectant, and is used in the medicinal sectors to treat thyroid [166]. In some cases, it has also been used in water purification [167]. Despite having several applications, it is also one of the radionuclides (<sup>129</sup>I and <sup>131</sup>I) waste generated from nuclear power plants [168]. Among them, <sup>129</sup>I has a half-life of around  $1.57 \times 10^7$  years, and if it encounters human health, it might cause incurable diseases like thyroid cancer [169]. <sup>131</sup>I is even more dangerous as it can easily interfere with the human metabolic system and can cause several fetal consequences, such as coma and death, though it has a half-life of eight days only [170,171]. Both radionuclides, being highly volatile in nature, might defuse in air and can reach human metabolic systems. Besides that, <sup>131</sup>I is used in cancer radiotherapy and generated in hospitals for therapeutic purposes [172,173]. Though in the vapor state, iodine exists in a classical molecular form  $(I_2)$ , which is sparingly soluble in water, several recent reports show the presence of polyiodides  $(I_3)$  in the vapor phase, which is water soluble in nature [174]. That makes the problem much more severe as diffusion of radio iodides into water increases the risk of human contact.

Iodine is essential for the synthesis of THs and the modulation of thyroid function. The production of THs (3,5,3',5'-tetraiodo-L-thyronine (T4) and 3,5,3'-triiodo-L-thyronine (T3)) mainly depends on thyrotropin-releasing hormones (TRHs) and thyroid-stimulating hormones (TSHs) [175]. As thyroid glands cannot differentiate between regular iodine and radioactive iodine if inhaled, the radioactive iodine gets adsorbed in the thyroid glands like the stable iodine, and that will ultimately lead to thyroid cancer.

Additionally, radioiodine poisoning dilutes the natural iodine sources in the body, decreasing the THs production rate and leading to hypothyroidism (**Figure 1.7**) *[176]*. Though the effect is short-lived, it affects the fetus and newborn children.



**Figure 1.7.** Schematic representation of radioiodine impact on human health. Reproduced with the permission of Frontiers Media [176].

Though there are several state-of-the-art materials like silver-based zeolites and activated carbons for iodine capture, their activity is restricted in terms of benchmark adsorption capacity due to low surface area and weak interaction of iodine with the adsorbents, slow adsorption kinetics, and lack of reusability [169,177,178]. The use of costly metals like silver in the adsorbents also increases the preparation cost of the material [179]. In this scenario, there is an urgent need to develop cost-efficient materials showing equal activity in capturing iodine from vapor and aqueous phases. Porous materials like metal-organic frameworks, covalent organic polymers, and molecular cages, though, established themselves as an efficient adsorbent for iodine capture in vapor and organic phases, they often lack activity in capturing iodine or iodide ions from aqueous solution [169,178]. Materials with polarizable pore surfaces and highly cationic skeletons with exchangeable ions could be efficient for the sequestration of iodine from

aqueous solution and from vapor and organic phases [180-185]. This thesis represents the development of ionic porous organic polymers by selecting viologen functionalities particularly, as it will not only provide cationic sites with exchangeable counter anions for selective capture of iodide from the aqueous solutions but also provide highly polarizable pore structures that will be helpful in the interaction with electron-rich moieties like neutral iodine. Additionally, this thesis proposed using iodine-containing polymers as antibacterial agents to combat microorganisms.

#### **1.8.3.** Detection of amines

Synthetic amines are vital in various laboratories, as they are significant components in multiple syntheses. They are also produced in millions of tons annually and used in dye, pharmaceutical, and polymer industries [186,187]. However, they are very volatile and corrosive and can damage human skin, eyes, and respiratory systems even in very low concentrations [188-190]. Being colorless in most cases and not having any chromophoric and fluorophoric properties, it isn't easy to detect amine vapors in the naked eye. Considering the toxic effect of volatile synthetic amines, the detection of amine vapor is very significant as it not only aids human health but also restricts environmental pollution. Though there are several techniques available for their detection, like high-performance liquid chromatography (HPLC), fluorometric detection, GC-coupled mass spectrometry, etc., due to the high cost and larger size of the instruments, they are not always affordable and not easily accessible on the spot [191-193]. Chromic materials are one such material that changes their color under the influence of external stimuli like light, chemicals, electricity, and temperature [194,195]. Developing a suitable chromic material that can readily interact with amines and detect them even in very low concentrations by change of color could be an alternative and convenient method for rapid and on-site detection. Though several materials reported in the literature have shown impressive results in detecting various amines, their compromised stability,

low reversibility, and high tendency to react with them make them insignificant at the industrial level [197-200]. Therefore, developing materials that are responsive to several amines but stable and reversible in nature are in high demand. Porous materials, due to their various interactive sites and inherent host-guest properties, proved to be promising in the field of amine sensing. Though there are several reports of porous material based amine sensors, the presence of reactive metal sites and the highly chelating nature of the amines leads to complex formation in the initial stages of sensing that hampers the reusability of the materials [201-207]. Dicationic ethyl-viologen molecules, being electron deficient and redox-active in nature, with a flexible chromic state, have shown their efficacy for detecting various amines [208-211]. Generation of ethyl viologen sites in the polymeric skeleton could be an efficient strategy for developing ethyl viologen-based ionic porous organic polymers for an efficient and robust platform for detecting amines. This thesis reports one such ionic porous organic polymer that shows fast response, high stability, and good reversibility in detecting ammonia vapor.

#### 1.8.4. Electrochromic device fabrication

Electrochromic materials refer to the materials that change color in response to electrical stimuli [212,213]. Electrochromic materials and devices are used in fields like reflectance mirrors, smart windows, emitting surfaces, etc. [214,215]. This technology is particularly getting attention due to its controllable light adsorption and release with the help of electrical bias. The reversible switching between transparent and opaque states can be achieved in these devices by modulating the electrical bias [216]. This helps in controlling the amount of solar irradiation, hence heat passing through the windows [217]. That ultimately helps to modulate the indoor heat and light. This capability helps to lower the use of artificial cooling systems on hot days, ultimately lowering cooling energy consumption [218]. Additionally, the ability of electrochromic materials to regulate light transmission can

impact the overall energy consumption in the buildings, which actively helps in lowering the carbon footprint and contributes to reducing greenhouse gas emissions [219,220]. Transition metal-based oxides like WO<sub>3</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, and Ta<sub>2</sub>O are some of the very well-known electrochromic materials [221]. Besides inorganic oxides, redox-active organic molecules have also shown considerable electrochromic properties. Among the very few organic electrochromic materials reported, most of them are anodically colored [222,223]. Cathodically colored materials, due to their instability in their radical states, are not being explored proficiently. Though the use of porous materials in electrochromic devices is comparatively new, the facile distribution of ions and electrolytes through the pore channels of the materials helps to achieve faster color switching and excellent color contrast [224-227]. Among the porous materials, metalorganic frameworks have shown good electrochromic properties owing to the presence of redox-active metal centers and organic ligands [228]; however, instability in the electrochemical conditions of such materials often restricts their applicability. Porous organic polymers, due to their robust nature and well-distributed pore channels, have shown their applicability to be used in solid-state electrochromic devices [229]. Among the very few cathodically colored organic molecules, ethyl viologen is one of the well-used molecules. Their applicability to show high color contrast and fast switching make them very efficient electrochromic materials [230,231]. Generating ethyl viologen centers in porous organic polymers could be useful for developing cathodically colored electrochromic material with high stability, fast switching, and good color contrast. This thesis reports one such example of fabricating an electrochromic device using a viologen-based porous organic polymer. The device shows excellent stability, fast switching, very high color contrast, and excellent stability.

#### 1.8.5. Sustainable hydrogen peroxide production

Hydrogen peroxide is one of the top most used chemicals. It is an ecofriendly oxidant, releasing water as a by-product during the oxidation reaction, whereas other oxidants, like oxychlorides, release toxic chlorine gas [232]. With its eco-friendly nature, it is in high demand and is used in huge amounts in several industrial sectors, such as chemical preparation, paper bleaching, water purification plants, etc. [233,234]. The current annual use of hydrogen peroxide is estimated to be around 2.2 million tons [235]. Though in high demand, the primary production of hydrogen peroxide largely depends on the traditional anthraquinone process [236]. This energy-intensive multistep oxidation-reduction process requires extensive operational facilities and expensive Pd-hydrogenation catalysts [237]. The organic by-products released from this process also have several toxic environmental effects [238]. Direct mixing of hydrogen and oxygen is another economically feasible alternative [239]. However, this process requires an expensive Pt-based catalyst that increases the preparation cost and the risk of explosion associated with storing highly compressible liquid hydrogen and oxygen, making its commercial application doubtful [240]. Another eco-friendly alternative is the electrochemical oxygen reduction to produce hydrogen peroxide in a fuel-cell setup. However, product selectivity is a significant issue in that case [241]. The 2e<sup>-</sup> reduction of oxygen to hydrogen peroxide is always countered by the parallel 4e<sup>-</sup> reduction of oxygen to water [242]. Several electrocatalysts have been developed in the recent past for oxygen reduction, but most of them show very poor selectivity in the 2e<sup>-</sup> reduction process [243]. Among the very few electrocatalysts that show good selectivity towards the 2e<sup>-</sup> reduction of oxygen are mostly noble metal-based catalysts that increase the preparation cost of the catalyst [244]. In this scenario, there is a requirement to develop metal-free electrocatalysts for selective reduction of oxygen to hydrogen peroxide.

Porous organic polymers have already established themselves as a class of emerging electrocatalysts, and there has been a significant advancement in

the field in the last couple of years [245]. Despite considerable advancement in green energy generation, there are limited reports on porous organic polymer-based electrocatalysts for sustainable chemical production. Among the very few reports of electrocatalytic hydrogen peroxide production by selective 2e<sup>-</sup> reduction of oxygen, most are metaldopped POPs [246-248], which not only affect the preparation cost of the electrocatalyst but the chances of metal leaching from the electrocatalyst in the harsh electrocatalytic condition hampers the catalytic performance. Among the very limited reports on POP-based metal-free electrocatalysts, most are sulfur-containing [249-253], which are unsafe to use at the industrial level, considering the known toxicity of the S-containing compounds [254,255]. In this situation, viologen-based porous organic polymers have shown promising results in selective hydrogen peroxide production (Chem comm paper). There is also a probability of manipulating the electronic properties of the polymeric skeleton by simply exchanging the counter anions, which might be beneficial in achieving better electrocatalytic performance. This thesis reports one such viologen-based ionic porous organic polymer synthesized using the Zincke reaction. The polymers show good selectivity for the selective production of hydrogen peroxide. Additionally, by exchanging the counter anions, the activity of the catalyst can be manipulated.

#### **1.9.** Overview of the thesis

The main objective of this thesis is to design and synthesize some novel ionic porous organic polymers and investigate their role as an ideal sustainable material for addressing some environmental challenges. The consecutive chapters discussed the design, synthesis, and characterization of some task-specific ionic porous organic polymers and tested their targeted applications.

Chapter 2 presents a thermally and chemically robust imidazolium-based ionic porous organic polymer **iPOP-ANT** with exchangeable counter anion

Cl<sup>-</sup>. The polymer was synthesized via a one-step condensation reaction between 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine and 9,10 bis(chloromethyl)anthracene under inert atmosphere. The chemical structure of the material was thoroughly characterized by <sup>13</sup>C-CPMAS NMR, FTIR spectroscopy, FESEM, EDX, XPS, and TGA. Owing to the presence of exchangeable counter anion Cl<sup>-</sup> in the polymeric skeleton, the polymer was used as a potential polymeric adsorbent in capturing toxic oxoanions ( $Cr_2O_7^{2-}$ ,  $MnO_4^{-}$ ) and anionic dyes (methyl orange, amaranth, congo red). The material shows high uptake capacity, fast kinetics, and selectivity toward capturing the anionic pollutants. The low optical band gap of the material (2.58 eV) makes it an ideal photocatalyst for the degradation of cationic dyes (rhodamine B, rhodamine 6G, and methylene blue) under solar irradiation.

Chapter 3 addresses an efficient strategy for designing highly efficient polymeric adsorbents. This chapter mainly explores the role of building blocks in optimizing the polymers' charge density and surface area to develop better polymeric adsorbents. Three cationic polymers, iPOP-ZN1, iPOP-ZN2, and iPOP-ZN3, were designed, synthesized, and characterized using standard characterization techniques. Among the three polymers, **iPOP-ZN1**, having the highest surface area and more significant charge density, comes up as the best adsorbent for anionic inorganic and organic pollutants in an aqueous medium. The polymers also reveal excellent adsorption capability in higher concentrations of competing ions and highly acidic and basic solutions. The polymers show excellent reusability up to several cycles. The polymers further show excellent adsorption capacity of iodine vapor at room temperature and 75°C. Among them, iodine adsorption by iPOP-ZN1 at 75°C is among the highest reported values in reported literature. The iodine-loaded polymers show impressive antibacterial properties against E. coli, B. subtilis, and H. pylori.

**Chapter 4** presents redox-active viologen sites containing multifunctional ionic porous organic polymer iPOP-Bpy. The materials show excellent iodine uptake capacity in vapor (540 wt%), organic (1009.77 mg/g), and aqueous phases (3921.47 mg/g), along with fast kinetics and reusability for several cycles. Due to the presence of redox-active viologen sites in the polymer, it also shows its utility in being used as a solid-state NH<sub>3</sub> vapor sensor as it shows ultrafast color switching from yellow to blue in the presence of electron-rich ammonia vapor and shows excellent efficiency as solid-state ammonia vapor sensor. Further, the material found application as a p-type complementary electrochromic electrode and was fabricated into a bilayer device. Bias-dependent in-situ transmission and electrochemical measurements of a solid-state ECD fabricated using iPOP-Bpy reveal its capability to be the best choice from the viologen family in fabricating an organic ECD. The above conclusion can be drawn from the excellent electrochromic performance parameter values of switching times (~0.5 s), color contrast ( $\sim$ 50%), and coloration efficiencies (up to 800 cm<sup>2</sup>/C).

**Chapter 5** explores another viologen-based ionic porous organic polymer (**iPOP-TAPA**) as an efficient electrocatalyst for selective 2e<sup>-</sup> reduction of oxygen to hydrogen peroxide. Electrochemical H<sub>2</sub>O<sub>2</sub> production by 2e<sup>-</sup> reduction of O<sub>2</sub> is a greener alternative to the traditional anthraquinone However, developing metal-free process. electrocatalysts that predominantly follow the 2e<sup>-</sup> reduction process over the more favorable 4e<sup>-</sup> reduction is challenging. iPOP-TAPA shows its efficiency as a metal-free electrocatalyst for the selective production of hydrogen peroxide  $(H_2O_2)$ from oxygen in an alkaline medium. The  $H_2O_2$  production ability of the catalyst was further tuned by exchanging the Cl<sup>-</sup> counter anion with other halide ions (F<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>). Among these catalysts, **iPOP-TAPA-F** shows exceptional catalytic activity towards the selective production of H<sub>2</sub>O<sub>2</sub> (98.5 %) with a significant current efficiency of 99 %.

#### 1.10. References

[1] Population | United Nations. https://www.un.org/en/globalissues/population (accessed 2024-07-21).

[2] Zhou H. (2009), Population Growth and Industrialization, Economic Inquiry, 47, 249–265 (DOI: 10.1111/j.1465-7295.2008.00151.x.)

[3] Saurabh Sonwani S. S., Vandana Maurya V. M. (2019), Impact of Air Pollution on the Environment and Economy, Air pollution: sources, impacts and controls, 113–134 (DOI: 10.1079/9781786393890.0113)

[4] Gaur N., Sharma S., Yadav N. (2024) Chapter 2 - Environmental Pollution. In Green Chemistry Approaches to Environmental Sustainability, Advances in Green and Sustainable Chemistry, Elsevier, 2024; pp 23–41 (DOI: 10.1016/B978-0-443-18959-3.00010-0)

[5] Le Monde (2022), Pollution Is Responsible for 9 Million Deaths EachYear Worldwide, www.lemonde.fr/en/environment/article/2022/05/18/.Accessed 21 July, 2024

[6] Hamanaka R. B., Mutl G. M. (2018), Particulate Matter Air Pollution:Effects on the Cardiovascular System, Front. Endocrinol. 9(DOI:10.3389/fendo.2018.00680)

[7] Anderson J. O., Thundiyil J. G., Stolbach A. (2012), Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health, J. Med. Toxicol., 8, 166–175 (DOI: 10.1007/s13181-011-0203-1)

[8] Kılıç Z. (2021), Water Pollution: Causes, Negative Effects and Prevention Methods, İZÜFBED 3 (2), 129–132 (DOI: 10.47769/izufbed.862679)

[9] Khatun R. (2017), Water Pollution: Causes, Consequences, Prevention Method and Role of WBPHED with Special Reference from Murshidabad District. 2017, 7 (8).

[10] Chaudhary FN., Malik MF. (2017) Factors Affecting Water Pollution: A Review, J Ecosyst. Ecography, 7, 1 (DOI: 10.4172/2157-7625.1000225)

[11] Liu Y., Wang P., Gojenko B., Yu J., Wei L., Luo D., Xiao T. (2021),
A Review of Water Pollution Arising from Agriculture and Mining Activities in Central Asia: Facts, Causes and Effects. Environ. Pollut., 291, 118209 (DOI: 10.1016/j.envpol.2021.118209)

[12] Makar P. A., Gong W., Milbrandt J., Hogrefe C., Zhang Y., Curci G.,
Žabka R.; Im U., Balzarini A., Baró R., Bianconi R., Cheung P., Forkel R.,
Gravel S., Hirtl M., Honzak L., Hou A., Jiménez-Guerrero P., Langer M.,
Moran M. D., Pabla B., Pérez J. L., Pirovano G., San José R., Tuccella P.
Werhahn J., Zhang J., Galmarini S. (2015), Feedbacks between Air
Pollution and Weather, Part 1: Effects on Weather, Atmos. Environ.115,
442–469 (DOI: 10.1016/j.atmosenv.2014.12.003)

[13] Makar P. A., Gong W., Hogrefe C., Zhang Y., Curci G., Žabkar R., Milbrandt J., Im U., Balzarini A., Baró R., Bianconi R., Cheung P., Forkel R., Gravel S., Hirtl M., Honzak L., Hou A., Jiménez-Guerrero P., Langer M., Moran M. D., Pabla B., Pérez J. L., Pirovano G., San José R., Tuccella P., Werhahn J., Zhang J., Galmarini S. (2015), Feedbacks between Air Pollution and Weather, Part 2: Effects on Chemistry. Atmos. Environ., 115, 499–526 (DOI: 10.1016/j.atmosenv.2014.10.021)

[14] Mandell J. T., Idarraga M., Kumar N., Galor A. (2020), Impact of Air Pollution and Weather on Dry Eye, J. Clin. Med., 9, 3740. (DOI: 10.3390/jcm9113740)

[15] Reddy V. R., Behera B. (2006), Impact of Water Pollution on Rural Communities: An Economic Analysis, Ecol. Econ., 58, 520–537. (DOI: 10.1016/j.ecolecon.2005.07.025)

[16] Schwarzenbach R. P., Egli T., Hofstetter T. B., Gunten U. von, Wehrli
B. (2010), Global Water Pollution and Human Health, Annu. Rev. Environ.
Resour., 35, 109–136 (DOI: 10.1146/annurev-environ-100809-125342)

[17] Bernstein J. A., Alexis N., Barnes C., Bernstein I. L., Nel A., Peden D.,
Diaz-Sanchez D., Tarlo S. M., Williams P. B., Bernstein J. A. (2004),
Health Effects of Air Pollution. J. Allergy Clin. Immunol., 114, 1116–1123
(DOI: 10.1016/j.jaci.2004.08.030)

[18] Wang Q., Yang Z (2016), Industrial Water Pollution, Water Environment Treatment, and Health Risks in China. Environ. Pollut., 218, 358–365 (DOI: 10.1016/j.envpol.2016.07.011)

[19] Brunekreef B., Holgate S. T. (2002), Air Pollution and Health, The Lancet, 360, 1233–1242 (DOI: 10.1016/S0140-6736(02)11274-8)

[20] Glencross D. A., Ho T. R., Camiña N., Hawrylowicz C. M., Pfeffer P.
E. (2020), Air Pollution and Its Effects on the Immune System, Free Radical Biol. Med., 151, 56–68 (DOI: 10.1016/j.freeradbiomed.2020.01.179)

[21] Forstinus N. O., Ikechukwu N. E., Emenike M. P., Christiana, A. O.
(2016), Water and Waterborne Diseases: A Review, Int. J. Trop. Dis. Health., 12, 1–14. https://doi.org/10.9734/IJTDH/2016/21895.

[22] Khan S., Naushad Mu., Lima E. C., Zhang S., Shaheen S. M., Rinklebe J. (2021), Global Soil Pollution by Toxic Elements: Current Status and Future Perspectives on the Risk Assessment and Remediation Strategies – A Review, J. Hazard. Mat., 417, 126039, (DOI: 10.1016/j.jhazmat.2021.126039)

[23] Zwolak A., Sarzyńska M., Szpyrka E., Stawarczyk K. (2019), Sources of Soil Pollution by Heavy Metals and Their Accumulation in Vegetables:
A Review, Water Air Soil Pollut, 230, 164 (DOI: 10.1007/s11270-019-4221-y)

[24] Hu Y., Liu X., Bai J., Shih K., Zeng E. Y., Cheng H. (2013), Assessing Heavy Metal Pollution in the Surface Soils of a Region That Had Undergone Three Decades of Intense Industrialization and Urbanization, Environ. Sci. Pollut. Res., 20, 6150–6159 (DOI: 10.1007/s11356-013-1668-z

[25] Modis K., Vatalis K. I. (2014), Assessing the Risk of Soil Pollution around an Industrialized Mining Region Using a Geostatistical Approach, Soil Sediment Contam. Int. J., 23, 63–75 (DOI: 10.1080/15320383.2013.777393)

[26] Wołejko E., Jabłońska-Trypuć A., Wydro U., Butarewicz A.,
Łozowicka B. (2020), Soil Biological Activity as an Indicator of Soil
Pollution with Pesticides – A Review, Appl. Soil. Ecol., 147, 103356. (DOI: 10.1016/j.apsoil.2019.09.006)

[27] Zhichkina, L., Nosov V., Zhichkin K., Zhenzhebir V., Abramov Y.,
Alborova M. (2020), Pesticide Monitoring of Agricultural Soil Pollution,
E3S Web Conf., 193, 01068 (DOI: 10.1051/e3sconf/202019301068)

[28] Cabrerizo A., Dachs J., Moeckel C., Ojeda M. J., Caballero G., Barceló D., Jones, K. C. (2011), Factors Influencing the Soil–Air Partitioning and the Strength of Soils as a Secondary Source of Polychlorinated Biphenyls to the Atmosphere, Environ. Sci. Technol., 45, 4785–4792 (DOI: 10.1021/es200400e)

[29] Manisalidis I., Stavropoulou E., Stavropoulos A., Bezirtzoglou E.(2020), Environmental and Health Impacts of Air Pollution: A Review,Front. Public Health, 8 (DOI: 10.3389/fpubh.2020.00014)

[30] Tiwary R. K. (2001), Environmental Impact of Coal Mining on Water Regime and Its Management Water, Air, & Soil Pollut., 132, 185–199 (DOI: 10.1023/A:1012083519667)

[31] Kampa M., Castanas E. (2008), Human Health Effects of Air Pollution.Environ. Pollut., 151, 362–367 (DOI: 10.1016/j.envpol.2007.06.012)

[32] Hansen J., Sato M., Ruedy R., Lo K., Lea D. W., Medina-Elizade M.(2006), Global Temperature Change, Proc. Natl. Acad. Sci. USA, 103 (39),14288–14293 (DOI: 10.1073/pnas.0606291103)

[33] Verones F., Hanafiah M. M., Pfister S., Huijbregts M. A. J., Pelletier G. J., Koehler A. (2010), Characterization Factors for Thermal Pollution in Freshwater Aquatic Environments, Environ. Sci. Technol., 44, 9364–9369 (DOI: 10.1021/es102260c)

[34] McMichael A. J., Woodruff R. E., Hales S. (2006), Climate Change and Human Health: Present and Future Risks, The Lancet, 367 (9513), 859–869 (DOI: 10.1016/S0140-6736(06)68079-3)

[35] Zecca A., Chiari L. (2010), Fossil-Fuel Constraints on Global Warming, Energy Policy, 38, 1–3 (DOI: 10.1016/j.enpol.2009.06.068)

[36] Hoel M., Kverndokk S. (1996), Depletion of Fossil Fuels and the Impacts of Global Warming, Resour. Energy Econ., 18, 115–136 (DOI: 10.1016/0928-7655(96)00005-X)

[37] Wigley T. M. L. (1991), Could Reducing Fossil-Fuel Emissions CauseGlobal Warming? Nature, 349, 503–506 (DOI: 10.1038/349503a0)

[38] Shepherd J. G., Brewer P. G., Oschlies A., Watson A. J. (2017), Ocean
Ventilation and Deoxygenation in a Warming World: Introduction and
Overview, Phil. Trans. R. Soc. A, 375, 20170240 (DOI: 10.1098/rsta.2017.0240)

[39] Slabbekoorn H. (2019) Noise Pollution, Curr. Biol., 29, R957–R960.(DOI: 10.1016/j.cub.2019.07.018)

[40] Gupta A., Gupta A., Jain K., Gupta S. (2018), Noise Pollution and Impact on Children Health, Indian J. Pediatr., 85, 300–306 (DOI: 10.1007/s12098-017-2579-7)

[41] Stansfeld S. A., Matheson M. P. (2003), Noise Pollution: Non-Auditory Effects on Health, Br. Med. Bull., 68, 243–257 (DOI: 10.1093/bmb/ldg033)

[42] Xie Z., Chen F., Li W. A., Geng X., Li C., Meng X., Feng, Y., Liu W.,
Yu F. (2017), A Review of Sleep Disorders and Melatonin, Neurol. Res.,
39, 559–565 (DOI: 10.1080/01616412.2017.1315864)

[43] Crowley K. (2011), Sleep and Sleep Disorders in Older Adults.Neuropsychol Rev., 21, 41–53 (DOI: 10.1007/s11065-010-9154-6)

[44] Nazeer M., Tabassum U., Alam S. (2016), Environmental Pollution and Sustainable Development in Developing Countries, Pak. Dev. Rev., 55, 589–604 (DOI: www.jstor.org/stable/44986005)

[45] Arora N. K. (20180 Environmental Sustainability—Necessary for Survival, Environ. Sustain., 1, 1–2 (DOI: 10.1007/s42398-018-0013-3)

[46] Holdgate, M. W. (1979) A Perspective of Environmental Pollution;CUP Archive, 1979.

[47] Mishra S., Chowdhary P., Bharagava R. N. (2019), Conventional Methods for the Removal of Industrial Pollutants, Their Merits and Demerits. Emerging and Eco-Friendly Approaches for Waste Management, Springer: Singapore, 2019; pp 1–31 (DOI: 10.1007/978-981-10-8669-4\_1)

[48] Lu B., Li B., Wang L., Yang J., Liu J., Wang X. V. (2014), Reusability
Based on Life Cycle Sustainability Assessment: Case Study on WEEE,
Procedia CIRP 15, 473–478 (DOI: 10.1016/j.procir.2014.06.046)

[49] Mohamed, F.; Jamil, M.; Zain, M. F. M. Sustainable Material: Challenges and Prospect, J. Adv. Res. Mater. Sci., 57, 7–18 (ISSN: 2289-7992)

[50] Florez, L., Castro-Lacouture D. (2013), Optimization Model for Sustainable Materials Selection Using Objective and Subjective Factors. Mater. Des., 46, 310–321 (DOI: 10.1016/j.matdes.2012.10.013)

[51] Ljungberg L. Y. (2007), Materials Selection and Design for Development of Sustainable Products, Mater. Des., 28, 466–479 (DOI: 10.1016/j.matdes.2005.09.006)

[52] Samanta P., Desai A. V., Let S. Ghosh, S. K. (2019), Advanced Porous Materials for Sensing, Capture and Detoxification of Organic Pollutants toward Water Remediation, ACS Sustainable Chem. Eng. 2019, 7 (8), 7456–7478 (DOI: 10.1021/acssuschemeng.9b00155)

[53] Mudassir M. A., Aslam H. Z., Ansari T. M., Zhang H., Hussain I. (2021), Fundamentals and Design-Led Synthesis of Emulsion-Templated Porous Materials for Environmental Applications. Advanced Science, 8, 2102540 (DOI: 10.1002/advs.202102540)

[54] Esquivel-Castro T. A., Martínez-Luévanos A., Estrada-Flores S., Cano-Salazar L. F. (2020), Porous Materials for Applications in Energy and Environment. In Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, Springer International Publishing: Cham, pp 1–19, (DOI: 10.1007/978-3-030-11155-7\_14-1)

[55] Al-Jubouri S. M., Al-Batty S., Al-Hamd R. Kh. S., Sims R., Hakami M. W., Sk M. H. (2023), Sustainable Environment through Using Porous Materials: A Review on Wastewater Treatment. Asia-Pacific J. Chem. Eng, 18, e2941 (DOI: 10.1002/apj.2941)

[56] Xue R., Guo H., Yang W., Huang S. L, Yang G. Y. (2022), Cooperation between Covalent Organic Frameworks (COFs) and Metal Organic

Frameworks (MOFs): Application of COFs-MOFs Hybrids, Adv. Compos. Hybrid Mater., 5, 1595–1611 (DOI: 10.1007/s42114-022-00432-3)

[57] Yuan N., Jiang Q., Li J., Tang J. (2020), A Review on Non-Noble Metal Based Electrocatalysis for the Oxygen Evolution Reaction, Arab. J. Chem., 13, 4294–4309 [DOI: 10.1016/j.arabjc.2019.08.006]

[58] Naz N., Manzoor M. H., Naqvi S. M. G., Ehsan U., Aslam M., Verpoort F. (2024), Porous Organic Polymers; an Emerging Material Applied in Energy, Environmental and Biomedical Applications, Appl. Mater. Today, 38, 102198 (DOI: 10.1016/j.apmt.2024.102198)

[59] Staudinger, H. On Polymerization. In On Polymerization; HarvardUniversityPress, 2013; pp259–264(DOI:10.4159/harvard.9780674366701.c90)

[60] Song W., Zhang Y., Tran C. H., Choi H. K., Yu D. G., Kim I. (2023),
Porous Organic Polymers with Defined Morphologies: Synthesis,
Assembly, and Emerging Applications, Prog. Polym. Sci., 142, 101691
(DOI: 10.1016/j.progpolymsci.2023.101691)

[61] Hu S., Yan J., Yang G., Ma C., Yin J. (2022) Self-Assembled Polymeric Materials: Design, Morphology, and Functional-Oriented Applications, Macromol. Rapid Commun., 43, 2100791. https://doi.org/10.1002/marc.202100791.

[62] Côté A. P., Benin A. I., Ockwig N. W., O'Keeffe, M.; Matzger, A. J.;
Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. Science 2005, 310 (5751), 1166–1170. https://doi.org/10.1126/science.1120411.

[63] Mohamed M. G., EL-Mahdy A. F. M., Kotp M. G., Kuo S. W. (2022), Advances in Porous Organic Polymers: Syntheses, Structures, and Diverse Applications, Mater. Adv., 3, 707–733 (DOI: 10.1039/D1MA00771H)

[64] Xiao J., Chen J., Liu J., Ihara H., Qiu H. (2023), Synthesis Strategies of Covalent Organic Frameworks: An Overview from Nonconventional Heating Methods and Reaction Media, Green Energy Environ., 8, 1596–1618 (DOI: 10.1016/j.gee.2022.05.003)

[65] Shi T., Wu Z., Wu Z., Zhang Q. F., Strømme M., Xu C. (2024),
Postsynthetic Amine Modification of Porous Organic Polymers for CO<sub>2</sub>
Capture and Separation, J. Appl. Polym. Sci., 62, 1554–1568 (DOI: 10.1002/pol.20230469)

[66] Zhang Y., Riduan S. N. (2012), Functional Porous Organic Polymers for Heterogeneous Catalysis, Chem. Soc. Rev., 41, 2083–2094 (DOI: 10.1039/C1CS15227K)

[67] Debruyne M., Speybroeck V. V., Voort P. V. D., Stevens C. V. (2021),Porous Organic Polymers as Metal Free Heterogeneous Organocatalysts,Green Chem., 23, 7361–7434 (DOI: 10.1039/D1GC02319E)

[68] Karatayeva U., Al Siyabi S. A., Brahma Narzary B., Baker B. C., Faul
C. F. J. (2024), Conjugated Microporous Polymers for Catalytic CO<sub>2</sub>
Conversion, Adv. Sci., 11, 2308228 (DOI: 10.1002/advs.202308228)

[69] Brahma Narzary B., Karatayeva U., Mintah J., Villeda-Hernandez M., Faul, C. F. J. (2023), Bifunctional Metal-Free Porous Polyimide Networks for CO<sub>2</sub> Capture and Conversion. Mater. Chem. Front., 7, 4473–4481 (DOI: 10.1039/D3QM00639E)

[70] Yuan S., White D., Mason A., Liu D. J. (2013), Porous Organic Polymers Containing Carborane for Hydrogen Storage, Int. J. Energy Res., 37, 732–740 (DOI: 10.1002/er.1886)

[71] Wang J., Wang L., Wang Y., Zhang D., Xiao Q., Huang J., Liu Y. N.
(2022), Recent Progress in Porous Organic Polymers and Their Application for CO<sub>2</sub> Capture, Chin. J. Chem. Eng., 42, 91–103. (DOI: 10.1016/j.cjche.2021.08.028)

[72] Cousins K., Zhang R. (2019) Highly Porous Organic Polymers for Hydrogen Fuel Storage. Polymers, 11, 690 (DOI: 10.3390/polym11040690)

[73] Bandyopadhyay S., Anil A. G., James A., Patra A. (2016),
Multifunctional Porous Organic Polymers: Tuning of Porosity, CO<sub>2</sub>, and H<sub>2</sub>
Storage and Visible-Light-Driven Photocatalysis, ACS Appl. Mater.
Interfaces, 8, 27669–27678 (DOI: 10.1021/acsami.6b08331)

[74] Lu Y., Liu W., Liu J., Li X., Zhang S. (2021), A Review on 2D Porous Organic Polymers for Membrane-Based Separations: Processing and Engineering of Transport Channels, Adv. Membr, 1, 100014 (DOI: 10.1016/j.advmem.2021.100014)

[75] Li Z., Yang Y. W. (2022), Macrocycle-Based Porous OrganicPolymers for Separation, Sensing, and Catalysis. Adv. Mater., 34, 2107401(DOI: 10.1002/adma.202107401)

[76] Mishra B., Alam A., Kumbhakar B., Díaz Díaz D., Pachfule P. (2023), Impact of the Crystallinity of Covalent Organic Frameworks on Photocatalytic Hydrogen Evolution, Cryst. Growth Des., 23, 4701–4719 (DOI: 10.1021/acs.cgd.3c00379)

(77) Prakash K., Mishra B., Díaz Díaz D., Nagaraja C M., Pachfule P.
(2023), Strategic Design of Covalent Organic Frameworks (COFs) for Photocatalytic Hydrogen Generation, J. Mater. Chem. A, 11 (27), 14489– 14538 (DOI: 10.1039/D3TA02189K)

[78] Sun H., Li J., Liang W., Gong X., Jing A., Yang W., Liu H., Ren S.
(2023), Porous Organic Polymers as Active Electrode Materials for Energy Storage Applications, Small Methods, 2301335 (DOI: 10.1002/smtd.202301335)

[79] Liu X., Liu C. F., Lai W. Y., Huang W. (2020), Porous OrganicPolymers as Promising Electrode Materials for Energy Storage Devices.Adv. Mater. Tech., 5, 2000154 (DOI: 10.1002/admt.202000154)

[80] Kang C. W., Son S. U. (2021), Redox-Active Porous Organic Polymers for Energy Storage, Bull. Korean Chem. Soc., 42, 159–167 (DOI: 10.1002/bkcs.12202)

[81] Maxwell J. C., Baker B. C., Faul C. F. J. (2023), Controlled Removal of Organic Dyes from Aqueous Systems Using Porous Cross-Linked Conjugated Polyanilines, ACS Appl. Polym. Mater., 5, 662–671 (DOI: 10.1021/acsapm.2c01718)

[82] Pan L., Liu Z., Hernandez M. V., Schroeder B. C., Sun Y., Faul, C. F.
J. (2024), Polyaniline-Based Cationic Porous Organic Polymers for Fast and Efficient Anion-Exchange-Driven Capture of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ACS Appl. Polym. Mater., 6, 6416–6424 (DOI: 10.1021/acsapm.4c00658)

[83] Li N., Huo L., Shen W., Qiang C., Wu M., Sun G., Li Q., Shi M., Ma,
J. (2023), Porous Organic Polymers for Superefficient Removal of Pollutants from Water: Design, Synthesis and Adsorption Performance, J. Clean. Prod., 396, 136558 (DOI: 10.1016/j.jclepro.2023.136558)

[84] Guo J., Yu L., Yue H. (2019), Bulk Fabrication of Porous Organic Framework Polymers on Flexible Nanofibers and Their Application for Water Purification, React. Funct. Polym., 135, 58–64 (DOI: 10.1016/j.reactfunctpolym.2018.12.007)

[85] Wang Y., Cui X., Zhang P., Wang Y., Lu W. (2023), Synthesis of Porphyrin Porous Organic Polymers and Their Application of Water Pollution Treatment: A Review, Environ. Technol. Innov., 29, 102972 (DOI: 10.1016/j.eti.2022.102972)

[86] Sun Q., Aguila B., Song Y., Ma S. (2020), Tailored Porous Organic
Polymers for Task-Specific Water Purification, Acc. Chem. Res., 53, 812–
821 (DOI: 10.1021/acs.accounts.0c00007)

[87] Bildirir H., Gregoriou G. V., Avgeropoulos A., Scherf U., L. ChochosC. (2017), Porous Organic Polymers as Emerging New Materials for
Organic Photovoltaic Applications: Current Status and Future Challenges, Mater. Horiz., 4, 546–556 (DOI: 10.1039/C6MH00570E)

[88] Keller N., Bein T. (2021), Optoelectronic Processes in Covalent Organic Frameworks. Chem. Soc. Rev., 50, 1813–1845 (DOI: 10.1039/D0CS00793E)

[89] Huang W., Zhang W., Yang S., Wang L., Yu G. (2024), 3D Covalent Organic Frameworks from Design, Synthesis to Applications in Optoelectronics, Small, 20, 2308019 (DOI: 10.1002/smll.202308019)

[90] Yadav V. K., Mir S. H., Mishra V., Gopakumar T. G., Singh, J. K. (2020), A Simple Molecular Design for Tunable Two-Dimensional Imine Covalent Organic Frameworks for Optoelectronic Applications, Phys. Chem. Chem. Phys., 22, 21360–21368 (DOI: 10.1039/D0CP02961K)

[91] Shi Y., Yang J., Gao F., Zhang Q. (2023) Covalent Organic
Frameworks: Recent Progress in Biomedical Applications, ACS Nano, 17, 1879–1905 (DOI: 10.1021/acsnano.2c11346)

[92] Mal A., Ding H., Li M., Li W., Wang C. (2022), Covalent OrganicFrameworks with Nanopores for Biological Applications: A Review, ACSAppl. Nano Mater., 5, 13972–13984 (DOI: 10.1021/acsanm.2c01517)

[93] Cho H. C., Lee H. S., Chun J., Lee S. M., Kim H. J., Son S. U. (2010), Tubular Microporous Organic Networks Bearing Imidazolium Salts and Their Catalytic CO<sub>2</sub> Conversion to Cyclic Carbonates, Chem. Commun., 47, 917–919 (DOI: 10.1039/C0CC03914D)

[94] Sun J. K., Antonietti M., Yuan J. (2016), Nanoporous Ionic Organic Networks: From Synthesis to Materials Applications, Chem Soc. Rev., 45, 6627–6656 (DOI: 10.1039/C6CS00597G)

[95] Xu D., Guo J., Yan F. (2018), Porous Ionic Polymers: Design, Synthesis, and Applications, Prog. Polym. Sci., 79, 121–143 (DOI: 10.1016/j.progpolymsci.2017.11.005)

[96] Jhariat P., Panda T. (2024), Recent Advancement in Viologen Functionalized Porous Organic Polymers (vPOPs) for Energy and Environmental Remediation. Mater. Adv., 5, 4055–4077 (DOI: 10.1039/D4MA00182F)

[97] Fang H., Sun S., Liao P., Hu Y., Zhang J. (2018), Gold Nanoparticles Confined in Imidazolium-Based Porous Organic Polymers to Assemble a Microfluidic Reactor: Controllable Growth and Enhanced Catalytic Activity, J. Mater. Chem. A, 6, 2115–2121 (DOI: 10.1039/C7TA08985F)

[98] Fang H., Chen J., Xiao Y., Zhang J. (2019), Platinum Nanoparticles Confined in Imidazolium-Based Ionic Polymer for Assembling a Microfluidic Reactor with Enhanced Catalytic Activity. Appl. Catal. A Gen., 585, 117186 (DOI: 10.1016/j.apcata.2019.117186)

[99] Bayatani M., Torabi M., Yarie M., Zolfigol M. A., Farajzadeh Z.
(2023), Fabrication of an Imidazolium-Based Magnetic Ionic Porous Organic Polymer for Efficient Heterogeneous Catalysis of Betti Reaction, J. Mol. Liq., 390, 122863 (DOI: 10.1016/j.molliq.2023.122863)

[100] Zhang Y., Su K., Hong Z., Han Z., Yuan D. (2020), Robust Cationic Calix[4]Arene Polymer as an Efficient Catalyst for Cycloaddition of Epoxides with CO<sub>2</sub>, Ind. Eng. Chem. Res., 59, 7247–7254 (DOI: 10.1021/acs.iecr.9b05312)

[101] Li J., Dai X., Zhu L., Xu C., Zhang D., Silver M. A., Li P., Chen L., Li Y., Zuo D., Zhang H., Xiao C., Chen J., Diwu J., Farha O. K., Albrecht-Schmitt T. E., Chai Z., Wang S. (2018), <sup>99</sup>TcO<sub>4</sub><sup>-</sup> Remediation by a Cationic Polymeric Network, Nat. Commun., 9, 3007 (DOI: 10.1038/s41467-018-05380-5)

[102] Gong Y., Zhong H., Liu W., Zhang B., Hu S., Wang R. (2018),
General Synthetic Route toward Highly Dispersed Ultrafine Pd–Au Alloy
Nanoparticles Enabled by Imidazolium-Based Organic Polymers, ACS
Appl. Mater. Interfaces, 10, 776–786 (DOI: 10.1021/acsami.7b16794)

[103] Skorjanc T., Mavrič A., Sørensen M. N., Mali G., Wu C., Valant M.
(2022), Cationic Covalent Organic Polymer Thin Film for Label-Free Electrochemical Bacterial Cell Detection, ACS Sens., 7, 2743–2749 (DOI: 10.1021/acssensors.2c01292)

[104] Zhang P., Qiao Z. A., Jiang X., Veith G. M., Dai S. (2015), Nanoporous Ionic Organic Networks: Stabilizing and Supporting Gold Nanoparticles for Catalysis. Nano Lett., 15, 823–828 (DOI: 10.1021/nl504780j)

[105] Kim K., Buyukcakir O., Coskun A. (2016), Diazapyrenium-Based Porous Cationic Polymers for Colorimetric Amine Sensing and Capture from CO<sub>2</sub> Scrubbing Conditions RSC Adv., 6, 77406–77409 (DOI: 10.1039/C6RA16714D)

[106] Das G., Skorjanc T., Prakasam T., Nuryyeva S., Olsen J. C., Trabolsi A. (2017), Microwave-Assisted Synthesis of a Viologen-Based Covalent Organic Polymer with Redox-Tunable Polarity for Dye Adsorption, RSC Adv., 7, 3594–3598 (DOI: 10.1039/C6RA26332A)

[107] Li Z. J., Liu J. Y., Yu Y., Chang K. J., Wang H., Li Y. J.; Gai K.
(2022), Rational Design of High-Performance Cationic Organic Network Adsorbents, ACS Appl. Mater. Interfaces, 14, 23868–23876 (DOI: 10.1021/acsami.2c03119)

[108] Hassan A., Das N. (2024), Triptycene-Based Cationic Porous Organic Polymer for the Swift and Effective Removal of Organic and Inorganic Anionic Water Pollutants, ACS Appl. Eng. Mater., 2, 56–66 (DOI: 10.1021/acsaenm.3c00562)

[109] Shang S., Li, S.; Peng, C.; Liu, H.; Hu, J. Building Internal Electric Fields in Porous Ionic Polymers for Fast Photocatalytic Degradation of Tetracycline Hydrochloride. J. Mater. Chem. C 2023, 11 (22), 7397–7404. https://doi.org/10.1039/D3TC01102J.

[110] Srinivasan P., Dhingra K., Kailasam K. (2023), A Critical Insight into Porous Organic Polymers (POPs) and Its Perspectives for next-Generation Chemiresistive Exhaled Breath Sensing: A State-of-the-Art Review, J. Mater. Chem. A, 11, 17418–17451 (DOI: 10.1039/D3TA02660D)

[111] Fu S. Q., Zhu M. Z., Xue B., Liu P. N. (2022), Synergy between Ionic Capacity and Intrinsic Porosity in Imidazolium-Based Cationic Organic Polymers and Its Effect on Anionic Dye Adsorption, Macromolecules, 55, 8784–8794 (DOI: 10.1021/acs.macromol.2c01127)

[112] Huang N., Wang P., Addicoat M. A., Heine T., Jiang D. (2017), Ionic
Covalent Organic Frameworks: Design of a Charged Interface Aligned on
1D Channel Walls and Its Unusual Electrostatic Functions, Angew. Chem.,
56, 4982–4986 (DOI: 10.1002/anie.201611542)

[113] Ma H., Liu B., Li B., Zhang L., Li Y. G., Tan H. Q., Zang H. Y., Zhu G. (2016), Cationic Covalent Organic Frameworks: A Simple Platform of Anionic Exchange for Porosity Tuning and Proton Conduction, J. Am. Chem. Soc., 138, 5897–5903 (DOI: 10.1021/jacs.5b13490)

[114] Luo H., Ji W., Guo W., Chen P., Zhang Z., Xu X., Yue B., Tan W., Zhou, B. (2022), A Photoactive Dual-Cationic Covalent Organic Framework Encapsulated Sodium Nitroprusside as Controllable NO-Releasing Material for Joint Cation/Photothermal/NO Antibacterial Therapy, Micropor. Mesopor. Mater., 346, 112281 (DOI: 10.1016/j.micromeso.2022.112281)

[115] Mitra S., Kandambeth S., Biswal B. P., Khayum M. A., ChoudhuryC. K., Mehta M., Kaur G., Banerjee S., Prabhune A., Verma S., Roy, S.,

Kharul U. K., Banerjee R. (2016), Self-Exfoliated Guanidinium-Based Ionic Covalent Organic Nanosheets (iCONs). J. Am. Chem. Soc., 138, 2823–2828 (DOI: 10.1021/jacs.5b13533)

[116] Ding L. G., Yao B. J., Li F., Shi S. C., Huang N., Yin H. B., Guan Q., Dong Y. B. (2019), Ionic Liquid-Decorated COF and Its Covalent Composite Aerogel for Selective CO<sub>2</sub> Adsorption and Catalytic Conversion. J. Mater. Chem. A, 7, 4689–4698 (DOI: 10.1039/C8TA12046C)

[117] Lin J., Bi S., Fan Z., Fu Z., Meng Z., Hou Z., Zhang F. (2021), A Metal-Free Approach to Bipyridinium Salt-Based Conjugated Porous Polymers with Olefin Linkages, Polym. Chem., 12, 1661–1667 (DOI: 10.1039/D0PY01743D)

[118] Zhang C. R., Cui W. R., Yi S. M., Niu C. P., Liang R. P., Qi J. X., Chen X. J., Jiang W., Liu X., Luo Q. X., Qiu J. D. (2022), An Ionic Vinylene-Linked Three-Dimensional Covalent Organic Framework for Selective and Efficient Trapping of ReO<sub>4</sub><sup>-</sup> or <sup>99</sup>TcO<sub>4</sub><sup>-</sup>, Nat. Commun., 13, 7621 (DOI: 10.1038/s41467-022-35435-7)

[119] Liu K., Xu Z., Huang H., Zhang Y., Liu Y., Qiu Z., Tong M., Long Z., Chen G. (2022), In Situ Synthesis of Pyridinium-Based Ionic Porous Organic Polymers with Hydroxide Anions and Pyridinyl Radicals for Halogen-Free Catalytic Fixation of Atmospheric CO<sub>2</sub>, Green Chem., 24, 136–141 (DOI: 10.1039/D1GC03465K)

[120] Liu T. T., Xu R., Yi J.D., Liang J., Wang X. S., Shi P. C., Huang Y. B., Cao R. (2018), Imidazolium-Based Cationic Covalent Triazine Frameworks for Highly Efficient Cycloaddition of Carbon Dioxide. ChemCatChem, 10, 2036–2040 (DOI: 10.1002/cctc.201800023)

[121] Buyukcakir O., Je S. H., Talapaneni S. N., Kim D., Coskun A. (2017)Charged Covalent Triazine Frameworks for CO<sub>2</sub> Capture and Conversion,

ACS Appl. Mater. Interfaces, 9, 7209–7216 (DOI: 10.1021/acsami.6b16769)

[122] Rose M., Notzon A., Heitbaum M., Nickerl G., Paasch S., Brunner E., Glorius F., Kaskel S. (2011), N-Heterocyclic Carbene Containing Element Organic Frameworks as Heterogeneous Organocatalysts, Chem. Commun., 47, 4814–4816 (DOI: 10.1039/C1CC10268K)

[123] Mousa A. O., Lin Z. I., Chaganti S. V., Chuang, C. H., Chen C. K., Kuo S. W., Mohamed M. G. (2024), Bifunctional Imidazolium Linked Tetraphenylethene Based Conjugated Microporous Polymers for Dynamic Antibacterial Properties and Supercapacitor Electrodes, Polym. Chem., 15, 397–411 (DOI: 10.1039/D3PY01303K)

[124] Su Y., Li X., Wang Y., Zhong H., Wang R. (2016), Gold Nanoparticles Supported by Imidazolium-Based Porous Organic Polymers for Nitroarene Reduction, Dalton Trans., 45, 16896–16903 (DOI: 10.1039/C6DT03050E)

[125] Das G., Skorjanc T., Sharma S. K., Gándara F., Lusi M., Shankar Rao D. S., Vimala S., Krishna Prasad S., Raya J., Han D. S., Jagannathan R., Olsen J. C., Trabolsi A. (2017), Viologen-Based Conjugated Covalent Organic Networks via Zincke Reaction, J. Am. Chem. Soc., 139, 9558–9565 (DOI: 10.1021/jacs.7b02836)

[126] Mi Z., Yang P., Wang R., Unruangsri J., Yang W., Wang C., Guo J.
(2019), Stable Radical Cation-Containing Covalent Organic Frameworks
Exhibiting Remarkable Structure-Enhanced Photothermal Conversion, J.
Am. Chem. Soc., 141, 14433–14442 (DOI: 10.1021/jacs.9b07695)

[127] Sarkar S., Ghosh S., Sani R., Seth J., Khan A., Islam Sk. M. (2023), Covalent Immobilization of Quaternary Ammonium Salts on Covalent Organic Framework: Sustainable Intensification Strategy for the Synthesis

of Cyclic Carbonates from CO<sub>2</sub>, ACS Sustainable Chem. Eng., 11, 14422–14434 (DOI: 10.1021/acssuschemeng.3c03041)

[128] Sharma R. K., Yadav P., Yadav M., Gupta R., Rana P., Srivastava A., Zbořil R., Varma R. S., Antonietti M., Gawande M. B. (2020), Recent Development of Covalent Organic Frameworks (COFs): Synthesis and Catalytic (Organic-Electro-Photo) Applications, Mater. Horiz., 7, 411–454 (DOI: 10.1039/C9MH00856J)

[129] Geng K., He T., Liu R., Dalapati S., Tan K. T., Li Z., Tao S., Gong Y., Jiang Q., Jiang D. (2020), Covalent Organic Frameworks: Design, Synthesis, and Functions. Chem. Rev., 120, 8814–8933 (DOI: 10.1021/acs.chemrev.9b00550)

[130] Bhagwat V. R. (2019), Chapter 9 - Safety of Water Used in Food Production. In Food Safety and Human Health, Academic Press, pp 219– 247 (DOI: 10.1016/B978-0-12-816333-7.00009-6)

[131] Lin L., Yang H., Xu X. (2022), Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review, Front. Environ. Sci., 10 (DOI: 10.3389/fenvs.2022.880246)

 [132] Rajaram T., Das A. (2008), Water Pollution by Industrial Effluents in India: Discharge Scenarios and Case for Participatory Ecosystem Specific Local Regulation, Futures, 40, 56–69 (DOI: 10.1016/j.futures.2007.06.002)

[133] Hou S., Zhao X., Liu Y., Tillotson M. R., Weng S., Wang H., Li Y., Liu B., Feng K., Zhang N. (2022), Spatial Analysis Connects Excess Water Pollution Discharge, Industrial Production, and Consumption at the Sectoral Level, npj Clean Water, 5, 1–9 (DOI: 10.1038/s41545-022-00152-7)

[134] Nallakaruppan M. K., Gangadevi E., Shri M. L., Balusamy B.,
Bhattacharya S., Selvarajan S. (2024), Reliable Water Quality Prediction and Parametric Analysis Using Explainable AI Models, Sci. Rep., 14, 7520 (DOI: 10.1038/s41598-024-56775-y)

[135] Zamora-Ledezma C., Negrete-Bolagay D., Figueroa F., Zamora-Ledezma E., Ni M., Alexis F., Guerrero V. H. (2021), Heavy Metal Water Pollution: A Fresh Look about Hazards, Novel and Conventional Remediation Methods, Environ. Technol. Innov., 22, 101504 (DOI: 10.1016/j.eti.2021.101504)

[136] von Burg R., Liu D. (1993), Chromium and Hexavalent Chromium,J. Appl. Toxicology, 13, 225–230 (DOI: 10.1002/jat.2550130315)

[137] Khezami L., Capart R. (2005), Removal of Chromium(VI) from Aqueous Solution by Activated Carbons: Kinetic and Equilibrium Studies, J. Hazard. Mater., 123, 223–231 (DOI: 10.1016/j.jhazmat.2005.04.012)

[138] Pellerin C., Booker S. M. (2000), Reflections on Hexavalent Chromium: Health Hazards of an Industrial Heavyweight, Environ. Health Perspect., 108, A402–A407 (DOI: 10.1289/ehp.108-a402)

[139] Lee M. S., Um W., Wang G., Kruger A. A., Lukens W. W., Rousseau R., Glezakou V. A. (2016), Impeding <sup>99</sup>Tc(IV) Mobility in Novel Waste Forms. Nat. Commun., 7, 12067 (DOI: 10.1038/ncomms12067)

[140] Banerjee D., Kim D., Schweiger M. J., Kruger A. A., Thallapally P.
K. (2016), Removal of TcO<sub>4</sub><sup>-</sup> Ions from Solution: Materials and Future Outlook, Chem. Soc. Rev., 45, 2724–2739 (DOI: 10.1039/C5CS00330J)

[141] Sun Q., Zhu L., Aguila B., Thallapally P. K., Xu C., Chen J., Wang S., Rogers D., Ma S. (2019), Optimizing Radionuclide Sequestration in Anion Nanotraps with Record Pertechnetate Sorption, Nat. Commun., 10, 1646 (DOI: 10.1038/s41467-019-09630-y)

[142] Mondal S. (2008), Methods of Dye Removal from Dye HouseEffluent—An Overview, Environ. Eng. Sci., 25, 383–396 (DOI: 10.1089/ees.2007.0049)

[143] Rovira J., Domingo J. L. (2019), Human Health Risks Due to Exposure to Inorganic and Organic Chemicals from Textiles: A Review. Environ. Res., 168, 62–69 (DOI: 10.1016/j.envres.2018.09.027)

[144] Zhou Y., Lu J., Zhou Y., Liu Y. (2019), Recent Advances for Dyes
Removal Using Novel Adsorbents: A Review. Environ. Pollut., 252, 352–365 (DOI: 10.1016/j.envpol.2019.05.072)

[145] Obotey Ezugbe E., Rathilal S. (2020), Membrane Technologies inWastewater Treatment: A Review, Membranes, 10, 89 (DOI: 10.3390/membranes10050089)

[146] Chen G. (2004), Electrochemical Technologies in Wastewater
Treatment, Sep. Purif. Technol., 38, 11–41 (DOI: 10.1016/j.seppur.2003.10.006)

[147] Liu Y., Tay J. H. (2004), State of the Art of Biogranulation Technology for Wastewater Treatment, Biotechnol. Adv., 22, 533–563 (DOI: 10.1016/j.biotechadv.2004.05.001)

[148] Gogate P. R., Pandit A. B. (2004), A Review of Imperative Technologies for Wastewater Treatment II: Hybrid Methods, Adv. Environ.
Res., 8, 553–597 (DOI: 10.1016/S1093-0191(03)00031-5)

[149] Wang J., Zheng S., Shao Y., Liu J., Xu Z., Zhu D. (2010), Amino-Functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Core–Shell Magnetic Nanomaterial as a Novel Adsorbent for Aqueous Heavy Metals Removal, J. Colloid Interface Sci., 349, 293–299 (DOI: 10.1016/j.jcis.2010.05.010)

[150] Shen N., Yang Z., Liu S., Dai X., Xiao C., Taylor-Pashow K., Li D.,
Yang C., Li J., Zhang Y., Zhang M., Zhou R., Chai Z., Wang S. (2020),
<sup>99</sup>TcO<sub>4</sub><sup>-</sup> Removal from Legacy Defense Nuclear Waste by an Alkaline-Stable 2D Cationic Metal Organic Framework, Nat. Commun., 11, 5571 (DOI: 10.1038/s41467-020-19374-9)

[151] Zhang Q., Yu J., Cai J., Zhang L., Cui Y., Yang Y., Chen B., Qian G. (2015), A Porous Zr-Cluster-Based Cationic Metal–Organic Framework for Highly Efficient  $Cr_2O_7^{2-}$  Removal from Water, Chem. Commun., 51, 14732–14734 (DOI: 10.1039/C5CC05927E)

[152] Desai A. V., Manna B., Karmakar A., Sahu A., Ghosh, S. K. (2016),
A Water-Stable Cationic Metal–Organic Framework as a Dual Adsorbent of Oxoanion Pollutants, Angew. Chem., 128, 7942–7946 (DOI: 10.1002/ange.201600185)

[153] Zhu L., Sheng D., Xu C., Dai X., Silver M. A., Li J., Li P., Wang Y., Wang Y., Chen L., Xiao C., Chen J., Zhou R., Zhang C., Farha O. K., Chai Z., Albrecht-Schmitt T. E., Wang S. (2017), Identifying the Recognition Site for Selective Trapping of  $^{99}$ TcO<sub>4</sub><sup>-</sup> in a Hydrolytically Stable and Radiation Resistant Cationic Metal–Organic Framework, J. Am. Chem. Soc., 139, 14873–14876, (DOI: 10.1021/jacs.7b08632)

[154] Loeb S. K., Alvarez P. J. J., Brame J. A., Cates E. L., Choi W., Crittenden J., Dionysiou D. D., Li Q., Li-Puma G., Quan X., Sedlak D. L., David Waite T., Westerhoff P., Kim J. H. (2019), The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? Environ. Sci. Technol., 53, 2937–2947 (DOI: 10.1021/acs.est.8b05041)

[155] Liu Y., Wang R., Yang Z., Du H., Jiang Y., Shen C., Liang K., Xu A.
(2015), Enhanced Visible-Light Photocatalytic Activity of Z-Scheme Graphitic Carbon Nitride/Oxygen Vacancy-Rich Zinc Oxide Hybrid Photocatalysts, Chinese J. Catal., 36, 2135–2144 (DOI: 10.1016/S1872-2067(15)60985-8)

[156] Gao X., Meng X. (2021), Photocatalysis for Heavy Metal Treatment:A Review, Processes, 9, 1729 (DOI: 10.3390/pr9101729)

[157] Fajal S. Dutta S. K., Ghosh S. (2023), Porous Organic Polymers (POPs) for Environmental Remediation, Mater. Horiz., 10, 4083–4138 (DOI: 10.1039/D3MH00672G)

[158] Liu Z. W., Cao C. X., Han B. H. (2019), A Cationic Porous Organic
Polymer for High-Capacity, Fast, and Selective Capture of Anionic
Pollutants, J. Hazard. Mater., 367, 348–355 (DOI: 10.1016/j.jhazmat.2018.12.091)

[159] Jiao S., Deng L., Zhang X., Zhang Y., Liu K., Li S., Wang L., Ma D.
(2021), Evaluation of an Ionic Porous Organic Polymer for Water Remediation, ACS Appl. Mater. Interfaces, 13, 39404–39413 (DOI: 10.1021/acsami.1c10464)

[160] Pan L., Liu Z., Hernandez M. V., Schroeder B. C., Sun Y., Faul, C.
F. J. (2024), Polyaniline-Based Cationic Porous Organic Polymers for Fast and Efficient Anion-Exchange-Driven Capture of Cr<sub>2</sub>O<sub>7</sub><sup>2–</sup>. ACS Appl.
Polym. Mater., 6, 6416–6424 (DOI: 10.1021/acsapm.4c00658)

[161] Ghanbari J., Mobinikhaledi A. (2023), Synthesis of a Novel Porous Organic Polymer Containing Triazine and Cyclohexanone Rings as an Efficient Methyl Red Adsorbent from Aqueous Solutions, Sci. Rep., 13, 12962 (DOI: 10.1038/s41598-023-40274-7)

[162] Song P., Zhang Z., Yu L., Wang P., Wang Q., Chen, Y. (2020), An Ionic Covalent Organic Polymer toward Highly Selective Removal of Anionic Organic Dyes in Aqueous Solution, New J. Chem., 44, 8572–8577 (DOI: 10.1039/D0NJ01132K)

[163] Shen X., Ma S., Xia H., Shi Z., Mu Y., Liu X. (2018), Cationic Porous Organic Polymers as an Excellent Platform for Highly Efficient Removal of Pollutants from Water, J. Mater. Chem. A, 6, 20653–20658 (DOI: 10.1039/C8TA09145E)

[164] Byun J., Zhang K. A. I. (2020), Designing Conjugated PorousPolymers for Visible Light-Driven Photocatalytic ChemicalTransformations, Mater. Horiz., 7, 15–31 (DOI: 10.1039/C9MH01071H)

[165] Leung A., Pearce E. N., Braverman L. E. (2010), Role of Iodine in Thyroid Physiology, Expert Rev. Endocrinol. Metab., 5, 593–602 (DOI: 10.1586/eem.10.40)

[166] Haymart M. R., Banerjee M., Stewart A. K., Koenig R. J., BirkmeyerJ. D., Griggs J. J. (2011), Use of Radioactive Iodine for Thyroid Cancer,JAMA, 306, 721–728 (DOI: 10.1001/jama.2011.1139)

[167] Backer H., Hollowell J. (2000), Use of Iodine for Water Disinfection:Iodine Toxicity and Maximum Recommended Dose, Environ. HealthPerspect., 108, 679–684 (DOI: 10.1289/ehp.00108679)

[168] Subrahmanyam K. S., Sarma D., Malliakas C. D., Polychronopoulou K., Riley B. J., Pierce D. A., Chun J., Kanatzidis M. G. (2015), Chalcogenide Aerogels as Sorbents for Radioactive Iodine, Chem. Mater., 27, 2619–2626 (DOI: 10.1021/acs.chemmater.5b00413)

[169] Xie W., Cui D., Zhang S. R., Xu Y. H., Jiang D. L. (2019) Iodine Capture in Porous Organic Polymers and Metal–Organic Frameworks Materials, Mater. Horiz., 6, 1571–1595 (DOI: 10.1039/C8MH01656A)

[170] Küpper F. C., Feiters M. C., Olofsson B., Kaiho T., Yanagida S., Zimmermann M. B., Carpenter L. J., Luther III G. W., Lu Z., Jonsson M., Kloo L. (2011), Commemorating Two Centuries of Iodine Research: An Interdisciplinary Overview of Current Research, Angew. Chem., 50, 11598–11620 (DOI: 10.1002/anie.201100028)

[171] Shimamoto Y. S., Takahashi Y., Terada Y. (2011), Formation of Organic Iodine Supplied as Iodide in a Soil–Water System in Chiba, Japan, Environ. Sci. Technol., 45, 2086–2092 (DOI: 10.1021/es1032162)

[172] Kinuya S., Yoshinaga K., Higuchi T., Jinguji M., Kurihara H., Kawamoto H. (2015) Draft Guidelines Regarding Appropriate Use of 1311-MIBG Radiotherapy for Neuroendocrine Tumors, Ann. Nucl. Med., 29, 543–552 (DOI: 10.1007/s12149-015-0960-z)

[173] Ferris T., Carroll L., Jenner S., Aboagye E. O. (2021), Use of Radioiodine in Nuclear Medicine—A Brief Overview, J. Label. Compd. Radiopharm., 64, 92–108 (DOI: 10.1002/jlcr.3891)

[174] Saiz-Lopez A., Plane J. M. C., Baker A. R., Carpenter L. J., von Glasow R., Gómez Martín J. C., McFiggans G., Saunders R. W. (2012), Atmospheric Chemistry of Iodine, Chem. Rev., 112, 1773–1804 (DOI: 10.1021/cr200029u)

[175] Sorrenti S., Baldini E., Pironi D., Lauro A., D'Orazi V., Tartaglia F.,
Tripodi D., Lori E., Gagliardi F., Praticò M., Illuminati G., D'Andrea V.,
Palumbo P., Ulisse S. (2021), Iodine: Its Role in Thyroid Hormone
Biosynthesis and Beyond, Nutrients, 13, 4469 (DOI: 10.3390/nu13124469)

[176] Calcaterra V., Mameli C., Rossi V., Massini G., Gambino M., Baldassarre P., Zuccotti G. (2022), The Iodine Rush: Over- or Under-Iodination Risk in the Prophylactic Use of Iodine for Thyroid Blocking in the Event of a Nuclear Disaster, Front. Endocrinol., 13 (DOI: 10.3389/fendo.2022.901620)

[177] Pan T., Yang K., Dong X., Han Y. (2023), Adsorption-Based Capture of Iodine and Organic Iodides: Status and Challenges, J. Mater. Chem. A, 11, 5460–5475 (DOI: 10.1039/D2TA09448G)

[178] Kurisingal J. F., Yun H., Hong C. S. (2023), Porous Organic Materialsfor Iodine Adsorption, J. Hazard. Mater., 458, 131835 (DOI: 10.1016/j.jhazmat.2023.131835)

[179] Elmekawy A., Quach Q., Abdel-Fattah T. M. (2024), Synthesis and Characterization of Silver-Modified Nanoporous Silica Materials for

Enhanced Iodine Removal, Nanomaterials, 14, 1143 (DOI: 10.3390/nano14131143)

[180] Jie K., Zhou Y., Li E., Li Z., Zhao R., Huang F. (2017), Reversible
Iodine Capture by Nonporous Pillar[6]Arene Crystals, J. Am. Chem. Soc.,
139, 15320–15323 (DOI: 10.1021/jacs.7b09850)

[181] Geng T., Zhu Z., Zhang W., Wang Y. (2017), A Nitrogen-Rich Fluorescent Conjugated Microporous Polymer with Triazine and Triphenylamine Units for High Iodine Capture and Nitro Aromatic Compound Detection, J. Mater. Chem. A, 5, 7612–7617 (DOI: 10.1039/C7TA00590C)

[182] Yin Z., Wang Q. X., Zeng M. H. (2012), Iodine Release and Recovery, Influence of Polyiodide Anions on Electrical Conductivity and Nonlinear Optical Activity in an Interdigitated and Interpenetrated Bipillared-Bilayer Metal–Organic Framework, J. Am. Chem. Soc., 134, 4857–4863 (DOI: 10.1021/ja211381e)

[183] Valizadeh B., Nguyen T. N., Smit B., Stylianou K. C. (2018), Porous Metal–Organic Framework@Polymer Beads for Iodine Capture and Recovery Using a Gas-Sparged Column, Adv. Funct. Mater., 28, 1801596 (DOI: 10.1002/adfm.201801596)

[184] Li B., Dong X., Wang H., Ma D., Tan K., Jensen S., Deibert B. J., Butler J., Cure J., Shi Z., Thonhauser T., Chabal Y. J., Han Y., Li, J. (2017) Capture of Organic Iodides from Nuclear Waste by Metal-Organic Framework-Based Molecular Traps, Nat. Commun., 8, 485 (DOI; 10.1038/s41467-017-00526-3)

[185] Yao S., Fang W. H., Sun Y., Wang S. T., Zhang J. (2021), Mesoporous Assembly of Aluminum Molecular Rings for Iodine Capture, J. Am. Chem. Soc., 143, 2325–2330 (DOI: 10.1021/jacs.0c11778)

[186] Audunsson G., Dalene M., Jönsson J. Å., Lövkvist P, Mathiasson L.,
Skarping G. (1985), Analysis of Amines in the Industrial Environment,
Inter. J. Environ. Anal. Chem., 20, 85–100 (DOI: 10.1080/03067318508077048)

[187] Froidevaux V., Negrell C., Caillol S., Pascault J.P., Boutevin B.
(2016), Biobased Amines: From Synthesis to Polymers; Present and Future, Chem. Rev., 116, 14181–14224 (DOI: 10.1021/acs.chemrev.6b00486)

[188] Dasarathy S., Mookerjee R. P., Rackayova V., Rangroo Thrane V., Vairappan B., Ott P., Rose C. F. (2017), Ammonia Toxicity: From Head to Toe? Metab. Brain Dis., 32, 529–538 (DOI: 10.1007/s11011-016-9938-3)

[189] Romano N., Zeng C. (2013), Toxic Effects of Ammonia, Nitrite, and Nitrate to Decapod Crustaceans: A Review on Factors Influencing Their Toxicity, Physiological Consequences, and Coping Mechanisms, Rev. Fish. Sci., 21, 1–21 (DOI: 10.1080/10641262.2012.753404)

[190] Johnston A. R. (1928), The Toxic Effects of Amines, J. Infect. Diseases, 42, 473–484.

[191] Fekete A., Malik A. K., Kumar A., Schmitt-Kopplin P. (2010),
Amines in the Environment, Crit. Rev. Anal. Chem., 40, 102–121 (DOI: 10.1080/10408340903517495)

[192] Timmer B., Olthuis W., Berg A. van den (2005), Ammonia Sensors and Their Applications—a Review, Sens. Actuators B, 107, 666–677 (DOI: 10.1016/j.snb.2004.11.054)

[193] Li D., Xu X., Li Z., Wang T., Wang, C. (2020), Detection Methods of Ammonia Nitrogen in Water: A Review. TrAC Trends Anal. Chem., 127, 115890 (DOI: 10.1016/j.trac.2020.115890)

[194] Chen W., Pan Y., Chen J., Ye F., Liu S. H., Yin, J. (2018), Stimuli-Responsive Organic Chromic Materials with near-Infrared Emission, Chin. Chem. Lett., 29, 1429–1435 (DOI: 10.1016/j.cclet.2018.08.011)

[195] Trovato V., Sfameni S., Rando G., Rosace G., Libertino S., Ferri A., Plutino M. R. (2022), A Review of Stimuli-Responsive Smart Materials for Wearable Technology in Healthcare: Retrospective, Perspective, and Prospective, Molecules, 27, 5709 (DOI: 10.3390/molecules27175709)

[196] Mallick A., Garai B., Addicoat A. M., Petkov St. P., Heine T., Banerjee R. (2015), Solid State Organic Amine Detection in a Photochromic Porous Metal Organic Framework, Chem. Sci., 6, 1420–1425 (DOI: 10.1039/C4SC03224A)

[197] Kossyvaki D., Barbetta A., Contardi M., Bustreo M., Dziza K., Lauciello S., Athanassiou A., Fragouli D. (2022), Highly Porous Curcumin-Loaded Polymer Mats for Rapid Detection of Volatile Amines, ACS Appl. Polym. Mater., 4, 4464–4475 (DOI: 10.1021/acsapm.2c00418)

[198] Jin P. P., Huang X., Zou Y. C., Zhou L. J., Wang X., Zhang F., Wang D., Li G. D. (2016), Effective Organic Amine Detection by Nanoparticle-Assembled Tin Dioxide Microspheres: The Importance of Interparticle Porosity on Sensing Properties, , 224, 381–390 (DOI: 10.1016/j.snb.2015.10.063)

[199] Siripongpreda T., Siralertmukul K., Rodthongkum N. (2020), Colorimetric Sensor and LDI-MS Detection of Biogenic Amines in Food Spoilage Based on Porous PLA and Graphene Oxide, Food Chem., 329, 127165 (DOI: 10.1016/j.foodchem.2020.127165)

[200] Mallick A., El-Zohry A. M. Shekhah O., Yin J., Jia, J., Aggarwal H., Emwas A. H., Mohammed O. F., Eddaoudi M. (2019), Unprecedented Ultralow Detection Limit of Amines Using a Thiadiazole-Functionalized

Zr(IV)-Based Metal–Organic Framework, J. Am. Chem. Soc., 141, 7245– 7249 (DOI: 10.1021/jacs.9b01839)

(201) Liu J. J., Shan Y. B., Fan C. R., Lin M. J., Huang C. C., Dai W. X. (2016), Encapsulating Naphthalene in an Electron-Deficient MOF to Enhance Fluorescence for Organic Amines Sensing, Inorg. Chem., 55, 3680–3684 (DOI: 10.1021/acs.inorgchem.6b00252)

[202] Leelasree T., Dixit M., Aggarwal, H. (2023), Cobalt-Based Metal– Organic Frameworks and Its Mixed-Matrix Membranes for Discriminative Sensing of Amines and On-Site Detection of Ammonia, Chem. Mater., 35, 416–423 (DOI: 10.1021/acs.chemmater.2c02706)

[203] Jia, P., He X., Yang J., Sun X., Bu T., Zhuang Y., Wang L. (2023),
Dual–Emission MOF–Based Ratiometric Platform and Sensory Hydrogel
for Visible Detection of Biogenic Amines in Food Spoilage, Sens. Actuators
B, 374, 132803 (DOI: 10.1016/j.snb.2022.132803)

[204] Xu Y., Zhang X., Zhang W., Liu X., Liu Q. (2021), Fluorescent Detector for NH<sub>3</sub> Based on Responsive Europium(III)–Salicylic Acid Complex Hydrogels, J. Photochem. Photobiol. A Chem., 404, 112901 (DOI: 10.1016/j.jphotochem.2020.112901)

[205] Hashemian H., Ghaedi M., Dashtian K., Khan S., Mosleh S., Hajati S., Razmjoue D. (2024), Highly Sensitive Fluorometric Ammonia Detection Utilizing Solenostemon Scutellarioides (L.) Extracts in MOF-Tragacanth Gum Hydrogel for Meat Spoilage Monitoring, Sens. Actuators B, 406, 135354 (DOI: 10.1016/j.snb.2024.135354)

[206] Yang D. H., Nguyen T. T. T., Navale S. T., Nguyen L. H. T., Dang Y. T., Mai N. X. D., Phan T. B., Kim J. Y., Doan T. L. H., Kim S. S., Kim H. W. (2022), Novel Amine-Functionalized Zinc-Based Metal-Organic Framework for Low-Temperature Chemiresistive Hydrogen Sensing, Sens. Actuators B, 368, 132120 (DOI: 10.1016/j.snb.2022.132120)

[207] Ladhi R., Kaur Dhillon A., Singh M. (2024), Ultrathin MOF Nanosheets and Their Mixed-Matrix Membranes for Ammonia and Aliphatic Amine Sensing in Water, Nanoscale, 16, 8836–8842 (DOI: 10.1039/D4NR00546E)

[208] Ding J., Zheng C., Wang L., Lu C., Zhang B., Chen Y., Li M., Zhai G., Zhuang X. (2019), Viologen-Inspired Functional Materials: Synthetic Strategies and Applications, J. Mater. Chem. A, 7, 23337–23360 (DOI: 10.1039/C9TA01724K)

[209] Striepe L., Baumgartner T. (2017), Viologens and Their Application as Functional Materials, Chem. - Eur. J., 23, 16924–16940 (DOI: 10.1002/chem.201703348)

[210] Li X., Yang J., Yang Y. W. (2023), Recent Advances of Stimuli-Responsive Viologen-Based Nanocomposites, Mater. Chem. Front., 7, 1463–1481 (DOI: 10.1039/D3QM00151B)

[211] Li L., Li S. H., Li Z. Y., Zhang N. N., Yu Y. T., Zeng J. G., Hua Y.
(2024), Advances in Viologen-Based Stimulus-Responsive Crystalline
Hybrid Materials, Coord. Chem. Rev., 518, 216064 (DOI: 10.1016/j.ccr.2024.2160640

[212] Gu C., Jia A. B., Zhang Y. M., Zhang S. X. A. (2022), Emerging Electrochromic Materials and Devices for Future Displays, Chem. Rev., 122, 14679–14721 (DOI: 10.1021/acs.chemrev.1c01055)

[213] Rai V., Singh R. S., Blackwood D. J., Zhili D. (2020), A Review on Recent Advances in Electrochromic Devices: A Material Approach. Adv. Eng. Mater., 22, 2000082 (DOI:10.1002/adem.202000082)

[214] Wang Z., Zhu H., Zhuang J., Lu Y., Chen Z., Guo W. (2024), Recent Advance in Electrochromic Materials and Devices for Display Applications, ChemPlusChem, 89, e202300770 (DOI: 10.1002/cplu.202300770)

[215] Fu H., Zhang L., Dong Y., Zhang C., Li W, Recent Advances in Electrochromic Materials and Devices for Camouflage Applications. Mater. Chem. Front., 7, 2337–2358 (DOI: 10.1039/D3QM00121K)

[216] Zhang L., Wang B., Li X., Xu G., Dou S., Zhang X., Chen X., Zhao J., Zhang K., Li Y. (2019), Further Understanding of the Mechanisms of Electrochromic Devices with Variable Infrared Emissivity Based on Polyaniline Conducting Polymers, J. Mater. Chem. C, 7, 9878–9891 (DOI: 10.1039/C9TC02126D)

[217] Rosseinsky D. R., Mortimer R. J. (2001), Electrochromic Systems and the Prospects for Devices, Adv. Mater., 13, 783–793 (DOI: 10.1002/1521-4095(200106)13:11<783::AID-ADMA783>3.0.CO;2-D)

[218] Cai G., Wang J., Lee P. S. (2016), Next-Generation Multifunctional Electrochromic Devices, Acc. Chem. Res., 49, 1469–1476 (DOI: 10.1021/acs.accounts.6b00183)

[219] Lu Z., Zhong X., Liu X., Wang J., Diao X. (2021), Energy StorageElectrochromic Devices in the Era of Intelligent Automation, Phys. Chem.Chem. Phys., 23, 14126–14145 (DOI: 10.1039/D1CP01398J)

[220] Kandpal S., Ghosh T., Rani C., Chaudhary A., Park J., Lee P. S.,
Kumar R. (2023), Multifunctional Electrochromic Devices for Energy
Applications, ACS Energy Lett., 8, 1870–1886 (DOI: 10.1021/acsenergylett.3c00159)

[221] Zhang W., Li H., Hopmann E., Elezzabi A. Y. (2021), Nanostructured Inorganic Electrochromic Materials for Light Applications, Nanophotonics, 10, 825–850 (DOI: 10.1515/nanoph-2020-0474)

[222] Österholm M. A., Nhon L., Eric Shen D., Dejneka M. A., Tomlinson L.A., Reynolds R. J. (2022), Conquering Residual Light Absorption in the Transmissive States of Organic Electrochromic Materials, Mater. Horiz., 9, 252–260 (DOI: 10.1039/D1MH01136G)

[223] Mortimer R. J. (1999), Organic Electrochromic Materials,
Electrochim. Acta, 44, 2971–2981 (DOI: 10.1016/S0013-4686(99)000468)

[224] Djaoued Y., Balaji S., Brüning R. (2012), Electrochromic DevicesBased on Porous Tungsten Oxide Thin Films, J. Nanomater., 2012, 674168(DOI: 10.1155/2012/674168)

[225] Li Y., Sun P., Chen J., Zha X., Tang X., Chen Z., Zhang Y., Cong S.,
Geng F., Zhao Z. (2023), Colorful Electrochromic Displays with High
Visual Quality Based on Porous Metamaterials, Adv. Mater., 35, 2300116
(DOI: 10.1002/adma.202300116)

[226] Qu H., Zhang H., Zhang X., Tian Y., Wang B., Li X., Zhao J., Li Y.
(2017), Review: Recent Progress in Ordered Macroporous Electrochromic Materials, J. Mater. Sci., 52, 11251–11268 (DOI: 10.1007/s10853-017-1077-7)

[227] Shchegolkov A. V., Jang S. H., Shchegolkov A. V., Rodionov Y. V., Sukhova A. O., Lipkin M. S. (2021), A Brief Overview of Electrochromic Materials and Related Devices: A Nanostructured Materials Perspective, Nanomaterials, 11, 2376 (DOI: 10.3390/nano11092376)

[228] Tao C., Li Y., Wang J. (2023), The Progress of Electrochromic Materials Based on Metal–Organic Frameworks, Coord. Chem. Rev., 475, 214891 (DOI: 10.1016/j.ccr.2022.214891)

[229] Sarkar M., Dutta T. K., Patra A. (2021), Two-Dimensional Covalent Organic Frameworks for Electrochromic Switching, Chem. Asian J., 16, 3055–3067 (DOI: 10.1002/asia.202100815)

[230] Madasamy K., Velayutham D., Suryanarayanan V., Kathiresan M.,
Ho K. C. (2019), Viologen-Based Electrochromic Materials and Devices. J.
Mater. Chem. C, 7, 4622–4637 (DOI: 10.1039/C9TC00416E)

[231] Wu W., Guo S., Bian J., He X., Li H., Li J. (2024), Viologen-BasedFlexible Electrochromic Devices, J. Energy Chem., 93, 453–470 (DOI: 10.1016/j.jechem.2024.02.027)

[232] Ping Teong S., Li X., Zhang Y. (2019), Hydrogen Peroxide as an Oxidant in Biomass-to-Chemical Processes of Industrial Interest, Green Chem., 21, 5753–5780 (DOI: 10.1039/C9GC02445J)

[233] Ventura M., Garboden G. (1999), A Brief History of Concentrated Hydrogen Peroxide Uses, In 35th Joint Propulsion Conference and Exhibit, American Institute of Aeronautics and Astronautics (DOI: 10.2514/6.1999-2739)

[234] Ventura M., Yuan S. (2000), Commercial Production and Use of Hydrogen Peroxide, In 36th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, American Institute of Aeronautics and Astronautics (DOI: 10.2514/6.2000-3556)

[235] Eul W., Moeller A., Steiner N. (2001), Hydrogen Peroxide. In Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley & Sons, Ltd (DOI: 10.1002/0471238961.0825041808051919.a01.pub2)

[236] Santacesaria E., Di Serio M., Russo A., Leone U., Velotti R. (1999), Kinetic and Catalytic Aspects in the Hydrogen Peroxide Production via Anthraquinone, Chem. Eng. Sci., 54, 2799–2806 (DOI: 10.1016/S0009-2509(98)00377-7)

[237] Campos-Martin J. M., Blanco-Brieva G., Fierro J. L. G. (2006),Hydrogen Peroxide Synthesis: An Outlook beyond the AnthraquinoneProcess, Angew. Chem., 45, 6962–6984 (DOI: 10.1002/anie.200503779)

[238] Chen Q. (2006), Toward Cleaner Production of Hydrogen Peroxide
in China, J. Cleaner Prod., 14, 708–712 (DOI: 10.1016/j.jclepro.2005.03.025)

[239] Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen: An Overview of Recent Developments in the Process (2008), Appl. Catal.A, 350, 133–149 (DOI: 10.1016/j.apcata.2008.07.043)

[240] Menegazzo F., Signoretto M., Ghedini E., Strukul G. (2019), Looking for the "Dream Catalyst" for Hydrogen Peroxide Production from Hydrogen and Oxygen, Catalysts, 9, 251 (DOI: 10.3390/catal9030251)

[241] Li S., Ma J., Xu F., Wei L., He D. (2023), Fundamental Principles and Environmental Applications of Electrochemical Hydrogen Peroxide Production: A Review, Chem. Eng. J., 452, 139371 (DOI: 10.1016/j.cej.2022.139371)

[242] Dan M., Zhong R., Hu S., Wu H., Zhou Y., Liu Z. Q. (2022), Strategies and Challenges on Selective Electrochemical Hydrogen Peroxide Production: Catalyst and Reaction Medium Design, Chem Catal., 2, 1919– 1960 (DOI: 10.1016/j.checat.2022.06.002)

[243] Tian Y., Deng D., Xu L., Li M., Chen H., Wu Z., Zhang S. (2023), Strategies for Sustainable Production of Hydrogen Peroxide via Oxygen Reduction Reaction: From Catalyst Design to Device Setup, Nano-Micro Lett. 2023, 15, 122 (DOI: 10.1007/s40820-023-01067-9)

[244] Jiang K., Zhao J., Wang H. (2020), Catalyst Design for Electrochemical Oxygen Reduction toward Hydrogen Peroxide, Adv. Funct. Mater., 30, 2003321 (DOI: 10.1002/adfm.202003321)

[245] Yang D. H., Tao Y., Ding X., Han B. H. Porous Organic Polymers for Electrocatalysis, Chem. Soc. Rev., 51, 761–791 (DOI: 10.1039/D1CS00887K)

[246] Yang S., Lu L., Li J., Cheng Q., Mei B., Li X., Mao J., Qiao P., Sun F., Ma J., Xu Q., Jiang Z. (2023), Boosting Hydrogen Peroxide Production via Establishment and Reconstruction of Single-Metal Sites in Covalent Organic Frameworks, SusMat, 3, 379–389 (DOI: 10.1002/sus2.125)

[247] Zhi Q., Jiang R., Yang X., Jin Y., Qi D., Wang K., Liu Y., Jiang J. (2024), Dithiine-Linked Metalphthalocyanine Framework with Undulated Layers for Highly Efficient and Stable H<sub>2</sub>O<sub>2</sub> Electroproduction, Nat Commun, 15, 678 (DOI: 10.1038/s41467-024-44899-8)

[248] Guo Y., Xu Q., Yang, S., Jiang Z., Yu C., Zeng G. (2021) Precise
Design of Covalent Organic Frameworks for Electrocatalytic Hydrogen
Peroxide Production, Chem. Asian J., 16, 498–502 (DOI: 10.1002/asia.202100030)

[249] Huang S., Zhang B., Wu D., Xu Y., Hu H., Duan F., Zhu H., Du M.,
Lu S. (2024), Linkage Engineering in Covalent Organic Frameworks as
Metal-Free Oxygen Reduction Electrocatalysts for Hydrogen Peroxide
Production, Appl. Catal. B., 340, 123216 (DOI: 10.1016/j.apcatb.2023.123216)

[250] Yang S., Cheng Q., Mao J., Xu Q., Zhang Y., Guo Y., Tan T., Luo W., Yang H., Jiang Z. (20210, Rational Design of Edges of Covalent Organic Networks for Catalyzing Hydrogen Peroxide Production, Appl. Catal. B., 298, 120605 (DOI: 10.1016/j.apcatb.2021.120605)

[251] Zhang Y., Qiao Z., Zhang R., Wang Z., Wang H.-J., Zhao J., Cao D.,
Wang S. (2023), Multicomponent Synthesis of Imidazole-Linked Fully
Conjugated 3D Covalent Organic Framework for Efficient Electrochemical
Hydrogen Peroxide Production, Angew. Chem., 62, e202314539 (DOI: 10.1002/anie.202314539)

[252] An S., Li X., Shang S., Xu T., Yang S., Cui C.-X., Peng C., Liu H., Xu Q., Jiang Z., Hu J. (2023), One-Dimensional Covalent Organic Frameworks for the 2e<sup>-</sup> Oxygen Reduction Reaction, Angew. Chem., 62, e202218742 (DOI: 10.1002/anie.202218742)

[253] Huang S., Lu S., Hu Y., Cao Y., Li Y., Duan F., Zhu H., Jin Y., DuM., Zhang W. (2023), Covalent Organic Frameworks with Molecular

Electronic Modulation as Metal-Free Electrocatalysts for Efficient Hydrogen Peroxide Production, Small Structures, 4, 220038 (DOI: 10.1002/sstr.202200387)

[254] Velempini T., Pillay K. (2019), Sulphur Functionalized Materials for Hg(II) Adsorption: A Review, J. Environ. Chem. Eng., 7, 103350 (DOI: 10.1016/j.jece.2019.103350)

[255] Komarnisky L. A., Christopherson R. J., Basu T. K. (2023), Sulfur:Its Clinical and Toxicologic Aspects, Nutrition, 19, 54–61 (DOI: 10.1016/S0899-9007(02)00833-X)

[256] Li W., Zhao Z., Hu W., Cheng Q., Yang L., Hu Z., Liu Y. A., Wen K., Yang H. (2020), Design of Thiazolo[5,4-d]Thiazole-Bridged Ionic Covalent Organic Polymer for Highly Selective Oxygen Reduction to H<sub>2</sub>O<sub>2</sub>, Chem. Mater., 32, 8553–8560 (DOI: 10.1021/acs.chemmater.0c02843)



# A Bifunctional Imidazolium Functionalized Ionic Porous Organic Polymer in Water Remediation

#### 2.1. Introduction

In the 21st century, freshwater accessibility is a global concern due to increasing water pollution [1]. With the massive industrialization in the current era, water sources get seriously contaminated by the uncontrolled discharge of industrial pollutants like heavy metal ions, organic dyes, and radioactive contaminants from textiles, electroplating, leather, paper, printing industries, nuclear power plants, etc. Remediation of these pollutants from water sources has gained attention worldwide [2-5]. Among the various contaminants, metal-based oxo-anions ( $Cr_2O_7^{2-}$ ,  $TcO_4^{-}$ ,  $SeO_4^{-}$ , AsO<sub>4</sub>) are one of the major threats, causing severe toxicity to the living organism by bioaccumulation [6]. Chromate is one of the major chemicals used in various industries. Industries like leather tanning, wood preservation, dyes and pigments, textiles, steel, etc., use chromate considerably in multiple applications. Among all these, only the tanning industry uses 30-35 liters of chromate for tanning 1 kilogram of leather, which is ultimately released to various natural water sources and pollutes the water [7]. Apart from chromate,  $TcO_4^-$  is another oxo-anion whose remediation is also a significant challenge [8,9].  $TcO_4^-$  is one of the forms of radioactive nuclide <sup>99</sup>Tc, evolved from the nuclear power industry with a very high half-life  $(2.1 \times 10^5 \text{ years})$  and is  $\beta$  emitting in nature [10,11]. It was estimated that till 2010, around 305 metric tons of <sup>99</sup>Tc were produced by nuclear industries and weapon testing [12]. Among the other prominent water pollutants, several organic dyes released from many industries are another major concern. Several printing, textile, and color industries use various dyes that are also discharged into multiple water sources, a major source of water contamination [13,14]. These pollutants can accumulate in living organisms and may cause several problems for both animals and humans, as most are carcinogenic, mutagenic, or teratogenic in nature [15].

There are many techniques reported in the literature for eliminating these anionic pollutants and dye, *viz* adsorption [16-18], electro- and photo-

catalysis [19,20], chemical precipitation [21,22], bioprocessing [23], etc. Among these techniques, adsorption [24-27] and photocatalysis [28-30] are the two most effective techniques due to their low cost and high feasibility, easy and safe operation, and green approach. Many emerging materials have been used so far for removing such pollutants, viz. porous materials like zeolites, activated carbons, MOFs, and COPs, which are mainly used for removing the contaminants by adsorption [31-37], whereas certain MOFs, carbon nitrides, and several traditional metal oxides are being used as photocatalyst [38-40]. However, these materials have several disadvantages, like low uptake capacities [zeolites and activated carbons], poor stability in water [MOF], effective reusability, low photocatalytic efficiency, etc. Therefore, challenges are still present in developing novel materials for quickly and efficiently removing toxic pollutants from water [41-44]. In this regard, ionic porous organic polymers could be an effective candidate for wastewater remediation due to their inherent charged and permanent nature.

To achieve anion pollutant capture using iPOPs, a stable cationic skeleton with exchangeable counter anions is the primary requirement [45-55], whereas the presence of electron-rich building blocks in the polymeric skeleton [56-58] and accumulation of a large number of N atoms in the material helps in increasing the photocatalytic performance [59]. Strategic incorporation of different binding sites in the polymeric network and the electron-rich moiety might contribute to the selective capture of anionic pollutants and enhance the material's photocatalytic performance. This Chapter discusses the synthesis of a novel cationic porous organic polymer **iPOP-ANT** with positive quaternized N site and exchangeable Cl<sup>-</sup> ions as counter anions along with electron-rich anthracene moiety. The material shows good adsorption properties towards the oxyanions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>) and anionic dyes (methyl orange, congo red, amaranth) and efficient photocatalytic degradation of the cationic dyes under solar irradiation (rhodamine B, rhodamine 6G and methylene Blue).

#### **2.2 Experimental section**

#### 2.2.1. Materials and methods

4-Bromomethylbenzonitrile, tri-fluoromethanesulfonic acid, and anthracene were purchased from Sigma-Aldrich; other reagents and solvents were purchased locally and were used without further purification. Fourier transform infrared (FTIR) analysis was carried out on PerkinElmer's spectrum II spectrometer. NMR spectra were obtained by an AVANCE III 500 Ascend Bruker Biospin machine at an ambient temperature using CDCl3. 13C CP/MAS NMR was carried out by ECZR series 600MHz NMR by JEOL. Thermogravimetric analysis (TGA) was analyzed using Mettler Toledo Thermal Analyzer with heating rate of 10 °C/min. Morphological data of the polymer were recorded in JEOL JSM-7400F field emission scanning electron microscopy (FESEM) and FEI Tecnai G2, F30 HR-TEM (300 kV). Gas adsorption measurements were carried out using Quantachrome, Autosorb iQ2 Brunauer-Emmett- Teller (BET) surface area analyzer was used. PXRD of the polymer was done on Empyrean, Malvern Panalytical, with Cu-K $\alpha$  radiation with 2 $\theta$  range from 2° to 80° and a step size of 0.02°. UV-DRS was obtained from Cary 5000 UV-Vis NIR Spectrometer. X-ray photoelectron spectroscopy (XPS) was performed through a Physical Electronics make PHI 5000 VersaProbe III (Mg K $\alpha$  X-rays, hv = 1253.6 eV).

#### 2.2.2. Synthesis of 9,10-Bis(chloromethyl)anthracene (ANT)

9,10-Bis(chloromethyl)anthracene (**ANT**) was synthesized following a reported procedure [60]. In a typical reaction, a mixture of anthracene (1.78 g, 10 mmol), anhydrous ZnCl<sub>2</sub> (1.64 g, 12 mmol), and paraformaldehyde (1.50 g, 50 mmol) in dioxane (20 mL) was added dropwise in concentrated aqueous hydrochloric acid (40 mL) at room temperature under stirring condition. The mixture was then gently refluxed for 3 h and allowed to stand for 16 h at room temperature. The resulting yellow-colored solid was separated by filtration and washed with a large amount of H<sub>2</sub>O and dioxane

to afford the crude product. The crude product was recrystallized from toluene to give a yellowish needle-shaped crystal as a pure product. Product yield: 1.80 g, 64%. <sup>1</sup>H NMR (400.13 MHz, 298 K, DMSO-d<sub>6</sub>):  $\delta$  8.53 (dd, 4H), 7.73 (dd, 4H), 5.88 (s, 4H). <sup>13</sup>C NMR (100.16 MHz, 298 K, DMSO-d<sub>6</sub>):  $\delta$  131.15, 129.69, 127.27, 125.19, 49.06.



Figure 2.1. <sup>1</sup>H NMR of 9,10-Bis(chloromethyl)anthracene (ANT)



Figure 2.2. <sup>13</sup>C NMR of 9,10-Bis(chloromethyl)anthracene (ANT)

## 2.2.3. Synthesis of 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5triazine (TTRB-IMZ)

2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine (TTRB-IMZ) was synthesized according to a reported procedure with slight modification *[61]*. In a typical reaction, imidazole (0.38 g, 5.61 mmol) and potassium hydroxide (0.57 g, 10.2 mmol) were dissolved in acetonitrile (25 mL) and stirred for 1 h at room temperature. To the solution, 1 g (1.7 mmol) of **TTRB-Br** was added and stirred overnight (**TTRB-Br** was synthesized as mentioned in Chapter 3, 3.2.4 section). The obtained precipitate was filtered and washed with a large amount of water. The precipitate was dried in a vacuum to obtain the final product as a white solid. Product yield: 0.84 g, 90%. <sup>1</sup>H NMR (400.13 MHz, 298 K, DMSO-d<sub>6</sub>):  $\delta$  8.65 (d, 6H), 7.84 (s, 3H), 7.47 (d, 6H), 7.26 (s, 3H), 6.98 (s, 3H), 5.36 (s, 6H). <sup>13</sup>C NMR (100.16 MHz, 298 K, DMSO-d<sub>6</sub>):  $\delta$  171.11, 143.35, 142.58, 135.22, 132.04, 129.54, 128.5, 128.02, 50.21.



**Figure 2.3.** <sup>1</sup>H NMR of 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine (TTRB-IMZ)



**Figure 2.4.** <sup>13</sup>C NMR of 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine (TTRB-IMZ)

### 2.2.4. Synthesis of iPOP-ANT

2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine was reacted with 9,10-Bis(chloromethyl)anthracene in 20 mL dry DMF in 1:1.5 molar ratio. The mixture was sonicated until a homogeneous mixture was obtained. The mixture was heated at 100 °C under N<sub>2</sub> atmosphere for 24 h. After being cooled to room temperature, the obtained precipitate was collected by centrifugation and washed successively with DMSO, DMF, water, MeCN, THF, DCM, and diethyl ether to remove the small chain oligomers and unreacted precursors. Furthermore, the obtained solid was dipped in a 1:1:1 mixture of MeOH, THF, and DCM solution for 72 h for solvent exchange. The solid was then collected by filtration and heated at 80 °C for 24 h to obtain the desolvated **iPOP-ANT** as a yellow solid. The successful synthesis of iPOP-ANT was confirmed from FTIR and <sup>13</sup>C solid-state NMR spectroscopy.



Scheme 2.1. Synthesis of iPOP-ANT

#### 2.2.5. Procedures for the time-dependent study of oxo-anion exchange

An aqueous solution of 3 mL of  $K_2Cr_2O_7$  (0.5 mM) was taken in a cuvette, and the initial absorption was recorded using UV-vis spectroscopy. 1.5 mg of the desolvated **iPOP-ANT** was added to the cuvette and shaken gently. The absorbance of the supernatant solution was monitored by liquid UV-vis spectroscopy with different adsorption times. UV-vis spectroscopy of the KMnO<sub>4</sub> solution was also recorded similarly. From the time-dependent study, the percentage of oxo-anion removal and decrease of concentration with time was calculated using the following equation.

$$D_t = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_t} \times 100\%$$

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  $A_t$  is the concentration and absorbance of the oxo-anion solution at specific times, respectively.

Kinetics data for removing  $Cr_2O_7^{2-}$  and  $MnO_4^{-}$  were fitted in the pseudosecond-order model using the following equation

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$$

Where t is the time in minutes, and  $Q_t$  and  $Q_e$  are the amounts of adsorbate (mg g<sup>-1</sup>) on the adsorbent at different time intervals and equilibrium, respectively.

## **2.2.6.** Selective adsorption of oxo-anions in the presence of competitive anions

This study used Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> ions as competing anions commonly present in ordinary water and wastewater sources. An equimolar (5 mM,1:1) aqueous solution of both the targeted oxo-anions and the competing anions was taken. 2 mg of the desolvated **iPOP-ANT** was added to the solution and stirred for 24 h. The solid particles were separated through filtration, the obtained supernatant was diluted ten times, and the UV-vis spectra were recorded. The capture efficiency of **iPOP-ANT** in the presence of competing ions was determined by comparison with a blank solution (0.5 mM aqueous of the oxo-anion).

In order to check the effect of excess competing ions on the adsorption of the targeted ions, adsorption experiments were also carried out by taking the excess concentrations of the competing ions in a ratio of 1:10 (5 mM:50 mM), 1:50 (5 mM:250 mM), 1:100 (5 mM:500 mM) and 1:1000 (5 mM:5000 mM).

#### 2.2.7. Procedures for the time-dependent study of anionic dye exchange

For this experiment, three common anionic dyes, methyl orange (MO), congo red (CR), and amaranth (AMR), and two common cationic dyes, rhodamine B (RhB) and rhodamine 6G (Rh6G) were taken.

In the case of the anion exchange study, in a typical experiment, an aqueous of 3 mL of MO (60 mgL<sup>-1</sup>) was taken in a cuvette, and the initial absorption was recorded using a UV-vis spectrophotometer. 1.5 mg of the desolvated **iPOP-ANT** was added to the cuvette and shaken gently. The corresponding absorbance of the supernatant solution was monitored by UV-Vis spectrophotometer with different adsorption times. UV-vis spectra of the other dye solutions were recorded similarly. From the time-dependent study, the percentage of dye removal and decrease of concentration with time was calculated.

#### 2.2.8. Calculation of capacity

5 mg of the desolvated **iPOP-ANT** was added to 2.5 mL of 5 mM of the oxo-anion solution or 60 mgL<sup>-1</sup> anionic dye solution. The mixture was stirred for 24 h; after one day, the solid particles were removed by filtration, and the filtrate was used for UV-vis studies by diluting the solution. The uptake capacity was calculated from the solutions' initial and final absorbance values using the following equation

$$Q_t = \frac{(C_0 - C_t) \times V}{m}$$

Where  $Q_t$  is the capacity of the adsorbent,  $C_0$ , and  $C_t$  are the initial concentration and concentration at time t, V is the volume of the solution, and m is the mass used for the adsorbent, respectively.

#### 2.2.9. The pseudo-second-order kinetic model

The linear form of the pseudo-second-order kinetic model is expressed as

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where  $Q_t$  and  $Q_e$  are the amount of pollutants adsorbed at time t and equilibrium (mg g<sup>-1</sup>), k<sub>2</sub> is the pseudo-second-order rate constant of the adsorption process (g mg<sup>-1</sup> min<sup>-1</sup>).

#### 2.2.10. Adsorption isotherm experiment

2.5 mg of **iPOP-ANT** was immersed in a 5 mL aqueous solution of oxoanion and dyes having different concentrations. After 12 h, the supernatant was collected, and UV-vis studies were carried out. The obtained data were fitted further with the following equation

Langmuir model

$$Q_e = \frac{Q_m C_e}{K_d + C_e}$$

where  $C_e$  (mM) and  $Q_e$  (mg g<sup>-1</sup>) are the concentration at equilibrium and the amount of oxo-anion adsorbed at equilibrium, respectively.  $Q_m$  (mg g<sup>-1</sup>) is the maximum amount of pollutant 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.

#### Freundlich model

$$Q_e = K_F C_e^{\frac{1}{n}}$$

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

#### 2.2.11. Recyclability test of iPOP-ANT

After capturing the pollutants, the original material was regenerated by treating them with saturated KCl solution for 24 h. The reusability of the regenerated material was examined with 5 mL of 0.5 mM of the oxo-anion solution and 60 mgL<sup>-1</sup> of anionic dye solution. The concentration of the anionic solutions was measured after 24h by UV-vis spectroscopy. These studies were repeated up to four cycles for each of the anions.

The same method was used for the column study, where the adsorbent was regenerated by passing saturated KCl solution through the column.

#### 2.2.12. Photocatalytic degradation of the cationic dyes

The photocatalytic performance of **iPOP-ANT** was investigated by monitoring the degradation of cationic dyes- rhodamine B (RhB), rhodamine-6G, and methylene blue (MLB) under solar irradiation. The dye solutions (10 ppm) were prepared in deionized water, and the pH of the solutions was regulated using 1N HCl or 0.1M KOH solution when required. A series of dye solutions were taken in 5 mL capacity glass vials, and 0.5 mg/mL **iPOP-ANT** were dispersed in the dye solutions. The vials were placed under solar light irradiation with occasional stirring. The
solutions were centrifuged at different time intervals; the supernatant was analyzed with the help of UV-vis spectroscopy to determine the concentration of the solution. After centrifugation, the solid **iPOP-ANT** was collected, washed with acetone, and dried at 75 °C to regenerate the photocatalyst. The regenerated material was reused, keeping all the conditions similar.

#### 2.2.13. Computational details

The structures of the pristine **iPOP-ANT** and various anionic and cationic binders were optimized at the B3LYP-D3 method, using a 6-31G(d) basis set for elements till period 3, whereas the SDD basis set was used for elements in the higher periods *[62-65]*. Confirmation of minimum geometry was performed by frequency analysis to obtain zero imaginary frequencies. For the iPOP-ANT and binders, electrostatic potential (ESP) maps were generated to understand the binding sites. Various sites were considered based on the relative electron density spread over the molecules, and the structures (complex after binding) with the lowest total energies are provided. The binding energy is then calculated by employing the formula:

Binding energy 
$$(BE) = E_{Complex} - E_{Binder} - E_{iPOP-ANT}$$

where  $E_{Complex}$ ,  $E_{Binder}$ , and  $E_{iPOP-ANT}$  are the total energies of complex, binder, and pristine **iPOP-ANT**, respectively. All calculations were performed using the Gaussian 16 program package [66].

#### 2.3. Results and Discussion

#### 2.3.1. Characterization of iPOP-ANT

In the present work, an imidazolium-based ionic porous organic polymer, iPOP-ANT, was synthesized via a one-step condensation reaction between 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine and 9,10 bis(chloromethyl)anthracene under N<sub>2</sub> atmosphere. The chemical structure of the material was thoroughly characterized by <sup>13</sup>C-CPMAS NMR, FTIR

spectroscopy, FESEM, EDX, XPS, and TGA. The <sup>13</sup>C-CPMAS NMR shows broad peaks in the range of ~124 ppm to ~134 ppm, corresponding to the aromatic ring carbons of imidazole, benzene, and anthracene. Peaks at ~45 ppm and ~51 ppm represent two types of methylenic carbons attached to the imidazolium nitrogens. A peak at ~168ppm corresponds to the carbons of the triazine core of the material (Figure 2.5).



Figure 2.5. Solid state <sup>13</sup>C NMR of **iPOP-ANT**.

FTIR spectra revealed band at ~1515 cm<sup>-1</sup> corresponds to the C=N stretching frequency of triazine and imidazole linkage, whereas the band at ~1417 cm<sup>-1</sup> indicates the presence of methylene (-CH<sub>2</sub>-) functional group. The band at ~1364 cm<sup>-1</sup> represents the triazine rings, while the band at ~1144 cm<sup>-1</sup> and 775 cm<sup>-1</sup> indicate the presence of imidazolium-based functional groups, whereas the absence of any band at 566 cm<sup>-1</sup> in **iPOP-ANT** confirms the complete consumption of the C-Cl bond during the formation of the polymer (Figure 2.6) [46-48].

**Chapter 2** 



Figure 2.6. FTIR spectra of iPOP-ANT.

The thermogravimetric analysis (TGA) showed almost negligible weight loss of the material up to 260 °C, giving evidence of its thermal stability. The minimal weight loss before 100 °C may be due to the removal of the trapped solvent molecules from the pores of the material (Figure 2.7).



Figure 2.7. Thermogravimetric analysis of iPOP-ANT.

The XPS analysis confirmed the presence of C, N, and Cl in the material (Figure 2.8a). The presence of three N-containing functional groups (C=N<sup>+</sup>,

C-N, and C=N) in the XPS of N 1s also confirmed the successful synthesis of the ionic polymer (Figure 2.8b).



**Figure 2.8.** (a) XPS survey spectra of **iPOP-ANT** (b) XPS spectra of N 1s for **iPOP-ANT**.

Gas adsorption analysis was carried out to explore the uptake capacity of the polymer. The lower uptake of N<sub>2</sub> (31.61 mLg<sup>-1</sup>) and CO<sub>2</sub> (11.14 mLg<sup>-1</sup>) by the polymers may be due to the occupation of Cl<sup>-</sup> ions in the pores of the polymer. The slight hysteresis in the CO<sub>2</sub> desorption profile suggests the interaction between Cl<sup>-</sup> and CO<sub>2</sub> molecules.



**Figure 2.9.** (a)  $N_2$  adsorption profile at 77K (b)  $CO_2$  adsorption profile at 298K.

The PXRD data showed a broad peak that indicates the amorphous nature of **iPOP-ANT** (Figure 2.10a), and it was further confirmed by the electron diffraction test data (Figure 2.10b), which proved that the material is an `amorphous pure carbon material.



**Figure 2.10.** (a) PXRD of **iPOP-ANT** (b) The electron diffraction pattern of **iPOP-ANT**.

The FESEM images revealed the agglomerated spherical morphology of the material (Figure 2.11a), which was further confirmed by the TEM imaging analysis (Figure 2.11b). The elemental mapping and the EDX analysis confirmed the presence of C, N, and Cl ions in **iPOP-ANT** (Figure 2.11c and 2.11d).



**Figure 2.11.** (a) FESEM image, (b) HRTEM image, (c) EDX analysis, and (d) elemental mapping of **iPOP-ANT** 

To check the chemical stability of **iPOP-ANT**, it was kept in 2N HCl and 2N KOH solution for seven days. It was observed that there was almost no significant change in the material, as confirmed by FTIR, TGA, and SEM analysis (Figure 2.12a-2.12d).



**Figure 2.12.** (a) FTIR spectra and (b) thermogravimetric analysis of **iPOP-ANT**. FESEM image of (c) acid and (d) base treated **iPOP-ANT**.

#### 2.3.2. Anionic contaminants capture from water

Encouraged by the physicochemical stability, cationic nature, and exchangeable counter anion in **iPOP-ANT**, its utility as an ion exchange material for the adsorption of toxic anions and dyes from water was investigated. The stability, insoluble nature, and easy dispersive nature of the material in water open up the possibility for prospective application of anion capture. First, the adsorption experiment on  $Cr_2O_7^{2-}$  was carried out by adding 1.5 mg of desolvated iPOP-ANT in 3 mL 0.5 mM solution of

 $Cr_2O_7^{2-}$ . The UV-vis spectra in different time intervals show a steady decrease in the peak at 258 and 352 nm, revealing the constant reduction in the concentration of the supernatant solution of  $Cr_2O_7^{2-}$ , and almost 97% adsorption was observed within five mins (Figure 2.13a and 2.13b). To check the material's ability to adsorb radioactive  $TcO_4^-$  ions, its nonradioactive surrogate  $MnO_4^-$  was chosen, considering the radioactive nature and operational difficulty of  $TcO_4^-$  in the lab.



**Figure 2.13.** UV-vis spectra in the presence of **iPOP-ANT** at different times for the aqueous solution of (a)  $Cr_2O_7^{2-}$ . Condition: Initial conc. of both the oxo-anions (C<sub>0</sub>) = 0.5 mM, mipop-ANT/V<sub>solution</sub> = 0.5mg/mL, contact time-5 mins and 4 mins for  $Cr_2O_7^{2-}$  and  $MnO_4^{-}$  respectively, pH of the solutions was kept neutral. Decrease in concentration and percentage of

removal of (c)  $Cr_2O_7^{2-}$  (d)  $MnO_4^-$  with time. Bar diagram representation of the removal efficiency of **iPOP-ANT** in the presence of competing anions  $(NO_3^-, Cl^-, Br^-)$  for (e)  $Cr_2O_7^{2-}$  (f)  $MnO_4^-$  ions.

1.5 mg of the material was dispersed in 3 mL of 0.5 mM solution of KMnO<sub>4</sub>, and the adsorption was monitored through UV-vis spectroscopy ( $\lambda_{max}$  for MnO<sub>4</sub><sup>-</sup> is 525 nm). Almost 95% adsorption of MnO<sub>4</sub><sup>-</sup> was observed within 1 minute, and nearly 99% was adsorbed in 4 minutes (Figure 2.13b and 2.13d). To mimic the wastewater environment and evaluate the material's ability to capture oxo-anions selectively, several competing anions, like Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, were chosen, ubiquitous in common water sources. The binary mixture study shows that the adsorption of the targeted oxo-anions remains unaffected even in the presence of the competing anions when the 1:1 molar ratio of oxo-anions and competing ions are taken into consideration (Figure 2.13e and 2.13f).

Further, to verify the observations, DFT studies were also performed, which also supports the experimental observation. Computed binding energies reveal that all anions have high binding energy (> 100 kcal/mol) (Figure 2.14).



**Figure 2.14**. Optimized geometries of anions (a) Br<sup>-</sup>, (b) Cl<sup>-</sup>, (c) NO<sub>3</sub><sup>-</sup>, (d)  $Cr_2O_7^{2-}$ , and (e) MnO<sub>4</sub><sup>-</sup> binding with **iPOP-ANT**, along with the corresponding binding energies (BE) computed at B3LYP-D3/SDD-6-31G(d) level of theory.

A cage-like formation of **iPOP-ANT** for all binding structures was observed, wherein the anions are captured within the cage. Among all anions,  $Cr_2O_7^{2-}$  displays the highest binding energy, which confirms the high binding affinity of the anion towards **iPOP-ANT** as observed experimentally. On the other hand, the binding of the Br<sup>-</sup> ion has the lowest binding energy relative to the other ions was observed. An attempt to explain the difference in the binding energies can be made from the anions' electrostatic potential (ESP) map (Figure 2.15). A larger difference in the potential between the positively charged iPOP-ANT and the negatively charged anions would lead to stronger binding between those two charged ions. The highest potential difference was observed for  $Cr_2O_7^{2-}$ . However, in the case of MnO<sub>4</sub><sup>-</sup> the theoretical findings predict smaller binding energy, which might arise due to the absence of solvation effects and bulk phenomenon in the computations, which can affect the binding of the anion.



**Figure 2.15.** Electrostatic potential (ESP) distribution maps (isodensity=0.001 a.u.) of **iPOP-ANT** and various anionic and cationic binders.

Owing to the highest computed binding energy of  $Cr_2O_7^{2-}$  with **iPOP-ANT**, the influence of excess competing ions on the adsorption capabilities of the  $Cr_2O_7^{2-}$  was further investigated. It was observed that the material shows excellent selectivity towards the oxo-anions even in the presence of 100 times competing ions.



**Figure 2.16.** Effect of excess competing anions on  $Cr_2O_7^{2-}$  uptake by **iPOP-ANT.** 

Inspired by the oxo-anion's excellent adsorbability and fast adsorption rate, the ability of the material to adsorb organic dyes was further explored. Three anionic dyes, methyl orange, congo red, and amaranth were selected. To 3 mL 60 mgL<sup>-1</sup> of each dye solution, 1.5 mg of **iPOP-ANT** was dispersed, and the adsorption was monitored under UV-vis spectroscopy.



Figure 2.17. UV-vis spectra in the presence of iPOP-ANT at different

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times for the aqueous solution of (a)methyl orange, (b) amaranth, and (c) congo red. Condition: Initial conc. of the dyes  $(C_0) = 60 \text{ mgL}^{-1}$ ,  $m_{iPOP-ANT}/V_{solution} = 0.5 \text{ mg/mL}$ , contact time-14 mins and 7 mins and 100 mins for MO, AMR, and CR, respectively, pH of the solutions were kept neutral. Decrease in concentration and percentage of removal of (d) methyl orange, (e) amaranth, (f) congo red.

The ability of the polymer to capture cationic dyes was further investigated using rhodamine B (RhB) and rhodamine 6G (Rh6G). Contrary to anionic dye adsorption, very low adsorption (4.38% for RhB, 2.84% for Rh6g) of the cationic dyes was observed (Figure 2.18).



**Figure 2.18.** UV-vis spectrum in the presence of **iPOP-ANT** at different times for the aqueous solution of (a) Rh6G and (b) RhB.

To check the ability of iPOP-ANT to selectively capture anionic dyes, a selectivity test was carried out by mixing methylene blue (MLB) and methyl orange (MO) in an equal concentration. Figure 2.19 shows that only anionic MO is wholly removed from the solution, showing the material's selectivity towards the anionic dyes.



Figure 2.19. Selective capture of anionic dyes over cationic dyes.

Computation of the binding energies of the organic dyes revealed that out of the three anionic dyes, the binding of amaranth is most favorable, with a high binding energy of -457 kcal/mol, followed by that of congo red (-306 kcal/mol) and methyl orange (-177 kcal/mol) (Figure 2.20 a-c). Contrary to this, positive binding energies for the cationic dyes were obtained (Figure 2.20 d-e). The binding of the anionic dyes would be favorable due to the attractive nature of the positive **iPOP-ANT**, in contrast to the electrostatic repulsion between **iPOP-ANT** and the cationic dye.



Figure 2.20. Optimized geometries of anionic dyes (a) methyl orange, (b)

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congo red, and (c) amaranth and cationic dyes, (d) rhodamine B, and (e) rhodamine 6G - binding with **iPOP-ANT**, along with the corresponding binding energies (BE) computed at B3LYP-D3/6-31G(d) level of theory.

The structural integrity of the material after adsorbing the contaminated was confirmed by FTIR spectroscopy. Observation of new peaks at 745 and 928 cm<sup>-1</sup> for the polymer after adsorbing  $Cr_2O_7^{2-}$  and at 913 cm<sup>-1</sup> after adsorbing with  $MnO_4^-$  along with the characteristic peaks of the polymer itself, indicate the successful adsorption of the oxo-anions. The FTIR spectrum confirmed that the material's structural integrity remains intact after the adsorption of the oxo-anions and dyes (Figure 2.21). The FESEM study demonstrates the unchanged morphology of the polymer after the adsorption (Figure 2.22).



Figure 2.21. FTIR spectra of (a)  $iPOP-ANT@Cr_2O_7^{2-}$  (b)  $iPOP-ANT@MnO_4^{-}$  (c) iPOP-ANT@MO (d) iPOP-ANT@AMR (e) iPOP-ANT@CR.



Figure 2.22. FESEM images of (a)  $iPOP-ANT@Cr_2O_7^{2-}$  (b)  $iPOP-ANT@MnO_4^-$  (c) iPOP-ANT@MO (d) iPOP-ANT@AMR (e) iPOP-ANT@CR.

XPS scan also shows the presence of Cr and Mn in the material, respectively (Figure 2.23)



Figure 2.23. XPS survey spectra of (a) iPOP-ANT@  $Cr_2O_7^{2-}$  (b) iPOP-ANT@MnO<sub>4</sub><sup>-</sup>.

To investigate the adsorption mechanism of the material, an XPS test was carried out on the materials after the adsorption of the pollutants. The typical N 1s spectra of our material (Figure 2.8) show the presence of three different N-containing functional groups *viz*.:  $C=N^+$  (401.9 eV), C=N (400.3 eV), and

C-N (399.3 eV). The N 1s data of the adsorbed materials show a shift in the binding energy of  $C=N^+$  in most cases (Figure 2.24), indicating a strong interaction between the cationic center of the material and the anionic contaminants.



Figure 2.24. XPS N1s spectra for (a)  $iPOP-ANT@Cr_2O_7^{2-}$  (b)  $iPOP-ANT@MnO_4^{-}$  (c) iPOP-ANT@MO (d) iPOP-ANT@AMR (e) iPOP-ANT@CR.

The anion trapping in all the cases is found to follow the pseudo-secondorder kinetics with a high  $R^2$  value (>0.99), indicating that the adsorption rate of the anionic pollutants and dyes depends on the availability of active sites (Figure 2.25).

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Figure 2.25. The pseudo-second-order kinetics model for (a) iPOP-ANT@ $Cr_2O_7^{2-}$  (b) iPOP-ANT@ $MnO_4^{-}$  (c) iPOP-ANT@MO (d) iPOP-ANT@AMR (e) iPOP-ANT@CR.

Langmuir adsorption isotherm model was also studied to evaluate the maximum adsorption capacity of our material. The obtained results show a good agreement with the Langmuir equation, indicating single-layer adsorption of the pollutants on the material's surface (Figure 2.26). After calculation, **iPOP-ANT** shows ultrahigh adsorption capacity for  $MnO_4^-$  (5372 mg/g) and amaranth (645.084 mg/g), which come out as one of the highest values reported among the porous materials (Table 2.2 and 2.4). The maximum adsorption capacity for  $Cr_2O_7^{2-}$ , MO, and CR is 330.75 mg/g,





**Figure 2.26.** The Langmuir and Freundlich adsorption isotherm model fitting for (a)  $Cr_2O7^{2-}$  (b)  $MnO_4^{-}$  (c) MO (d) AMR (e) CR.

Table 2.1. A comparison table of $Cr_2O_7^{2-}$ capture (mg/g) with some well-	-
studied examples in the literature (ND-Not done).	

Compound	Capacity(mg/g)	Selectivity	Reference	
iPOP-ANT	330.75	Cl⁻, Br⁻, NO <sub>3</sub> ⁻	This work	
FIR-53	100	ND	67	
1-Br	128	ND	68	
CON-LDU-2	325	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	69	
CON-1	293	ND	70	
UiO-66- NH <sub>2</sub> @silica	277.4	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	71	
FJI-C11	321	ND	72	
1-NO <sub>3</sub> -OH	154.8	ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	73	
1-SO <sub>4</sub>	116	ND	32	
COP-NH <sub>2</sub>	304.9	ND	75	
1-Cl	28.7	ClO <sub>4</sub> -, BF <sub>4</sub> -, CF <sub>3</sub> SO <sub>3</sub> -	76	
ZJU-101	245	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> l <sup>-</sup> , F <sup>-</sup>	77	
DUT-52	120.68	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-,</sup> CO <sub>3</sub> <sup>2-</sup>	78	
QUST-iPOP-1	396	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	46	
{Zn <sub>1.5</sub> L} <sub>n</sub>	469	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	80	
C-NSA <sub>Naph</sub> -HCP@Br	745	F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> ,OAc <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> PO <sub>4</sub> <sup>3</sup>	81	

**Table 2.2.** A comparison table of  $MnO_4^-$  capture (mg/g) with some wellstudied examples in the literature (ND-Not done).

Compound	Surrogate ion used	Capacity(mg/g)	Selectivity	Reference
iPOP-ANT	MnO₄⁻	5372	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> -	This work
Ox-FVESP	MnO₄ <sup>-</sup>	1428.57	ND	82
[Cu <sub>3</sub> Cl(L)(H <sub>2</sub> O) <sub>2</sub> ]·Cl· 4DMA·8H <sub>2</sub> O	MnO₄⁻	106	ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> PF <sub>6</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	83
ZrIT-1	MnO₄⁻	276.6	ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , BF <sub>4</sub> <sup>-</sup>	84
SLUG-21	MnO₄⁻	283	NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	85
SCNU-Z1-Cl	MnO₄⁻	313.5	Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> NO <sub>3</sub> <sup>-</sup> , N <sub>3</sub> <sup>-</sup> ,SO <sub>4</sub> <sup>2-</sup>	86
Compound-1	MnO₄⁻	297.3	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	48
Ag(btr)·PF <sub>6</sub> ·0.5CH <sub>3</sub> CN	MnO₄⁻	163	NO <sub>3</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	87
QUST-iPOP-1	MnO <sub>4</sub> - ReO <sub>4</sub> -	514.86 441.6	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	46
SCU-CPN-1	ReO <sub>4</sub> -	876	NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	52
SCU-CPN-4	ReO <sub>4</sub> -	437	NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	53
SCU-COF-1	ReO₄⁻	367.65	NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-,</sup> SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	54
SCU-CPN-2	ReO <sub>4</sub> -	1467	NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	55
iPOP-3	ReO <sub>4</sub> -	515.5	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	49
iPOP-3	ReO₄ <sup>−</sup>	350.3	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	49

**Table 2.3.** A comparison table of MO capture (mg/g) with some wellstudied examples in the literature (ND-Not done).

Compound	Capacity(mg/g)	Recycling	Reference
ipop-ant	574.63	4	This work
Fe <sub>3</sub> O <sub>4</sub> -PEI/β-CD	192.2	4	88
MWCNTs@Fe <sub>3</sub> O <sub>4</sub> /PE I	1727.6	6	89
CANEX1000	180.25	10	90
CANEX300	160.2	10	90
Fe/MCM-41	500	ND	91
4Czpyz-poly	204	ND	92
QUST-iPOP-1	300	3	46
NH <sub>2</sub> -MWCNTs	160	ND	93
[Cd(INA) <sub>2</sub> ·(H <sub>2</sub> O)].ISB	384	ND	94
SCNU-Z1-Cl	285	ND	86

**Table 2.4.** A comparison table of AMR capture (mg/g) with some well-studied examples in the literature (ND-Not done).

Compound	Capacity(mg/g)	Recycling	Reference
iPOP-ANT	645.084	4	This work
MIL-100(Fe)	386.05	5	[36]
МСВ	404.18	ND	[37]

 Table 2.5. A comparison table of CR capture (mg/g) with some well-studied examples in the literature (ND-Not done)

Compound	Capacity(mg/g)	Recycling	Reference
ipop-ant	587.82	4	This work
Fe₃O₄/PEG	133.3	ND	97
MCB {[Tb(L)(H <sub>2</sub> O) (DMF)]·DMF} <sub>n</sub>	636.94	ND	98
SCNU-Z1-Cl	585	ND	86
AmMAC1.35	319.49	ND	99
QUST-iPOP-1	1074.9	3	46
Co-MOF	996.7	ND	100
ZIF-67	998.5	ND	100
ZIF-8@CS sponge	987	5	101

The recyclability of sorbent materials restricts its practicability in real-time wastewater processing. In this regard, the reusability experiment of **iPOP-ANT** was examined by dipping the post-captured material in saturated KCl solution for 24h after each capture cycle to regenerate the material. No significant change in the adsorption efficiency of the material was observed up to four cycles (Figure 2.27).



**Figure 2.27.** Reusability test of **iPOP-ANT** for (a)  $Cr_2O_7^{2-}$  (b)  $MnO_4^{-}$  (c) MO (d) AMR (e) CR.

A chromatographic column was prepared with **iPOP-ANT** to separate the pollutants in the water (Figure 2.28). 0.5 mM stock solutions of  $MnO_4^-$  and AMR were poured on the top of the column. The solution coming out of the column showed a significant drop in color intensity, revealing efficient capture of the contaminants, which was further confirmed by UV-vis spectroscopy. From this observation (Figure 2.28), it can be claimed that the **iPOP-ANT**-based column is proficient enough to eradicate many anionic pollutants from wastewater.



**Figure 2.28.** Images of (a)  $MnO_4^-$  and (b) AMR solution before and after passing through the polymer-packed column. UV-vis spectra of (c)  $MnO_4^-$  (d) AMR solution before and after passing through polymer packed column. Condition: Initial conc. of both  $MnO_4^-$  and AMR ( $C_0$ ) = 0.5 mM, the pH of the solutions was kept neutral.

#### 2.3.3. Photocatalytic degradation of cationic dyes

After investigating the anionic pollutant removal efficiency of iPOP-ANT, the cationic dyes present in the wastewater were dealt with, as the polymer has not shown the capability of adsorbing the cationic dyes. The promising thermal stability of the polymer logically leads to exploring its photocatalytic activity. The high thermal stability is beneficial for the practical application of photocatalysis under harsh conditions. The UV-DRS shows that the material has the ability to absorb light in the visible region and shows an absorption profile with an absorption edge adjacent to

540 nm, suggesting that it could utilize solar energy. The Tauc plot then determined the optical bandgap of the material [the curve of converted  $(\alpha hv)^r$  versus hv from the UV-vis spectrum, where  $\alpha$ , h, and v are the absorption coefficient, Planck constant, and light frequency, respectively, and r = 2 for a direct bandgap material and r = 1/2 for an indirect bandgap material]. The optical bandgap of the material was found to be 2.58 eV (Figure 2.29a), lower than ZnO, the widely used photocatalyst. The band gap was further computed based on the HOMO-LUMO separation of the optimized structure of **iPOP-ANT** and obtained an estimate of ~2.30 eV, which is in good agreement with the experimental result. Based on the orbital distribution, we find that HOMO is mainly distributed over the anthracene moiety, while the LUMO is spread over the central triazine group (Figure 2.29b).



Figure 2.29. (a) UV-vis DRS spectrum of iPOP-ANT from Tauc's relation.
(b) The theoretical band gap of iPOP-ANT was obtained from HOMO-LUMO separation at the optimized geometry, computed at B3LYP-D3/6-31G(d) level of theory.

The energy gap of ZnO is 3.24 eV, which confines its light absorption range in the UV region [85]. The sunlight that reaches the earth's surface contains only approximately 10% of the UV light. Hence, the useability of the sun by ZnO is minimal. The low band gap of iPOP-ANT and the possibility of absorption of visible light opens the possibility of using them as

photocatalytic material. It is also to be noted that such a low bandgap can lead to the charge transfer interaction, leading to the free radical generation.

The photocatalytic activity of the material was investigated by monitoring the degradation of RhB, Rh6G, and MLB under solar irradiation. The photocatalytic degradation of the dyes was monitored at different time intervals using UV-vis spectroscopy at a particular  $\lambda_{max}$  for a specific dye (552 nm for RhB, 525 nm for Rh6G, 663 nm for MLB). A constant decrease in the intensity of the absorbance with time was observed.



**Figure 2.30.** UV-vis absorbance spectra of RhB (a), Rh6G (b), and MLB (c) degradation under solar irradiation at different time intervals.  $ln(C_0/C_t)$ 

vs. Time plot shows the kinetics of the dyes' photocatalytic degradation for (d) RhB, (e) Rh6G, and (f) MLB.

Almost 94% degradation of RhB and 97% degradation of Rh6G under solar irradiation was obtained within 140 min and 160 min, respectively, at a pH of 4.5, whereas for MB, 99.8% degradation was obtained within 210 min at a pH of 10 (Figure 2.30a-c) The photocatalytic degradation of the dyes was fitted with the pseudo-first-order kinetic equation having rate constants 0.0192 min<sup>-1</sup>, 0.018 min<sup>-1,</sup> and 0.024 min<sup>-1</sup> for RhG, Rh6G, and MB, respectively as estimated by using the Langmuir–Hinshelwood kinetics model:

$$ln\frac{C_0}{C_t} = kt$$

where  $C_0$  and  $C_t$  are the initial concentration and concentration at time t minutes of the dyes in the photocatalytic degradation, k is the slope of the linear curve representing the rate constant of the reaction, and t is the time of the reaction in minutes (Figure 2.30d-f).

Recycling experiments were performed to estimate the photostability of the material, and the results revealed constant photocatalytic activity of the material even after three cycles (Figure 2.31).



**Figure 2.31.** The percentage degradation efficiency of observed recyclability for(a) RhB, (b) Rh6G, and (c) MLB.

The stability of the material after 4<sup>th</sup> cycle of degradation was analyzed by FTIR and FESEM analysis. The results confirmed almost no change in the material even after the 4<sup>th</sup> cycle (Figure 2.32 and 2.33).



Figure 2.32. FT-IR spectra of iPOP-ANT before and after the reaction.



**Figure 2.33**. FESEM images of **iPOP-ANT** after photodegradation of (a) RhB, (b) Rh6G, (c) MLB.

It is well known from the literature that superoxide radicals, hydroxyl radicals, singlet oxygen, and photogenerated holes are mainly responsible for the photodegradation of organic pollutants [102,103]. Several scavengers like p-benzoquinone (BQ,  $O_2^-$  scavenger), isopropanol (IPA, OH scavenger), sodium azide (NaN<sub>3</sub>,  $O_2$  scavenger), and EDTA (h<sup>+</sup> scavenger) were added separately to ascertain the presence of radical species, which might be responsible for the degradation of the dyes.



**Figure 2.34.** The effects of different radical scavenging agents on the degradation of (a) RhB, (b) Rh6G, and (c) MLB.

In the case of RhB and Rh6G, upon the addition of BQ and NaN<sub>3</sub>, no significant change in the photodegradation was observed, whereas, upon the introduction of IPA and EDTA as sacrificial agents, a significant decrease in the photodegradation was observed. This observation indicates that hydroxyl radical and photogenerated holes are the main active species for degrading RhB and Rh6G. In the case of MB, upon the addition of BQ and EDTA, the degradation rate decreased significantly, whereas NaN<sub>3</sub> and IPA did not show any significant reduction in the degradation rate, indicating the active role of superoxide radicals and photogenerated holes in the degradation of MB (Figure 2.34). The comparative photocatalytic performance of iPOP-ANT with the other reported COPs is presented in Table 2.6.

 Table 2.6. Comparative studies of our designed iPOP-ANT with the reported COPs in terms of photocatalytic dye degradation.

Material	Dye used	Source of irradiation	Degradation time	% of degradation	Reference
	RhB		140 min	94 %	
iPOP-ANT	Rh6G	Solar Light	160 min	97 %	This
	MB		210 min	99.8 %	work
TP-COP	RhB	Solar Light	160 min	95 %	104
POP-1	RhB	LED Light	180 min	93 %	105
sp2c-CTP-4.	MB	Vis Light	90 min	98 %	106
PDA-COP 1	MO	Vis-light	120 min	92 %	107
	MO		600 min	67 %	
CON-TP	RhB	Vis-Light	240 min	78 %	108
	MB		100 min	57 %	
	RhB		30	>99 %	
TpSD	Rh6G	Vis-Light (Xe arc lamp)	60	99.2 %	109
	MB		60	95.8 %	

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#### 2.4. Conclusion

In this study, a thermally and chemically stable ionic polymer **iPOP-ANT** was designed and synthesized by a one-step condensation reaction. It was well-characterized by various spectroscopic and imaging techniques. The polymer was found to be suitable for acting as a dual functionalized material for the rapid and selective capture of oxo-anions and anionic dyes from water and photocatalytic degradation of cationic dyes under solar irradiation. The material can show significantly higher uptake capacities, fast kinetics, and selectivity towards capturing the oxo-anions and anionic dyes. The same material can also degrade the cationic dyes efficiently. In both cases, the material was found to be remarkably reusable. These findings open a new avenue for developing dual-functionalized material with excellent adsorption and photocatalytic properties.

#### 2.5. Declaration

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#### 2.6. References

[1] Bouwer H. (2002), Integrated Water Management for the 21st Century: Problems and Solutions, J. Irrig. Drain Eng., 128, 193–202 (DOI: 10.1061/(ASCE)0733-9437(2002)128:4(193)).

[2] Jury W. A., Vaux H. (2005), The Role of Science in Solving the World's Emerging Water Problems, Proc. Natl. Acad. Sci. USA, 102, 15715–15720 (DOI: 10.1073/pnas.050646710)

[3] Oliver, S. R. J. (2009), Cationic Inorganic Materials for Anionic Pollutant Trapping and Catalysis, Chem. Soc. Rev., 38, 1868-1881 (DOI: 10.1039/B710339P)

[4] Watharkar A. D., Kadam S. K., Khandare R. V., Kolekar P. D. Jeon B.
H., Jadhav J. P., Govindwar S. P. (2018), Asparagus Densiflorus in a Vertical Subsurface Flow Phytoreactor for Treatment of Real Textile Effluent: A Lab to Land Approach for in Situ Soil Remediation, Ecotoxicol. Environ. Saf., 161, 70–77 (DOI: 10.1016/j.ecoenv.2018.05.078)

[5] Schwarzenbach R. P., Egli T., Hofstetter T. B., von Gunten U., Wehrli
B. (2010), Global Water Pollution and Human Health, Annu. Rev. Environ.
Resour., 35, 109–136 (DOI: 10.1146/annurev-environ-100809-125342)

[6] Zamora-Ledezma C., Negrete-Bolagay D., Figueroa F. Zamora-Ledezma E., Ni M., Alexis F., Guerrero V. H. (2021), Heavy Metal Water Pollution: A Fresh Look about Hazards, Novel and Conventional Remediation Methods, Environ. Technol. Innov., 22, 101504 (DOI: 10.1016/j.eti.2021.101504)

[7] Khezami L., Capart R. (2005), Removal of Chromium (VI) from Aqueous Solution by Activated Carbons: Kinetic and Equilibrium Studies, J. Hazard. Mater., 123, 223–231 (DOI: 10.1016/j.jhazmat.2005.04.012)

[8] Sun Q., Zhu L., Aguila B., Thallapally P. K., Xu C., Chen J., Wang S., Rogers D. Ma S. (2019), Optimizing Radionuclide Sequestration in Anion Nanotraps with Record Pertechnetate Sorption, Nat. Commun., 10, 1646 (DOI: 10.1038/s41467-019-09630-y).

[9] Lee M.S., Um W., Wang G., Kruger A. A., Lukens W. W., Rousseau R., Glezakou V.A. (2016), Impeding <sup>99</sup>Tc (IV) Mobility in Novel Waste Forms, Nat. Commun., 7, 12067 (DOI: 10.1038/ncomms12067).

[10] Banerjee D., Kim D., Schweiger M. J., Kruger A. A., Thallapally P. K. (2016), Removal of  $TcO_4^-$  Ions from Solution: Materials and Future Outlook, Chem. Soc. Rev., 45, 2724–2739 (DOI: 10.1039/C5CS00330J)

[11] Smith F. N., Taylor C. D., Um W., Kruger A. A. (2015), Technetium Incorporation into Goethite (α-FeOOH): An Atomic-Scale Investigation, Environ. Sci. Technol., 49, 13699–13707 (DOI: 10.1021/acs.est.5b03354)

[12] Wang S., Yu P., Purse B. A., Orta M. J., Diwu J., Casey W. H., Phillips B. L., Alekseev E. V., Depmeier W., Hobbs D. T., Albrecht-Schmitt T. E. (2012), Selectivity, Kinetics, and Efficiency of Reversible Anion Exchange with  $TcO_4^-$  in a Supertetrahedral Cationic Framework, Adv. Funct., Mater., 22, 2241–2250 (DOI: 10.1002/adfm.201103081)

[13] Solís M., Solís A., Pérez H. I., Manjarrez N., Flores M. (2012),
Microbial Decolouration of Azo Dyes: A Review, Process Biochem., 47,
1723–1748 (DOI: 10.1016/j.procbio.2012.08.014)

[14] Mondal S. (2008), Methods of Dye Removal from Dye House Effluent-An Overview, Environ. Eng. Sci., 25, 383–396 (DOI: 10.1089/ees.2007.0049)

[15] Zhou Y., Lu J., Zhou Y., Liu Y. (2019), Recent Advances for Dyes
Removal Using Novel Adsorbents: A Review, Environ. Pollut., 252, 352–365 (DOI: 1016/j.envpol.2019.05.072)

[16] Gupta V. K., Suhas (2009), Application of Low-Cost Adsorbents for Dye Removal – A Review, J. Environ. Manag., 90, 2313–2342 (DOI: 10.1016/j.jenvman.2008.11.017)

[17] Rafatullah Mohd., Sulaiman O., Hashim R., Ahmad A. (2010),
Adsorption of Methylene Blue on Low-Cost Adsorbents: A Review, J.
Hazard. Mater, 177, 70–80 (DOI: 10.1016/j.jhazmat.2009.12.047)

[18] Yagub M. T., Sen T. K., Afroze S., Ang H. M. (2014), Dye and Its Removal from Aqueous Solution by Adsorption: A Review, Adv. Colloid Interface Sci., 209, 172–184 (10.1016/j.cis.2014.04.002)

[19] Brillas E., Martínez-Huitle C. A. (2015), Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods. An Updated Review, App. Catal. B, 166–167, 603–643 (DOI: 10.1016/j.apcatb.2014.11.016)

[20] Cardoso J. C., Bessegato G. G., Boldrin Zanoni M. V. (2016), Efficiency Comparison of Ozonation, Photolysis, Photocatalysis and Photoelectrocatalysis Methods in Real Textile Wastewater Decolorization, Water Research, 98, 39–46 (DOI: 10.1016/j.watres.2016.04.004)

[21] Fu F., Wang Q. (2011) Removal of Heavy Metal Ions from Wastewaters: A Review, J. Environ. Manag., 92, 407–418 (DOI: 10.1016/j.jenvman.2010.11.011)

[22] Barakat M. A. (2011), New Trends in Removing Heavy Metals from Industrial Wastewater, Arab. J. Chem., 4, 361–377 (DOI: 10.1016/j.arabjc.2010.07.019)

[23] Abdel-Raouf N., Al-Homaidan A. A., Ibraheem I. B. M. (2012)
Microalgae and Wastewater Treatment, Saudi J. Bio. Sci., 19, 257–275
(DOI: 10.1016/j.sjbs.2012.04.005)

[24] Sheng D., Zhu L., Xu C., Xiao C., Wang Y., Wang Y., Chen L., Diwu J., Chen J., Chai Z., Albrecht-Schmitt T. E., Wang S. (2017), Efficient and Selective Uptake of  $TcO_4^-$  by a Cationic Metal-Organic Framework Material with Open Ag<sup>+</sup> Sites, Environ. Sci. Technol., 51, 3471–3479, (DOI: 10.1021/acs.est.7b00339)

[25] Wang G. Q., Huang J. F., Huang X. F., Deng S. Q., Zheng S.R., Cai S.L., Fan J., Zhang W. G. (2021), A Hydrolytically Stable Cage-Based Metal-Organic Framework Containing Two Types of Building Blocks for the Adsorption of Iodine and Dyes, Inorg. Chem. Front., 8, 1083–1092 (DOI: 10.1039/D0QI01257B)

[26] Zhang R. T., Xiao H. P., Li Z., Wang M., Xie Y. F., Ye Y. D., Li X. X.
Zheng S. T. (2021), Two Highly Stable Inorganic–Organic Hybrid 3D
Frameworks Based on Cu–Ln Incorporated Polyoxometalates for Selective
Dye Removal and Proton Conduction, CrystEngComm, 23, 2973–2981
(DOI: 10.1039/D1CE00218J)

[27] Karthikeyan P., Elanchezhiyan S. S. D., Banu H. A. T., Hasmath Farzana M., Park C. M. (2021), Hydrothermal Synthesis of Hydroxyapatite-Reduced Graphene Oxide (1D–2D) Hybrids with Enhanced Selective Adsorption Properties for Methyl Orange and Hexavalent Chromium from Aqueous Solutions, Chemosphere, 276, 130200 (DOI: 10.1016/j.chemosphere.2021.130200)

[28] Schlichter S., Sapag K., Dennehy M., Alvarez M. (2017), Metal-Based Mesoporous Materials and Their Application as Catalysts for the Degradation of Methyl Orange Azo Dye, J. Environ. Chem. Eng., 5, 5207– 5214 (DOI: 10.1016/j.jece.2017.09.039)

[29] Wen T., Zhang D. X., Liu J., Lin R., Zhang J. (2013), A Multifunctional Helical Cu(I) Coordination Polymer with Mechanochromic, Sensing and Photocatalytic Properties, Chem. Commun., 49, 5660–5662 (DOI: 10.1039/C3CC42241K)

[30] Chen H., Liu P. X., Xu N., Meng X., Wang H. N., Zhou Z.Y. (2016),
A visible light-driven photocatalyst of a stable metal-organic framework
based on Cu<sub>4</sub>Cl clusters and TIPE spacers, Dalton Trans., 45, 13477–13482
(DOI: 10.1039/C6DT02659A)

[31] Wang J., Zheng S., Shao Y., Liu J., Xu Z., Zhu D. (2010), Aminofunctionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal, J. Colloid. Interfaces Sci., 349, 293–299 (DOI: 10.1016/j.jcis.2010.05.010)

[32] Desai A. V., Manna B., Karmakar A., Sahu A., Ghosh S. K. (2016), A
Water-stable cationic metal-organic framework as a dual adsorbent of oxoanion pollutants, Angew. Chem., 128, 7942–7946 (DOI: 10.1002/anie.201600185)

[33] Zhang Q., Yu J., Cai J., Zhang L., Cui Y., Yang Y., Chen B., Qian G. (2015), A porous Zr-cluster-based cationic metal-organic framework for highly efficient  $Cr_2O_7^{2-}$  removal from water, Chem. Commun., 51, 14732–14734 (DOI: 10.1039/c5cc05927e)

[34] Zhu L., Sheng D., Xu C., Dai X., Silver M. A., Li J., Li P. Wang Y., Wang Y., Chen L., Xiao C., Chen J., Zhou R., Zhang C., Farha O. K., Chai Z., Albrecht-Schmitt T. E., Wang S. (2017), Identifying the recognition site for selective trapping of  ${}^{99}$ TcO<sub>4</sub><sup>-</sup> in a hydrolytically stable and radiation resistant cationic metal-organic framework, J. Am. Chem. Soc., 139, 14873–14876 (DOI: 10.1021/jacs.7b08632)

[35] Shen N., Yang Z., Liu S., Dai X., Xiao C., Taylor-Pashow K., Li D., Yang C., Li J., Zhang Y., Zhang M., Zhou R., Chai Z., Wang S. (2020), <sup>99</sup>TcO<sub>4</sub><sup>-</sup> removal from legacy defense nuclear waste by an alkaline-stable 2D cationic metal-organic framework, Nat. Commun., 11, 5571 (DOI: 10.1038/s41467-020-19374-9)

[36] Samanta P., Chandra P., Desai A. V., Ghosh S. (2017), Chemically stable microporous hyper-cross-linked polymer (HCP): an efficient selective cationic dye scavenger from an aqueous medium, Mater. Chem. Front., 1, 1384–1388 (DOI: 10.1039/C6QM00362A)

[37] Shen X., Faheem M., Matsuo Y., Aziz S., Zhang X., Li Y., Song J., Tian Y., Zhu G. (2019), Polarity engineering of porous aromatic frameworks for specific water contaminant capture, J. Mater. Chem. A, **7**, 2507–2512 (DOI: 10.1039/C8TA11343B)

[38] Jiao L., Wang Y., Jiang H. L., Xu Q. (2018) Metal–organic frameworks as platforms for catalytic applications, Adv. Mater., 30, 1703663 (DOI: 10.1002/adma.201703663)

[39] Pei C. Y., Chen Y. G., Wang L., Chen W., Huang G. B. (2021), Stepscheme  $WO_3/CdIn_2S_4$  hybrid system with high visible light activity for tetracycline hydrochloride photodegradation, Appl. Surf. Sci., 535, 147682 (DOI: 10.1016/j.apsusc.2020.147682)

[40] Mollick S., Mandal T. N., Jana A., Fajal S., Desai A. V. Ghosh S. K. (2019), Ultrastable luminescent hybrid bromide perovskite@MOF nanocomposites for the degradation of organic pollutants in water, ACS Appl. Nano Mater. 2, 1333–1340 (DOI: 10.1021/acsanm.8b02214)

[41] Trewin A., Cooper A. I. (2010), Porous organic polymers: distinctionfrom disorder? Angew. Chem., 49, 1533–1535 (DOI: 10.1002/anie.200906827)

[42] Zhang T., Xing G., Chen W., Chen L. (2020), Porous organic polymers: A promising platform for efficient photocatalysis, Mater. Chem. Front., 4, 332–353 (DOI: 10.1039/C9QM00633H)

[43] Chen D., Liu C., Tang J., Luo L., Yu G. (2019), Fluorescent porous organic polymers, Polym. Chem., 10, 1168–1181 (DOI: 10.1039/C8PY01620H)

[44] Taylor D., Dalgarno S. J., Xu Z., Vilela F. (2020), Conjugated porous polymers: incredibly versatile materials with far-reaching applications, Chem. Soc. Rev., 49, 3981–4042 (DOI: 10.1039/C9CS00315K)

[45] Li Z., Li H., Guan X., Tang J., Yusran Y., Li Z., Xue M., Fang Q., Yan Y., Valtchev V., Qiu S. (2017), Three-dimensional ionic covalent organic frameworks for rapid, reversible, and selective ion exchange, J. Am. Chem. Soc., 139, 17771–17774 (DOI: 10.1021/jacs.7b11283)

[46] Jiao S., Deng L., Zhang, X., Zhang Y., Liu K., Li S., Wang L. Ma D.
(2021), Evaluation of an ionic porous organic polymer for water remediation, ACS Appl. Mater. Interfaces, 13, 39404–39413 (DOI: 10.1021/acsami.1c10464)

[47] Liu Z. W., Cao C. X., Han B.H. (2019), A cationic porous organic polymer for high-capacity, fast, and selective capture of anionic pollutants, J. Hazard. Mater., 367, 348–355 (DOI: 10.1016/j.jhazmat.2018.12.091)

[48] Samanta P., Chandra P., Dutta S., Desai A. V., Ghosh S. K. (2018), Chemically stable ionic viologen-organic network: an efficient scavenger of toxic oxo-anions from water, Chem. Sci., 9, 7874–7881 (DOI: 10.1039/C8SC02456A)

[49] Sen, A., Dutta S., Dam G. K., Samanta P., Let S., Sharma S., Shirolkar M. M., Ghosh S. K. (2021), Imidazolium-functionalized chemically robust ionic porous organic polymers (iPOPs) toward toxic oxo-pollutants capture from water, Chem. – Eur. J., 27, 13442–13449 (DOI: 10.1002/chem.202102399)

[50] Wang Y., Zhao H., Li X., Wang R. (2016), A durable luminescent ionic polymer for rapid detection and efficient removal of toxic  $Cr_2O_7^{2-}$ , J. Mater. Chem. A, 4, 12554–12560 (DOI: 10.1039/C6TA03516G)

[51] Wang S. Meng X., Luo H., Yao L., Song X., Liang Z. (2022), Postsynthetic modification of conjugated microporous polymer with imidazolium for highly efficient anionic dyes removal from water, Sep. Purif. Technol, 284, 120245, (DOI: 10.1016/j.seppur.2021.120245)

[52] Li J., Dai X., Zhu L., Xu C., Zhang D., Silver M. A., Li P., Chen L., Li Y., Zuo D., Zhang H., Xiao C., Chen J., Diwu J., Farha O. K., Albrecht-Schmitt T. E., Chai Z., Wang S. (2018), <sup>99</sup>TcO<sub>4</sub><sup>-</sup> remediation by a cationic polymeric network, Nat. Commun., 9, 3007 (DOI: 10.1038/s41467-018-05380-5)
[53] Li J., Li B., Shen N., Chen L., Guo, Q., Chen L., He L., Dai X., Chai Z., Wang S. (2021), Task-specific tailored cationic polymeric network with high base-resistance for unprecedented  $^{99}$ TcO<sub>4</sub><sup>-</sup> cleanup from alkaline nuclear waste, ACS Cent. Sci., **7**, 1441–1450 (DOI: 10.1021/acscentsci.1c00847)

[54] He L., Liu S., Chen L., Dai X., Li J., Zhang M., Ma F., Zhang C., Yang, Z., Zhou R., Chai Z., Wang S. (2019), Mechanism unravelling for ultrafast and selective <sup>99</sup>TcO<sub>4</sub><sup>-</sup> uptake by a radiation-resistant cationic covalent organic framework: A combined radiological experiment and molecular dynamics simulation study, Chem. Sci. 10, 4293–4305 (DOI: 10.1039/C9SC00172G)

[55] Li J., Chen L., Shen N., Xie R., Sheridan M. V., Chen X., Sheng D., Zhang D., Chai Z., Wang S. (2021) Rational design of a cationic polymer network towards record high uptake of <sup>99</sup>TcO<sub>4</sub>- in nuclear waste., Sci. China Chem., 64, 1251–1260 (DOI: 10.1007/s11426-020-9962-9)

[56] Preet K., Gupta G., Kotal M., Kansal S. K., Salunke D. B., Sharma H. K., Chandra Sahoo S., Van Der Voort P., Roy S. (2019), Mechanochemical synthesis of a new triptycene-based imine-linked covalent organic polymer for degradation of organic dye, Cryst. Growth Des., 19, 2525–2530 (DOI: 10.1021/acs.cgd.9b00166)

[57] Xu N., Wang R. L., Li D. P., Meng X., Mu J. L., Zhou Z. Y., Su Z. M.
(2018), A new triazine-based covalent organic polymer for efficient photodegradation of both acidic and basic dyes under visible light, Dalton Trans. 47, 4191–4197 (DOI: 10.1039/C8DT00148K)

[58] Xue, H., Xiong S. Mi K., Wang Y. (2023), Visible-light degradation of azo dyes by imine-linked covalent organic frameworks, Green Energy Environ., 8, 194-199 (DOI: 10.1016/j.gee.2020.09.010)

[59] Zheng X., Ruan Q., Jiang Q., Wang K., Wang Q., Tang Y., Huang H., Zhong C. (2018), Integrated adsorption and catalytic degradation of safranine T by a porous covalent triazine-based framework, J. Colloid Interface Sci., 532, 1–11 (DOI: 10.1016/j.jcis.2018.07.113)

[60] Dawson R., Adams D. J., Cooper A. I. (2011), Chemical tuning of CO<sub>2</sub> sorption in robust nanoporous organic polymers, Chem. Sci., 2, 1173–1177 (DOI: 10.1039/C1SC00100K)

[61] Kumar A., Zangrando E., Mukherjee P. S. (2019), Self-assembledPd3L2 cages having flexible tri-imidazole donors, Polyhedron, 172, 67-73(DOI: 10.1016/j.poly.2019.03.014)

[62] Lee C. T., Yang W. T., Parr R. G. (1988), Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B. 37, 785 (DOI: 10.1103/PhysRevB.37.785)

[63] Grimme S., Antony J., Ehrlich S., Krieg H. (2010), A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys., 132, 154104 (DOI: 10.1063/1.33823440)

[64] Hehre W. J., Ditchfie R., Pople J. A. (1972), Self-consistent molecular orbital methods. XII. Further extensions of gaussian—type basis sets for use in molecular orbital studies of organic molecules, J. Chem. Phys., 56, 2257 (DOI: 10.1063/1.16775270)

[65] Andrae D., Häußermann U., Dolg M., Stoll H., Preuß H. (1990), Energy-adjustedab initio pseudopotentials for the second and third row transition elements, Theor. Chim. Acta, 77, 123 (DOI: 10.1007/BF01114537)

[66] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Petersson G.A., Nakatsuji H., Li X., Caricato M., Marenich A.V., Bloino J., Janesko B.G., Gom-perts R.,

Mennucci B., Hratchian H.P., Ortiz J.V., Izmaylov A.F., Sonnenberg J.L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V. G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Mont-gomery J. A. Jr., Peralta J. E., Ogliaro F., Bearpark M. J., Heyd J. J., Brothers E. N., Kudin K. N., Staroverov V. N., Keith T. A., Kobayashi R., Normand J., Raghavachari K., Rendell A.P., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Millam J. M., Klene M., Adamo C., Cammi R., Ochterski J. W., Martin R. L., Morokuma K., Farkas O., Foresman J. B., Fox D. J. (2016).: Gaussian 16 Revision C.01. Gaussian Inc. Wallingford CT.

[67] Fu H. R, Xu Z. X., Zhang J. (2015), Water-stable metal–organic frameworks for fast and high dichromate trapping via single-crystal to single-crystal ion exchange, Chem. Mater., 27, 205-210 (DOI: 10.1021/cm503767r)

[68] Lv X. X., Shi L. L., Li K., Li B. L., Li H. Y. (2017), An unusual porous cationic metal–organic framework based on a tetranuclear hydroxyl-copper(II) cluster for fast and highly efficient dichromate trapping through a single-crystal to single-crystal process, Chem. Commun., 53, 1860-1863. (DOI: 10.1039/C6CC09676J)

[69] Li Z. J., Xue H. D., Ma Y. X., Zhang Q., Li Y. C., Xie M., Qi H. L.,
Zheng X.D. (2019), Dual-functionalized fluorescent cationic organic network: highly efficient detection and removal of dichromate from water,
ACS Appl. Mater. Interfaces, 11, 46197-46204 (DOI: 10.1021/acsami.9b17074)

[70] Li Z. J., Xue H. D., Zhang Y. Q., Hu H. S., Zheng X. D. (2019), Construction of a cationic organic network for highly efficient removal of

anionic contaminants from water, New J. Chem., 43, 11604-11609 (DOI: 10.1039/C9NJ00886A)

[71] El-Mehalmey W. A., Ibrahim A. H., Abugable A. A., Hassan M. H., Haikal R. R., Karakalos S. G., Zaki O., Alkordi M. H. (2018), Metal– organic framework@Silica as a stationary phase sorbent for rapid and costeffective removal of hexavalent chromium, J. Mater. Chem. A, 6, 2742-2751 (DOI: 10.1039/C7TA08281A)

[72] Zou Y. H., Liang J., He C., Huang Y. B., Cao R. (2019), A mesoporous cationic metal–organic framework with a high density of positive charge for enhanced removal of dichromate from water, Dalton Trans., 48, 6680-6684 (DOI: 10.1039/C9DT01622H)

[73] Zheng T. R, Qian L. L., Li M., Wang Z. X., Li K., Zhang Y. Q., Li B. L., Wu B. (2018), A bifunctional cationic metal–organic framework based on unprecedented nonanuclear copper(ii) cluster for high dichromate and chromate trapping and highly efficient photocatalytic degradation of organic dyes under visible light irradiation, Dalton Trans., 47, 9103-9113 (DOI: 10.1039/C8DT01685B)

[75] Kong K., Cheng B., Liang J., Guo Y., Wang R. (2022), The aminated covalent organic polymers for reversible removal of concurrent perfluorooctane sulfonate and dichromate, Chem. Eng. J., 446, 137343 (DOI: 10.1016/j.cej.2022.137343)

[76] Ma L., Yang J., Lu B. B., Li C. P., J.-F. Ma (2018), Water-stable metalorganic framework for effective and selective  $Cr_2O_7^{2-}$  capture through single-crystal to single-crystal anion exchange, Inorg. Chem. 57, 11746-11752 (DOI: 10.1021/acs.inorgchem.8b01879)

[77] Sousa-Herves A., Wedepohl S., Calderón M. (2015), One-pot synthesis of doxorubicin-loaded multiresponsive nanogels based on hyperbranched

polyglycerol, Chem. Commun., 51, 5264-5267 (DOI: 10.1039/C5CC00644A)

[78] Shen Y., Duan R., Qian J., Li Q. (2022), Preparation of highly stableDUT-52 materials and adsorption of dichromate ions in aqueous solution,ACS Omega, 19, 16414-16421 (DOI: 10.1021/acsomega.2c00373)

[80] Jena S. R., Choudhury J. (2021), 3D Metallo-organic coordination assembly-based anion-enriched supramolecular material for fast and efficient removal of  $Cr_2O_7^{2-}$ , J. Hazard. Mater., 405, 124242 (DOI: 10.1016/j.jhazmat.2020.124242)

[81] Shen X., Ma S., Xia H., Shi Z., Mu Y., Liu X. (2018), Cationic porous organic polymers as an excellent platform for highly efficient removal of pollutants from water, J. Mater. Chem. A, 6, 20653-20658 (DOI: 10.1039/C8TA09145E)

[82] Bani-Atta S. A. (2022), Potassium permanganate dye removal from synthetic wastewater using a novel, low-cost adsorbent, modified from the powder of Foeniculum vulgare seeds, Sci. Rep., 12, 4547 (DOI: 10.1038/s41598-022-08543-z)

[83] Li Y., Yang J., Ma J. F. (2021), A copper(ii)-based porous metalorganic framework for the efficient and rapid capture of toxic oxo-anion pollutants from water, Dalton Trans., 50, 3832-3840 (DOI: 10.1039/D0DT04252H)

[84] Hou B., Gu X., Gan H., Zheng H., Zhu Y., Wang X., Su Z., Face-Directed construction of a metal–organic isohedral tetrahedron for the highly efficient capture of environmentally toxic oxoanions and iodine, Inorg. Chem., 61, 7103-7110 (DOI: 10.1021/acs.inorgchem.2c00584)

[85] Fei H., Rogow D. L., Oliver S. R. J. (2010), Reversible anion exchange and catalytic properties of two metal–organic frameworks Bbased on Cu(I) and Ag(I), J. Am. Chem. Soc., 132, 7202-7209 (DOI: 10.1021/ja102134c)

[86] Deng S. Q., Mo X. J., Zheng S. R., Jin X., Gao Y., Cai S. L., Fan J., Zhang W. G. (2019), Hydrolytically stable nanotubular cationic metal– organic framework for rapid and efficient removal of toxic oxo-anions and dyes from water, Inorg. Chem., 58, 2899-2909 (DOI: 10.1021/acs.inorgchem.9b00104)

[87] Li X., Gong Y., Zhao H., Wang R. (2014), Anion-directed assemblies of cationic metal–organic frameworks based on 4,4'-Bis(1,2,4-triazole): syntheses, structures, luminescent and anion exchange properties, Inorg. Chem., 53, 12127-12134 (DOI: 10.1021/ic501978u)

[88] Chen B., Chen S., Zhao H., Liu Y., Long F., Pan X. (2019), A versatile  $\beta$ -cyclodextrin and polyethyleneimine bi-functionalized magnetic nanoadsorbent for simultaneous capture of methyl orange and Pb(II) from complex wastewater, Chemosphere, 216, 605-616 (DOI: 10.1016/j.chemosphere.2018.10.157)

[89] Chen B., Yue W., Zhao H., Long F., Cao Y., Pan X. (2019), Simultaneous capture of methyl orange and chromium(vi) from complex wastewater using polyethylenimine cation decorated magnetic carbon nanotubes as a recyclable adsorbent, RSC Adv. 9, 4722-4734 (DOI: 10.1039/C8RA08760A)

[90] Dragan E. S., Dinu M. V. (2018), Spectacular selectivity in the capture of methyl orange by composite anion exchangers with the organic part hosted by DAISOGEL microspheres, ACS Appl. Mater. Interfaces, 10, 20499-20511 (DOI: 10.1021/acsami.8b04498)

[91] Albayati T. M., Alwan G. M., Mahdy O. S. (2017), High performance methyl orange capture on magnetic nanoporous MCM-41 prepared by incipient wetness impregnation method, Korean J. Chem. Eng., 34, 259-265 (DOI: 10.1007/s11814-016-0231-2)

[92] Al-Hetlani E., Rajendran N., BabuVelappan A., Amin M. O., Ghazal B., Makhseed S. (2021), Design and synthesis of a nanopolymer for CO<sub>2</sub> capture and wastewater treatment, Ind. Eng. Chem. Res., 60, 8664-8676 (DOI: 10.1021/acs.iecr.1c01492)

[93] Liu Y., Cui G., Luo C., Zhang L., Guo Y., Yan S. (2014), Synthesis, characterization and application of amino-functionalized multi-walled carbon nanotubes for effective fast removal of methyl orange from aqueous solution, RSC Adv., 4, 55162-55172 (DOI: 10.1039/C4RA10047F)

[94] Tella A. C., Olawale M. D., Neuburger M., Obaleye J. A. (2017), Synthesis and crystal structure of Cd-based metal-organic framework for removal of methyl-orange from aqueous solution, J. of Solid State Chem., 255, 157-166 (DOI: 10.1016/j.jssc.2017.07.019)

[95] Zhao R., Tian Y., Li S., Ma T., Lei H., Zhu G. (2019), An electrospun fiber based metal–organic framework composite membrane for fast, continuous, and simultaneous removal of insoluble and soluble contaminants from water, J. Mater. Chem. A, 7, 22559-22570 (DOI: 10.1039/C9TA04664J)

[96] F. Wang, L. Li, J. Iqbal, Z. Yang, Y. Du (2022), Preparation of magnetic chitosan corn straw biochar and its application in adsorption of amaranth dye in aqueous solution, Int. J. Biol. Macromolecules, 199, 234-242 (DOI: 10.1016/j.ijbiomac.2021.12.195)

[97] Pi C., He Z., Wang Y., Li C., Wang W., Yang Y., Li W. (2022), Efficient removal of Congo red from wastewater by gas-assisted lowgradient magnetic separation, J. Disper. Sci. Tech., 44, 1972–1978 (DOI: 10.1080/01932691.2022.2053704)

[98] Ding B., Cheng Y., Wu J., M. Wu X., M. Zhang H., Luo Y., Shi X. F., Wu X. X., Huo J. Z., Liu Y. Y, Li Y. (2017), A unique multifunctional cluster-based nano-porous Terbium organic material: Real-time detection

of benzaldehyde, visually luminescent sensor for nitrite and selective high capacity capture of Congo Red, Dyes Pigm., 146, 455-466 (DOI: 10.1016/j.dyepig.2017.07.044)

[99] Tian C., Feng C., Wei M., Wu Y. (2018), Enhanced adsorption of anionic toxic contaminant Congo Red by activated carbon with electropositive amine modification, Chemosphere, 208, 476-483 (DOI: 10.1016/j.chemosphere.2018.06.005)

[100] Guo X., Kong L., Ruan Y., Diao Z., Shih K., Su M., Hou L., Chen D.
(2020), Green and facile synthesis of cobalt-based metal–organic frameworks for the efficient removal of Congo red from aqueous solution, J. Colloid Interface Sci., 578, 500-509 (DOI: 10.1016/j.jcis.2020.05.126)

[101] L. Liu, Y. Ma, W. Yang, C. Chen, M. Li, D. Lin, Q. Pan (2020), Reusable ZIF-8@chitosan sponge for the efficient and selective removal of congo red, New J. Chem., 44, 15459-15466 (DOI: 10.1039/D0NJ02699A)

[102] Nakagawa S., Sakakibara K., Gotoh H. (2016), Novel degradation mechanism for triarylmethane dyes: acceleration of degradation speed by the attack of active oxygen to halogen groups (2016), Dyes Pigm., 124, 130–132 (DOI: 10.1016/j.dyepig.2015.09.006)

[103] Yin M., Li Z., Kou J., Zou Z. (2009), Mechanism investigation of visible light-induced degradation in a heterogeneous TiO2/Eosin Y/Rhodamine B system, Environ. Sci. Technol., 43, 8361–8366 (DOI: 10.1021/es902011h)

[104] Preet K., Gupta G., Kotal M., Kansal S. K., Salunke D. B., Sharma H. K., Sahoo S. C., Van Der Voort P., Roy S. (2019), Mechanochemical synthesis of a new triptycene-based imine-linked covalent organic polymer for degradation of organic dye, Cryst. Growth Des. 19, 2525–2530 (DOI: 10.1021/acs.cgd.9b00166)

[105] Liu P., Xing L., Lin H., Wang H., Zhou Z., Su Z. (2017), Construction of porous covalent organic polymer as photocatalysts for RhB degradation under visible light, Science Bulletin, 62, 931-937 (DOI: 10.1016/j.scib.2017.05.031)

[106] Xu C., Xie Q., Zhang W., Xiong S., Pan C., Tang J., Yu G. (2020), A vinylene-bridged conjugated covalent triazine polymer as a visible-light-active photocatalyst for degradation of methylene blue, Macromol. Rapid Commun., 41, 2000006 (DOI: 10.1002/marc.202000006)

[107] Bhowmik S., Jadhav R. G., Das A. K. (2018), Nanoporous conducting covalent organic polymer (COP) nanostructures as metal-free high performance visible-light photocatalyst for water treatment and enhanced CO<sub>2</sub> capture, J. Phys. Chem. C, 122, 274-284 (DOI: 10.1021/acs.jpcc.7b07709)

[108] Xu N., Wang R. L., Li D. P., Meng X., Mu J. L., Zhou Z. Y., Su Z.
M. (2018), A new triazine-based covalent organic polymer for efficient photodegradation of both acidic and basic dyes under visible light, Dalton Trans., 47, 4191-4197 (DOI: 10.1039/C8DT00148K)

[109] Cao Y., Liu W., Qian J., Cao T., Wang J., Qin W. (2019), Porous organic polymers containing a sulfur skeleton for visible light degradation of organic dyes, Chem. - Asian J., 14, 2883 (DOI: 10.1002/asia.201900477)



Investigation of the Role of Charge Density and Surface Area of High-Performance ionic Porous Organic Polymer Adsorbents and their Antibacterial Actions

#### **3.1. Introduction**

With the rapid growth of human civilization, industrialization is also increasing exponentially. Rapid industrialization around the globe is one of the leading causes of environmental pollution, slowly threatening the sustainability of life on Earth. Among various types of environmental pollution, water, and air pollution are two of the main stakeholders around the globe, and they are a direct threat to human health *[1]*.

The toxic effects of several inorganic and organic pollutants are already discussed in the previous chapters. Along with several heavy metal-based oxo-anions and organic dyes, radioactive iodine and iodides are other potential pollutants. Though iodine has excellent antibacterial effects and is used widely for medical purposes, some nuclear waste contains radioactive iodide residues <sup>129</sup>I and <sup>131</sup>I, which, due to their very high volatility, are very hard to control. Due to their very volatile nature, they might diffuse into the air and ultimately reach the human metabolic system, causing several problems [2,3]. Other than that, iodine is also widely used in medical science. The medical waste was eventually dumped on several water bodies, causing iodine contamination in the water. An efficient strategy to mitigate such pollution is urgently needed in this scenario. Though ionic porous organic polymers have established themselves as one of the better adsorbents in the field of wastewater remediation in the last couple of years [4-7], the research is still in its infancy, and there is an urgent need to develop an efficient strategy to design a highly effective iPOP-based adsorbent. It is well known from earlier studies that the surface properties of a porous material play a very crucial role in determining its adsorption properties [8]. The role of higher surface area in the porous adsorbents in achieving higher adsorption for scavenging foreign elements is well established [9,10]. The structure activity relationship is a crucial phenomenon that often remains unnoticed when designing iPOP-based polymeric adsorbents. However, the charge density in the active sites of the adsorbents is a critical factor that almost remains unexplored. Charge

density in the active sites of the ionic polymers might play an important role in achieving higher adsorption capacity as it can increase the effective surface charge close to the binding site in the materials. Using smaller building blocks could be an effective strategy in developing iPOPs with higher charge density in the binding sites. The use of smaller building units will put the cationic sites in proximity, thereby helping achieve a higher charge density in the binding site [11]. At the same time, choosing an electron-rich building block over a comparatively less electron-rich entity might also decrease the positive charge density at the active binding site, hampering the adsorption property of polymeric adsorption. Therefore, integrating high positive charge density around the active binding site by choosing an appropriate building block and the high surface area in an ionic porous organic polymer might result in an efficient polymer adsorbent.

In this Chapter, to establish the hypothesis, three ionic porous organic polymers (iPOPs), **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**, have been designed and synthesized by using a viologen-based cationic building block ZN-NH<sub>2</sub>. Three building blocks with different sizes and electron densities were considered. All the polymers were very efficient in adsorbing inorganic anions and anionic organic dyes from water and iodine vapor in the solid state. Among the three polymers, **iPOP-ZN1** appears to be the best adsorbent owing to its higher positive charge density at the active center and higher surface areas. Additionally, considering the antibacterial properties of iodine, the antibacterial actions of the iodine-loaded polymers were further explored. All the iodine-loaded polymers show impressive antibacterial properties against *E. coli*, *B. subtilis*, and *H. pylori*.

#### **3.2 Experimental section**

#### 3.2.1. Materials and methods

4,4'-Bipyridine, 2,4-dinitro-chlorobenzene, p-phenylenediamine, 4-(Bromomethyl)benzonitrile, 1,3,5-Tribromobenzene, Cyanuric chloride were obtained from Sigma-Aldrich. All the other chemicals, dyes, and

solvents were purchased locally and used without further purifying. DI water was used to prepare all the solutions. For characterizing the materials the same characterization techniques were used as mentioned in Chapter 2, 2.2.1 section



**Scheme 3.1.** Synthesis of 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'diium chloride (ZN-NH2)

# **3.2.2.** Synthesis of 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'diium dichloride

4,4'-Bipyridine (1.56 g, 10 mmol) and 2,4-dinitro-chlorobenzene (5.66 g, 28 mmol) were dissolved in 15 mL acetonitrile, and the solution was refluxed for 24 h. After completion of the reaction, the obtained precipitate was collected by filtration and washed with hot acetonitrile and hexane to obtain the product as a yellowish solid. <sup>1</sup>H NMR (400.13 MHz, 298 K, D<sub>2</sub>O):  $\delta$  9.44 (d, 4H), 9.37 (s, 2H), 8.91 (d, 2H), 8.89 (d, 4H), 8.27 (d. 2H). <sup>13</sup>C NMR (100.16 MHz, 298K, D<sub>2</sub>O):  $\delta$  152.59, 149.87, 146.85, 142.81, 138.23, 131.10, 130.73, 127.54, 122.80.



**Figure 3.1.** <sup>1</sup>H NMR of 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'diium dichloride.



**Figure 3.2.** <sup>13</sup>C NMR of 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride.

# 3.2.3. Synthesis of 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (ZN-NH<sub>2</sub>)

1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (500 mg, 0.89 mmol) and p-phenylenediamine (281 mg, 2.6 mmol) were dissolved in 15 mL of ethanol and the solution was heated to reflux for 12 h. After completion of the reaction, the solvent was removed using a rotary evaporator to obtain the desired product as a dark red solid. (Product yield: 336mg, 96%). <sup>1</sup>H NMR (400.13 MHz, 298 K, D<sub>2</sub>O):  $\delta$  9.20 (d, 4H), 8.62 (d, 4H), 7.52 (d, 4H), 6.98 (d, 4H), 5.37 (s, 4H). <sup>13</sup>C NMR (100.16 MHz, 298 K, D<sub>2</sub>O):  $\delta$  150.33, 149.17, 144.54, 133.37, 126.67, 125.04, 116.68.



**Figure 3.3.** <sup>1</sup>H NMR 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride.



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 Chemical Shift (ppm)

**Figure 3.4.** <sup>13</sup>C NMR spectra of 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride.

# **3.2.4.** Synthesis of 2,4,6-tris (-(bromomethyl) phenyl)-1,3,5-triazine (TTRB-Br)

2.0 g of 4-bromomethyl benzonitrile was taken in an oven-dried two-neck round bottom flask, and CF<sub>3</sub>SO<sub>3</sub>H (3.0 mL) was injected at 0 °C. After some time, the ice bath was removed, and the reaction mixture was allowed to stir at room temperature for 24 h. After completion of the reaction, the reaction mixture was added to ice-cold water and neutralized with a dropwise addition of liquid NH<sub>3</sub>. The obtained precipitate was filtered and dried under a vacuum to get the product as a white solid. Yield: 94%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.64 (d, 6H), 7.51 (d, 6H), 4.52 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  171.18, 142.30, 136.11, 129.45, 124.39, 32.71.



**Figure 3.5.** <sup>1</sup>H NMR of 2,4,6-tris (-(bromomethyl) phenyl)-1,3,5-triazine (TTRB-Br).



**Figure 3.6.** <sup>13</sup>C NMR of 2,4,6-tris (-(bromomethyl) phenyl)-1,3,5-triazine (TTRB-Br).

#### 3.2.5. Synthesis of iPOP-ZN1, iPOP-ZN2 and iPOP-ZN3

1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (**ZN-NH**<sub>2</sub>) (261 mg) and NaHCO<sub>3</sub> (213 mg) were charged in an oven-dried two-neck round bottom flask under N<sub>2</sub> atmosphere and 5 mL dry DMF was added. The reaction mixture was stirred for two hours. To the mixture, 1,3,5-Tribromobenzene (**TBrBnZ**) (100 mg) in dry DMF (5 mL) was added dropwise, and the final reaction mixture was refluxed for 24 h. It was then cooled to room temperature. The obtained precipitate was filtered and washed with DMSO, DMF, brine, water, acetone, methanol, and DCM. The obtained dark-colored solid was dipped in a 1:1 mixture of methanol and chloroform for two days. Finally, the solid was filtrated and dried at 100°C for 24 h to obtain the desolvated **iPOP-ZN1**.

**iPOP-ZN2** and **iPOP-ZN3** were synthesized by following the same procedure. In the synthesis of **iPOP-ZN2**, Cyanuric chloride (**Cn-Cl**) (100 mg) was reacted with 445 mg of 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (**ZN-NH**<sub>2</sub>) and 365 mg NaHCO<sub>3</sub>.

For synthesizing **iPOP-ZN3** 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (**TTRB-Br**) (100 mg) was reacted with 140 mg of 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (**ZN-NH**<sub>2</sub>) and 115 mg NaHCO<sub>3</sub>.



Scheme 3.2. Synthesis of iPOP-ZN polymers

# **3.2.6.** Procedures for the adsorption of anionic pollutants from aqueous solution and time-dependent study

For this study similar procedure was followed as mentioned in **Chapter 2-2.2.5 section**. In this study, 0.5 mM  $Cr_2O_7^{2-}$ ,  $MnO_4^{-}$ , and  $I_3^{-}$  as inorganic pollutants, and 50 ppm methyl orange (MO) and amaranth (AMR) organic dyes.  $I_3^{-}$  was prepared by dissolving equimolar  $I_2$  and KI in water.

# **3.2.7.** Selective adsorption of oxo-anions in the presence of competitive anions

Five widely found anions in wastewaters (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>) in different concentrations with respect to the targeted ions [1:0 (2.5 mM:0 mM), 1:1 (2.5 mM:2.5 mM), 1:10 (2.5 mM:25 mM), 1:100 (2.5 mM:250 mM) and 1:1000 (2.5 mM:2500 mM)] were introduced as interfering ions along with the targeted ions to check the selectivity of the adsorbent polymers. 2.5 mg of the adsorbent polymer was dispersed in 5 mL of the prepared solution and stirred for 12 h. After 12 h, the supernatant was collected by filtration. The concentration was adjusted to 0.5 mM with

respect to the standard solution, and the concentration was evaluated using UV-vis spectroscopy.

#### 3.2.8. The pseudo-second-order kinetic model

The pseudo-second-order kinetic model was used to obtain the kinetic data. The details are mentioned in **Chapter 2- 2.2.9 section**.

#### 3.2.9. Langmuir/ Freundlich adsorption isotherm experiment

This experiment was performed similarly as mentioned in **Chapter 2-2.2.10** section.

#### 3.2.10. Reusability test of polymers

After capturing the pollutants, the adsorbent polymers are reactivated by immersing them in a saturated KCl solution overnight. The polymers were then washed with water, MeOH, and chloroform, dried at 100° C for 6 h, and used directly in the next cycle. Experimental details are mentioned in **Chapter 2-2.2.11 section**.

# **3.2.11.** pH-dependent capture study of the inorganic pollutants and anionic dyes

For this study, water solutions of different pH (2-10) were prepared using HCl and NaOH. 0.5 mM of anionic solutions and 50 ppm of the dye solutions were prepared using the acidic and basic solutions. In the experiment, 2.5 mg of the polymers were dispersed in 5 ml of the solutions and same experiment was repeated as mentioned and the solutions were left for the exact time as mentioned in 3.2.6 section. After that, the polymers were separated from the solutions and were analyzed using UV-vis spectroscopy. The % of removal was calculated using the given formula:

$$D_t = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\%$$

# **3.2.12.** Selectivity study of the polymers towards targeted inorganic in the presence of competing ions in acidic and basic solutions.

This experiment was performed following the same procedure mentioned in the **2.2.7 section**. Here, the solutions were prepared with water of different pH, and  $Br^{-}$ ,  $SO_4^{2-}$ , and  $PO_4^{3-}$  were used in different concentrations as competing ions.

#### 3.2.13. Preparation of iPOP-ZN1 coated nylon membrane filter

100 mg of **iPOP-ZN1** was dispersed in 50 mL water and sonicated until a homogeneous dispersion was obtained. 10 ml of the polymeric dispersion was injected into the nylon filter; the 1<sup>st</sup> layer of polymer-coated nylon filter was dried at 80 °C for 12 h. The same process was repeated for another 4 times. The polymer-coated nylon membrane was then used for further applications.

#### 3.2.14. Procedure for iodine capture in vapor-state

In this study, a small glass vial containing 10 mg of the desolvated polymers was placed in a glass chamber containing an excess amount of iodine granules and sealed properly. The whole chamber was placed on a heating plate at 75°C, and the weight of the glass vial containing polymer was measured gravimetrically every 2 h interval. The iodine uptake in the vapor state was evaluated using the following equation:

$$\alpha = \frac{m_t - m_0}{m_0} \times 100\%$$

where  $\alpha$  is the I<sub>2</sub> uptake capacity of the polymers, m<sub>t</sub> and m<sub>0</sub> represent the initial mass weight and mass weight at time t of adsorption of the solid polymeric adsorbents.

#### 3.2.15. Reusability of iodine-loaded polymers

Iodine-loaded polymers were immersed in 10 mL ethanol and allowed to stand. Every 2h, the brown-colored ethanol solution was replaced with fresh

ethanol until a clear ethanol solution was obtained. The polymers were then collected by filtration, dried at 100°C, and used for the next cycle.

#### 3.2.16. Computational methodology

The optimized geometries were obtained using the density functional M062X-D3 *[12,13]* (incorporating dispersion corrections) using the 6-311G(d,p) basis set for C, N, O, and H, and SDD for Cr, Mn, and I atoms. Vibrational frequencies were computed to confirm the optimization of the geometries to a minimum. The binding energies of various iPOPs with the interacting molecules were computed using the following:

Binding energy =  $E_{Complex} - (E_{iPOP} + E_{Binder})$ 

 $E_{Complex}$ ,  $E_{iPOP}$ , and EBinder are the energies of the iPOP-Binder complex, iPOP, and the interacting molecule (binder), respectively. All calculations were performed using Gaussian 16 software [14].

#### 3.2.17. Antibacterial study

#### **3.2.17a. Bacterial strains**

Two gram-negative bacterial strains were used to check for the antibacterial activity of polymer compounds. *Helicobacter pylori* strain (I10) was a kind gift from Dr. Asish Kumar Mukhopadhyay (NICED, ICMR, Kolkata, India). *Escherichia coli* (DH5α) was used in this study. *E. coli* was cultured in Luria Broth agar (Becton, Dickinson and Company, New Jersey, USA), and *Bacillus subtilis* was cultured in Nutrient broth agar, incubated at 37 °C for 12 h. Pure colonies were picked up and cultured in Luria broth media (Becton, Dickinson and Company, New Jersey, USA) overnight in a rotary shake of 220 rpm at 37°C. Similarly, I10 strain was cultured in Brain Heart Infusion (BHI) agar (Becton, Dickinson and Company, New Jersey, USA) augmented with 10% FBS and selective antibiotics such as Trimethoprim (Sigma, life sciences, Sigma-Aldrich, St. Louis, USA, C8145-

100MG), Vancomycin (Sigma, life sciences, Sigma-Aldrich, St. Louis, USA, SBR00001-10ML) and Amphotericin B (Himedia, Mumbai, India, TC019-1G). Pure colonies were obtained and inoculated in BHI broth (Sigma, Life Sciences, Sigma-Aldrich, St. Louis, USA) supplemented with 10% FBS (Himedia, Mumbai, India) and selective antibiotics. I10 was grown at 37 °C with micro-aerophilic conditions, as mentioned in earlier literature [15-16].

#### 3.2.17b. Disc diffusion method

The antibacterial activity of the compounds was tested using the disk diffusion method [17,18]. The E. coli, B. subtilis, and I10 bacterial strains were spread on the LB agar, NB agar, and BHI agar plates, respectively. The I<sub>2</sub>@iPOP-ZN1, I<sub>2</sub>@iPOP-ZN2, and I<sub>2</sub>@iPOP-ZN3 compounds were dissolved in H<sub>2</sub>O (Himedia, Mumbai, India). The compound concentration was 100  $\mu$ g/ $\mu$ L, and 10  $\mu$ L of each solution was impregnated into sterile, blank discs of 6 mm diameter. H<sub>2</sub>O was used as a negative control. Ampicillin (Himedia, Mumbai, India, MB104-5G) (100  $\mu$ g/ $\mu$ L), Kanamycin (Himedia, Mumbai, India, TC136-5G) (50  $\mu$ g/ $\mu$ L) and Amoxicillin (Sigma, life sciences, Sigma-Aldrich, St. Louis, USA, A8523-1G) (1  $\mu$ g/ $\mu$ L) were used as positive control in E. coli, B. subtilis and I10 strain respectively. The plate was incubated at 37 °C for 24 h in their respective conditions, and the zone of inhibition was measured. Antimicrobial activity was determined by measuring the zone of inhibition diameter (mm) around the discs. The assay was performed twice.

#### **3.2.17c. Detection of ROS in bacterial cell**

Intracellular reactive oxygen species (ROS) levels were assessed through the 2',7'-dichlorodihydrofluorescein diacetate (H2DCFDA) method [19]. Briefly, compound treatment was given for 24h timepoint. After that, bacteria were subjected to H2DCFDA (10  $\mu$ M) for 30 mins in the dark. The net fluorescence was measured after negating the autofluorescence from

bacterial cells and background fluorescence from the buffer. Subsequently, the fluorescence intensity was measured using a microplate reader at excitation and emission wavelengths of 488 nm and 530 nm, respectively. The experiment was performed in triplicate.

#### **3.3. Results and Discussion**

In designing the polymers, it was hypothesized that the larger building blocks might lower the positive charge density around the active binding site of the polymeric adsorbent. At the same time, the introduction of heteroatom-containing building blocks like triazine in place of benzene might also decrease the positive charge density of the polymer. In this regard, three iPOPs, **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**, using three building blocks of identical sizes, 1,3,5-tri bromobenzene (TBrBnZ), Cyanuric chloride (Cn-Cl), and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (TTRB-Br) have been designed. Compared to the first two building blocks, owing to the larger size of TTRB-Br, it might have the lowest positive charge density in its active site compared to the other two polymers. Among the first two building blocks, the presence of a triazine ring in **iPOP-ZN2** might impart a slightly higher electron-rich environment in its active site compared to the **iPOP-ZN1**.

#### 3.3.1. Characterization of iPOPs

In designing the polymers, it was hypothesized that the larger building blocks might lower the positive charge density around the active binding site of the polymeric adsorbent. At the same time, introducing heteroatom-containing building blocks like triazine in place of benzene might also decrease the positive charge density of the polymer. In this regard, three iPOPs, **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**, have been designed using three building blocks of identical sizes, 1,3,5-tri bromobenzene (TBrBnZ), Cyanuric chloride (Cn-Cl), and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (TTRB-Br). Compared to the first two building blocks, owing to the

larger size of TTRB-Br, it might have the lowest positive charge density in its active site compared to the other two polymers. Among the first two building blocks, a triazine ring in **iPOP-ZN2** might impart a slightly higher electron-rich environment in its active site compared to **iPOP-ZN1**. Three polymers, **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3** were synthesized by reacting 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (ZN-NH<sub>2</sub>) with 1,3,5-tri bromobenzene (TBrBnZ), Cyanuric chloride (Cn-Cl), and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (TTRB-Br) respectively, in DMF in the presence of NaHCO<sub>3</sub> at 100°C for 24 h to obtain polymers as insoluble dark brown solid. The successful synthesis of the polymers was confirmed by FTIR and solid-state <sup>13</sup>C-NMR spectroscopy.

In the <sup>13</sup>C-CPMAS NMR spectra, the peaks in the range of 100-155 ppm represent the presence of aromatic carbons in the polymers (Figure 1a-1c). Sharp peaks at 165.49 ppm in **iPOP-ZN2** and 169.41 ppm in **iPOP-ZN3** indicate the presence of triazine carbon (Figure 1b and 1c). The peak at 59.37 in **iPOP-ZN3** represents the methylene (-CH<sub>2</sub>-) functionality in the polymer (Figure 3.7).



Figure 3.7. Solid state <sup>13</sup>C-CPMAS NMR spectra of **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**.

In the FTIR spectra of the **iPOP-ZN1**, the complete disappearance of the aromatic C-Br stretching band of TBrBnZ at 648 cm<sup>-1</sup> confirms the successful synthesis of the polymer. The bands at 1594 cm<sup>-1</sup> and 1622 cm<sup>-1</sup> represent the polymer's N-H bending and C=C stretching (Figure 3.8a). In **iPOP-ZN2**, the characteristic C-Cl stretching frequency of the Cn-Cl

molecule at 833 cm<sup>-1</sup> almost disappears in the polymer, confirming its successful synthesis. Additionally, the bands at 1328 cm<sup>-1</sup> and 1505 cm<sup>-1</sup> represent the presence of the triazine unit in the polymer. The bands at 1602 cm<sup>-1</sup> and 1624 cm<sup>-1</sup> correspond to the bending of N-H and stretching of the C=C bond (Figure 3.8b). In **iPOP-ZN3**, the band at 598 cm<sup>-1</sup> that represents the C-Br stretching in the starting material is absent in the polymer, confirming the complete consumption of the starting material. The bands at 1357 cm<sup>-1</sup> and 1506 cm<sup>-1</sup> confirm the presence of the triazine unit, further clarifying the successful synthesis of the polymer (Figure 3.8c). A broad band at 3336 cm<sup>-1</sup> in **iPOP-ZN1** and **iPOP-ZN2** and 3332 cm<sup>-1</sup> in **iPOP-ZN3** represents the N-H stretching frequencies of the secondary amine center of the polymers.



Figure 3.8. FTIR spectra of (a) iPOP-ZN1, (b) iPOP-ZN2, and (c) iPOP-ZN3.

The broad spectrum obtained in the PXRD analysis confirms the amorphous nature of all the polymers (Figure 3.9) [20].

**Chapter 3** 



Figure 3.9. PXRD data for iPOP-ZN1, iPOP-ZN2 and iPOP-ZN3.

The morphology of the synthesized polymers was investigated using FESEM imaging (Figure 3.10). The FESEM imaging shows flake-like morphology of **iPOP-ZN1**, whereas **iPOP-ZN2** and **iPOP-ZN3** appear to be spherical and aggregated spherical, respectively.



Figure 3.10. FESEM images of iPOP-ZN1, iPOP-ZN2 and iPOP-ZN3.

The thermal stability of the polymers was investigated by the thermogravimetric analysis (TGA). The TGA data shows all the polymers were stable over 275 °C. The minimal weight loss of the polymers up to 100 °C may be due to the removal of entrapped solvent molecules from the pores of the polymers (Figure 3.11).



Figure 3.11. TGA profiles of the polymers.

Additionally, to check the robustness of the polymers, the polymers were treated in several lab solvents, showing the insoluble nature of the polymers with a negligible loss in the residual weight percentage (Figure 3.12). Almost the same pattern in the FTIR profiles of the solvent-treated polymers confirms their high stability and robust nature. (Figure 3.13).



**Figure 3.12.** The residual weight percentage of the polymers after exposure to different solvents.



**Figure 3.13.** Comparative FTIR spectra of the polymers in various lab solvents, showing the chemical robustness of the polymers. (a) **iPOP-ZN1** (b) **iPOP-ZN2** and (c) **iPOP-ZN3**.

The EDX analysis shows the presence of C, N, and Cl in the polymers (Figure 3.14).



155 | P a g e

# Figure 3.14. EDX profiles of (a) iPOP-ZN1 (b) iPOP-ZN2 and (c) iPOP-ZN3

The XPS survey spectra further confirmed the presence of all the elements (Figure 3.15).



Figure 3.15. XPS survey spectra of the polymers.

The specific surface area and porosity of the synthesized polymers were determined from the  $N_2$  adsorption-desorption experiments at 77 K (Figure 3.16a).





It was observed that the amount of  $N_2$  adsorption decreases significantly in the order **iPOP-ZN1**> **iPOP-ZN2**> **iPOP-ZN3**, and so the BET surface area, average pore size, and pore volume (Table 3.1). The BET surface area

for **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3** appeared to be  $35.052 \text{ m}^2\text{g}^{-1}$ ,  $26.726 \text{ m}^2\text{g}^{-1}$ , and  $11.620 \text{ m}^2\text{g}^{-1}$ , respectively, whereas pore size distribution calculated from the BJH method was 2.81 nm, 2.89 nm, and 2.79 nm, respectively (Figure 3.16b).

**Table 3.1.** Comparative data regarding avg. pore size, avg. pore volume andsurface area of **iPOP-ZN1**, **iPOP-ZN2** and **iPOP-ZN3**.

Parameter	iPOP-ZN1	iPOP-ZN2	iPOP-ZN3
N <sub>2</sub> uptake (77K) (cc/g)	295.43	183	55.46
$CO_2$ uptake (298K) (cc/g)	20.47	17.25	16.73
$CO_2$ uptake (273K) (cc/g)	26.5	25.14	22.02
Avg. pore size (nm)	6.86	3.28	2.98
Avg. pore vol. (cc/g)	0.486	0.287	0.0807
BET surface area $(m^2/g)$	35.052	26.726	11.620
Langmuir surface area (m <sup>2</sup> /g)	1289.075	593.277	160.760



Figure 3.17. CO<sub>2</sub> adsorption-desorption isotherm at 273K and 298K.

The CO<sub>2</sub> adsorption capacity of the polymers at 298 K and 273 K were further investigated. It was observed that the adsorption capacities are 20.47 cc/g, 17.25 cc/g and 16.73 cc/g at 298K and 26.5 cc/g, 25.14 cc/g and 22.02 cc/g at 273K for **iPOP-ZN1**, **iPOP-ZN2** and **iPOP-ZN3**.

#### 3.3.2. Anionic contaminants capture from water

Owing to the high thermal and chemical stability and cationic nature of the polymers, these polymers were used as polymeric adsorbents to capture several anionic pollutants. In this regard,  $I_3^-$ ,  $Cr_2O_7^{2-}$ , and  $MnO_4^-$  were taken as inorganic ions, and Methyl Orange (MO) and Amaranth (AMR) were considered model organic pollutants.

To 0.5 mM aqueous solution of  $I_3^-$ , 0.5 mg/mL of the desolvated polymers was added, and the solution was monitored under UV-vis spectroscopy in one-minute intervals (Figure 3.18a-c).



**Figure 3.18.** UV-vis spectrum of aqueous  $I_3^-$  solution in the presence of (a) **iPOP-ZN1** (b) **iPOP-ZN2** (c) **iPOP-ZN3** at 1 min intervals. Condition: Initial conc. of the  $I_3^-$  (C<sub>0</sub>) = 0.5 mM, m<sub>adsorbent</sub>/V<sub>solution</sub> = 0.5 mg/mL, contact time-4 mins for **iPOP-ZN1** and **iPOP-ZN2** and 5 min for **iPOP-ZN3**.

It was observed that over 85% of I<sub>3</sub><sup>-</sup> gets adsorbed within one minute in the case of **iPOP-ZN1** and **iPOP-ZN2**, and over 80% in the case of **iPOP-ZN3** and within 5 minutes, around 97.4%, 95.67%, and 92.8% of iodine gets adsorbed in **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3** respectively (Figure 3.19a). All the adsorption follows pseudo-second-order kinetics with rate constants 0.076 mgg<sup>-1</sup>min<sup>-1</sup>, 0.0026 mgg<sup>-1</sup>min<sup>-1</sup> and 0.000368 mgg<sup>-1</sup>min<sup>-1</sup> (Figure 3.19b).



**Figure 3.19.** (a) Pseudo second model fitting for  $I_3^-$  adsorption by the polymers (b) % removal of  $I_3^-$  from water with time.

The maximum iodine adsorption capacity from the water was calculated using the Langmuir adsorption isotherm model. The maximum adsorption capacities for **iPOP-ZN1**, **iPOP-ZN2** and **iPOP-ZN3** were 3880.43 mgg<sup>-1</sup>, 2296.86 mgg<sup>-1</sup> and 1017.37 mgg<sup>-1</sup>, respectively (Figure 3.20). Among them, the adsorption capacity of **iPOP-ZN1** is one of the highest values in the literature (Table 3.2). The good arrangement of the experimental results with the Langmuir adsorption isotherm model compared to the Freundlich adsorption model indicates the monolayer adsorption of iodide ions in the polymeric matrices (Figure 3.20).



**Figure 3.20.** Langmuir and Freundlich adsorption isotherm model for I<sub>3</sub><sup>-</sup>. (a)**iPOP-ZN1** (b)**iPOP-ZN2** and (c)**iPOP-ZN3**.
Material	Maximum	Selectivity	Reference		
	adsorption				
	capacity				
iPOP-ZN1	3880.41 mg/g	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-,</sup>			
iPOP-ZN2	2296.86 mg/g	PO <sub>4</sub> <sup>3-</sup>	This work		
iPOP-ZN3	1017.37 mg/g				
іРОР-Вру	3921.47 mg/g	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2023, 15, 23, 28453–28464		
Compound-	3.5 g/g				
1		Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces		
Compound- 2	3.04 g/g		2021, 13, 34188–34196		
CaCOP1	<mark>240 wt%</mark>				
CaCOP2	<mark>281 wt%</mark>	ND	Mater. Chem. Phys. 2020, 239,		
CaCOP3	310 wt%		<mark>122328.</mark>		
SCNU-Z4	CNU-Z4 331.7 mg/g N		Inorg. Chem. Front. 2021, 8, 1083–1092.		
TNHCP1	729 mg/g				
TNHCP2	854 mg/g	ND	Sep. Purif. Tech. 2021, 257,		
ТNНСР3	819 mg/g		11/923		
CalCOP1	2.318 g/g				
CalCOP2	1.758 g/g	ND	J. Mater. Sci. 2020, 55, 1854–		
CalCOP3	0.346 g/g		1864.		
CalCOP4	0.156 g/g				

**Table 3.2.** Comparison table of  $I_3$ <sup>-</sup> uptake with well-studied literature report.

The iodide-adsorbed polymers were further reactivated by soaking them in a saturated KCl solution. The polymers were then reused for four consecutive cycles. The results show almost no changes in the adsorption capacities after four cycles (Figure 3.21).



**Figure 3.21.** Reusability study of the polymeric adsorbent for four consecutive cycles.



**Figure 3.22**. UV-vis spectrum of  $Cr_2O_7^{2-}$  solution in the presence of (a) **iPOP-ZN1** (b) **iPOP-ZN2** (c) **iPOP-ZN3**. Condition: Initial conc. of the  $Cr_2O_7^{2-}$  (C<sub>0</sub>) = 0.5 mM, m<sub>adsorbent</sub>/V<sub>solution</sub> = 0.5 mg/mL, contact time 5 mins for **iPOP-ZN1**, 10 mins for **iPOP-ZN2** and 12 mins for **iPOP-ZN3**.

In the adsorption study of  $Cr_2O_7^{2-}$ , in 3 mL of 0.5 mM K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution,1.5 mg of the desolvated polymers were dispersed. The removal of  $Cr_2O_7^{2-}$  from water was monitored with the help of UV-vis spectroscopy (Figure 3.22).

 $MnO_4^-$  was chosen as a nonradioactive surrogate of  $TcO_4^-$  due to operational difficulties of radioactive  $TcO_4^-$  ions in the laboratory [21]. Here, 1.5 mg of desolvated polymers were dispersed in 3 mL 0.5 mM KMnO<sub>4</sub> solution, and the supernatant was analyzed under UV-vis spectroscopy in one-minute intervals (Figure 3.23)



**Figure 3.23.** UV-vis spectrum of MnO<sub>4</sub><sup>-</sup> solution in the presence of (a) **iPOP-ZN1** (b) **iPOP-ZN2** (c) **iPOP-ZN3**. Condition: Initial conc. of the MnO<sub>4</sub><sup>-</sup> (C<sub>0</sub>) = 0.5 mM,  $m_{adsorbent}/V_{solution} = 0.5$  mg/mL, contact time- 4 mins for **iPOP-ZN1** and **iPOP-ZN2** and 5 mins for **iPOP-ZN3**.

A steady decrease in the characteristic peak of both ions with increasing time indicates the continuous decrease in the concentration of the ions with time in water.

Among the three polymers, **iPOP-ZN1** was the fastest to remove  $Cr_2O_7^{2-}$  from water, and almost 99% removal was observed within 5 minutes. Whereas it takes 10 minutes and 12 minutes for **iPOP-ZN2** and **iPOP-ZN3** to remove 99% of  $Cr_2O_7^{2-}$  from water (Figure 3.24a). The adsorption kinetics was very fast for all three polymers for MnO<sub>4</sub><sup>-</sup>, and it took only 4 minutes to remove around 98% of MnO<sub>4</sub><sup>-</sup> (Figure 3.24b). Removal of both oxo-anions follows the pseudo-second-order kinetics in all three polymers (Figure 3.24c and d).



**Figure 3.24.** % Removal of (a)  $Cr_2O_7^{2-}$  (b)  $MnO_4^{-}$  with time in the presence of the polymers. Pseudo-second-order kinetic model fitting for removing (c)  $Cr_2O_7^{2-}$  (d)  $MnO_4^{-}$  by the polymers.

The maximum  $Cr_2O_7^{2-}$  and  $MnO_4^-$  adsorption capacities of the polymers were further investigated using Langmuir adsorption isotherm model.



**Figure 3.25.** Langmuir and Freundlich adsorption isotherm for  $Cr_2O_7^{2-}$ .

**Table 3.3.** Comparison table of  $Cr_2O_7^{2-}$  uptake with some well-studied examples in the literature.

Material	Maximum Material adsorption capacity (mg/g)		Reference		
iPOP-ZN1 759.97 iPOP-ZN2 558.496		Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-,</sup> PO <sub>4</sub> <sup>3-</sup>	This work		
iPOP-ZN3	333.83				
iPOP-ANT	330.75	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	Mater. Chem. Front., 2022,6, 3070- 3083		
FIR-53	100	ND	Chem. Mater. 2015, 27, 205		
1-Br	128	ND	Chem. Commun. 2017, 53, 1860.		
CON-LDU-2	325	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2019, 11, 46197		
CON-1	293	ND	New J. Chem. 2019, 43, 11604.		
UiO-66- NH <sub>2</sub> @silica	277.4	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	J. Mater. Chem. A 2018, 6, 2742.		
FJI-C11	321	ND	Dalton Trans. 2019, 48, 6680.		
1-NO3-OH	154.8	CIO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CI <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	Dalton Trans. 2018, 47, 9103.		
1-SO <sub>4</sub>	116	ND	Angewandte Chemie 2016, 128, 7942		
1-Cl	28.7	CIO <sub>4</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	Inorg. Chem. 2018, 57, 11746		
ZJU-101	245	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> l <sup>-</sup> , F <sup>-</sup>	Chem. Commun. 2015, 51, 5264		
QUST-iPOP-1	396	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2021, 13, 39404.		
{Zn <sub>1.5</sub> L} <sub>n</sub>	469	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	Journal of Hazardous Materials 2021, 405, 124242.		
C-NSA <sub>Naph</sub> -HCP@Br	745	F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> OAc <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> PO <sub>4</sub> <sup>3</sup>	J. Mater. Chem. A 2018, 6, 20653		



The maximum adsorption capacities  $(Q_m)$  for  $Cr_2O_7^{2-}$  was 759.97 mgg<sup>-1</sup>, 558.496 mgg<sup>-1</sup> and 333.83 mgg<sup>-1</sup> for **iPOP-ZN1**, **iPOP-ZN2** and **iPOP-ZN3** respectively (Figure 3.25). Among them,  $Cr_2O_7^{2-}$  adsorption capacity of **iPOP-ZN1** is one of the highest values in the literature (Table 3.3).

Whereas the calculated  $Q_m$  for MnO<sub>4</sub><sup>-</sup> were 4085.46 mgg<sup>-1</sup>, 2917.67 mgg<sup>-1</sup>, and 1516.87 mgg<sup>-1</sup> for **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3** respectively (Figure 3.26), which are also comparable with some well-studied literature reports (Table 3.4).



Figure 3.26. Langmuir and Freundlich adsorption isotherm for MnO<sub>4</sub><sup>-</sup>.

**Table 3.4.** Comparison table of  $MnO_4^-$  uptake with some well-studied examples in the literature.

Material	Maximum adsorption	Selectivity	Reference		
	capacity(mg/g)				
iPOP-ZN1	4085.46	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> ,	This work		
iPOP-ZN2	2917.67	SO4 <sup>2-,</sup> PO4 <sup>3-</sup>			
iPOP-ZN3	1516.87				
iPOP-ANT	5372	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	Mater. Chem. Front. 2022,6, 3070-3083.		
Ox-FVESP	1428.57	ND	Sci Rep. 2022, 12, 4547.		
[Cu <sub>3</sub> Cl(L)(H <sub>2</sub> O) <sub>2</sub> ]·Cl· 4DMA·8H <sub>2</sub> O	106 ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> PF <sub>6</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub>		Dalton Trans. 2021, 50, 3832.		
ZrIT-1	276.6	ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> ,BF <sub>4</sub> <sup>-</sup>	Inorg. Chem. 2022, 61, 7103.		
SLUG-21	283	NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	J. Am. Chem. Soc. 2010, 132, 7202.		
SCNU-Z1-CI	313.5	Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> NO <sub>3</sub> <sup>-</sup> , N <sub>3</sub> <sup>-,</sup> SO <sub>4</sub> <sup>2-</sup>	Inorg. Chem. 2019, 58, 2899.		
Compound-1	297.3	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	Chem. Sci. 2018, 9, 7874.		
Ag(btr)·PF <sub>6</sub> ·0.5CH <sub>3</sub> CN	163	NO <sub>3</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	Inorg. Chem. 2014, 53, 12127		
QUST-iPOP-1	514.86	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2021, 13, 39404.		

Similar experiments were performed to investigate the capabilities of the polymeric adsorbents in removing anionic organic dyes from wastewater. In a cuvette of 3 mL 50 ppm of dye solution (MO and AMR), 1.5 mg of the desolvated polymers were dispersed, and the concentration of the supernatant solution was monitored under UV-vis spectroscopy in one-minute intervals. A steady decrease in the characteristic peak of the dyes with time suggested a steady decrease in the concentration of the dyes with time (Figures 3.27 and 3.28).



**Figure 3.27.** UV-vis spectrum of Methyl Orange (MO) solution in the presence of (a) **iPOP-ZN1**, (b) **iPOP-ZN2**, (c) **iPOP-ZN3**. Condition: Initial conc. of the MO ( $C_0$ ) = 50 ppm, adsorbent/V solution = 0.5 mg/mL, contact time: 5 mins for **iPOP-ZN1**, 6 mins for **iPOP-ZN2**, and **iPOP-ZN3**.



**Figure 3.28.** UV-vis spectrum of Amaranth (AMR) solution in the presence of (a) **iPOP-ZN1** (b) **iPOP-ZN2** (c) **iPOP-ZN3**. Condition: Initial conc. of the AMR ( $C_0$ ) = 50 mM, adsorbent/V solution = 0.5 mg/mL, contact time: 5 mins for **iPOP-ZN1**, 7 mins for **iPOP-ZN2**, and 10 mins for **iPOP-ZN3**.

In the case of both the dyes, **iPOP-ZN1** was the fastest and removed around 99% of the dyes from the water in only 5 minutes in both cases (Figure 3.29a and 3.29b). Both adsorption mechanisms follow the pseudo-second-order kinetics (Figure 3.29c and S3.29d).



**Figure 3.29.** % Removal of (a) MO (b) AMR with time in the presence of the polymers. Pseudo-second-order kinetic model fitting for removing (c) MO (d) AMR by the polymers.

Langmuir adsorption isotherm model was studied for both dyes to examine the maximum adsorption capacities of the polymers towards capturing the dyes. As calculated, the maximum adsorption capacities for adsorbing MO were 648.74 mgg<sup>-1</sup>, 566.93 mgg<sup>-1</sup>, and 592.83 mgg<sup>-1</sup> for **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3** respectively (Figure 3.30 and Table 3.5). Whereas in the case of Amaranth it was 1370.55 mgg<sup>-1</sup>, 711.92 mgg<sup>-1</sup> and 480.37 mgg<sup>-1</sup>

<sup>1</sup> for **iPOP-ZN1**, **iPOP-ZN2** and **iPOP-ZN3**, respectively (Figure 3.31 and Table 3.6).



**Figure 3.30.** Langmuir and Freundlich adsorption isotherm model fitting for MO.

**Table 3.5.** Comparison table of MO uptake with some well-studied examples in the literature.

Material	Maximum adsorption capacity(mg/g)	Recycling	Reference		
iPOP-ZN1	648.74				
iPOP-ZN2	566.93	4	This work		
iPOP-ZN3	592.83				
iPOP-ANT	574.63	4	Mater. Chem. Front. 2022,6, 3070-3083.		
Fe <sub>3</sub> O <sub>4</sub> -PEI/β-CD	192.2	4	Chemosphere 2019, 216, 605		
MWCNTs@Fe <sub>3</sub> O <sub>4</sub> /PEI	1727.6	6	RSC Adv. 2019, 9, 4722		
CANEX1000	180.25	10	ACS Appl. Mater. Interfaces 2018, 10, 20499		
CANEX300	160.2	10	ACS Appl. Mater. Interfaces 2018, 10, 20499		
Fe/MCM-41	500	-	J. Chem. Eng. 2017, 34, 259		
4Czpyz-poly	204	-	Ind. Eng. Chem. Res. 2021, 60, 8664		
QUST-iPOP-1	300	3	ACS Appl. Mater. Interfaces 2021, 13, 39404.		
NH <sub>2</sub> -MWCNTs	160	-	ACS Appl. Mater. Interfaces 2021, 13, 39404.		
[Cd(INA)₂·(H₂O)].ISB	384	-	Journal of Solid State Chemistry 2017, 255, 157.		
SCNU-Z1-Cl	285	-	Inorg. Chem. 2019, 58, 2899		





**Figure 3.31.** Langmuir and Freundlich adsorption isotherm model fitting for AMR.

**Figure 3.6.** Comparison table of AMR uptake with some well-studied examples in the literature.

Material	Maximum adsorption capacity(mg/g)	Recycling	Reference	
iPOP-ZN1	1370.55	4	This work	
iPOP-ZN2	711.92			
iPOP-ZN3	470.37			
MIL-100(Fe)	386.05	5	J. Mater. Chem. A 2019, 7, 22559	
МСВ	404.18	-	International Journal of Biological Macromolecules 2022, 199, 234	
<b>iPOP-ANT</b> 645.084		4	Mater. Chem. Front. 2022,6, 3070-3083	

#### 3.3.3. Iodine vapor capture

Considering the cationic nature of the ionic polymers, the iodine vapor uptake capacity of the polymers in the solid state was further explored, as

recent studies show the presence of iodide and polyiodide ions in the vapor state along with molecular I<sub>2</sub> [22]. The iodine adsorption capacity was explored by exposing the polymers to iodine vapor at room temperature and 75 °C for 12 h, and iodine uptake by the solids was monitored using gravimetric analysis. It was observed that as the surface area decreases from **iPOP-ZN1** to **iPOP-ZN3**, iodine adsorption capacity also decreases. Iodine adsorption capacities were around 278%, 222%, and 189% at room temperature and 675%, 482%, and 325% at 75°C, for **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**, respectively (Figure 3.32).



**Figure 3.32.** Gravimetric iodine vapor adsorption by the polymers with time at room temperature and 75 °C and ambient pressure.

**Table 3.7.** Comparison table of I<sub>2</sub> uptake in the vapor phase with some wellstudied examples in the literature.

	Experiment	Adsorption	Maximum	
Material	lemperature	time	uptake capacity	Reference
iPOP-ZN1	RT		278 wt%	
iPOP-ZN2	RT		222 wt%	
iPOP-ZN3	RT	12h	189 wt%	This work
iPOP-ZN1	75°C		675 wt%	
iPOP-ZN2	75°C		482 wt%	
iPOP-ZN3	75°C		325 wt%	
iPOP-Bpy	75°C	7h	540 wt%	ACS Appl. Mater. Interfaces 2023, 15, 23, 28453–28464
Compound-1	70°C	24h	7.3 g/g	ACS Appl. Mater. Interfaces 2021, 13, 34188–34196
Compound-2	70°C	24h	4 g/g	ACS Appl. Mater. Interfaces 2021, 13, 34188–34196
TPT-BD COF	75°C	48h	543 wt%	Chem. Mater. 2018, 30, 7, 2299–2308
НСР	75°C	~11h	460 wt%	Sep. Purif. Technol. 2019, 210, 995-1000
ТТРВ	80°C	24h	443 wt%	J. Mater. Chem. A 2017, 5, 7612-7617
PSIF-1a	75°C	15h	485 wt%	ACS Appl. Mater. Interfaces 2018, 10, 19964–19973
SIOC-COF-7	75°C	60h	481 wt%	Chem. Commun. 2017, 53, 7266-7269
CMP-LS6	81°C	12 hours	440 wt%	Polym. Chem. 2019, 10, 2608-2615
COP <sub>0</sub> <sup>1</sup>	60°C	~1 hours	380 wt%	J. Mater. Chem. A 2016, 4, 15361-15369
SCMPs	81°C	24h		Chem. Commun. 2016,
			345 wt%	52, 9797-9800
Azo-Trip	77°C	48h	238 wt%	Polym. Chem. 2016, 7, 643–647
CMP-E1	75°C	48h	215 wt%	Angew. Chem. Int. Ed. 2015, 54, 12733- 12737
PB-TT COF	75°C	48h	5.97 g/g	Chinese Chemical Letters 2023, 34, 107201
PA-TT-COF			5.1 g/g	

The iodine adsorption capacity of **iPOP-ZN1** at 75 °C is comparable to some highly performed materials in the literature, as summarised in the literature (Table 3.7).

The iodine-loaded polymers could maintain their weight for several days, indicating their ability to store iodine (Figure 3.33a). The TGA analysis of the iodine-loaded polymers shows a significant weight loss after ~90  $^{\circ}$ C, indicating the loss of the captured iodine molecules from the pores of the polymers (Figure 3.33b).



**Figure 3.33.** (a) Weight retention of the iodine-loaded polymer upon exposure to air at room temperature (b) Comparative TGA profiles of the iodine-loaded polymers and the pristine polymers.

The PXRD pattern of the polymers post iodine adsorption shows an amorphous nature, confirming the absence of any iodine crystals in the polymers [23]. That indicates the chemisorption of iodine in the pores of the polymers (Figure 3.34a-c).



**Figure 3.34.** Comparative PXRD data of (a) I<sub>2</sub>@**iPOP-ZN1** (b) I<sub>2</sub>@**iPOP-ZN2**, and (c) I<sub>2</sub>@**iPOP-ZN3** with their pristine polymers.

Though there are no significant changes in the morphologies were observed in the iodine-loaded polymers, as shown in the FESEM imaging (Figure 3.35), the EDX analysis shows a significant presence of iodide residues in the polymer matrices (Figure 3.36).



Figure 3.35. FESEM images of the iodine-loaded polymer matrices.



Figure 3.36. EDX analysis of (a)  $I_2@iPOP-ZN1$  (b)  $I_2@iPOP-ZN2$  (c)  $I_2@iPOP-ZN3$ .

The mechanistic aspect of iodine uptake by the polymers was further investigated by XPS analysis. The XPS survey spectra of the iodine-loaded polymers show the presence of iodine, confirming the successful encapsulation of iodine in the polymeric bed (Figure 3.37a-c).



Figure 3.37. (a-c) XPS survey spectra of post-iodine adsorbed polymers.

The presence of two intense peaks in the region of 618 eV and 629 eV in deconvoluted I3d spectra of the iodine-loaded polymers indicates the presence of  $3d_{3/2}$  and  $3d_{5/2}$  orbital electrons in the adsorbed polymer matrices (Figure 3.38). That further shows the adsorption of iodine in the form of polyiodides in the polymeric bed.



Figure 3.38. Deconvoluted I3d spectra of (a) I<sub>2</sub>@iPOP-ZN1 (b) I<sub>2</sub>@iPOP-ZN2 (c) I<sub>2</sub>@iPOP-ZN3.

The deconvoluted N1s and C1s spectra further show the shifting of peaks corresponding to C-N, C=N, C-N<sup>+</sup>, and C=N<sup>+</sup> in the higher binding energies, clearly indicating the interaction of the adsorbed iodine and polyiodide molecules with the cationic N center and triazine ring in the polymer matrices (Figure 3.39a-c, 3.40a-c and Table 3.8).



**Figure 3.39.** Comparative deconvoluted N1s spectra of the iodine-loaded polymers with the pristine polymers.



**Figure 3.40.** Comparative deconvoluted C1s spectra of the iodine-loaded polymers with the pristine polymers.

(a)	B.E. (eV)	iPOP-ZN1		iPOP-ZN2		iPOP-ZN3	
	Units	Pristine	I <sub>2</sub> loaded	Pristine	I <sub>2</sub> loaded	Pristine	I <sub>2</sub> loaded
	N-H	399.09	399.13	398.92	399.12	398.73	399.44
	C-N	399.63	399.62	399.95	400.16	399.13	400.15
	C=N	-	-	400.78	400.99	400.03	401.35
	C=N+	400.72	401.32	401.55	401.92	401.7	401.93
	C-N <sup>+</sup>	401.89	402.12	402.48	403.07	402.96	403.16
(b)ì							
(~)	B.E. (eV)	iPOP-ZN1		iPOP-ZN2		iPOP-ZN3	
	Units	Pristine	I <sub>2</sub> loaded	Pristine	I <sub>2</sub> loaded	Pristine	I <sub>2</sub> loaded
	C-C/C=C	284.29	284.43	284.52	284.57	283.93	284.07
	C-N	284.94	285.12	285.07	285.39	284.31	285.27
	C-N <sup>+</sup>	285.53	285.83	285.73	286.50	284.76	285.94
	C=N+	286.15	286.80	286.55	287.31	285.59	286.66

**Table 3.8.** Comparative binding energies obtained from XPS (a) N1s and(b) C1s data.

The reusability of such polymeric solid-state adsorbents is an important parameter that often restricts their practical use. The polymers were recovered by immersing the iodine-loaded polymers in ethanol and reused for six consecutive cycles.





A slight but steady decrease in the iodine uptake abilities in the consecutive cycles may be due to some residual iodine entrapped in the polymeric bed (Figure 3.41). The recovered polymers were further characterized with FTIR, PXRD, and FESEM imaging. The FESEM imaging of the recovered polymers after six consecutive cycles shows almost no changes in their morphologies (Figure 3.42). In the FTIR and PXRD analysis, virtually no change was observed, confirming the excellent stability of the polymers after several cycles (Figures 3.43 and 3.44).



Figure 3.42. FESEM images of the recovered polymers.



**Figure 3.43.** Comparative FTIR profiles of the recovered and pristine polymers.



**Figure 3.44.** Comparative PXRD profiles of the recovered and pristine polymers.

The release of the adsorbed iodine in ethanol was monitored under UV-vis spectroscopy, which showed a very rapid release and attained saturation within ten minutes in all the cases (Figure 3.45).



**Figure 3.45.** Release of loaded iodine from the polymers in ethanol: (a) **iPOP-ZN1** (b) **iPOP-ZN2** (c) **iPOP-ZN3**.

The oxo-anions and dye-loaded polymers were further reactivated, as was done in the case of  $I_3^-$  loaded polymers. The pollutant-loaded polymers were reactivated by treating them with a saturated solution of KCl. The reusability of the polymers was checked up to four cycles, and the activity of the polymers almost remained unaltered even after the 4<sup>th</sup> cycle (Figure 3.46).



Figure 3.46. Recyclability of the polymers for four consecutive cycles.

The stability of the polymer after being used for four consecutive cycles was checked using FTIR spectra and FESEM imaging. The results show almost no change in the FTIR profile, and the morphology of the used polymer is nearly the same as the pristine polymer, confirming their stability even after use for four consecutive cycles (Figure 3.47).



Figure 3.47. FTIR spectra of the used polymer after the 4<sup>th</sup> cycle

In the above experiments, it was observed that with the decrease in the surface area of the polymers, the adsorption capacity decreases significantly. Though the increased surface area of **iPOP-ZN1** could be a possible reason, the role of positive charge density in the polymers is also a deciding factor that cannot be ignored. It was hypothesized that, compared to **iPOP-ZN3**, smaller building blocks in **iPOP-ZN1** and **iPOP-ZN2** increase the density of positive charge sites around the active sites in **iPOP-ZN1** and **iPOP-ZN2**, improving their adsorption efficiency. In the case of **iPOP-ZN1** and **iPOP-ZN2**, the electron-rich triazine moiety in **iPOP-ZN2** makes the system less positive than **iPOP-ZN1**.

DFT calculations were further performed to establish the hypothesis. The electrostatic potential (ESP) maps show all polymers to be highly electron deficient, with the electron density being the lowest at the pyridine rings (Figure 3.48). Among them, **iPOP-ZN3** shows a slightly lower positive potential compared to the other two polymers. This indicates that **iPOP-ZN3** would show a lower binding affinity to negatively charged ions compared to **iPOP-ZN1** and **iPOP-ZN2**.



**Figure 3.48.** Electrostatic potential (ESP) distribution maps (isodensity=0.001 a.u.) of iPOPs.

Further, to evaluate the interaction energies of the pollutants with the polymers, the chemical structure of pollutants and active monomeric units of the polymers were computationally optimized, and the binding energy of the pollutants with the polymers was then calculated (Figure 3.49-3.53).

The results show that the computed binding energies of the ionic pollutants with the polymers were very high. Among all the polymers, the binding of the pollutants with **iPOP-ZN1** appeared to be the highest, explaining its higher pollutant binding ability compared to the other polymers. These results reinforced our claim that the higher positive charge density around the active site of **iPOP-ZN1** makes it a better adsorbent than the other two polymers (Table 3.9). Therefore, the higher surface area and increased positive charge density in **iPOP-ZN1** make it superior to the other two polymers.



Figure 3.49. Optimized structures of the binders.



Figure 3.50. Optimized structures of the polymers.



Figure 3.51. Optimized geometry of iPOP-ZN1 interacting with the binders.



Figure 3.52. Optimized geometry of iPOP-ZN2 interacting with the binders.



Figure 3.53. Optimized geometry of iPOP-ZN3 interacting with the binders.

	iPOP-ZN1		iPOP-ZN2		iPOP-ZN3	
Binders	Energy (Hartree)	Energy (kcal/mol)	Energy (Hartree)	Energy (kcal/mol)	Energy (Hartree)	Energy (kcal/mol)
l <sub>2</sub>	-0.0109986	-6.9016545	-0.010359	-6.500303577	-0.0095773	-6.00978448
l <sub>3</sub> -	-0.3351626	-210.315537	-0.326364	-204.7943891	-0.2729923	-171.303487
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	-0.7646825	-479.840563	-0.7309849	-458.6952177	-0.6064412	-380.543672
MnO₄ <sup>-</sup>	-0.3550904	-222.820291	-0.3535048	-221.762572	-0.3026051	-189.885608
Methyl orange	-0.3741096	-234.754896	-0.3748302	-235.207075	-0.3195819	-200.538901
Amaranth	-1.1143155	-699.236319	-1.0256524	-643.599958	-0.9317178	-584.655715

**3.9.** The computed binding energy of the pollutants with the polymers.

To check the selectivity of the polymers in capturing targeted pollutants and to mimic industrial wastewater, several competing ions with different concentrations were introduced with the targeted inorganic ions. In all the cases, the polymers show significant selectivity in capturing the targeted ions even in a higher concentration of competing ions (Figure 3.54-3.56). An impressive 75-80% adsorption was achieved in the presence of 1000-fold excess Cl<sup>-</sup> ions compared to  $Cr_2O_7^{2-}$  and  $MnO_4^-$ , whereas in the case of  $I_3^-$  around 65-70% adsorption was achieved. In the presence of  $SO_4^{2-}$  and  $PO_4^{3-}$  ions, the adsorption capacity of the ions decreases significantly compared to Cl<sup>-</sup> and Br<sup>-</sup> ions, and around 55-60% adsorption was achieved in the case of  $I_3^-$ . In contrast, around 70% adsorption was achieved in the case of the oxo-anions.



Figure 3.54. Effect of competing ions in the adsorption of  $Cr_2O_7^{2-}$ 



Figure 3.55. Effect of competing ions in the adsorption of MnO<sub>4</sub><sup>-</sup>.



**Figure 3.56.** Effect of competing ions in the adsorption of  $I_3^-$ .

Industrial wastewater comes with different pH values [24]. Therefore, any adsorbent used for industrial wastewater remediation must be stable in acidic and basic solutions. Therefore, the stability of the polymers was investigated in acidic and basic solutions. The FTIR and PXRD data show almost no change in the polymers after treating them with 3M acidic and basic solutions (Figures 3.57 and 3.58).



Figure 3.57. FTIR spectra of acid and base-treated polymers.



Figure 3.58. PXRD spectra of acid and base-treated polymers.

Inspired by the high acid and base tolerance of the polymers, the ability of the polymers to adsorb the pollutants from water of different pH values was further explored. In the case of inorganic anions, it was observed that when the solutions are at extreme pH, the adsorption abilities of the polymers decrease compared to the adsorption ability of polymers in neutral solution. This may be due to the increasing acidity or basicity of the solutions; the competing Cl<sup>-</sup> and OH<sup>-</sup> increase periodically, and a decrease in the adsorption of the targeted anions is observed (Figure 3.59). Additionally, in the basic solutions, the higher decrease in the adsorption properties compared to the acidic solutions may be due to the partial reduction of the dicationic viologen centers to radical cations in the presence of bases [25]. The formation of radical cations decreases the positive charge density in the polymers, resulting in a reduction in the adsorption.



**Figure 3.59.** Percentage of removal of the anions removal by the polymers from different pH of water solution. (a)  $Cr_2O_7^{2-}$  (b)  $MnO_4^{-}$  (c)  $I_3^{-}$  (d) MO (e) AMR.

To check the potential of the polymers in realistic scenarios, different competing ions were introduced in the acidic and basic solutions along with the targeted inorganic anions. In this study. 0.5 mM of  $I_3^-$ ,  $Cr_2O_7^{2-}$  and  $MnO_4^-$  solutions were prepared with water of different pH (2-10) having different concentrations of competing ions (here Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> were taken as competing ions in 1:1, 1:10 and 1:100 ration with respect to the targeted ions). The study shows that even in these harsh conditions, the polymers were able to adsorb around 50% of the pollutants most of the time



(Figures 3.60-3.62). The obtained results show the ability of the polymers to work in industrial wastewater remediation.

**Figure 3.60.** Percentage removal of  $Cr_2O_7^{2-}$  in the presence of different counter-anions in different pH solutions. a, b and c are the percentage removal by **iPOP-ZN1** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively. d, e and f are the percentage removal by **iPOP-ZN2** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively. g, h and i are the percentage removal by **iPOP-ZN3** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively.



**Figure 3.61.** Percentage removal of  $I_3^-$  in the presence of different counteranions in different pH solutions. a, b and c are the percentage removal by **iPOP-ZN1** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively. d, e and f are the percentage removal by **iPOP-ZN2** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively. g, h and i are the percentage removal by **iPOP-ZN3** Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively.



Figure 3.62. Percentage removal of  $MnO_4^-$  in the presence of different counter-anions in different pH solutions. a, b and c are the percentage
removal by **iPOP-ZN1** Br<sup>-</sup>,  $SO_4^{2-}$  and  $PO_4^{3-}$  respectively. d, e and f are the percentage removal by **iPOP-ZN2** Br<sup>-</sup>,  $SO_4^{2-}$  and  $PO_4^{3-}$  respectively. g, h and i are the percentage removal by **iPOP-ZN3** Br<sup>-</sup>,  $SO_4^{2-}$  and  $PO_4^{3-}$  respectively.

The ability of the polymers to adsorb cationic dyes was further explored. For this purpose, Rhodamine B (RhB), Methylene blue (MLB), and Malachite green (MG) were chosen as model cationic dyes. It was observed that the adsorption of the cationic dyes was negligible even after one hour (Figure 3.63, 3.64).



**Figure 3.63.** UV-vis spectrum of Rhodamine B (RhB) solution in the presence of the polymers. Condition: Initial conc. of the RhB ( $C_0$ ) = 50 ppm,adsorbent/V solution = 0.5 mg/mL, contact time: 60 mins.



**Figure 3.64.** UV-vis spectrum of Methylene blue (MLB) solution in the presence of the polymers. Condition: Initial conc. of the MLB ( $C_0$ ) = 50 ppm, adsorbent/V solution = 0.5 mg/mL, contact time: 60 mins.

Since the polymers are incapable of adsorbing cationic dyes and show a very high affinity towards anionic dyes, the efficiency of the polymers in removing the anionic dyes from the mixture of dye solution selectively was further explored. In this regard, different combinations of dye mixtures were considered. Three dye solutions of 10 ppm were prepared by mixing two

cationic dyes, methylene blue and rhodamine B, and one anionic dye, methyl orange. The dye solutions were treated with desolvated **iPOP-ZN1** overnight. The supernatant was analyzed with UV-vis spectroscopy (Figure 3.65). The results show that from the mixture of the dye solution, the polymer selectively captured the anionic dye MO.



**Figure 3.65.** Selective separation of anionic dye MO from the mixture of (a) MO and RhB, (b) MO and MLB, and (c) MO, RhB, and MLB.

To check the real-life use of the polymers, a nylon membrane filter was coated with **iPOP-ZN1** (Figure 3.66).



**Figure 3.66.** (a) Nylon membrane filter (b) **iPOP-ZN1** coated nylon membrane syringe filter.

0.5 mM of  $MnO_4^-$  and 50 ppm MO solution was passed through the polymer-coated membrane filter.



**Figure 3.67.** UV-vis spectra of (c)  $MnO_4^-$  (d) MO solution before and after passing through **iPOP-ZN1** coated nylon membrane filter. Condition: Initial conc. (C<sub>0</sub>) of  $MnO_4^- = 0.5$  mM and MO (C<sub>0</sub>) = 50 ppm, the pH of the solutions was kept neutral.

Only colorless water was obtained after passing the dye and ion-containing solutions through the membrane filter, revealing the efficiency of the polymer-coated membrane in capturing the contaminants. The obtained supernatant was characterized by UV-vis spectroscopy, which showed no sign of the contaminants in the supernatant. (Figure 3.67).

#### 3.3.4. Antibacterial properties of the iodine-loaded polymer matrices

Since iodine is a known antibacterial agent [26,27] and polymers were highly capable of trapping and storing iodine for several days, the potential of the polymers as delivery vehicles of iodine for antibacterial action was further investigated. To check the potential of the iodine-loaded polymers for antibacterial action, the antimicrobial activity of iodine-loaded polymers was monitored against different bacterial strains such as *E. coli*, *B. subtilis*, and I10 through disc diffusion assay. The formation of a clear zone around the compound-containing disk suggests that these compounds can inhibit the growth of these pathogens and possess antibacterial activity.

In the case of *E. coli*, the maximum zone of inhibition was observed in  $I_2@iPOP-ZN1$  compared to other compounds and negative control. The  $I_2@iPOP-ZN1$  formed a significantly more (p<0.01) zone of inhibition than

the other compounds, such as  $I_2@iPOP-ZN2$  and  $I_2@iPOP-ZN3$ . On the other hand, the zone of inhibition of  $I_2@iPOP-ZN2$  and  $I_2@iPOP-ZN3$  were less than positive control, i.e., ampicillin. In contrast, the formed zone in all compounds was more significant than the negative control, i.e.,  $H_2O$  in the case of *E. coli*. The result of a zone of inhibition is summarized in Table 3.10, and the zone of inhibition formed by the compounds against E. coli is shown in Figure 3.68a.

In the case of *B. subtilis*, the zone of inhibition was observed more in positive control, i.e., Kanamycin. The zone of inhibition was in the order of Kanamycin  $\sim I_2@iPOP-ZN2 > I_2@iPOP-ZN3 > I_2@iPOP-ZN1$ . I\_2@iPOP-ZN2 was found to be more effective as compared to I\_2@iPOP-ZN1 and I\_2@iPOP-ZN3. The result of a zone of inhibition is summarized in Table 3.11, and the zone of inhibition formed by the compounds against *B. subtilis* is shown in Figure 3.68b.

In the case of I10, the zone of inhibition was observed in positive control, i.e., amoxicillin was comparable to the zone of inhibition of  $I_2@iPOP-ZN1$ . The diameter of the zone of inhibition was reduced in the order of Amoxicillin  $\sim I_2@iPOP-ZN1 > I_2@iPOP-ZN2 > I_2@iPOP-ZN3$ . However, the effect of polymers was lesser than the positive control but more from the negative control, suggesting the compound showed lesser antibacterial activity inhibiting the growth of the *H. pylori* (I10) strain. The result of a zone of inhibition was summarized in Table 3.12, and the zone of inhibition formed by the polymers against I10 is shown in Figure 3.68c.

The present investigation employed DCFDA to quantify ROS levels (Figure 3.68d). After 24h of polymer treatment, a significant increase in ROS was observed in the *H. pylori* or *B. subtilis* groups treated with the compounds compared to the untreated group. *B. subtilis*, a Gram-positive bacterium, exhibits a more significant fold change in ROS generation relative to the untreated group. With the increase in the compound concentration, the ROS generation was more prominent in *B. subtilis*. On the other hand, ROS

generation in gram-negative bacteria, i.e., *H. pylori*, was less than in grampositive bacteria, i.e., *B. subtilis*. This discrepancy may be attributed to structural distinctions in the cell membrane, which influence permeability characteristics *[28]*. These findings suggest that these iodine-loaded polymeric compounds can generate ROS in water, consequently damaging bacterial cell membranes, protein structures, and intracellular systems. Further, recent research has elucidated a correlation between the antibacterial efficacy of polymers and the generation of free radicals *[29]*. Notably, the free radicals produced by these polymers have been demonstrated to induce damage to bacterial cell membranes. Under specific conditions, elevated levels of reactive oxygen species (ROS) may precipitate oxidative stress within cells, damaging various cellular components, including the membrane, proteins, DNA, and intracellular systems, such as the respiratory apparatus.



Figure 3.68. Antibacterial activity of different polymers against grampositive and negative bacteria. Different polymers form a representative,

clear zone of inhibition in (a) E. coli, (b) B. subtilis, and (c) H. pylori. Relative intensity in terms of fold change shows the ROS generation in (d) H. pylori and (e) B. subtilis. C0 is the untreated bacteria, C1 is the polymer treatment to the bacteria with 0.5 mg/mL, and C2 is the polymer treatment with 0.25 mg/mL. The experiment was performed for two biological replicates, and the results are shown as the mean  $\pm$  SD for two independent experiments. Data were statistically analyzed using an unpaired t-test. p values were estimated using GraphPad Prism version 8, and p values of 0.05, 0.01, and 0.001 were considered statistically significant and \*\*\*/###. represented \*/#. \*\*/##. and denoting by upregulation/downregulation, respectively.

**Table 3.10.** Zone of Inhibition of different compounds on *E. coli* bacteria

 using disk-diffusion method.

Compounds	Concentration s (μg/μl)	Volume used (µl)	Zone of inhibition (mm)
I <sub>2</sub> @iPOP-ZN1	100	10	9.96±0.49
I <sub>2</sub> @iPOP-ZN2	100	10	9.74±1.20
I <sub>2</sub> @iPOP-ZN3	100	10	7.8±1.25
Ampicillin	100	10	12.75±0.64

 Table 3.11. Zone of Inhibition of different compounds on *B. subtilis* 

 bacteria using disk-diffusion method.

Compounds	Concentrations (µg/µl)	Volume used (µl)	Zone of inhibition (mm)
I <sub>2</sub> @iPOP-ZN1	100	10	10.89±0.68
I <sub>2</sub> @iPOP-ZN2	100	10	13.94±0.64
I <sub>2</sub> @iPOP-ZN3	100	10	13.05±1.06
Kanamycin	50	10	18.91±1.06

Compounds	Concentrations (µg/µl)	Volume used (µl)	Zone of inhibition (mm)
I <sub>2</sub> @iPOP-ZN1	100	10	8.60±0.56
I <sub>2</sub> @iPOP-ZN2	100	10	8.35±0.82
I₂@iPOP-ZN3	100	10	7.63±0.31
Amoxicillin	1	10	18.93±0.18

**Table 3.12.** Zone of Inhibition of different compounds on *H. pylori* (I10)

 bacteria using disk-diffusion method.

#### 3.4. Conclusion

In summary, three physically and chemically robust ionic porous organic iPOP-ZN1, iPOP-ZN2, and iPOP-ZN3, polymers, viz., have been designed and synthesized using a cationic building block. The study established the role of charge density and surface area in the polymers to be a better adsorbent, which was further established by DFT calculations. Among the three polymers, **iPOP-ZN1**, having the highest surface area and larger charge density, is found to be the best adsorbent for anionic inorganic and organic pollutants in an aqueous medium. The polymers also show excellent adsorption capability in the presence of higher concentrations of competing ions and highly acidic and basic solutions. The polymers show excellent reusability up to several cycles. The polymers further show excellent adsorption capacity of iodine in vapor state with the adsorption of 278 wt.%, 222 wt.%, and 189 wt.% at room temperature and 675 wt.%, 482 wt.% and 325 wt.% at 75°C was achieved for iPOP-ZN1, iPOP-ZN2, and iPOP-ZN3 respectively. Among them, the adsorption of iodine by iPOP-ZN1 at 75°C is one of the highest reported values in reported literature. The iodine-loaded polymers show impressive antibacterial properties against E. coli, B. subtilis, and H. pylori. This study presents a strategy for designing polymeric adsorbents with high performance and shows a glimpse of how

contaminant-loaded polymeric matrices could be used for further applications.

#### **3.5. References**

[1] Nahar N., Mahiuddin S., Hossain Z. (2021), The Severity of Environmental Pollution in the Developing Countries and Its Remedial Measures, Earth, 2, 124–139 (DOI: 10.3390/earth2010008)

[2] Xie W., Cui D., Zhang S. R., Xu Y. H., Jiang D. L. (2019), Iodine Capture in Porous Organic Polymers and Metal–Organic Frameworks Materials, Mater. Horiz., 6, 1571–1595. (DOI: 10.1039/C8MH01656A)

[3] Ojovan M. I., Lee W. E., Kalmykov S. N. (2019), An Introduction to Nuclear Waste Immobilisation; Elsevier.

[4] Sarkar S., Chakraborty A., Ranjan R., Nag P., Reddy Vennapusa S., Mukhopadhyay S. (2022) A Bifunctional Imidazolium-Functionalized Ionic Porous Organic Polymer in Water Remediation, Mater.Chem. Front., 6, 3070–3083. (DOI:1039/D2QM00636G)

[5] Sarkar S., Ghosh T., Chakrobarty A., Majhi J., Nag P., Bandyopadhyay A., Vennapusa S. R., Kumar R., Mukhopadhyay S. (2023), Exploring a Redox-Active Ionic Porous Organic Polymer in Environmental Remediation and Electrochromic Application, ACS Appl. Mater. Interfaces, 15, 28453–28464. (DOI: 10.1021/acsami.3c01800)

[6] Fajal S., Hassan A., Mandal W., Shirolkar M. M., Let S., Das N., Ghosh S. K. (2023), Ordered Macro/Microporous Ionic Organic Framework for Efficient Separation of Toxic Pollutants from Water, Angew. Chem., 135, e202214095 (DOI: 10.1002/ange.202214095)

[7] Mandal W., Fajal S., Mollick S., Shirolkar M. M., More Y. D., Saurabh S., Mahato D. Ghosh S. K. (2022), 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, ACS Appl. Mater. Interfaces, 14, 20042–20052 (DOI: 10.1021/acsami.2c02174)

[8] Ma X., Li L., Chen R., Wang C., Zhou K., Li H. (2018), Porous Carbon Materials Based on Biomass for Acetone Adsorption: Effect of Surface Chemistry and Porous Structure, App. Surface Sci., 459, 657–664 (DOI: 10.1016/j.apsusc.2018.07.170)

[9] Delmelle P., Villiéras F., Pelletier M. Surface Area, Porosity and Water Adsorption Properties of Fine Volcanic Ash Particles, Bull Volcanol, 67, 160–169 (DOI: 10.1007/s00445-004-0370-x)

[10] de Lange M. F., Lin L.C., Gascon J., Vlugt T. J. H., Kapteijn F. (2016),
Assessing the Surface Area of Porous Solids: Limitations, Probe Molecules,
and Methods, Langmuir, 32, 12664–12675 (DOI: 10.1021/acs.langmuir.6b03531)

[11] Li J., Chen L., Shen N., Xie R., Sheridan M. V., Chen X., Sheng D., Zhang D. Chai Z., Wang S. (2021), Rational Design of a Cationic Polymer Network towards Record High Uptake of  ${}^{99}\text{TcO}_4^-$  in Nuclear Waste, Sci. China Chem., 64, 1251–1260 (DOI: 10.1007/s11426-020-9962-9)

[12] Zhao Y., Truhlar D. G. (2008), The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals, Theor. Chem. Account, 120, 215–241 (DOI: 10.1007/s00214-007-0310-x)

[13] Grimme S., Antony J., Ehrlich S., Krieg H. (2010), A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu., J. Chem. Phy., 132, 154104 (DOI: 10.1063/1.3382344)

[14] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E. Robb M. A., Cheeseman J., Scalmani G., Barone V., Petersson G. A., Nakatsuji H., Li X., Caricato M., Marenich A.V., Bloino J., Janesko B. G., Gomperts R., Mennucci B., Hratchian H. P., Ortiz J. V., Izmaylov A. F., Sonnenberg J. L., Williams Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V. G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Mont-gomery J.A. Jr., Peralta J.E., Ogliaro F., Bearpark M. J., Heyd J. J., Brothers E. N., Kudin K. N., Staroverov, V. N., Keith T. A., Kobayashi R., Normand J., Raghavachari K., Rendell A. P., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Millam J. M., Klene M., Adamo C., Cammi R., Ochterski J. W., Martin R. L., Morokuma K., Farkas O., Foresman J. B., Fox D. J.: Gaussian 16 Revision C.01. Gaussian Inc. Wallingford CT(2016).

[15] Sonkar C., Verma T., Chatterji D., Jain A. K., Jha H. C. (2020) Status of Kinases in Epstein-Barr Virus and Helicobacter Pylori Coinfection in Gastric Cancer Cells, BMC Cancer, 20, 925 (DOI: 10.1186/s12885-020-07377-0)

[16] Kashyap D., Baral B., Verma T. P., Sonkar C., Chatterji D., Jain A. K.,
Jha H. C. (2020), Oral Rinses in Growth Inhibition and Treatment of
Helicobacter Pylori Infection, BMC Microbiology, 20, 45 (DOI: 10.1186/s12866-020-01728-4)

[17] Razmavar S., Abdulla M. A., Ismail S. B., Hassandarvish P. (2014), Antibacterial Activity of Leaf Extracts of *Baeckea Frutescens* against Methicillin-Resistant *Staphylococcus Aureus*. BioMed Res.Intern., 2014, e521287 (DOI: 10.1155/2014/521287)

[18] Ngamsurach P., Praipipat P. (2022) Antibacterial Activities against Staphylococcus Aureus and Escherichia Coli of Extracted Piper Betle Leaf

Materials by Disc Diffusion Assay and Batch Experiments RSC Adv., 12, 26435–26454 (DOI: 10.1039/D2RA04611C)

[19] Dewachter L., Herpels P., Verstraeten N., Fauvart M., Michiels J.(2016), Reactive Oxygen Species Do Not Contribute to ObgE\*-MediatedProgrammed Cell Death, Sci Rep, 6, 33723 (DOI: 10.1038/srep33723).

[20] Jiao S., Deng L., Zhang X., Zhang Y., Liu K. Li S., Wang L., Ma D.
(2021), Evaluation of an Ionic Porous Organic Polymer for Water Remediation, ACS Appl. Mater. Interfaces, 13, 39404–39413 (DOI: 10.1021/acsami.1c10464)

[21] Samanta P., Chandra P., Dutta S., Desai A. V., Ghosh S. K. (2018),
Chemically Stable Ionic Viologen-Organic Network: An Efficient Scavenger of Toxic Oxo-Anions from Water, Chem. Sci. 9, 7874–7881 (DOI: 10.1039/C8SC02456A)

[22] Saiz-Lopez A., Plane J. M. C., Baker A. R., Carpenter L. J., von Glasow R., Gómez Martín J. C., McFiggans G., Saunders R. W. (2012), Atmospheric Chemistry of Iodine. Chem. Rev., 112, 1773–1804 (DOI: 10.1021/cr200029u)

[23] Sarkar S., Ghosh T., Chakrobarty A., Majhi J., Nag P., Bandyopadhyay A., Vennapusa, S. R., Kumar R., Mukhopadhyay S. (2023), Exploring a Redox-Active Ionic Porous Organic Polymer in Environmental Remediation and Electrochromic Application, ACS Appl. Mater. Interfaces, 15, 28453–28464 (DOI: 10.1021/acsami.3c01800)

[24] Mehrpour P., Mirbagheri S. A., Kavianimalayeri M., Sayyahzadeh A.
H., Ehteshami M. (2023), Experimental pH Adjustment for Different Concentrations of Industrial Wastewater and Modeling by Artificial Neural Network, Environ. Techn. Innov., 31, 103212. (DOI: 10.1016/j.eti.2023.103212)

[25] Das G., Prakasam T., Nuryyeva S., Suk Han D., Abdel-Wahab A., Olsen J. C. Polychronopoulou, K.; Platas-Iglesias, C.; Ravaux, F.; Jouiad, M.; Trabolsi, A. (2016), Multifunctional Redox-Tuned Viologen-Based Covalent Organic Polymers, J. Mater. Chem. A, 4, 15361–15369 (DOI:10.1039/C6TA06439F)

[26] Xu N., Ding D. (2015), Preparation and Antibacterial Activity of Chitosan Derivative Membrane Complexation with Iodine. RSC Adv., 5, 79820–79828 (DOI: 10.1039/C5RA13227D)

[27] Tang Y., Xie L., Sai M., Xu N. Ding D. (2015), Preparation and Antibacterial Activity of Quaternized Chitosan with Iodine, Mater.Sci. Eng.
C, 48, 1–4 (DOI: 10.1016/j.msec.2014.11.019)

[28] Maher C., Hassan K. A. (2023), The Gram-Negative Permeability Barrier: Tipping the Balance of the in and the Out, mBio, (DOI: 10.1128/mbio.01205-23)

[29] Olmos D., González-Benito J. (2021), Polymeric Materials with Antibacterial Activity: A Review, Polymers, 13, 613. (DOI: 10.3390/polym13040613)



# Exploring Redox-Active Ionic Porous Organic Polymer in Environmental Remediation & Electrochromic Application

#### 4.1. Introduction

Molecules that respond to external stimuli in a programmable and reversible way have been generating lots of interest in the recent past with their materialistic properties, which can be controlled and manipulated intelligently. This provides the basis for generating smart (multifunctional) materials, and they are finding applications in energy, environment, catalysis, sensing, and biology [1-5]. The stimuli for smart materials can range from the application of light, heat, electrical potential, pressure, or even chemicals. The fundamental understanding of the mechanism of the response of smart materials toward external stimuli is essential in designing and fabricating such materials [6-8]. Extensive research on smart materials opens the opportunity to bring in newer technologies in the field of commercially and industrially relevant applications like smart windows, self-healing coatings, chemicals and gas separations, optical switches, artificial intelligence, electrochromic devices, etc [9-14]. Interestingly, the number of examples of incorporating such stimuli-responsive building blocks in fabricating covalent organic polymers (COPs) is relatively rare [15]. In this Chapter, the advantage of incorporation of viologens, N, N'-Disubstituted-4,4-'bipyridinium moiety, which is an electron-accepting dicationic organic structure with an excellent reversible redox property and fast electron transfer ability have been utilized [16], to generate an ionic porous organic polymer (iPOP-Bpy). The polymer contains an electronwithdrawing triazine moiety in the core, which is a suitable electron acceptor with favorable electron-conducting properties[17-19]. The cationic nature of the polymer, nitrogen-rich structure, physicochemical stability, and presence of an aromatic skeleton make it a suitable candidate for exploring its capacity in iodine adsorption. Furthermore, as electrondeficient dicationic viologen moiety tends to get easily reduced in the presence of electron-rich substances like amines, the polymer is also tested for its ability to sense ammonia in the vapor state. This is important because a moderate to high concentration of ammonia in the air can cause several

damages to human health, such as immediate burning of the eyes, nose, and respiratory tract, and can also cause blindness. Even a low concentration of ammonia inhalation can cause coughing and nose and throat irritation [20]. Therefore, developing sensors for ammonia vapor is a part of industrial waste management. **iPOP-Bpy** has shown a significant capability to work as a solid-state ammonia gas sensor.

However, the most interesting aspect of the viologen remains its electrochromic property, as a high degree of control on its redox process can be externally achieved, and the range of colors for the viologen varies from being colorless  $(V^{2+})$  to green/blue/purple  $(V^{+})$  [21]. Therefore, a potential application of the iPOP-Bpy can be found in electrochromic devices (ECD), a rapidly growing technology due to its various multifunctional applications, including energy-saving/storage due to its capability to change optical properties when influenced by an applied bias [22-26]. To fabricate a solid-state ECD, preferably without liquid electrolyte, proper choices of complimentary electrodes and electrolyte are essential. Compatable electrode materials helps in acheiving superior performance as measured/quantified using parameters like multicolor switching, faster switching speeds, high color contrast, and good stability/reversibility [27-30]. In this Chapter, the newly developed cathodic **iPOP-Bpy** has been used with an anodic polymeric species to design a bilayer solid-state ECD, which shows improved coloration performance, making the iPOP-Bpy molecule a potential candidate, ready to be explored in the field of solid-state ECD.

#### 4.2 Experimental section

#### 4.2.1. Materials and methods

The required materials were obtained as mentioned in Chapter 3, 3.2.1 section. The same characterization techniques were used as mentioned in Chapter 2, 2.2.1 section.

# 4.2.2. Synthesis of 2,4,6-tris (-(bromomethyl) phenyl)-1,3,5-triazine (TTRB-Br)

TTRB-Br was synthesized using the procedure mentioned in chapter 3, 3.2.4.

#### 4.2.3. Synthesis of iPOP-Bpy

TTRB-Br and 4,4'-bipyridine were reacted in a 1 : 1.5 molar ration in 20 mL of dry DMF under an inert atmosphere at 373K for 24 h. The reaction mixture was cooled to room temperature. The obtained precipitate was collected by centrifugation and washed successively with DMF, water, acetone, MeOH, THF, DCM, and diethyl ether to remove the small chain oligomers and unreacted precursors. Furthermore, the obtained solid was dipped in a 1:1:1 mixture of MeOH, THF, and DCM solution for 72 h to remove the trapped solvents with a high boiling point. The yellow-colored compound was filtered off and heated at 373K for 24 h to obtain the desolvated compound.



4.1. Synthesis of iPOP-Bpy and iPOP-Bpy-PF6

### 4.2.4. Synthesis of iPOP-Bpy-PF6<sup>-</sup>

The dispersibility of the material was strategically increased with the exchange of the counter anion  $Br^-$  with  $PF_6^-$  as it supports the fabrication of the electrochromic device. To the water dispersion of **iPOP-Bpy**, a saturated aqueous solution of potassium hexafluorophosphate was added dropwise at room temperature. The mixture was allowed to be stirred overnight. The precipitate was collected by filtration, washed with excess water, and dried overnight under a vacuum to obtain the final product.

#### 4.2.5. Preparation of cationic radical form of iPOP-Bpy

50 mg of the desolvated **iPOP-Bpy** was added to the degassed water under an  $N_2$  atmosphere. The mixture was sonicated to make a homogeneous dispersion. A saturated aqueous solution of  $Na_2S_2O_4$  was added dropwise to the solution. The color change was observed instantly. The obtained bluecolored solid was collected by centrifugation and washed with excess water to remove the remaining  $Na_2S_2O_4$ . The solid was then washed with methanol and DCM a couple of times and dried to get the deep blue-colored powder.

## 4.2.6. Procedure for iodine capture in solid-state

For this experiment same procedure was followed as mentioned in the 3.2.14 section in chapter 3.

# 4.2.7. Procedures for the iodine adsorption in the solution phase and time-dependent study

For this study, 3 mL iodine solution in n-hexane (2 mM) was taken in a cuvette, and the initial absorption was recorded using UV-vis spectroscopy. 1.5 mg of the desolvated **iPOP-Bpy** was added to the cuvette and shaken gently. The corresponding absorbance of the supernatant solution was recorded in two-minute time intervals for 18 minutes. From the time-

dependent study, the percentage of iodine adsorption and decrease of concentration with time was calculated using the following equation:

where  $D_t$  is the exchange capacity,  $C_0$  and  $A_0$  are the initial concentration and absorbance of the iodine solution, respectively, and  $C_t$  and  $A_t$  is the concentration and absorbance of the iodine solution at specific times, respectively.

Kinetics data for adsorbing iodine were fitted in the pseudo-secondorder model using the following equation:

Where t is the time in minutes, and  $Q_t$  and  $Q_e$  are the amounts of adsorbate (mg g<sup>-1</sup>) on the adsorbent at different time intervals and equilibrium, respectively.

For the aqueous phase iodide capture study, 0.625 M of  $I_3^-$  solution was prepared by dissolving an equimolar amount of  $I_2$  and KI in water. The corresponding absorbance of the supernatant solution was recorded in 0.5 min time intervals for 2.5 mins.

#### 4.2.8. Effect of different competitive anions in the adsorption of I<sub>3</sub>-

For this study, four competitive anions, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were taken in different concentrations [1:1 (5 mM:5 mM), 1:10 (5 mM:50 mM), 1:50 (5 mM:250 mM), 1:100 (5 mM:500 mM) and 1:1000 (5 mM:5000 mM)]. To the 5 mL of the prepared solution, 2.5 mg of the desolvated polymer was dispersed and allowed to stand for 24 h. The supernatant aqueous solution was collected by centrifugation and diluted accordingly to 0.5 mM. The UV- vis spectra were recorded with the diluted solutions.

#### 4.2.9. Recyclability test of iPOP-Bpy

 $iPOP-Bpy@I_2$  was added to 20 mL ethanol and allowed to stand for 2 h. The brown-colored solution was decanted, and the process was repeated multiple times until the colorless solution was obtained. The solid was

filtered off, washed with excess alcohol and ether, dried under vacuum, and used further for the next cycle.

### 4.2.10. Ammonia vapour (NH<sub>3</sub>) sensing in solid state

A pad of **iPOP-Bpy** was placed in a chamber containing a 25% aqueous ammonia solution. A change in color from yellow to blue was observed within seconds. The blue-colored pad returns to its original yellow-colored state upon exposing it to air within a couple of minutes. The cycle was repeated ten times.

## 4.2.11. Computational Methodology

All structures were optimized using the DFT method by utilizing the M062X-D3 [31,32] functional (incorporating dispersion corrections) in combination with the 6-311G(d,p) basis set for C, N, H, and SDD for I atoms. Harmonic frequencies were calculated to confirm the convergence of the geometries to a minimum. Binding energies of iPOP-Bpy with  $I_2/I_3^-$  were computed using the following equation:

Binding energy =  $E_{Complex} - (E_{iPOP-Bpy} + E_{I2/I3})$ 

where  $E_{Complex}$ ,  $E_{iPOP-Bpy}$  and  $E_{I2/I3}$  are the energies of the iPOP-Bpy-I<sub>2</sub>/I<sub>3</sub><sup>-</sup> complex, **iPOP-Bpy** and I<sub>2</sub>/I<sub>3</sub><sup>-</sup>, respectively. All calculations were performed using Gaussian 16 software [33].

## 4.2.12. Fabrication of the solid-state electrochromic device (ECD)

A solid-state ECD was fabricated using ITO-coated glass using a flip-chip technique. First, a layer of Poly-3-hexyl thiophene (P3HT) was spin-coated onto an ITO-coated glass, and the same was sandwiched with another ITO-coated glass onto which the **iPOP-Bpy-PF**<sub>6</sub> molecule was incorporated into a gel electrolyte. In-situ bias-dependent color modulation was studied using a Lambda 365 spectrophotometer (PerkinElmer make), and a Keithley 2450 workstation was used for the electrochemical measurements.

#### 4.3. Results and Discussion

#### 4.3.1. Characterization of iPOP-Bpy

**iPOP-Bpy** was synthesized via a one-step condensation reaction between 4,4'-bipyridine and 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (A) in 20 mL of dry DMF under an inert atmosphere at 373K for 24 h, as depicted in Scheme 4.1. The material was thoroughly characterized using <sup>13</sup>C-CPMAS NMR (cross-polarization magic angle spinning nuclear magnetic resonance), Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX), and thermogravimetric analysis (TGA).

In the <sup>13</sup>C-CPMAS NMR spectrum, the peak at 60.47 ppm corresponds to the -CH<sub>2</sub>- carbon, and the peak at around 168 ppm represents the triazine carbon; other peaks ranging from 127-151 ppm (b, c, d, e) indicate the presence of aromatic carbons in the material (Figure 4.1).



**Figure 4.1.** <sup>13</sup>C-CPMAS NMR of **iPOP-Bpy** [(a) indicates the (-CH<sub>2</sub>) carbon at 60.47 ppm, (b-e) represents the aromatic protons, (f) represents the C atoms in the triazine ring].

In the FTIR spectra, the band at 1636 cm<sup>-1</sup> represents aromatic C=C stretching, and bands at 1517 cm-1 and 1365 cm-1 indicate the triazene ring's presence in the polymer. The shifting of the methylene (-CH<sub>2</sub>-) band from 1412 cm<sup>-1</sup> in the TTRB-Br to 1408 cm<sup>-1</sup> in the iPOP-Bpy not only

indicates the development of a positive charge in the N center, whereas the disappearance of the band at 598 cm<sup>-1</sup> in the polymer indicates the complete consumption of the C-Br bond during the formation of the polymer (Figure 4.2a). The PXRD pattern of the material confirms its amorphous nature (Figure 4.2b). The TGA analysis shows that the material is thermally stable up to 260° C. The minimum weight loss before 100 °C may be due to the removal of entrapped solvents in the material via desolvation (Figure 4.2c). The material's insoluble nature and minimal residual weight loss in various lab solvents like MeOH, EtOH, acetone, acetonitrile, DCM, DMF, toluene, THF, chloroform, and DMSO also establish its chemical stability (Figure 4.2d).



**Figure 4.2.** (a) FTIR spectrum of **iPOP-Bpy** (b) PXRD of **iPOP-Bpy** (c) TGA of **iPOP-Bpy** (d) Residual weight percentage **iPOP-Bpy** after exposing in different solvents.

The morphology of the material was investigated from FESEM imaging (Figure 4.3).

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Figure 4.3. FESEM imaging of iPOP-Bpy

Elemental mapping and EDS further confirm the presence of C, N, and Br in the polymer.



Figure 4.4. EDS and Elemental mapping of iPOP-Bpy

The presence of the elements was further confirmed by the XPS survey spectrum (Figure 4.5a). The Deconvoluted XPS N1s spectrum of the material shows the presence of two types of functionalities (C=N, C=N<sup>+</sup>) in

the material, which also confirms the successful synthesis of the material (Figure 4.5b).



Figure 4.5. (a) XPS survey spectra of iPOP-Bpy (b) XPS N1s spectra of iPOP-Bpy

The polymer shows lower uptake of N<sub>2</sub> and CO<sub>2</sub>, which may be due to the presence of bulky Br<sup>-</sup> ion in the pores of the material (Figure 4.6a, 4.6b). The porosity of the material was analyzed using N<sub>2</sub> adsorption-desorption isotherm, adsorbing N<sub>2</sub> at 77K and 1 bar pressure. The Langmuir surface area was calculated as  $364.43 \text{ m}^2/\text{g}$ . The pore size distribution calculated by the NLDFT method confirmed the mesoporous nature of the material with a pore diameter of 2.89 nm (Figure 4.6c). The average pore size was found to be 1.94 nm, and the average pore volume was 0.21 cc/g.



**Figure 4.6.** (a)  $N_2$  adsorption and desorption profile at 77K (b)  $CO_2$  adsorption and desorption profile at 298K (c) The pore size distribution profile obtained from the adsorption branch by the NLDFT method.

#### 4.3.2. Adsorption of iodine vapor by iPOP-Bpy

Inspired by the physicochemical stability, aromatic skeleton, cationic nature, and exchangeable Br<sup>-</sup> ions in **iPOP-Bpy**, its iodine vapor capture capacity was investigated by exposing the material to iodine vapor at 75 °C under ambient pressure to mimic the typical nuclear fuel processing condition *[42]*. Instant color change from yellow to brown-black was observed within the initial few minutes. The gravimetric measurements were carried out to evaluate the iodine uptake capacity with time (Figure 4.7a). The adsorption kinetics was observed to be very rapid in the initial hours and reached equilibrium with time. In the initial 3 h, the I<sub>2</sub> uptake was around 502% with respect to the initial weight of pristine polymer taken for I<sub>2</sub> capture, and a gradual decrease in the uptake rate was observed after that, and within 7 h, it reached the equilibrium. The iodine uptake value in the

vapor phase was calculated to be ~540%. The I<sub>2</sub>-loaded polymer (I<sub>2</sub>@iPOP-Bpy) was observed to maintain its weight for several days upon exposure to air at room temperature, indicating that the material not only has the capability to adsorb I<sub>2</sub> but also in I<sub>2</sub> storage (Figure 4.7b).



**Figure 4.7.** (a) Gravimetric iodine vapor uptake of **iPOP-Bpy** with time at 75°C and ambient pressure. (b) Iodine retention of **I**<sub>2</sub>@**iPOP-Bpy** upon exposure to air at room temperature.

The thermogravimetric analysis of the post-captured material shows a significant weight loss in the temperature range of 85-335 °C, which signifies the volatilization of the adsorbed  $I_2$  molecules from the pocket of the polymer (Figure 4.8). The adsorption of iodine vapor by **iPOP-Bpy** is comparable to that of some highly-performed materials in the literature.



Figure 4.8. Thermogravimetric analysis (TGA) of I2@iPOP-Bpy

**Table 4.1.** A comparison table of  $I_2$  uptake in hexene with some wellstudied examples in the literature.

Material	Maximum adsorption capacity	Reference
іРОР-Вру	1009.77 mg/g	This work
Meo-CTF600	849 mg/g	ACS Appl. Nano Mater. 2022, 5, 7, 8783–8793
TatPOP-2	1239 mg/g	Chem. Commun. 2018, 54, 8450-8453
ТТРРА	300 mgL <sup>-1</sup>	J. Mater. Chem. A 2018, 6, 2808– 2816
КОН-АС	460 mg/g	J. Mater. Sci. 2015, 50, 7326– 7332
SCMPs	500 mgL <sup>-1</sup>	Chem. Commun. 2016, 52, 9797-9800
AzoPPN	735 mg/g	Chem. Eur. J. 2016, 22, 11863-11868
NiP-CMP	326 mg/g	Chem. Commun. 2014, 50, 8495-8498
COP1 ++	212 wt%	J. Mater. Chem. A, 2016,4, 15361

FTIR, Raman spectroscopy, and XPS analysis were performed to investigate the interaction between the polymer and adsorbed iodine. FTIR spectra of **iPOP-Bpy@I**<sub>2</sub> show some shifting of the triazine representative bands, indicating the interaction of the adsorbed iodine with the triazine core of the polymer (Figure 4.9a). The Raman spectra show the nature of the adsorbed iodine molecule. Broad Raman band at 165 cm<sup>-1</sup> indicates the symmetric mode of the adsorbed di-iodine molecule, whereas the band at 109 cm<sup>-1</sup> indicates the symmetric stretching vibration, and the band at 135 cm<sup>-1</sup> indicates the asymmetric stretching vibrations of the I<sub>3</sub><sup>-</sup> molecule (Figure 4.9b).



Figure 4.9. (a) FTIR and (b) Raman spectra of iPOP-Bpy and I<sub>2</sub>@iPOP-Bpy

The XPS survey spectra of  $I_2@iPOP-Bpy$  show the presence of iodine in the material (Figure 4.10a). XPS N1s spectrum of  $I_2@iPOP-Bpy$  shows a shift in the binding energies of C=N+ and C=N from 400.7eV and 398.87eV to 402.5eV and 400.27eV, respectively, which indicate the interaction of the adsorbed iodine and iodide molecules with the N centers of the material (Figure 4.10b). Two intense peaks at 618.4eV and 629.78eV in the deconvoluted I3d spectra of  $I_2@iPOP-Bpy$  indicate the 3d<sub>3/2</sub> and 3d<sub>5/2</sub> orbital electrons of the adsorbed iodine (Figure 4.10c).



**Figure 4.10.** (a) XPS survey spectra of **I**<sub>2</sub>@**iPOP-Bpy** (b) XPS N1s spectra of **I**<sub>2</sub>@**iPOP-Bpy** (c) XPS I3d spectra of **I**<sub>2</sub>@**iPOP-Bpy** 

The FESEM image confirms the unchanged morphology of the material after iodine adsorption (Figure 4.11).



Figure 4.11. FESEM image of I<sub>2</sub>@iPOP-Bpy

The elemental mapping and EDS analysis further confirm the presence of iodine in the material (Figure 4.12).



Figure 4.12. EDS and elemental mapping of I<sub>2</sub>@iPOP-Bpy

The PXRD pattern of **I**<sub>2</sub>@**iPOP-Bpy** shows the amorphous nature of the post-adsorbed material, which indicates the absence of any iodine crystals, indicating that the iodine is encapsulated inside the pores of the material (Figure 4.13).



### Figure 4.13. PXRD of I2@iPOP-Bpy

The reusability of the material was tested by simply immersing the  $I_2$ -loaded material in ethanol. A slight but constant decrease in the adsorption capacity of the recycled material compared to the freshly prepared polymer was observed after each cycle (Figure 2d).





The reduction in the material's adsorption capacity after each cycle may be due to the residual iodine trapped in the material due to the strong interaction with the material and cannot be removed entirely after the ethanol wash (Figure 4.15)



**Figure 4.15.** Photographs of the recovered polymer after the 4th cycle of iodine adsorption in the vapor phase.

The material's morphology and thermal stability remained unaltered after the regeneration (Figure 4.16a and 4.16b).



**Figure 4.16.** (a) TGA and (b) FESEM image of recovered **iPOP-Bpy** after the 4th cycle of I<sub>2</sub> adsorption in the vapor phase.

The  $I_2$  release from  $I_2@iPOP-Bpy$  in ethanol was also investigated with time-dependent UV-vis spectroscopic technique. It was observed that the kinetics of the  $I_2$  release was very fast and attained saturation within 6 minutes (Figure 4.17).



**Figure 4.17.** Time-dependent UV-vis spectra of iodine release in ethanol from vapor phase iodine loaded **iPOP-Bpy** 

The change in color of the material from yellow to brown-black upon exposing it to  $I_2$  vapor is an obvious indication of the optical bandgap alteration of the material. The solid-state UV-vis spectra of the material before and after the  $I_2$  adsorption show a significant red shift of the spectra after adsorption, indicating the color change (Figure 4.18a). The corresponding bandgap calculated by the Tauc plot method also shows the decrease in the material's band gap after  $I_2$  adsorption from 2.92 eV to 1.62 eV (Figure 4.18b).



Figure 4.18. (a) Solid-state UV-vis spectra of iPOP-Bpy and I2@iPOP-

**Bpy**. (b) The band gap of **iPOP-Bpy** and **I**<sub>2</sub>@**iPOP-Bpy** was calculated by the Tauc plot method

It was well established in the literature that I<sub>2</sub> is used as a chemical doping for enhancing the electrical conductivity of host materials [34]. Encouraged by the earlier reports, the electrical conductivity ( $\sigma$ ) of the I<sub>2</sub>-loaded **iPOP-Bpy** was further investigated. The current-voltage (*I-V*) measurement was carried out on palletized samples of both **iPOP-Bpy** and I<sub>2</sub>-loaded **iPOP-Bpy** to estimate the electrical conductivity using a four-probe method. The results show an increase in the electrical conductivity of the material after I<sub>2</sub> doping from 1.19×10<sup>-6</sup> S/m to 27.03×10<sup>-6</sup> S/m (Figure 4.19a). The EPR measurement was carried out to investigate the enhancement in conductivity after I<sub>2</sub> doping in the host material. As can be seen in Figure 4.19b, though **iPOP-Bpy** shows a very weak paramagnetic signal, upon I<sub>2</sub> doping, the paramagnetic signal increases many folds with a g value of 2.00148, indicating the formation of a large number of free radicals upon iodine doping. These formations of free radicals are possibly the cause of the enhanced electrical conductivity.



**Figure 4.19.** (a) *I-V* curve of **iPOP-Bpy** and **I**<sub>2</sub>@**iPOP-Bpy** (b) EPR spectra of **iPOP-Bpy** and **I**<sub>2</sub>@**iPOP-Bpy**.

#### 4.3.3. Adsorption of iodine from organic and aqueous medium

Iodine capture in the organic solution was also investigated. 1.5 mg of **iPOP-Bpy** was added to a 3 mL 2 mM  $I_2$  solution in n-hexane; the purple

color of the solution gradually faded over time upon adding the polymer powder, indicating the capture of I<sub>2</sub> by the polymer. The decrease in the concentration of I<sub>2</sub> was monitored in two-minute time intervals under UVvis spectroscopy. A steady decrease in the peak at 520 nm in UV-vis spectra indicates the constant decrease in the concentration of I<sub>2</sub> in the supernatant solution (Figure 4.20a). It was observed that around 75.3% of I<sub>2</sub> was adsorbed in the initial two minutes, the adsorption reached equilibrium in 18 minutes, and about 96.2% of I<sub>2</sub> was adsorbed (Figure 4.20b). The adsorption was found to be following pseudo-second-order kinetics with an R<sup>2</sup> value of 0.9949 (Figure 4.20c). Langmuir adsorption was also studied to evaluate the maximum adsorption capacity of the material. After calculation, it shows an adsorption capacity of 1009.77 mgg<sup>-1</sup>, one of the highest values reported in the literature (Figure 4.20d, Table 4.2).



**Figure 4.20.** (a) UV-vis spectrum of I<sub>2</sub> solution in n-hexane (b) Decrease in concentration and % of removal of iodine from I<sub>2</sub> solution in n-hexane. (c) Pseudo second model fit for I<sub>2</sub> adsorption by **iPOP-Bpy** in n-hexane

solution (d) The Langmuir and Freundlich model fit for  $I_2$  adsorption in n-hexane solution.

**Table 4.2.** Comparison table of I<sub>2</sub> uptake in hexene with some well-studied examples in the literature.

Material	Maximum adsorption capacity	Reference
іРОР-Вру	1009.77 mg/g	This work
Meo-CTF600	849 mg/g	ACS Appl. Nano Mater. 2022, 5, 7, 8783–8793
TatPOP-2	1239 mg/g	Chem. Commun. 2018, 54, 8450-8453
ТТРРА	300 mgL <sup>-1</sup>	J. Mater. Chem. A 2018, 6, 2808– 2816
КОН-АС	460 mg/g	J. Mater. Sci. 2015, 50, 7326– 7332
SCMPs	500 mgL <sup>-1</sup>	Chem. Commun. 2016, 52, 9797-9800
AzoPPN	735 mg/g	Chem. Eur. J. 2016, 22, 11863-11868
NiP-CMP	326 mg/g	Chem. Commun. 2014, 50, 8495-8498
COP1 ++	212 wt%	J. Mater. Chem. A, 2016, 4, 15361

Though several studies regarding iodine capture are reported in the literature, these studies are limited to the vapor phase and some organic solvents like hexane. Significant attention is not being paid to the iodine capture from the aqueous medium [35-39], which is equally important in keeping the highly volatile nature of iodine in mind. In the nuclear power industries, the radioactive iodide nuclides might enter the environment during the nuclear fission process, contaminating the natural water resources. There is extensive use of radioiodine nuclides in medical science as a diagnostic and therapeutic tool, which is also a significant source of radioiodine water contamination. In an aqueous medium, iodine predominantly exists as a polyiodide (triiodide-I<sub>3</sub><sup>-</sup>). Owing to the high-

capacity iodine adsorption by the material in the vapor and organic phase, the potential of **iPOP-Bpy** was further explored in capturing iodine capture in the aqueous phase. To the 0.625 mM aqueous  $I_3^-$  solution, 0.5 mg/mL **iPOP-Bpy** was dispersed. The adsorption of  $I_3^-$  was monitored under UV-vis spectroscopy at different time intervals (Figure 4.21a). The adsorption kinetics was extremely fast, and around 99%  $I_3^-$  gets removed within 2.5 mins (Figure 4.21b). The adsorption was found to be following pseudo-second-order kinetics ( $R^2$ =0.97), with a rate constant of 0.00247 mgg<sup>-1</sup>min<sup>-1</sup> (Figure 4.21c). The highest iodide adsorption capacity of the material from the water was calculated to be 3921.47 mgg<sup>-1</sup> is also comparable to some well-performed previous materials reported in the literature (Figure 4.21d, Table 4.3).



**Figure 4.21.** (a) UV-vis spectrum of aqueous  $I_3^-$  solution in the presence of **iPOP-Bpy**. (b) Decrease in concentration and % of removal of  $I_3^-$  with time (c) Pseudo second model fit for  $I_3^-$  adsorption by **iPOP-Bpy** (d) The Langmuir and Frundlich model fit for  $I_3^-$  adsorption by **iPOP-Bpy**.
**Table 4.3.** A comparison table of  $I_3$  uptake in water with some well-studied examples in the literature.

Material	Maximum adsorption capacity	Selectivity	Reference
іРОР-Вру	3921.47 mg/g	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	This work
Compound-1	3.5 g/g	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2021, 13, 34188–34196
Compound-2	3.04 g/g	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	ACS Appl. Mater. Interfaces 2021, 13, 34188–34196
CaCOP1	240 wt%	ND	Mater. Chem. Phys. 2020, 239, 122328.
CaCOP2	281 wt%	ND	Mater. Chem. Phys. 2020, 239, 122328.
CaCOP3	310 wt%	ND	Mater. Chem. Phys. 2020, 239, 122328.
SCNU-Z4	331.7 mg/g	ND	Inorg. Chem. Front. 2021, 8, 1083–1092.
TNHCP1	729 mg/g	ND	Sep. Purif. Tech. 2021, 257, 117923
TNHCP2	854 mg/g	ND	Sep. Purif. Tech. 2021, 257, 117923
ТNНСР3	819 mg/g	ND	Sep. Purif. Tech. 2021, 257, 117923
CalCOP1	2.318 g/g	ND	J. Mater. Sci. 2020, 55, 1854– 1864.
CalCOP2	1.758 g/g	ND	J. Mater. Sci. 2020, 55, 1854– 1864.
CalCOP3	0.346 g/g	ND	J. Mater. Sci. 2020, 55, 1854– 1864.
CalCOP4	0.156 g/g	ND	J. Mater. Sci. 2020, 55, 1854– 1864.

To check the practicability of the material, the normal wastewater condition was simulated by introducing different competitive anions like Cl<sup>-</sup>, Br<sup>-</sup>,  $NO_3^-$ , and  $SO_4^{2-}$  in different concentrations. It was observed that the material was efficient enough in removing  $I_3^-$  from water even after the presence of competitive anions 1000 times excess compared to  $I_3^-$  (Figure 4.22).



Figure 4.22. Effect of excess competing anions I<sub>3</sub><sup>-</sup> uptake by iPOP-Bpy

Further, to get more insight into how  $I_2$  and  $I_3^-$  bind with **iPOP-Bpy**, DFT studies were performed on the model system of **iPOP-Bpy** (Figure 4.23a).



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**Figure 4.23.** (a) Optimized structure of **iPOP-Bpy** model system (b) Optimized geometry of **iPOP-Bpy** binds with  $I_2$  (c) Optimized geometry of  $I_3^-$  binding with **iPOP-Bpy**. Intermolecular bond distances are given in Å.

The binding energy of  $I_2$  with the positively charged **iPOP-Bpy** is small, with a stabilization energy of ~7.26 kcal/mol (Figure 4.23b). On the other hand, the negatively charged  $I_3^-$  has a large binding energy of ~216.21 kcal/mol, owing to the electrostatic interaction between the positively charged iPOP and the anion (Figure 4.23c).

#### 4.3.4. NH<sub>3</sub> vapor sensing

It is well established from the literature that viologen derivatives undergo facile charge transfer due to low-energy LUMO as an electron acceptor [40,41]. The noticeable color change in the dicationic viologen derivatives by forming radical-cation clearly indicates electron transfer in the presence of electron-rich chemicals such as ammonia. Though there are several reports of the viologen-based systems for ammonia sensing in the literature, only a few reports of the viologen-based solid-state materials in ammonia sensing are there [35,40,42,43]. In **iPOP-Bpy**, due to having similar viologen linkage, its ability to sense ammonia vapor was further explored.

A pad of solid polymer was exposed to ammonia gas, and a rapid color change of the polymer from yellow to blue was observed. The color change can indicate the polymer's reduction from the dicationic state to the cationic radical state (Figure 4.24a). Solid-state EPR spectra of the NH<sub>3</sub>-treated blue-colored polymer powder were further carried out. The sharp peak in the EPR spectra (g = 2.0025) indicates the presence of cationic radical species in the polymer (Figure 4.24b). To further confirm the observation, the polymer was treated with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, a commonly used reducing agent in reducing the viologen derivative. The instant color change of the material from yellow to deep blue was observed post-

treatment, similar to the ammonia-treated polymer, and confirmed the cationic radical formation (Figure 4.24c).



**Figure 4.24.** (a) Color change of **iPOP-Bpy** in the presence of NH<sub>3</sub> vapor (b) EPR spectra of **iPOP-Bpy** and **iPOP-Bpy@NH**<sub>3</sub> (c) Photograph of iPOP-Bpy after treatment with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.

The solid-state UV-vis spectra of the iPOP-Bpy show a strong adsorption band around 200-400 nm, which is a clear indication of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ charge transition in the material. The appearance of a shoulder peak in the range of 415-518 nm post NH<sub>3</sub> treatment may be due to the intermolecular charge transfer from NH<sub>3</sub> to the electron-deficient viologen moiety [44] (Figure 4.25)

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Figure 4.25. Solid state UV-vis spectra of iPOP-Bpy and iPOP-Bpy@NH3

The observation was further established with the help of DFT calculation. The computed results show that the HOMO and LUMO energies of **iPOP-BPy** are -17.72 eV and -12.29 eV, respectively, lower than the HOMO of electron-rich NH<sub>3</sub>. The obtained results suggested the facile electron transfer from the HOMO of NH<sub>3</sub> to the LUMO of **iPOP-BPy** (Figure 4.26).



**Figure 4.26.** HOMO and LUMO energies of **iPOP-Bpy** model system and HOMO of NH<sub>3</sub>

The material can be regenerated by exposing the blue-colored polymeric pad to air. Surprisingly, the rates of these two processes are different. The polymer changes its color to blue upon exposure to ammonia vapor within a few seconds, whereas the color regeneration takes a couple of minutes. The cycle was continued ten times, and the same observation was noticed in each cycle. No morphological and structural changes in the polymer were observed after ten cycles, as confirmed by the FTIR and FESEM imaging (Figure 4.27).



Figure 4.27. (a) FTIR and (b) FESEM of NH<sub>3</sub> treated iPOP-Bpy

#### 4.3.5. Investigation of the electrochromic properties of iPOP-Bpy

Viologen-based derivatives are one of the key materials used to develop efficient electrochromic devices. Inspired by the rapid color change of the material upon exposure to electron-rich amines, its electrochromic properties were further explored. Here, **iPOP-Bpy-PF**<sub>6</sub><sup>-</sup> was used to fabricate the electrochromic device. The successful ion exchange was confirmed by <sup>31</sup>P CPMAS NMR, XPS, EDS, and elemental analysis. The multiplate at around -145 ppm in the <sup>31</sup>P CPMAS NMR spectra indicates the presence of PF<sub>6</sub><sup>-</sup> ions in the material, where the multiplate originates from the <sup>31</sup>P-<sup>19</sup>F coupling (Figure 4.28).



Figure 4.28. <sup>31</sup>P CPMAS NMR of iPOP-Bpy-PF6<sup>-</sup>

The complete absence of Br and clear presence of P and F in XPS, EDS, and elemental mapping data confirm the complete ion exchange upon treatment with  $PF_6^-$  (Figure 4.29a and 4.30).

A shift in the C=N<sup>+</sup> binding energy in XPS N1S spectra post-ion exchange from 400.7eV to 401.6eV indicates the interaction of  $PF_6^-$  ions with the cationic center in the polymer (Figure 4.29b).



Figure 4.29. (a)XPS survey spectra and (b) deconvoluted N1s spectra of iPOP-Bpy-PF6<sup>-</sup>



Figure 4.30. EDS and elemental mapping of iPOP-Bpy-PF6-

There is no change in the PXRD pattern after ion exchange (Figure 4.31a), whereas FESEM imaging shows similar morphology (Figure 4.31b).



Figure 4.31. (a) PXRD and (b) FESEM of iPOP-Bpy-PF6<sup>-</sup>

An electrochromic device was developed using P3HT as a complimentary auxiliary electrode along with the molecule of interest to fabricate a bilayer ECD in the form of ITO/P3HT/**iPOP-Bpy-PF6**-/ITO. Here, P3HT has been chosen as the complementary layer mainly due to its familiarity with its electrochromic properties [45,46], besides being a highly stable conducting polymer. Secondly, the molecule under study is an n-type material, i.e., it changes color when applied with negative bias; P3HT, being a p-type

material, is thus the best-suited choice of incorporation for achieving an overall enhancement of performance [47,48]. The fabricated device can be visualized using the schematic shown in Figure 4.32, which also shows the actual photographs of the device corresponding to the applied bias (Figures 4.32a-c).



**Figure 4.32.** Schematic of the solid-state electrochromic device under a bias of (a) 0V (as-prepared), (b) 2V, (c) -2V applied with respect to the P3HT layer. The insets show actual photographs of the device under corresponding applied bias.

Since the **iPOP-Bpy** molecule is transparent in the neutral state, the original color of the as-prepared device (unbiased) appears magenta, owing to the inherent color of P3HT (Figure 4.32a). When applied with +2V (with respect to P3HT) bias, the P3HT electrode turns transparent due to the formation of polarons as a consequence of dynamic doping, a process of bias-induced oxidation from a neutral state to a polaronic state [49,50]. Along with this dynamic doping of the P3HT electrode, the **iPOP-Bpy** molecule gains electrons at the other electrode, reducing it to the corresponding cationic state. This causes a change in its color from transparent to blue, giving an overall appearance of blue color to the device (Figure 4.32b). On bias reversal, the device color switches back to magenta (Figure 4.32c) as reduction occures in the P3HT electrode, pulling the electrons back and reversing the overall redox processes at both layers. The two visible color states of the device achieved at respective biases have been then validated by performing in situ UV-visible measurements.

The in-situ bias-dependent transmittance spectra of the device at three different bias states (Figure 4.33a) clearly show a bias-dependent color modulation in the device, and the spectral response can also be correlated with the actual color perceived from the device (corresponding insets). The black curve represents the initial color of the device (magenta in appearance), as can be validated by the RGB color scheme [45] as follows. Higher transmittance in the red & blue regions with a dip in the green region corresponds to the magenta appearance (the combination of red & blue) [47]. Under the +2V, the transmittance increases (red curve, Figure 4.33a) in the blue region, thus giving the device an overall blue appearance (inset). Next, when the bias was reversed to -2V bias, the initial magenta state of the device was restored with the reinstallation of the transmittance curve similar to the initial state (blue curve, Figure 4.33a), indicating the perfect reversibility. Analysis of the transmittance spectra reveals a color contrast value of ~50%, corresponding to 515 nm wavelength, and ~48%, corresponding to ~700 nm (black arrows, Figure 4.33a). Looking at the good color contrast, the electrochromic performance of the ECD was studied for these two wavelengths to test multi-wavelength switching capabilities. To check the stability, cycle life was tested for which a  $\pm 2V$ pulse of 5s duration was applied to the device while recording the corresponding optical changes in the device (Figure 4.33b). A dynamic switching in absorbance corresponding to 515 nm wavelength shows that the reversibility is well maintained for at least 500s (100 switching pulses) while the contrast decreases only a little, indicating that the device might be storing some charges on each switching pulse. A dynamic switching in absorbance corresponding to 515 nm wavelength can be seen. After a few ON/OFF fluctuations cycles, the device gets stabilized, and not much variation is seen. It is clear that the device retains its stability for more than 1000s, and reversibility is well maintained while the contrast decreases only a little, indicating that the device might be storing some charges on each switching pulse.



**Figure 4.33.** (a) Bias-dependent transmittance spectra of the device and its actual images as inset (b) Absorbance V/s Time spectra of the device recorded at 2V/-2V for 2500s (250 cycles) (c) Coloration ( $\tau_c$ ) and Bleaching ( $\tau_b$ ) times calculated at 515nm (d) Voltage and current V/s time graph recorded along with coloration efficiencies at (e) 515nm and (f) 700 nm wavelength with inset image showing coloration and bleaching time.

To measure the switching time of the device, one switching cycle of the device has been analyzed carefully (Figure 4.33c) to reveal coloration and bleaching times of 0.5s and 0.7s, respectively. A switching time of less than one second represents one of the fastest ECDs in the family. Coloration efficiency (CE) is one of the most important device performance parameters that quantify the power efficiency of an ECD. To estimate the CE of the device, the current response of the device as a consequence of the voltage pulse train to the device is first recorded (Figure 4.33d)... Since the CE is defined as the change in optical density ( $\Delta$ OD) of the device per unit charge insertion/exertion (Q), it can be calculated using the slope of the " $\Delta$ OD v/s Q curve" (Figure 4.33e). The CE value for this device was obtained to be ~800 cm<sup>2</sup>/C for color switching, corresponding to 515 nm. This is a high value as compared to the reported ECDs in the EV-based ECD family, as can be seen from the comparison table (Table 4.4). Furthermore, the solid-

state ECD also shows fast and efficient electrochromic switching performance corresponding to 700 nm with color-switching times of 0.4s/0.5s and CE of 670 cm<sup>2</sup>/C (Figure 4.33f). The overall study of electrochromic performance from the newly developed iPOP-Bpy molecule reveals that this molecule has the potential to be used in a power-efficient and fast solid-state electrochromic device which shows great color contrast of more than 50% at a voltage of as low as 2V.

**Table 4.4** Comparison table for current work with already reported work onPTH-incorporated ECDs.

Serial No.	Device structure	Switching speed	Coloration Efficiency	References
1	PHT/Viologen	1.5/2s	222	Solar Energy Materials and Solar Cells 2018, 188, 249–254.
2	PHT/ iPOP-Bpy	0.5/0.7s	800	This work
3	PHT/CNT/Viologen	1.0/0.5s	401	Appl. Phys. Lett. 2021, 118 (15), 153301
4	PHT/WO <sub>3</sub>	1.3/5.1s	Not reported	Electrochemistry Communications 2015, 57, 65– 69
5	PHT/MOS <sub>2</sub> /Viologen	0.8/0.4s	580	Solar Energy Materials and Solar Cells 2022, 236, 111502
6	РНТ	3.2/3.2s	239.5	ACS Appl. Mater. Interfaces 2009, 1 (12), 2821–2828
7	РНТ	2.5/2.5s	230	Chin. J. Chem. 2008, 26 (4), 677–680.

#### 4.4. Conclusion

Here, a thermally and chemically stable, multifunctional ionic porous organic polymer containing redox-active viologen sites was designed and synthesized and well characterized with various spectroscopic and imaging techniques. The materials show excellent iodine uptake capacity in vapor, organic, and aqueous phases, fast kinetics, and multiple-time reusability. Due to the presence of redox-active viologen sites in the material, it shows ultrafast color switching from yellow to blue in the presence of electron-

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rich ammonia vapor. It shows excellent efficiency as a solid-state ammonia vapor sensor. Bias-dependent in-situ transmission and electrochemical measurements of a solid-state ECD fabricated using **iPOP-Bpy** reveal that it can be the best choice from the viologen family in manufacturing an organic ECD. The above conclusion can be drawn from the excellent electrochromic performance parameter values of switching times (~0.5 s), color contrast (~50%), and coloration efficiencies (up to 800 cm<sup>2</sup>/C). In addition, the device shows color switching for multiple wavelengths with a low applied bias of 2V while showing the abovementioned performance parameters. The material can be applied in a n-type electrochromic auxiliary electrode, preferably in combination with an p-type material.

#### 4.5. Declaration

This chapter is adapted from ACS Appl. Mater. Interfaces 2023, 15, 23, 28453–28464 (DOI: 10.1021/acsami.3c01800).

#### 4.6. References

[1] Klajn R., Stoddart J. F., Grzybowski B. A. (2010), Nanoparticles Functionalised with Reversible Molecular and Supramolecular Switches, Chem. Soc. Rev., 39, 2203–2237 (DOI: 10.1039/B920377J)

[2] Kundu P. K., Olsen G. L., Kiss V., Klajn R. (2014), Nanoporous Frameworks Exhibiting Multiple Stimuli Responsiveness, Nat. Commun., 5, 3588 (DOI: 10.1038/ncomms4588)

[3] Sun H., Liu S., Lin W., Zhang K. Y. Lv, W., Huang X., Huo F., Yang H., Jenkins G., Zhao Q., Huang W. (2014), Smart Responsive Phosphorescent Materials for Data Recording and Security Protection, Nat. Commun., 5, 3601 (DOI: 10.1038/ncomms4601)

[4] Sun J., Wu Y., Wang Y., Liu Z., Cheng C., Hartlieb K. J., WasielewskiM. R., Stoddart, J. F. (2015), An Electrochromic Tristable Molecular

Switch, J. Am. Chem. Soc., 137, 13484–13487 (DOI: 10.1021/jacs.5b09274)

[5] Mura S., Nicolas J. Couvreur P. (2013), Stimuli-Responsive Nanocarriers for Drug Delivery, Nature Mater, 12, 991–1003 (DOI: 10.1038/nmat3776)

[6] Berkovic G., Krongauz V., Weiss V. (2000), Spiropyrans and Spirooxazines for Memories and Switches, Chem. Rev., 100, 1741–1754 (DOI: 10.1021/cr9800715)

[7] Minkin V. I. (2004), Photo-, Thermo-, Solvato-, and Electrochromic Spiroheterocyclic Compounds, Chem. Rev., 104, 2751–2776 (DOI: 10.1021/cr020088u)

[8] Wang Y., Zhang Y. M., Zhang S. X. A. (2021), Stimuli-Induced Reversible Proton Transfer for Stimuli-Responsive Materials and Devices, Acc. Chem. Res., 54, 2216–2226 (DOI: 10.1021/acs.accounts.1c00061)

[9] Zhang X., Hou L., Samorì P. (2016), Coupling Carbon Nanomaterials with Photochromic Molecules for the Generation of Optically Responsive Materials, Nat. Commun., 7, 11118 (DOI: 10.1038/ncomms11118)

[10] Burnworth M., Tang L., Kumpfer J. R., Duncan A. J., Beyer F. L.,
Fiore G. L., Rowan S. J., Weder C. (2011), Optically Healable
Supramolecular Polymers, Nature, 472, 334–337 (DOI: 10.1038/nature09963)

[11] Zhai L. (2013), Stimuli-Responsive Polymer Films, Chem. Soc. Rev.42, 7148–7160 (DOI: 10.1039/C3CS60023H)

[12] Vassalini I., Alessandri I., de Ceglia D (2014), Stimuli-ResponsivePhase Change Materials: Optical and Optoelectronic Applications,Materials, 14, 3396 (DOI: 10.3390/ma14123396)

[13] Zhang X., Chen L., Lim K. H., Gonuguntla S., Lim K. W., Pranantyo D., Yong W. P., Yam W. J. T., Low Z., Teo W. J., Nien H. P., Loh Q. W., Soh S. (2019), The Pathway to Intelligence: Using Stimuli-Responsive Materials as Building Blocks for Constructing Smart and Functional Systems, Adv. Mater., 31, 1804540 (DOI: 10.1002/adma.201804540)

[14] Malik N., Elool Dov N., de Ruiter G., Lahav M. van der Boom M. E.
(2019), On-Surface Self-Assembly of Stimuli-Responsive Metallo-Organic
Films: Automated Ultrasonic Spray-Coating and Electrochromic Devices,
ACS Appl. Mater. Interfaces, 11, 22858–22868 (DOI: 10.1021/acsami.9b05512

[15] Škorjanc T., Shetty D., Olson M. A., Trabolsi A. (2019), Design Strategies and Redox-Dependent Applications of Insoluble Viologen-Based Covalent Organic Polymers, ACS Appl. Mater. Interfaces, 11, 6705–6716 (DOI: 10.1021/acsami.8b20743)

[16] Murugavel K. (2014), Benzylic Viologen Dendrimers: A Review of Their Synthesis, Properties and Applications, Polym. Chem., 5, 5873–5884 (DOI: 10.1039/C4PY00718B)

[17] Zhang W., Zhu C., Huang Z., Gong C., Tang Q., Fu X. (2019), Electrochromic 2,4,6-triphenyl-1,3,5-triazine Based Esters with Electron Donor-Acceptor Structure, Org. Electron., 67, 302-310 (DOI: 10.1016/j.orgel.2018.12.041)

[18] Data P., Zassowski P., Lapkowski M., Grazulevicius J. V., Kukhta N.
A., Reghu R. R. (2016) Electrochromic Behaviour of Triazine Based Ambipolar Compounds, Electrochim. Acta 192, 283-295 (DOI: 10.1016/j.electacta.2016.01.208)

[19] Wu N., Ma L., Zhao S., Xiao D. (2019), Novel Triazine-Centered
 Viologen Analogues for Dual-band Electrochromic Devices, Sol. Energy
 Mater. Sol. Cells, 195, 114–121 (DOI: 10.1016/j.solmat.2019.03.005)

[20] Chen C., Cai L. X., Tan B., Zhang Y. J., Yang X. D., Zhang J. (2015), Ammonia Detection by Using Flexible Lewis Acidic Sites in Luminescent Porous Frameworks Constructed from a Bipyridinium Derivative, Chem. Commun., 51, 8189–8192 (DOI: 10.1039/C5CC01239B)

[21] Madasamy K., Velayutham D., Suryanarayanan V., Kathiresan M.,
Ho K. C. (2019), Viologen-Based Electrochromic Materials and Devices, J.
Mater. Chem. C, 7, 4622–4637 (DOI: 10.1039/C9TC00416E)

[22] Granqvist C. (1994), Electrochromic Oxides: A BandstructureApproach, Sol. Energy Mater. Sol. Cells, 32, 369–382. (DOI: 10.1016/0927-0248(94)90100-7)

[23] Chaudhary A., Pathak D. K., Ghosh T., Kandpal S., Tanwar M., Rani C., Kumar R. (2020), Prussian Blue-Cobalt Oxide Double Layer for Efficient All-Inorganic Multicolor Electrochromic Device, ACS Appl. Electron. Mater., 2, 1768–1773 (DOI: 10.1021/acsaelm.0c00342)

[24] Pathak D. K., Chaudhary A., Tanwar M., Kandpal S., Ghosh T.,
Rani C., Kumar R. (2021), Low Voltage Colour Modulation in
Hydrothermally Grown Ni-Co Nanoneedles for Electrochromic
Application, IET Nanodielectrics, 4, 75–80 (DOI: 10.1049/nde2.12012)

[25] Kandpal S., Ghosh T., Rani C., Rani S., Pathak D. K., Tanwar M., Bhatia R., Sameera I., Kumar R. (2022), MoS<sub>2</sub> Nano-Flower Incorporation for Improving Organic-Organic Solid State Electrochromic Device Performance, Sol. Energy Mater. Sol. Cells, 236, 111502 (DOI: 10.1016/j.solmat.2021.111502)

[26] Argun A. A., Cirpan A., Reynolds J. R. (2003), The First Truly All-Polymer Electrochromic Devices, Adv. Mater., 15, 1338–1341 (DOI: 10.1002/adma.200305038)

[27] Cai G., Wang J., Lee P. S. (2016), Next-Generation Multifunctional Electrochromic Devices. Acc. Chem. Res., 49, 1469–1476 (DOI: 10.1021/acs.accounts.6b00183)

[28] Mishra S., Lambora S., Yogi P., Sagdeo P. R., Kumar R. (2018),
Organic Nanostructures on Inorganic Ones: An Efficient Electrochromic
Display by Design, ACS Appl. Nano Mater., 1, 3715–3723 (DOI: 10.1021/acsanm.8b00871)

[29] Chaudhary A., Sivakumar G., Pathak D. K., Tanwar M., Misra R., Kumar R. (2021), Pentafluorophenyl Substituted Fulleropyrrolidine: A Molecule Enabling the Most Efficient Flexible Electrochromic Device with Fast Switching, J. Mater. Chem. C, 9, 3462–3469 (DOI: 10.1039/D0TC04991C)

[30] Pathak D. K., Chaudhary A., Tanwar M., Goutam, U. K., Kumar R.
(2020), Nano-Cobalt Oxide/Viologen Hybrid Solid State Device: Electrochromism beyond Chemical Cell, Appl. Phys. Lett., 116, 141901 (DOI: 10.1063/1.5145079)

[31] Zhao Y., Truhlar D. G. (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc., 120, 215-41 (DOI: 10.1007/s00214-007-0401-8)

[32] Grimme S., Antony J., Ehrlich S., Krieg H. (2010), A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys., 132, 154104 (DOI: 10.1063/1.3382344)

[33] M.J. Frisch, et al Gaussian 16 Revision C.01. Gaussian Inc.Wallingford CT (2016).

[34] Li R., Xing G., Li H., Li S., Chen L. (2022) A Three-Dimensional Polycyclic Aromatic Hydrocarbon Based Covalent Organic Framework Doped with Iodine for Electrical Conduction, Chinese Chemical Letters, https://doi.org/10.1016/j.cclet.2022.04.052.

[35] Das M., Sarkar S. K., Patra Y. S., Manna A., Mukherjee S., Das, S. (2022), Soft Self-Templating Approach-Derived Covalent Triazine Framework with Bimodal Nanoporosity for Efficient Radioactive Iodine Capture for Safe Nuclear Energy, ACS Appl. Nano Mater., 5, 8783–8793 (DOI: 10.1021/acsanm.2c00564)

[36] Sen A., Sharma S., Dutta S., Shirolkar M. M., Dam G. K., Let S.,
Ghosh S. K. (2021), Functionalized Ionic Porous Organic Polymers
Exhibiting High Iodine Uptake from Both the Vapor and Aqueous Medium,
ACS Appl. Mater. Interfaces, 13, 34188–34196 (DOI: 10.1021/acsami.1c07178)

[37] Zhang Z., Li L., An D., Li H., Zhang X. (2020), Triazine-Based Covalent Organic Polycalix[4]Arenes for Highly Efficient and Reversible Iodine Capture in Water, J Mater Sci, 55, 1854–1864 (DOI: 10.1007/s10853-019-04164-6)

[38] Lin Y., Jiang X., Kim S. T., Alahakoon S. B., Hou X., Zhang Z., Thompson C. M., Smaldone R. A., Ke C. (2017), An Elastic Hydrogen-Bonded Cross-Linked Organic Framework for Effective Iodine Capture in Water, J. Am. Chem. Soc., 139, 7172–7175 (DOI: 10.1021/jacs.7b03204)

[39] An D., Li L., Zhang Z., Asiri A. M., Alamry K. A., Zhang X. (2020),
Amino-Bridged Covalent Organic Polycalix[4]Arenes for Ultra Efficient
Adsorption of Iodine in Water, Mater. Chem. Phys., 239, 122328 (DOI: 10.1016/j.matchemphys.2019.122328)

[40] Shi W., Xing F., Bai Y. L., Hu M., Zhao Y., Li M. X., Zhu S. (2015),High Sensitivity Viologen for a Facile and Versatile Sensor of Base and

Solvent Polarity in Solution and Solid State in Air Atmosphere, ACS Appl. Mater. Interfaces, 7, 14493–14500 (DOI: 10.1021/acsami.5b03932)

[41] Li M., Wei Y., Zheng J., Zhu D., Xu C. (2014), Highly Contrasted and Stable Electrochromic Device Based on Well-Matched Viologen and Triphenylamine. Org. Electronics, 15, 428–434 (DOI: 10.1016/j.orgel.2013.11.018)

[42] Tan B., Chen C. Cai L. X., Zhang Y. J.; Huang X. Y., Zhang J.
(2015), Introduction of Lewis Acidic and Redox-Active Sites into a Porous
Framework for Ammonia Capture with Visual Color Response, Inorg.
Chem., 54, 3456–3461 (DOI: 10.1021/acs.inorgchem.5b00023)

[43] Das G., Prakasam T., Nuryyeva S., Han D. S., Abdel-Wahab A.,
Olsen J. C., Polychronopoulou K., Platas-Iglesias C., Ravaux F., Jouiad M.,
Trabolsi A. (2016), Multifunctional Redox-Tuned Viologen-Based
Covalent Organic Polymers, J. Mater. Chem. A, 4, 15361–15369 (DOI: 10.1039/C6TA06439F)

[44] Li Z., Cai W., Yang X., Zhou A., Zhu Y., Wang H., Zhou X., Xiong K., Zhang Q., Gai Y. (2020), Cationic Metal-Organic Frameworks Based on Linear Zwitterionic Ligands for  $Cr_2O_7^{2-}$  and Ammonia Sensing, Cryst. Growth Des., 20, 3466–3473 (DOI: 10.1021/acs.cgd.0c00247)

[45] Chen R., Chen S., Zhou Y., Wei Z., Wang H., Zheng Y., Li M., Sun K., Li Y. (2020), Unsubstituted Polythiophene Film Deposited via In-Situ Sequential Solution Polymerization for Chemo-/Electrochromism, Macromolecule, 53, 4247–4254 (DOI: 10.1021/acs.macromol.0c00297)

[46] Nicho M. (2004), Synthesis of Derivatives of Polythiophene and Their Application in an Electrochromic Device, Sol. Energy Mater. Sol. Cells, 82, 105–118 (DOI: 10.1016/j.solmat.2004.01.009)

[47] Chaudhary A., Pathak D. K., Mishra S., Yogi P., Sagdeo P. R.,Kumar R. (2018), Polythiophene -Viologen Bilayer for Electro-Trichromic Device, Sol. Energy Mater. Sol. Cells, 188, 249–254.

[48] Chaudhary A., Pathak D. K., Tanwar M. Koch J., Pfnür H., Kumar R. (2020), Polythiophene-NanoWO<sub>3</sub> Bilayer as an Electrochromic Infrared Filter: A Transparent Heat Shield. J. Mater. Chem. C, 8, 1773–1780 (DOI: 10.1039/C9TC05523A)

[49] Chaudhary A., Pathak D. K., Tanwar M., Yogi P., Sagdeo P. R.,
Kumar R. (2019), Polythiophene–PCBM-Based All-Organic
Electrochromic Device: Fast and Flexible. ACS Appl. Electron. Mater., 1,
58–63 (DOI: 10.1021/acsaelm.8b00012)

[50] Barman S., Deng F., McCreery R. L. (2008) Conducting Polymer Memory Devices Based on Dynamic Doping, J. Am. Chem. Soc., 130, 11073–11081 (DOI: doi.org/10.1021/ja802673w)





Exploring Counter Anions in a Redox-Active Viologen-Based ionic Porous Organic Polymer (iPOP) for Highly Selective Reduction of Oxygen to H<sub>2</sub>O<sub>2</sub>

#### 5.1. Introduction

With the increasing globalization, the demand for commercial reagents has increased significantly. Among the various chemical reagents in massive demand in different industrial and commercial projects,  $H_2O_2$ , an environment-friendly oxidant, is significant [1-4]. Though in high demand, the production of H<sub>2</sub>O<sub>2</sub> still largely depends on the anthraquinone process, which is energy-consuming, only operational in centralized facilities, and is a cause of significant environmental pollution [5,6]. Mixing hydrogen and oxygen in the presence of Pd-based catalysts, though, is a green and achievable alternative [7]; implementation of such a process at the industrial level is always problematic not only due to the high processing cost of the catalyst but also due to the risk of explotion of the H<sub>2</sub>/O<sub>2</sub> gas mixture. Considering the high demand and low producibility of H<sub>2</sub>O<sub>2</sub> and the high risk involved in the traditional  $H_2O_2$  production processes, there is an pressing need to find cost-efficient and environmentally friendly alternatives. In this regard, synthesizing H<sub>2</sub>O<sub>2</sub> electrochemically in a fuelcell setup using water and oxygen could be a green and cost-efficient alternative. Selective production of H<sub>2</sub>O<sub>2</sub> over water is always challenging in a fuel-cell setup as the competitive and predominant 4e<sup>-</sup> reduction pathway severely hampers the  $2e^{-1}$  reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> [8-12]. Therefore, developing a suitable catalyst that could selectively reduce O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> is essential. In the past few years, several noble metal-based catalysts have evolved that show considerably low overpotential and good selectivity toward the production of  $H_2O_2$  [13-16]. At the same time, there are several heteroatom-dopped carbon materials show significant oxygen reduction reactions. However, their reduced selectivity for the H<sub>2</sub>O<sub>2</sub> production, high cost of pyrolyzing, disrupted pore structure, and loss of N atoms during the pyrolysis process always make them inefficient [17-21]. Recently, porous organic polymer-based materials have evolved into new types of porous material with unique pore structures, stable skeletons, high surface areas, and high physicochemical stability [22]. Though porous organic polymers

are extensively explored in several domains of research, their applicability in the selective electrochemical production of H<sub>2</sub>O<sub>2</sub> still remains largely unexplored. Among the very few reports of porous organic polymer-based electrocatalysts for selective hydrogen peroxide production, most are metaldoped catalysts [23-25]. The use of metals not only increases the preparation cost of the catalyst but also the leaching of the metal ions from the polymeric skeleton during the electrocatalysis might hamper the catalytic activity of the materials. Among the reported metal-free electrocatalysts [26-30], most of them use sulfur as the active element, which is also not safe to use at the industrial level, considering the known toxicity of S-containing compounds towards mammals and aquatic creatures [31,32]. Using viologen-based materials in the polymeric skeleton is particularly helpful in increasing the ORR activity [33,34]. In this work, viologen-based ionic porous organic polymer (iPOP-TAPA-Cl) was synthesized by reacting Zincke salt with a non-planar building block Tris(4aminophenyl)amine (TAPA), to check the efficiency of the polymers in the selective electrochemical production of H<sub>2</sub>O<sub>2</sub>. The electron-rich TAPA building block, owing to its strong electron-donating nature, increases the O<sub>2</sub> adsorption strength in the active site of the catalyst [35]. Additionally, the switchable redox states from dicationic to radical cations help to polarize the dissolved oxygen, which is beneficial in prioritizing the 2e<sup>-</sup> reduction pathway [36,37]. At the same time, the exchangeable counter anion in the cationic skeleton is further helpful in tuning the electronic property of the polymeric skeleton by simple ion exchange that might help to control the catalytic activity of the polymer. In this study, a series of polymeric electrocatalysts is prepared by simply exchanging counter anions with other halide anions. Among the polymer electrocatalysts, iPOP-TAPA-F has come up as the most active catalyst with high selectivity for  $H_2O_2$  (98.5%) and excellent current efficiency (99%).

### **5.2 Experimental section**

### 5.2.1. Materials

1-fluoro-4-nitrobenzene, 4-nitroaniline, and 4,4'-Bipyridine and Pd/C were purchased from Sigma Aldrich. 2,4-dinitro-chlorobenzene and hydrazine monohydrate were purchased from Avra Chemicals. All the salts and solvents were obtained from a local vendor and used without further purification.

#### 5.2.2. Physical measurements

The same characterization techniques were used, as mentioned in 2.2.1 section in charpter 2

# 5.2.3. Synthesis of 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'diium dichloride (ZN-Cl2)

The building block was synthesized using the same method described in Chapter 3, 3.2.2 section.

### 5.2.4. Synthesis of Tris(4-aminophenyl)amine (TAPA)

4-nitroaniline (5 g, 36.20 mmol) and  $K_2CO_3$  (30 g, 217.07 mmol) were taken in dry DMSO, and the solution was stirred under an N<sub>2</sub> atmosphere for 20 mins. To the solution, 1-fluoro-4-nitrobenzene (8 mL, 0.08 mmol) was added dropwise to the solution and the whole mixture was heated at 120°C for 48 h. The mixture was then cooled to room temperature and poured into 100 mL of ice-cold water to obtain a bright yellow solid. The solid was then collected by filtration and washed with a large amount of water. Finally, the solid was dried at 70°C, and the obtained solid was directly used in the next step.

The yellow solid (10 g) and Pd/C (0.66 g) were dispersed in 30 mL 2:1 dioxane ethanol mixture under an N<sub>2</sub> atmosphere, and the mixture was heated at 80°C for 1h. After that, hydrazine monohydrate (26.3 mL) was

added dropwise to the suspension, and the whole system was heated for 48 h. After completion of the reaction, the reaction mixture was filtered hot, and the filtrate was cooled to obtain a precipitate. The precipitate was washed with a large amount of ethanol and dried to obtain Tris(4-aminophenyl)amine (TAPA) as a gray-colored solid. Product yield 68%, 5.23 g. <sup>1</sup>H NMR (500 MHz, 298 K, DMSO-d<sub>6</sub>):  $\delta = 6.60$  (d, 6H), 6.45 (d, 6H), 5.92 (s, 6H). 13C NMR (125 MHz, 298K, DMSO-d<sub>6</sub>):  $\delta$  143.66, 139.13, 124.54, 115.20.



Figure 5.1. <sup>1</sup>H NMR of Tris(4-aminophenyl)amine (TAPA)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 Chemical Shift (ppm)

# Figure 5.2. <sup>13</sup>C NMR of Tris(4-aminophenyl)amine (TAPA) 5.2.5. Synthesis of iPOP-TAPA-Cl

An oven-dried pressure tube was charged with 0.1 g of TAPA and 0.29 g of ZN-CL2, then 10 mL of acetonitrile-water (4:1) was added as a solvent. It was sonicated for 30 min to obtain a deep violet homogeneous mixture. The whole system was heated at 90°C for 6 h. After cooling the reaction tube to room temperature, the obtained precipitate was separated by vacuum filtration. The isolated solid was washed frequently with DMF, water, acetone, MeOH, and chloroform several times. Finally, the black-colored solid was dipped in a solvent mixture of MeOH and chloroform (1:1) overnight. The solid was then separated by centrifugation and dried overnight at 100°C in a hot-air oven to obtain desolvated **iPOP-TAPA-Cl** as a black-colored powder.

#### 5.2.6. Synthesis of iPOP-TAPA-X (X= F, Br, and I)

To prepare **iPOP-TAPA-X**, to a saturated solution of KX (X= F, Br, I) (10 mL), 0.1 g of desolvated **iPOP-TAPA-Cl** was added and heated overnight at  $60^{\circ}$ C with constant stirring. The obtained solid was then separated by

centrifugation and again added to 10 mL of saturated solution of KX, and the same process was repeated. Finally, the recovered solid was washed with hot water and MeOH and dried in a hot air oven for 24 h to obtain **iPOP-TAPA-X** powder.



Scheme 5.1. Synthesis of iPOP-TAPA-Cl and its halogenated derivatives.

#### 5.2.7. Preparation of the iPOP-TAPA-Cl radical cation

For this experiment, the same procedure was followed as described in Chapter 4 section 4.2.5 section.

### 5.2.8. Chemical stability test of iPOP-TAPA-Cl

To check the chemical stability of the polymer, 5 mg of the polymer was added individually to different solvents and was allowed to stand for 24 h. The residual solid was collected by filtration and repeatedly washed with MeOH and DCM. The solid was then dried in a hot air oven at 100 °C for another 24 h. Finally, the weight of the polymer was measured gravimetrically and characterized with FTIR spectroscopy.

#### 5.2.9. Electrochemical Measurements

The electrochemical activities of the series of synthesized **iPOP-TAPA-X** (F, Cl, Br, I) samples were carried out using a three-electrode setup in a Metroohm Autolab 204 workstation. The glassy carbon rotating disk electrode with drop-casted electrocatalyst, Ag/AgCl, and Pt wire were used

as working, reference, and counter electrodes, respectively. Homogeneous sample ink was prepared by mixing 2.5 mg of **iPOP-TAPA-X** into a 450  $\mu$ L solution of isopropanol and water mixture and adding 50  $\mu$ L of 0.01 wt% PVDF as binder under ultrasonication condition for 30 minutes. After sonicating, the working electrode was prepared by drop-casting 7  $\mu$ L of prepared ink onto the glassy carbon disk. Approximately 180  $\mu$ g cm<sup>-2</sup> mass loading was found to be optimal for showing the best catalytic activity.

To evaluate the ORR performance of electrocatalyst **iPOP-TAPA-X**, LSV measurements were recorded at different rpm at a scan rate of 10 mV s<sup>-1</sup> in  $O_2$ -saturated 0.1 M KOH electrolyte, keeping the ring potential fixed at 1.4V vs. RHE. The CV curves were recorded at a scan rate of 50 mV s<sup>-1</sup> in both  $O_2$  and  $N_2$ -saturated 0.1 M KOH electrolytes for comparative electrochemical study.

The number of electron transfers during the ORR process is experimentally evaluated by the Koutecky–Levich (K–L) equations as described below:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{Bw^{1/2}}$$

where J is the measured current density,  $J_K$  and  $J_d$  are kinetic current density and the diffusion-limited current density, respectively (mA cm<sup>-2</sup>), d is the diffusion-limited current density, and w is the rotating speed of the electrode (rad s<sup>-1</sup>). B is the Levich Constant.

$$B = 0.62 n F A v^{-1/6} C_{O2} D^{2/3}$$

Where n is the number of transferred electrons, F is the Faraday constant (96500 C mol<sup>-1</sup>), v is the kinematic viscosity (0.011 cm<sup>2</sup> s <sup>-1</sup>), C<sub>02</sub> is the bulk concentration of O<sub>2</sub> ( $1.2 \times 10^{-6}$  mol cm<sup>-3</sup>), and D is the diffusion coefficient of O<sub>2</sub> ( $1.9 \times 10^{-5}$  cm<sup>2</sup> s <sup>-1</sup>) in 0.1 M KOH solution.

Hydrogen peroxide selectivity, electron transfer number (n), and Faraday efficiency (%) were calculated based on the following equations:

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$
$$H_2 O_2(\%) = \frac{200 I_r}{N|I_d| + I_r}$$
Faraday efficiency (%) =

 $\frac{\frac{I_r}{N}}{I_d}$ 

where  $I_d$  and  $I_r$  are the disk current and the ring current, respectively. N is the collection efficiency was determined to be 0.23 from the reduction of K<sub>4</sub>Fe[CN]<sub>6</sub>.

#### 5.3. Results and Discussion

#### 5.3.1. Characterization of iPOP-TAPA-Cl

The polymer **iPOP-TAPA-Cl** was synthesized by the Zincke reaction, reacting TAPA and ZN-Cl2 (Zincke salt) in a 1:1.5 molar ratio in acetonitrile-water (4:1) solvent mixture at 90°C for 6 h (Scheme 5.1). The polymer was isolated as a black powder. The successful synthesis of the polymer was confirmed by FTIR and <sup>13</sup>C-CPMAS NMR spectroscopy. In the <sup>13</sup>C-CPMAS NMR spectra, broad peaks in the 149.42-123.62 ppm region represent all aromatic carbons in the polymeric skeleton. Peaks at 149.42,135.22, and 123.62 ppm correspond to the viologen moiety present in the polymeric backbone, whereas peaks at 145.17, 132.56, 130.64, and 127.52 ppm represent the carbons of the TAPA molecule in the polymer (Figure 5.3 a).



**Figure 5.3.** (a) <sup>13</sup>C CPMAS NMR spectra of **iPOP-TAPA-Cl** (b) FTIR spectra of **iPOP-TAPA-Cl**.

In the FTIR spectra of iPOP-TAPA-Cl, the complete disappearance of the bands at 3403 and 3320 cm<sup>-1</sup>, which corresponds to the -NH<sub>2</sub> stretching frequencies of the TAPA building block and band at 1545 cm<sup>-1,</sup> which corresponds to the -NO<sub>2</sub> stretching frequencies of the ZN-Cl2 building blocks represents the successful consumption of the starting materials in the polymer (Figure 5.3b). PXRD analysis shows the amorphous nature of the polymer (Figure 5.4a). The TGA analysis shows the polymer is thermally stable over 250 °C, depicting its high thermal stability (Figure 5.4b).



**Figure 5.4.** (a) PXRD of **iPOP-TAPA-X** (X= F, Cl, Br, and I) (b) TGA profiles of **iPOP-TAPA-X** (X= F, Cl, Br, and I)

The polymer **iPOP-TAPA-Cl** appeared to be insoluble in every possible lab solvent (Figure 5.5).



Figure 5.5. Residual weight of the polymer in different lab solvents

Additionally, its stable nature in weak acidic and basic solutions, which was confirmed by FTIR spectra (Figure 5.6), further confirms its robust nature.



**Figure 5.6.** Comparative FTIR spectra of the polymers in (a) various lab solvents and (b) after treatment in different pH solutions, showing the chemical robustness of the polymers.

The FESEM image shows an aggregated spherical morphology of the polymer. The elemental analysis and EDX further confirm the presence of C, N, and Cl in the polymer (Figures 5.7 and 5.8).



Figure 5.7. FESEM imaging and elemental mapping of iPOP-TAPA-Cl



Figure 5.8. EDX analysis of iPOP-TAPA-Cl

The XPS analysis confirms the presence of these elements only in the polymer (Figure 5.9a). The deconvoluted XPS N1s and C1s spectra show the presence of C-C/C=C, C-N, C=N<sup>+,</sup> and C-N<sup>+</sup> functionalities in the polymer (Figures 5.9b and 5.9c). The deconvoluted Cl 2p spectra further confirm the presence of Cl<sup>-</sup> as a counter-anion in the polymer (Figure 5.9d).



**Figure 5.9.** (a) XPS survey spectra of **iPOP-TAPA-Cl**. (b) Deconvoluted N1s spectra, (c) Deconvoluted C1s spectra, and (d) Deconvoluted Cl2p spectra of **iPOP-TAPA-Cl**.

The N<sub>2</sub> adsorption-desorption study was performed at 77 K to investigate the porosity of the polymer (Figure 5.10a). The calculated BET surface area of the polymer was  $45.174 \text{ m}^2/\text{g}$ . The pore size distribution of the polymer was evaluated using the BJH method, showing a mesoporous nature with a pore diameter of 3.089 nm (Figure 5.10b).



**Figure 5.10.** (a) N<sub>2</sub> adsorption-desorption isotherm and (b) the pore size distribution of **iPOP-TAPA-Cl** calculated using the BJH method.

#### **5.3.2. Electrochemical performance of iPOP-TAPA-Cl**

The ORR performances of synthesized pristine polymer **iPOP-TAPA-Cl** were tested with both  $O_2$  and  $N_2$ -saturated alkaline 0.1 M KOH electrolyte using the RRDE technique. The CV curve **iPOP-TAPA-Cl** in both  $N_2$  and  $O_2$ -saturated electrolytes (Figure 5.11a) reflected the presence of a well-defined reduction peak at 0.48-0.51 V vs. RHE, confirming its redox-active nature. More importantly, the increase in reduction current density in  $O_2$ -saturated electrolyte compared to that of  $N_2$  saturated indicates its oxygen reduction property. The LSV polarisation plot at a scan rate of 10 mV s<sup>-1</sup> with different rotating speeds in  $O_2$ -saturated alkaline electrolytes further confirms its pronounced ORR activity (Figure 5.11b).



**Figure 5.11.** (a) CV curve of **iPOP-TAPA-Cl** at a scan rate of 50 mV s<sup>-1</sup> in N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH electrolyte. (b) LSV curve of **iPOP-TAPA-Cl** in O<sub>2</sub>-saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s<sup>-1</sup> with different rotating speeds.

However, it is well known that oxygen reduction reaction may follow either the 2e<sup>-</sup> transfer pathway to produce  $H_2O_2$  or the 4e<sup>-</sup> transfer pathway to form  $O_2$ . The Koutecky–Levich plot, as displayed in Figure 5.12a, revealed that the 2e<sup>-</sup> pathway is preferred here. Additionally, the selectivity towards  $H_2O_2$ production as quantified from the RRDE measurement (Figure 5.12b) for

**iPOP-TAPA-Cl** was found to be notably high at around 86%, which is comparable with the recently reported catalysts [34,37].



**Figure 5.12.** (a) Koutecky–Levich plot and (b)  $H_2O_2$  selectivity and electron transfer number (n) of **iPOP-TAPA-Cl**.

#### 5.3.3. Characterization of iPOP-TAPA-X

Owing to the presence of exchangeable Cl<sup>-</sup> ions in the polymeric skeleton, the role of different halogen ions in the H<sub>2</sub>O<sub>2</sub> production activity was further investigated. The variable electronegativity of the halogen ions might manipulate the electronic properties in the polymeric skeleton, making a difference in the activity of the H<sub>2</sub>O<sub>2</sub> production. The Cl<sup>-</sup> counter anion in the polymeric skeleton was exchanged with F<sup>-</sup>, Br<sup>-,</sup> and I<sup>-</sup> by simply immersing **iPOP-TAPA-Cl** in the saturated solution of the corresponding potassium salt of the halogens (KF, KBr, and KI) (Scheme 5.1). The XPS analysis confirmed the successful replacement of Cl<sup>-</sup> with other halides (Figures 5.13a and 5.13d). The deconvoluted C 1s and N 1s of **iPOP-TAPA-Cl** with slightly shifted values, further indicating the interaction of the halogen anions with the polymeric skeleton (Figures 5.13b, 5.13c and Table 5.1 and 5.2).


**Figure 5.13.** (a) Comparative XPS survey spectra (b) Comparative deconvoluted N 1s spectra of **iPOP-TAPA-X** (X=F, Cl, Br, and I) (c) Deconvoluted C 1s spectra of **iPOP-TAPA-X** (X=F, Br, and I) (d) Deconvoluted F 1s, Br 3d, and I 3d spectra of **iPOP-TAPA-F**, **iPOP-TAPA-Br**, and **iPOP-TAPA-I**.

**Table 5.1.** Comparative binding energies of the functionalities obtained from deconvoluted N 1s spectra of **iPOP-TAPA-X** (X= F, Cl, Br, and I).

Polymer	Binding Energy (eV)				
	CN	C=N+	C-N+		
iPOP-TAPA-Cl	398.85	399.74	401.89		
ipop-tapa-i	398.83	399.63	401.75		
iPOP-TAPA-Br	398.74	399.69	401.93		
ipop-tapa-f	398.88	399.72	401.83		

Polymer	Binding Energy (eV)				
	C-C/C=C	C-N	C-N⁺	C=N+	
iPOP-TAPA-Cl	284.01	284.55	285.53	287.86	
ipop-tapa-i	283.87	284.37	285.39	286.32	
iPOP-TAPA-Br	284.12	284.55	285.75	287.27	
ipop-tapa-f	283.98	284.58	285.58	286.65	

**Table 5.2.** Comparative binding energies of the functionalities obtained from deconvoluted C 1s spectra of **iPOP-TAPA-X** (X= F, Cl, Br, and I).

The TGA data shows that thermal stability remains intact after the halogen ion exchange. Only in the case of **iPOP-TAPA-I**, the initial weight loss to 100 °C may be due to the removal of entrapped solvent molecules or the removal of volatile iodine molecules from the skeleton upon heating (Figure 5.14a). The FTIR spectra of the ion-exchanged polymers show almost no changes compared to the pristine **iPOP-TAPA-Cl**, indicating no chemical change in the polymer upon halogen exchange (Figure 5.14b).



**Figure 5.14.** (a) TGA profiles and (b) comparative FTIR spectra of **iPOP-TAPA-X** (X= F, Cl, Br, and I)

The FESEM images show the aggregated spherical type of morphology in the polymer (Figure 5.15), whereas the elemental mapping and EDX

analysis further confirm the presence of the respective elements in the polymer (Figure 5.15 and 5.16).



**Figure 5.15.** FESEM and elemental mapping of **iPOP-TAPA-X** (X= F, Br and I)



Figure 5.16. EDX analysis of iPOP-TAPA-X (X=F, Br and I)

The  $N_2$  adsorption-desorption study was conducted to check any changes in the porosity of the polymer. As shown in Figure 5.17a, there is a slight but

steady increase in the N<sub>2</sub> adsorption capability in the polymer when going from F<sup>-</sup> to I<sup>-</sup>. The calculated BET surface area was 35.87 m<sup>2</sup>/g, 56.41 m<sup>2</sup>/g, and 69.28 m<sup>2</sup>/g, respectively, where the pore diameter varies from 3.05-3.44 nm (Figure 5.17b).



**Figure 5.17.** (a) N<sub>2</sub> adsorption-desorption isotherm of **iPOP-TAPA-X** (X= F, Cl, Br, and I) at 77K (b) Pore size distribution of **iPOP-TAPA-X** calculated using the BJH method.

#### 5.3.4. Electrochemical performance of iPOP-TAPA-X

The ORR performances of developed polymers obtained after exchanging the Cl<sup>-</sup> anion of **iPOP-TAPA-Cl** by F<sup>-</sup>/Br<sup>-</sup>/l<sup>-</sup> were also evaluated under an O<sub>2</sub>-saturated alkaline 0.1 M KOH electrolyte. Nevertheless, mass loading is a pivotal part of any electrocatalyst in showing its activity. Figure 5.18 revealed 180  $\mu$ g cm<sup>-2</sup> was the optimal loading for **iPOP-TAPA-F** in terms of current, H<sub>2</sub>O<sub>2</sub> selectivity, and number of electron transfers, and thereby, all electrochemical experiments were performed using 180  $\mu$ g cm<sup>-2</sup> of catalyst loading.



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**Figure 5.18.** (a) LSV polarisation curve of **iPOP-TAPA-F** at 1600 rpm at a scan rate of 10 mV s<sup>-1</sup> with different mass loading. (b) The  $H_2O_2$  selectivity and electron transfer number (n).

Figure 5.19a compares LSV plots of all four iPOP-TAPA-X at a scan rate of 10 mV s<sup>-1</sup> with 1600 rpm rotating speed. Clearly, the enhanced ORR performance of **iPOP-TAPA-F** was evidenced by its onset potential value of 0.78V, which is in good agreement with CV results (0.8V). The corresponding Tafel plot for iPOP-TAPA-F, as displayed in Figure 5.19b, with the smallest Tafel slope value of 65 mV dec<sup>-1</sup> among all, reveals its faster reaction kinetics towards ORR. Impressively, the ORR selectivity of **iPOP-TAPA-F** towards H<sub>2</sub>O<sub>2</sub> formation turned out to be highest (~98.5 %) with the selectivity trend of **iPOP-TAPA-X** as **iPOP-TAPA-F** (~98.5 %) > iPOP-TAPA-Cl (~86 %) > iPOP-TAPA-Br (~76 %) > iPOP-TAPA-I (~70 %), as compared in Figure 5.19c. Indeed, the electronegativity of the counteranion in iPOP greatly influences such a selectivity trend and is believed to be responsible for such high selectivity towards  $H_2O_2$ . Furthermore, the highest ORR performance of iPOP-TAPA-F was also evidenced by its excellent current efficiency of 99 %, as can be seen in Figure 5.19d.



**Figure 5.19.** (a) LSV polarization curves of **iPOP-TAPA-X** (X = F, Cl, Br, and I) at 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH electrolyte; (b) Tafel slope plot; (c)  $H_2O_2$  selectivity and electron transfer number (n) and (d) The current efficiencies of **iPOP-TAPA-X** for ORR.

The detailed electrochemical characterization of iPOP-TAPA-F was also evaluated in both  $O_2$  and  $N_2$  saturated 0.1 M KOH solution in Figure 5.20.



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**Figure 5.20.** (a) CV curve of **iPOP-TAPA-F** at a scan rate of 50 mV s<sup>-1</sup> in N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH electrolyte. (b) LSV curve of **iPOP-TAPA-F** at a scan rate of 10 mV s<sup>-1</sup> with different rotating speeds. (c) The Koutecky–Levich plot and (d) The H<sub>2</sub>O<sub>2</sub> selectivity and electron transfer number (n) of **iPOP-TAPA-F**.

With such a significant ORR performance, the stability of **iPOP-TAPA-F** was further examined by evaluating the disc current as well as ring current at specific applied potentials, which shows quite stable performances over 16 h, as shown in Figure 5.21a. LSV polarization curve of **iPOP-TAPA-F** before and after performing 1000 CV cycles showed negligible decay in its activity, revealing outstanding stability in alkaline media (Figure 5.21b).



**Figure 5.21.** (a) Stability test of **iPOP-TAPA-F** in 0.1 M KOH electrolyte showing disc current at a fixed voltage of 0.1 V vs. RHE and ring current at 1.4 V vs. RHE. (b) LSV polarization curve plotted before and after 1000 CV cycles.

Importantly, FE-SEM and EDX analysis were performed after the chronoamperometry test in order to check the structural stability of the **iPOP-TAPA-F**.



**Figure 5.22.** FE-SEM image, EDX, and elemental mapping of **iPOP-TAPA-F** after 4 h stability in 0.1 M KOH electrolyte.

Figure 5.22 displayed that the morphology and halide content of the polymer did not change significantly after the 4h stability test. Undoubtedly, the modulated iPOP systems exhibited comparable or, in some cases, much superior performances compared to some recently reported polymers, as tabulated in Table 5.3.

**Table 5.3.** Activity controlling parameters of **iPOP-TAPA-X** (X= F, Cl, Br, and I) in comparison with recently reported polymers.

D.I.		<b>.</b>	но	G. 1.114	D.f.
Polymer	Onset	Limiting	$H_2O_2$	Stability (b)	Reference
	(V vs	density	tv	(11)	
	RHE)	(mA cm <sup>-2</sup> )	(%)		
	, , , , , , , , , , , , , , , , , , ,	at 0.2 V vs			
		RHE			
iPOP-TAPA-F	0.78	2.25	98.5	16	This work
iPOP-TAPA-Cl	0.7	1.8	86		
iPOP-TAPA-Br	0.68	1.6	76		
iPOP-TAPA-I	0.65	1.65	70		
cCTN:Cl	0.75	2	85	8	Chem. Commun., 2018, 54, 4433-4436
BPyTTz-COP:F	0.72	1.5	98.5	10	Chem. Mater. 2020, 32, 8553–8560
CONs	0.695	2	99	10	Applied Catalysis B: Environmental 298 (2021) 120605
MgP-DHTA-COF	0.68	2	96	12	Chem Asian J. 2021, 16, 498 –502
Py-TD-COF	0.834	3	80–92	16	Applied Catalysis B: Environmental 340 (2024) 123216
PYTA-TPEDH- COF	0.69	2.1	86-84	1	Angew. Chem. Int. Ed. 2023, 62, 202218742
DFTAPB-TFTA- COF	0.698	1.7	96	3.47	Angew. Chem. Int. Ed. 2023, 62, 202313940
TP-TD-COF	0.71	2.6	50.9– 67.4	2.7	Small Struct. 2023, 4, 2200387
CoPc-S-COF	0.81	2.4	>95	10	Nature Communications   (2024) 15:678
COF-CN	0.72	1.7	97.2	28	Nano Today 49 (2023) 101792
PtCl-COF	0.675	1.83	81.6- 87.2	10	SusMat. 2023;3:379– 389.

In order to establish the plausible mechanism of the  $H_2O_2$  production by the polymer, EPR analysis of both **iPOP-TAPA-Cl** and **iPOP-TAPA-Cl**<sup>+</sup> was performed. **iPOP-TAPA-Cl**<sup>+</sup> was prepared by treating the polymer with a saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in the presence of N<sub>2</sub>. Though no visible change in color was observed after the reduction of the polymer, the

appearance of a sharp peak in the ERP spectrum (g=2.002) confirms the formation of the radical cation (Figures 5.23a and 5.23b).



**Figure 5.23.** EPR spectra of (a) **iPOP-TAPA-Cl** (b) **iPOP-TAPA-Cl** $\cdot$  (c) Mechanism of H<sub>2</sub>O<sub>2</sub> generation on **iPOP-TAPA-Cl**.

This data proves that the redox-active polymer can be reduced to radical cation (**iPOP-TAPA-Cl**<sup>+</sup>), and this can be done by both chemical and electrochemical procedures. Subsequently, the dissolved oxygen is reduced to generate superoxygen radical (HO<sub>2</sub><sup>-</sup>) and further to H<sub>2</sub>O<sub>2</sub> by accepting one more electron from the electrolyte (Figure 5.23c) [34,38].

Further, to establish the effect of the counter anions, the Zeta potential of all the polymers was recorded, which appears to be 74.07, 57.27, 54.69, and 42.81 for **iPOP-TAPA-F**, **iPOP-TAPA-Cl**, **iPOP-TAPA-Br**, and **iPOP-**

**TAPA-I respectively** (Figure 5.24). The obtained data indicates a direct correlation between the counter anions' electronegativity and the positive charge density of the polymer. This leads to better ORR activity of the polymer with higher positive charge density on the surface and higher activation of the O<sub>2</sub> molecule. The enhanced positive charge density of **iPOP-TAPA-F** also might help to achieve the higher desorption of the intermediate \*OOH to the catalyst surface, leading to the highest catalysis efficiency of **iPOP-TAPA-F** compared to the other polymers.



**Figure 5.24.** Zeta potential measurements of iPOP-TAPA-X (X = F, Cl, Br, I)

#### **5.4.** Conclusion

In summary, viologen-based ionic porous organic polymer, **iPOP-TAPA-Cl** was synthesized via Zincke reaction by reacting 1,1'-bis(2,4dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (ZN-Cl2) and Tris(4-aminophenyl)amine (TAPA) in acetonitrile-water mixture at 90 °C for 6 h. The obtained polymer shows its efficiency as a metal-free electrocatalyst for the selective production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) from oxygen in an alkaline medium. The H<sub>2</sub>O<sub>2</sub> production ability of the catalyst was further tuned by exchanging the Cl<sup>-</sup> counter anion with other

halide ions ( $F^-$ ,  $Br^-$ , and  $I^-$ ). Among these catalysts, **iPOP-TAPA-F** shows exceptional catalytic activity towards the selective production of H<sub>2</sub>O<sub>2</sub> (98.5 %) with a significant current efficiency of 99 %. This type of viologenbased polymeric system could open a new avenue toward designing a metalfree electrocatalyst with controllable catalytic performance for the electrocatalytic production of H<sub>2</sub>O<sub>2</sub>.

#### 5.5. Declaration

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#### 5.5. References

[1] Sun Y., Han L., Strasser P. (2020), A Comparative Perspective of Electrochemical and Photochemical Approaches for Catalytic H2O2 Production, Chem. Soc. Rev., 49, 6605–6631 (DOI: 10.1039/D0CS00458H)

[2] Yang Q., Xu W., Gong S., Zheng G., Tian Z., Wen Y., Peng L., Zhang L., Lu Z., Chen L. (2020), Atomically Dispersed Lewis Acid Sites Boost 2-Electron Oxygen Reduction Activity of Carbon-Based Catalysts, Nat Commun, 11, 5478 (DOI:10.1038/s41467-020-19309-4)

[3] Tang C., Zheng Y., Jaroniec M., Qiao S. Z. (2021), Electrocatalytic Refinery for Sustainable Production of Fuels and Chemicals, Angewandte Chemie International Edition, 60, 19572–19590 (DOI: 10.1002/anie.202101522)

[4] Perry S. C., Pangotra D., Vieira L., Csepei L. I., Sieber V., Wang L.,
Ponce de León C., Walsh F. C. (2019), Electrochemical Synthesis of
Hydrogen Peroxide from Water and Oxygen, Nat Rev Chem, 3, 442–458
(DOI: 10.1038/s41570-019-0110-6)

[5] Ciriminna R., Albanese L., Meneguzzo F., Pagliaro M. (2016),
Hydrogen Peroxide: A Key Chemical for Today's Sustainable
Development, ChemSusChem, 9, 3374–3381 (DOI: 10.1002/cssc.201600895)

[6] Nishimi T., Kamachi T., Kato K., Kato T., Yoshizawa K. (2011), Mechanistic Study on the Production of Hydrogen Peroxide in the Anthraquinone Process, European Journal of Organic Chemistry, 2011, 4113–4120 (DOI: 10.1002/ejoc.201100300)

[7] Pizzutilo E., Freakley S. J., Cherevko S., Venkatesan S., Hutchings G.
J., Liebscher C. H., Dehm G., Mayrhofer K. J. J. (2017), Gold–Palladium Bimetallic Catalyst Stability: Consequences for Hydrogen Peroxide Selectivity, ACS Catal., 7, 5699–5705 (DOI: 10.1021/acscatal.7b01447)

[8] Campos-Martin J. M., Blanco-Brieva G., Fierro J. L. G. (2006), Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process, Angewandte Chemie International Edition, 45, 6962–6984 (DOI: 10.1002/anie.200503779)

[9] Jiang Y., Ni P., Chen C., Lu Y., Yang P., Kong B., Fisher A., Wang X.
(2018), Selective Electrochemical H<sub>2</sub>O<sub>2</sub> Production through Two-Electron
Oxygen Electrochemistry, Advanced Energy Materials, 8, 1801909 (DOI: 10.1002/aenm.201801909)

[10] Wang N., Ma S., Zuo P., Duan J., Hou B. (2021), Recent Progress of Electrochemical Production of Hydrogen Peroxide by Two-Electron Oxygen Reduction Reaction, Advanced Science, 8, 2100076 (DOI: 10.1002/advs.202100076)

[11] Bu Y., Wang Y., Han G.-F., Zhao Y., Ge X., Li F., Zhang Z., Zhong Q., Baek J.-B. (2021), Carbon-Based Electrocatalysts for Efficient Hydrogen Peroxide Production, Advanced Materials, 33, 2103266 (DOI: 10.1002/adma.202103266)

[12] Wang Y., Waterhouse G. I. N., Shang L., Zhang T. (2021), Electrocatalytic Oxygen Reduction to Hydrogen Peroxide: From Homogeneous to Heterogeneous Electrocatalysis. Advanced Energy Materials, 11, 2003323, (DOI: 10.1002/aenm.202003323)

[13] Yang X., Zeng Y., Alnoush W., Hou Y., Higgins D., Wu G. (2022), Tuning Two-Electron Oxygen-Reduction Pathways for H<sub>2</sub>O<sub>2</sub> Electrosynthesis via Engineering Atomically Dispersed Single Metal Site Catalysts, Advanced Materials, 34, 2107954 (DOI: 10.1002/adma.202107954)

[14] Jirkovský J. S., Panas I., Ahlberg E., Halasa M., Romani S., Schiffrin D. J. (2011), Single Atom Hot-Spots at Au–Pd Nanoalloys for Electrocatalytic H<sub>2</sub>O<sub>2</sub> Production, J. Am. Chem. Soc., 133, 19432–19441 (DOI: 10.1021/ja206477z)

[15] Verdaguer-Casadevall A., Deiana D., Karamad M., Siahrostami S., Malacrida P., Hansen T. W., Rossmeisl J., Chorkendorff I., Stephens I. E. L. (2014), Trends in the Electrochemical Synthesis of H<sub>2</sub>O<sub>2</sub>: Enhancing Activity and Selectivity by Electrocatalytic Site Engineering, Nano Lett., 14, 1603–1608 (DOI: 10.1021/nl500037x)

[16] Siahrostami S., Verdaguer-Casadevall A., Karamad M., Deiana D., Malacrida P., Wickman B., Escudero-Escribano M., Paoli E. A., Frydendal R., Hansen T. W., Chorkendorff I., Stephens I. E. L., Rossmeisl J. (2014), Erratum: Enabling Direct H2O2 Production through Rational Electrocatalyst Design. 13. 213-213 Nature Mater. (DOI: 10.1038/nmat3871)

[17] Yang S., Kim J., Tak Y. J., Soon A., Lee H. (2016), Single-Atom Catalyst of Platinum Supported on Titanium Nitride for Selective Electrochemical Reactions, Angewandte Chemie International Edition, 55, 2058–2062 (DOI: 10.1002/anie.201509241)

[18] Jung E., Shin H., Lee B.-H., Efremov V., Lee S., Lee H. S., Kim J.,
Hooch Antink W., Park S., Lee K.-S., Cho S.-P., Yoo J. S., Sung Y.-E.,
Hyeon T. (2020), Atomic-Level Tuning of Co–N–C Catalyst for HighPerformance Electrochemical H<sub>2</sub>O<sub>2</sub> Production, Nat. Mater., 19, 436–442
(DOI: 10.1038/s41563-019-0571-5)

[19] Liu Y., Quan X., Fan X., Wang H., Chen S. (2015), High-Yield Electrosynthesis of Hydrogen Peroxide from Oxygen Reduction by Hierarchically Porous Carbon, Angewandte Chemie, 127, 6941–6945 (DOI: 10.1002/ange.201502396)

[20] Han L., Sun Y., Li S., Cheng C., Halbig C. E., Feicht P., Hübner J. L., Strasser P., Eigler S. (2019), In-Plane Carbon Lattice-Defect Regulating Electrochemical Oxygen Reduction to Hydrogen Peroxide Production over Nitrogen-Doped Graphene, ACS Catal., 9, 1283–1288 (DOI: 10.1021/acscatal.8b03734)

[21] Chang Q., Zhang P., Mostaghimi A. H. B., Zhao X., Denny S. R., Lee J. H., Gao H., Zhang Y., Xin H. L., Siahrostami S., Chen J. G., Chen Z. (2020), Promoting H<sub>2</sub>O<sub>2</sub> Production via 2-Electron Oxygen Reduction by Coordinating Partially Oxidized Pd with Defect Carbon, Nat Commun, 11, 2178 (DOI: 10.1038/s41467-020-15843-3)

[22] Das S., Hasman P., Ben T., Qiu S. (2017), Porous Organic Materials:
Strategic Design and Structure–Function Correlation. Chem. Rev., 117, 1515–1563 (DOI: 10.1021/acs.chemrev.6b00439)

[23] Yang S., Lu L., Li J., Cheng Q., Mei B., Li X., Mao J., Qiao P., Sun F., Ma J., Xu Q., Jiang Z. (2023), Boosting Hydrogen Peroxide Production via Establishment and Reconstruction of Single-Metal Sites in Covalent Organic Frameworks, SusMat, 3, 379–389 (DOI: 10.1002/sus2.125)

[24] Zhi Q., Jiang R., Yang X., Jin Y., Qi D., Wang K., Liu Y., Jiang J. (2024), Dithiine-Linked Metalphthalocyanine Framework with Undulated

Layers for Highly Efficient and Stable H<sub>2</sub>O<sub>2</sub> Electroproduction, Nat Commun, 15, 678 (DOI: 10.1038/s41467-024-44899-8)

[25] Guo Y., Xu Q., Yang, S., Jiang Z., Yu C., Zeng G. (2021) Precise Design of Covalent Organic Frameworks for Electrocatalytic Hydrogen Peroxide Production, Chemistry – An Asian Journal, 16, 498–502 (DOI: 10.1002/asia.202100030)

[26] Huang S., Zhang B., Wu D., Xu Y., Hu H., Duan F., Zhu H., Du M., Lu S. (2024), Linkage Engineering in Covalent Organic Frameworks as Metal-Free Oxygen Reduction Electrocatalysts for Hydrogen Peroxide Production, Applied Catalysis B: Environmental, 340, 123216 (DOI: 10.1016/j.apcatb.2023.123216)

[27] Yang S., Cheng Q., Mao J., Xu Q., Zhang Y., Guo Y., Tan T., Luo W.,
Yang H., Jiang Z. (20210, Rational Design of Edges of Covalent Organic Networks for Catalyzing Hydrogen Peroxide Production, Applied Catalysis
B: Environmental, 298, 120605 (DOI: 10.1016/j.apcatb.2021.120605)

[28] Zhang Y., Qiao Z., Zhang R., Wang Z., Wang H.-J., Zhao J., Cao D., Wang S. (2023), Multicomponent Synthesis of Imidazole-Linked Fully Conjugated 3D Covalent Organic Framework for Efficient Electrochemical Hydrogen Peroxide Production, Angewandte Chemie International Edition, 62, e202314539 (DOI: 10.1002/anie.202314539)

[29] An S., Li X., Shang S., Xu T., Yang S., Cui C.-X., Peng C., Liu H., Xu Q., Jiang Z., Hu J. (2023), One-Dimensional Covalent Organic Frameworks for the 2e– Oxygen Reduction Reaction, Angewandte Chemie International Edition, 62, e202218742 (DOI: 10.1002/anie.202218742)

[30] Huang S., Lu S., Hu Y., Cao Y., Li Y., Duan F., Zhu H., Jin Y., Du M., Zhang W. (2023), Covalent Organic Frameworks with Molecular Electronic Modulation as Metal-Free Electrocatalysts for Efficient Hydrogen Peroxide Production, Small Structures, 4, 220038 (DOI: 10.1002/sstr.202200387)

[31] Velempini T., Pillay K. (2019), Sulphur Functionalized Materials for Hg(II) Adsorption: A Review, Journal of Environmental Chemical Engineering, 7, 103350 (DOI: 10.1016/j.jece.2019.103350)

[32] Komarnisky L. A., Christopherson R. J., Basu T. K. (2023), Sulfur: Its Clinical and Toxicologic Aspects, Nutrition, 19, 54–61 (DOI: 10.1016/S0899-9007(02)00833-X)

[33] Li W., Zhao Z., Hu W., Cheng Q., Yang L., Hu Z., Liu Y. A., Wen K.,
Yang H. (2020), Design of Thiazolo[5,4-d]Thiazole-Bridged Ionic
Covalent Organic Polymer for Highly Selective Oxygen Reduction to H<sub>2</sub>O<sub>2</sub>,
Chem. Mater., 32, 8553–8560 (DOI: 10.1021/acs.chemmater.0c02843)

[34] Peng L.-Z., Liu P., Cheng Q.-Q., Hu W. J., Liu Y. A., Li J.-S., Jiang B., Jia X.-S., Yang H., Wen K. (2018), Highly Effective Electrosynthesis of Hydrogen Peroxide from Oxygen on a Redox-Active Cationic Covalent Triazine Network, Chem. Commun., 54, 4433–4436 (DOI: 10.1039/C8CC00957K)

[35] Fellinger T.-P., Hasché F., Strasser P., Antonietti M. (2012), Mesoporous Nitrogen-Doped Carbon for the Electrocatalytic Synthesis of Hydrogen Peroxide, J. Am. Chem. Soc., 134, 4072–4075 (DOI: 10.1021/ja300038p)

[36] Sidik R. A., Anderson A. B., Subramanian N. P., Kumaraguru S. P.,
Popov B. N. (2006), O<sub>2</sub> Reduction on Graphite and Nitrogen-Doped
Graphite: Experiment and Theory, J. Phys. Chem. B, 110, 1787–1793
(DOI: 10.1021/jp055150g)

[37] Lenarda A., Bevilacqua M., Tavagnacco C., Nasi L., Criado A., Vizza F., Melchionna M., Prato M., Fornasiero P. (2019), Selective Electrocatalytic H2O2 Generation by Cobalt@N-Doped Graphitic Carbon Core–Shell Nanohybrids, ChemSusChem, 12, 1664–1672 (DOI: 10.1002/cssc.201900238)

[38] Pegis M. L., Wise C. F., Martin D. J., Mayer J. M. (2018), Oxygen Reduction by Homogeneous Molecular Catalysts and Electrocatalysts, Chem. Rev., 118, 2340–2391 (DOI: 10.1021/acs.chemrev.7b00542)





# **Conclusion and Future Aspects**

#### 6.1. Conclusion

The conclusions of the thesis can be outlined as follows:

1. **iPOP-ANT** was found to be an excellent bifunctional material for removing toxic oxo-anions ( $Cr_2O_7^{2-}$ ,  $MnO_4^{-}$ ) and anionic dyes (methyl orange, amaranth, congo red) from wastewater and photocatalytic degradation of cationic dyes (rhodamine b, rhodamine 6G and methylene blue) under solar light irradiation. All the adsorption processes follow pseudo-second-order kinetics and the Langmuir adsorption model, whereas the dye degradation follows the pseudo-first-order kinetics. The materials show excellent stability in adsorption and degradation studies for several cycles.

2. The role of charge density and surface area in the development of highly efficient iPOP-based adsorbent was established in Chapter 2. Three iPOPs, **iPOP-ZN1**, **iPOP-ZN2**, and **iPOP-ZN3**, have been designed and synthesized. Among the three polymers, **iPOP-ZN1**, owing to its high charge density around the active site and comparatively higher surface area, proves to be the better adsorbent for capturing various inorganic pollutants from water and iodine in the vapor phase. Owing to the antibacterial activity of the iodine, the iodine-loaded polymers were further tested for antibacterial actions. The iodine-loaded polymers show impressive antibacterial properties against *E. coli*, *B. subtilis*, and *H. pylori*.

3. The multifunctionality of a viologen-based ionic porous organic polymer, **iPOP-Bpy**, has been explored in Chapter 3. The polymer shows excellent iodine adsorption capacity in the vapor phase, as well as in organic and aqueous mediums. Utilizing the redox-switching nature of the viologen molecule, the polymer was further utilized as a solid-state NH<sub>3</sub> gas sensor. Further, an electrochromic device has been fabricated using iPOP-Bpy. The device shows excellent switching times (~0.5 s), color contrast (~50%), and coloration efficiencies (up to 800 cm<sup>2</sup>/C).

4. Hydrogen peroxide, an environment-friendly oxidant, is in high demand in various industrial sectors. Viologen-based iPOPs, owing to their redox-

active nature, could be an efficient metal-free electrocatalyst for selective  $2e^{-}$  reduction of oxygen to hydrogen peroxide. In Chapter 4, **iPOP-TAPA-Cl** was explored as a metal-free electrocatalyst for selective reduction of oxygen to hydrogen peroxide. Further, the electronic property of the polymer was tuned by simply changing the counter anions of the polymer by other halogen ions. Among all the polymers, **iPOP-TAPA-F** was found to be the selective production of H<sub>2</sub>O<sub>2</sub> (98.5 %) with a significant current efficiency of 99 %.

#### **6.2.** Future aspects

Ionic porous organic polymers (iPOPs) are an exciting material class known for their distinctive structural and functional properties. This thesis explores their potential in environmental sustainability, but their applications extend beyond this field. For instance, ionic POPs show promise in metal ion batteries, with viologen-based POPs proving to be excellent electrocatalysts for various electrochemical reactions. In wastewater remediation, while iPOPs have made notable progress, further research is needed to develop industrial-scale adsorbents. Chapter 3 of this thesis highlights the critical role of surface charge in improving adsorption properties, but factors like heteroatoms, pore structure, and pore size also play a significant role. Additionally, surface charge modulation, as discussed in Chapter 5 through simple ion exchange, could be beneficial in various applications beyond wastewater treatment. The concept of relating structural properties to functionality in porous organic polymers is new and has the potential to greatly enhance their use if further explored.