

Cite this: *Mater. Adv.*, 2024,
5, 4055

Recent advancement in viologen functionalized porous organic polymers (vPOPs) for energy and environmental remediation

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A rise in the concentration of hazardous and noxious substances in the environment due to industrialization and population expansion has begun to disrupt the ecological equilibrium. It is of utmost importance to monitor and efficiently manage these pollutants through adsorption techniques or catalytic degradation. Viologen-based porous organic polymers (vPOPs) are a class of porous polymeric materials composed of 4,4'-bipyridinium ions along with other small organic molecules linked together by strong covalent bonds. They have garnered attention as a viable platform for many applications, particularly in the realm of effective environmental remediation. This advancement has generated prospects for the development of more advanced techniques for eliminating contaminants, segregating chemicals, converting gases, and transforming energy. The purpose of this study is to provide an overview of the most recent advancements and successes in the production, utilization, and structural engineering of vPOPs and associated composite materials to remediate environmental problems. This detailed study seeks to provide insights into the potential of vPOPs as viable materials for addressing environmental challenges and stimulating additional research in this emerging sector. This paper provides an analysis of the perspectives about the challenges, opportunities, practical applications, and prospects of these materials in advanced remediation technology for the next generation.

Received 22nd February 2024,
Accepted 14th April 2024

DOI: 10.1039/d4ma00182f

rsc.li/materials-advances

Introduction

Environmental remediation is a methodical procedure designed to address pollution- or contamination-related environmental issues. The main goals are to safeguard human health and the ecosystem while returning the impacted region to its pre-pollution condition.¹ The worldwide population had a notable upsurge throughout the twentieth century, resulting in considerable growth in both commercial and agricultural sectors. Significant human endeavours generate enormous quantities of environmentally detrimental garbage from industrial and agricultural sources,^{2,3} significantly contributing to many environmental challenges, such as global warming and the contamination of land, air, and water bodies. Furthermore, the rapid depletion of fossil fuel supplies as a result of extensive global energy use has presented enormous obstacles to the progress and long-term viability of the human population.⁴⁻⁷ To accomplish the goals of protecting human health and the ecosystem, it is essential to actively participate in the development and investigation of novel materials that are

specifically designed to meet certain criteria. This is crucial for fostering socioeconomic development and supporting the promotion of ecologically sustainable activities.⁸

The rise and notable advancement of porous materials in recent years have highlighted the significant influence of porosity in enhancing the outstanding performance of a material across many applications.^{9,10} Porous materials are crucial for many developing technologies and applications because of their unique inherent qualities, including an extensive surface area, versatile synthetic capabilities, adaptive structure, and other notable features.¹¹⁻¹³

In recent decades, numerous novel porous materials have emerged and progressed, encompassing microporous, mesoporous, and macroporous structures. These materials consist of porous organic polymers (POPs), covalent-organic frameworks (COFs), and metal-organic frameworks (MOFs).¹⁴⁻¹⁷ Amidst the proliferation of recently developed materials, there has been a renewed scientific interest in POPs owing to their unique capacity to combine the properties of porous and polymeric substances. POPs are metal-free polymeric organic materials that are predominantly composed of complex molecular structures made up of lightweight elements including carbon, hydrogen, oxygen, nitrogen, and boron.¹⁸⁻²⁰

In general, porous organic polymers (POPs) exhibit numerous structural and physicochemical benefits in comparison to

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conventional and modern porous materials.²¹ These benefits placed them at the vanguard of the forthcoming generation of multipurpose functional materials. POPs offer many advantages compared to traditional inorganic substances such as activated carbons, zeolites, *etc.* These advantages include a significant surface area, low density, and strong physico-chemical durability. In addition, it is possible to incorporate functional components into POP structures *via* modifications that occur both before and after synthesis. The pre-synthetic methods offer an extensive range of chemical reactions and the adaptability of monomer design affords considerable potential for the modification of functionalities.^{22–24} On the other hand, post-synthetic modification functions as a potent mechanism to enhance the porous architecture's functional versatility. Redox switches are the most frequently observed molecular switch types in POPs.^{25,26} These switches are susceptible to alteration when the redox potential of their surroundings alters. A variety of applications of redox switches involve the removal of substances from the environment, such as dyes, iodine, and oxoanions. They are also utilized as electrochemical devices, drug delivery systems, actuators, and sensors.^{27–29} Different forms of 4,4'-bipyridine, often referred to as viologens, are specific types of redox molecular switches that have been the subject of extensive research. Owing to their positive charge, these switches are amenable to reversible reduction *via* chemical or electrical reduction methods to radical cationic or neutral species (Scheme 1).^{30–33} The incorporation of viologen moieties into polymeric frameworks to form viologen-based porous organic polymers (vPOPs) presents a multitude of benefits: (i) the radical cationic species remain in an unstable state for prolonged durations under ambient conditions as the extended polymeric structures stabilize the radicals. (ii) In applications that rely on the *in situ* generation of radical cationic species, polymeric viologens frequently demonstrate enhanced performance in comparison to monomers and dimers, owing to their improved charge transfer capabilities. (iii) The porosity of vPOPs makes them highly suitable for applications requiring significant surface areas, such as gas adsorption and separation, including reaction catalysis. (iv) The inherent cationic property of vPOPs facilitates the dispersion of insoluble substances. (v) The capacity to regulate the redox state of their viologen moieties enables vPOPs to recognize a variety of substances (such as hydrophobic, hydrophilic, anionic, cationic and other substances) selectively.^{34–40} In light of the exponential growth of scientific investigation and recognizing the promising possibilities of new materials, we present a thorough analysis that explores the current state and recent



Fig. 1 Representative examples of synthetic methods of vPOPs (right side) including solvothormal, microwave and room temperature synthesis approaches. The left side of the figure represents the application of vPOPs towards energy storage and conversion, water remediation, gas storage and separation, *etc.*

advancements in various categories of vPOPs used in the diverse environmental context. Their diverse functionalization techniques and synthetic strategies are given particular emphasis. As illustrated in Fig. 1, the review subsequently undertakes a comprehensive analysis of the pragmatic implementations of vPOPs in environmental remediation endeavours, including the storage/segregation of hazardous vapors, elimination of organic/inorganic contaminants, iodine adsorption, and energy storage/conversion. Especially, we shed light on the present obstacles, along with possible advantages, and prospects of these promising materials for energy and environmental remediation. To the best of our knowledge, this review is unique in terms of the application of ionic vPOPs for energy and environmental remediation.

Synthetic methods of vPOPs

As previously mentioned, vPOPs are composed of viologen units, specifically 4,4'-bipyridinium salts, covalently bonded with other organic building blocks. The fabrication of such



Scheme 1 Schematic representation of different redox states of a viologen moiety. The viologen moiety undergoes two reversible reduction reactions. The dicationic state of the viologen moiety is the most stable state of viologen. [R = alkyl/aromatic].



covalent connections, that link 4,4'-bipyridinium ions with organic linkers to build vPOPs, involves several methodical synthetic approaches which are further classified and outlined below. Comprehensive discussions on these synthetic techniques are presented subsequently.

Microwave synthesis

Microwave irradiation presents a viable substitute for traditional techniques utilized in the provision of energy or heat to a given system. This approach functions by using the ability of mobile electric charges in liquids or conducting ions in solids to transform electromagnetic energy into heat. Microwave radiation, consisting of electromagnetic pulses, occupies a position in the electromagnetic spectrum between infrared radiation and radio waves. The frequency spectrum of microwaves spans from 0.3 to 300 GHz, with wavelengths varying from 1 mm to 1 m. A multitude of applications, including microwave radar devices and telecommunications, employ distinct frequencies from this spectrum. By capitalizing on the ability of particular liquids and solids to transform electromagnetic radiation into thermal energy, this method enables chemical reactions to proceed more efficiently. This technological methodology grants synthetic chemists the ability to investigate novel reactions that are unfeasible through the use of conventional thermal techniques.^{41,42} In the year 2017,

Trabolsi *et al.* reported⁴³ for the first time the synthesis of a viologen-based covalent organic gel framework (COGF) through the microwave-assisted Zincke reaction. A triamine-based reactant [1,3,5-tris(4-aminophenyl)benzene] was combined with a Zincke salt (1,1-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1-dium dichloride) in an EtOH-water (4:1) solvent mixture and the resulting mixture was then subjected to 2.45 GHz microwave irradiation for one hour at 100 °C in a 100 mL microwave reaction vessel. The outcome of this procedure was a sheet-like viscoelastic/gel organic framework (COGF). Following the completion of these reactions, the synthesized COGF was utilized to extract iodine in the cyclohexane phase in an efficient manner, as discussed later in the section I₂ uptake. Furthermore, the aforementioned research group utilized microwave irradiation to incorporate azacalix[4]arene, an organic macrocycle, into the structure of a viologen-based covalent organic framework (ACA-COF).⁴⁴ The ACA-COF has been utilized in the adsorption of uric acid and creatinine, which are critical byproducts produced during hemodialysis in patients suffering from renal failure. The detailed reports of other microwave-synthesized vPOPs are presented in Table 1.

Solvothermal synthesis

Solvothermal synthesis is a well-known technique for synthesizing vPOPs, which has resulted in the development of a wide

Table 1 Tabular representation of synthesis methods of vPOPs

S. no.	vPOPs	Methods for synthesis of vPOPs	Name reactions for the synthesis of vPOPs	Reaction conditions	Ref.
T1.1	COGF	Microwave	Zincke reaction	EtOH : H ₂ O (1 : 1), 100 °C, 2 h	43
T1.2	COP ₁ ⁺⁺	Microwave	Menshutkin reaction	MeCN, 89 °C, 1 h	59
T1.3	ACA-COF	Microwave	Zincke reaction	EtOH : H ₂ O (1 : 1), 100 °C, 2 h	44
T1.4	TFAM-BDNP	Microwave	Zincke reaction	EtOH : H ₂ O (4 : 1), 100 °C, 2 h	67
T1.5	PV-COF	Microwave	Zincke reaction	EtOH : H ₂ O (1 : 1), 100 °C, 2 h	82
T1.6	CONS	Solvothermal	Zincke reaction	EtOH : H ₂ O (1 : 1), 120 °C, 72 h	89
T1.7	COTS	Solvothermal	Zincke reaction	EtOH : H ₂ O (1 : 1), 120 °C, 72 h	89
T1.8	cCTN:Cl ⁻	Solvothermal	Zincke reaction	MeCN : H ₂ O (10 : 1), 120 °C, 72 h	45
T1.9	HS	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	43
T1.10	HT	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	
T1.11	Compound-1	Solvothermal	Zincke reaction	1,4-Dioxane : EtOH : chlorobenzene (1 : 1 : 1), 120 °C, 72 h	46
T1.12	V-PCIF-X	Solvothermal	Zincke reaction	DMF, 180 °C, 48 h	78
T1.13	VBCOP	Solvothermal	Zincke reaction	MeOH : dioxane (1 : 1), 120 °C, 72 h	65
T1.14	TZ-PAF	Solvothermal	Zincke reaction	THF : H ₂ O (1 : 1), 100 °C, 72 h	66
T1.15	PC-COF	Solvothermal	Zincke reaction	AcOH : EtOH : H ₂ O, 100 °C, 168 h	60
T1.16	vGC	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	80
T1.17	vGAC	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	
T1.18	vMEL	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	
T1.19	vBPDP	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	
T1.20	VIP-X	Solvothermal	Menshutkin reaction	MeCN, 100 °C, 48 h	88
T1.21	Por(Co)-Vg-COF	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 90 °C, 72 h	84
T1.22	IISERP-POF9	Solvothermal	Bakelite bond formation	Dioxane : THF, 200 °C, 72 h	83
T1.23	IISERP-POF9	Solvothermal	Bakelite bond formation	Dioxane : THF, 200 °C, 72 h	83
T1.24	IISERP-POF9	Solvothermal	Bakelite bond formation	Dioxane : THF, 200 °C, 72 h	
T1.25	AN-POP	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	85
T1.26	BD-POP	Solvothermal	Zincke reaction	EtOH : H ₂ O (4 : 1), 120 °C, 72 h	
T1.27	SCU-COF-1	Solvothermal	Schiff base reaction	<i>o</i> -DCB : BuOH : acetic acid (19 : 1 : 2), 120 °C, 144 h	86
T1.28	TpVCB[7]	Room temperature	Schiff base reaction	DCM : H ₂ O, 72 h	48
T1.29	V2DP	Room temperature	Schiff base reaction	TfOH, 144 h	47
T1.30	RT-iCOF	Room temperature	Schiff base reaction	<i>o</i> -DCB : BuOH (7 : 3), 24 h	87
T1.31	IPOP	Solvothermal	Menshutkin reaction	MeCN, 90 °C, 72 h	102
T1.32	VCR-POP-1	Solvothermal	Knoevenagel condensation	DMSO, CS ₂ CO ₃ , 120 °C, 72 h	110



array of vPOPs utilized in numerous disciplines. This synthetic approach generates vPOPs by combining two or more different monomers or, occasionally, by self-coupling a single monomer. The reaction takes place in a solvent mixture heated to a high temperature, typically (ranging between 90 and 150 °C) for one to three days. Numerous organic monomers are chemically bonded together to form stable covalent bonds under these artificial circumstances. Afterward, these bonds undergo expansion in two or three dimensions, leading to the creation of a kinetically regulated network of vPOPs. Numerous instances of effective vPOP synthesis utilizing the solvothermal technique are examined and listed in Table 1. For example, Wen *et al.* documented the solvothermal synthesis of a redox-active covalent triazine network based on viologen. The vPOP that was produced was subsequently employed in fuel cell applications as an electrochemical catalyst.⁴⁵ Ghosh *et al.* also described the synthesis of viologen-based vPOPs (compound 1) using a solvothermally aided Zincke reaction.⁴⁶ Compound-1 displayed remarkable capacity values for a range of oxoanions, which were comparable to those of several exceptionally efficient compounds documented in the extant literature.

Room temperature synthesis

In this method, the reactants are mixed in a designated solvent or a blend of solvents, often with the inclusion of a catalyst. The mixture is then stirred or kept undisturbed at room temperature for a set period to accomplish the reaction. Using this straightforward synthesis approach, several vPOPs have been synthesized, as mentioned in Table 1. Feng and his group constructed one high-performance electrochemical device with a fully crystalline viologen-based 2D polymer (denoted as V2DP) thin film.⁴⁷ The thin film was synthesized through a two-dimensional polycondensation approach at room temperature. The resulting V2DP manifests as a self-supporting, crystalline film with a substantial area (exceeding 100 cm²) along with adjustable thickness (ranging from 1 to 65 nm) which was further used in solar cell application, discussed in the section Energy storage and conversion. Trabolsi *et al.* synthesized a thin film of a polyrotaxanated covalent organic network at room temperature.⁴⁸ The film, encapsulated with CB[7], exhibited enhanced mechanical and thermal robustness, along with increased luminescence. Table 1 contains information on additional room-temperature synthesized vPOPs.

The reaction involved in the synthesis of vPOPs

Zincke reaction

The Zincke reaction, a widely recognized name reaction for the synthesis of vPOPs, has been pivotal in the creation of a wide range of vPOPs that are utilized across multiple disciplines. The Zincke reaction converts bipyridine into a quaternary pyridinium salt in two steps. The initial stage involves the S_N2 reaction between 4,4'-bipyridine and 1-chloro-2,4-dinitrobenzene to produce the Zincke salt. A primary amine attacks the most

electrophilic carbon in the Zincke salt and opens the pyridine ring in the second phase. This results in the elimination of 2,4-dinitroaniline, the closing of the ring, and the formation of a quaternized pyridinium ion. It is believed that the rate-determining step is the opening of the ring, and the reversibility of the reaction produces a crystalline substance and likely permits error correction.³³ In the year 2017, Trabolsi *et al.* reported⁴³ for the first time the synthesis of crystalline viologen-based covalent organic gel frameworks (COGFs) through the microwave-assisted Zincke reaction and amorphous vPOPs through the solvothermal assisted Zincke reaction (HS and HT). At the same time, Ghosh *et al.* also described the synthesis of viologen-based vPOPs (compound 1) using the solvothermal-assisted Zincke reaction.⁴⁶ Compound-1 demonstrated extraordinary capture capacity of oxoanions from wastewater. Very recently, our group synthesized a series of vPOPs (vGC, vGAC, vMEL and vBPDP) through the solvothermal assisted Zincke reaction and utilized these vPOPs as metal-free bifunctional electrocatalysts for the oxygen reduction and oxygen evolution reaction which is discussed thoroughly in the Energy storage and conversion section.⁸⁰ Several vPOPs have been synthesized through the Zincke reaction, as mentioned in Table 1.

Menshutkin reaction

An exhaustively researched S_N2 reaction, the Menshutkin reaction, is one of the foundational S_N2 reactions in organic and bioorganic chemistry. The reactants are neutral during the reaction, whereas the two products acquire negative and positive charges, respectively. The mechanism underlying the Menshutkin reaction in solution differs significantly from that observed in the gas phase. Specifically, the reaction occurs at a significantly faster rate in a solvent with high polarity compared to that with reduced polarity. In general, polymers comprise a monomer that is modified with an aliphatic alkyl halide, such as chloride. In straightforward S_N2 Menshutkin reactions, halides function well as leaving groups when subjected to nucleophilic attack by the electron-rich nitrogen centres of 4,4'-bipyridine. The crosslinked vPOPs have been synthesized using this methodology.³³ There are several vPOPs reported, synthesized through this name reaction and documented in Table 1. For example, Trabolsi *et al.* reported a vPOP (COP₁⁺⁺) through the microwave-assisted Menshutkin reaction and further employed this vPOP in iodine vapor adsorption.⁴³ Very recently, Moorthy *et al.* reported a vPOP (IPOP) synthesized through a solvothermal-assisted Menshutkin reaction where they used twisted biaryl as a monomer. They utilized the IPOP as a phase transfer catalyst for the Michal addition reaction (discussed in the Catalysis section).

Schiff-base reaction

Schiff-base condensation is one of the most significant categories of reactions in the synthesis of porous organic polymers. The process, which utilizes amine and aldehyde to functionalize monomers, generates an imine link. For vPOP synthesis, this name reaction is very rarely explored. Very few vPOPs, synthesized through the Schiff base reaction, are reported and



tabulated in Table 1. Feng *et al.* constructed one high-performance electrochemical device with a fully crystalline viologen-based 2D polymer (denoted as V2DP) thin film through the Schiff base reaction at room temperature.⁴⁷ Similarly, Trabolsi *et al.* synthesized a thin film of a polyrotaxanated covalent organic network through the Schiff base reaction at room temperature.⁴⁸

Application

vPOPs for water remediation

One of the extensively explored realms within environmental science focuses on eliminating organic and inorganic pollutants from water. Several methods have been devised to treat polluted wastewater, and among them, the adsorption method stands out as a very promising technology owing to its economical nature, substantial capacity to adsorb pollutants, and ability to selectively remove certain contaminants. Crucial characteristics of adsorbents for pollution removal include high adsorption capacity, rapid kinetics, reusability, and stability.^{49,50} The implementation of vPOPs in these kinds of applications provides advantages, notably because of their modifiable charge. Dicationic vPOPs can interact with various anionic poisonous dyes and anions present in polluted water. On the other hand, neutral vPOPs may function as Lewis bases and interact with hydrophobic substances in water.^{27,51}

The increasing demand of a growing human population, coupled with accelerated industrial development and global environmental issues, has profoundly affected the availability of clean water for civilization, leading to serious problems such as water shortages and mounting water pollution. Water pollution has become a major worldwide problem, and the preservation of micro contaminants in water has drawn a significant deal of scientific attention.^{52,53} Several sustained enhanced chemical separation technologies have been employed or are being tested to decontaminate clogged water systems, including effluent and salt water, to provide a fresh and pure water supply. Of these, adsorption-based purification technologies have been acknowledged as feasible and eco-friendly alternatives to conventional treatments, which may be attributable to their exceptional efficiency, effortless operation, and cost-effectiveness. Significant progress has been made in developing very effective adsorbents for separation methods that rely on sorption in the last several years.^{54,55} In the field of pollutant removal from water and wastewater treatment, vPOPs have been regarded as highly promising adsorbent substances because of their distinctive properties such as redox activity, tuneable pore diameter, free exchangeable anions and so on. Here, we have categorized pollutants into two classes, namely: (i) organic pollutants and (ii) inorganic pollutants, and discussed the role of vPOPs in removing them from water thoroughly. Iodine removal from water and iodine capture through vPOPs are also subject to in-depth discussion.

Organic pollutants removal from water. Water bodies worldwide have been shown to contain organic pollutants, including

organic colors, pesticides, antibiotics, pharmaceuticals, personal care items, and chemicals produced from oil. This finding has sparked apprehensions over possible adverse effects on both aquatic environments and human well-being. Consequently, there is a growing focus on studying effective methods to remove these pollutants from diverse water sources. In this specific context, research indicates that porous organic polymers based on viologen (vPOPs) demonstrate significant efficacy in efficiently capturing these organic toxins from water solutions.^{56,57}

In a recent exploration, Ghosh *et al.* delved into the potential of a vPOP (named iVOFm) to effectively eliminate several harmful anionic organic compounds, including pigments, antimicrobial agents, as well as inorganic pollutants (Fig. 2(a)).⁵⁸ The study introduced a solid-state acid vapor-aided approach utilizing silica nanoparticles as templates for designing and synthesizing a macro-micro hierarchical iVOFm. The resulting iVOFm underwent thorough characterization, revealing unique features such as a cationic backbone with densely distributed free counter anions, hierarchical porosity at macro and micro scales, and exceptional chemical stability. Notably, the size and quantity of macropores in iVOFm could be easily adjusted using an appropriate SiO₂ nanoparticle template. Here, the customized design of iVOFm employs a synergistic approach, integrating electrostatically induced ion exchange processes, macro-micro pores, and specialized binding sites, to efficiently target and remove the desired contaminants. The efficacy of iVOFm in removing organic dyes, specifically alizarin red S and methyl orange, and antibiotics such as sulfamethazine (SMT) and sulfadimethoxine (SDM) from water was assessed. iVOFm demonstrated swift adsorption capabilities for diverse organic toxins, iodine, and metal-based oxoanions, achieving a clearance efficiency exceeding 93% within 30 s (Fig. 2(b) and (c)). The research further illustrated the successful removal of the antibiotic SDM from water, highlighting a rapid sorption capacity that maintained high effectiveness even in the presence of coexisting anions such as nitrates, chloride, and bromide. The investigation suggested that the exceptional pollutant-trapping efficiency could be attributed to the rapid diffusion of pollutants facilitated by well-structured and interconnected macropores, synergistically interacting with the cationic backbone.

Simultaneously, a comprehensive investigation was carried out to assess how the redox state of the viologen moieties of vPOPs influences the capture of hydrophilic and hydrophobic dyes. Trabolsi *et al.* synthesized a new type of phosphazene based vPOP (COP₁), for the absorption of neutral fluorescein dye (hydrophilic), cationic rhodamine B dye (hydrophilic), and anionic Nile red dye (hydrophobic) (Fig. 2(d)). The study revealed that both the charge and the level of hydrophilic or hydrophobic nature of both the adsorbent and the dye play a crucial role in determining the absorption capacity. Efficient adsorption of fluorescein by the dicationic COP₁²⁺ was observed, achieving a remarkable removal rate of 99% in just 4 minutes (Fig. 2(e)).⁵⁹ This high efficiency can be attributed to robust hydrophilic-hydrophilic associations, which are not feasible between fluorescein and radical cationic (COP₁^{•+}) or neutral



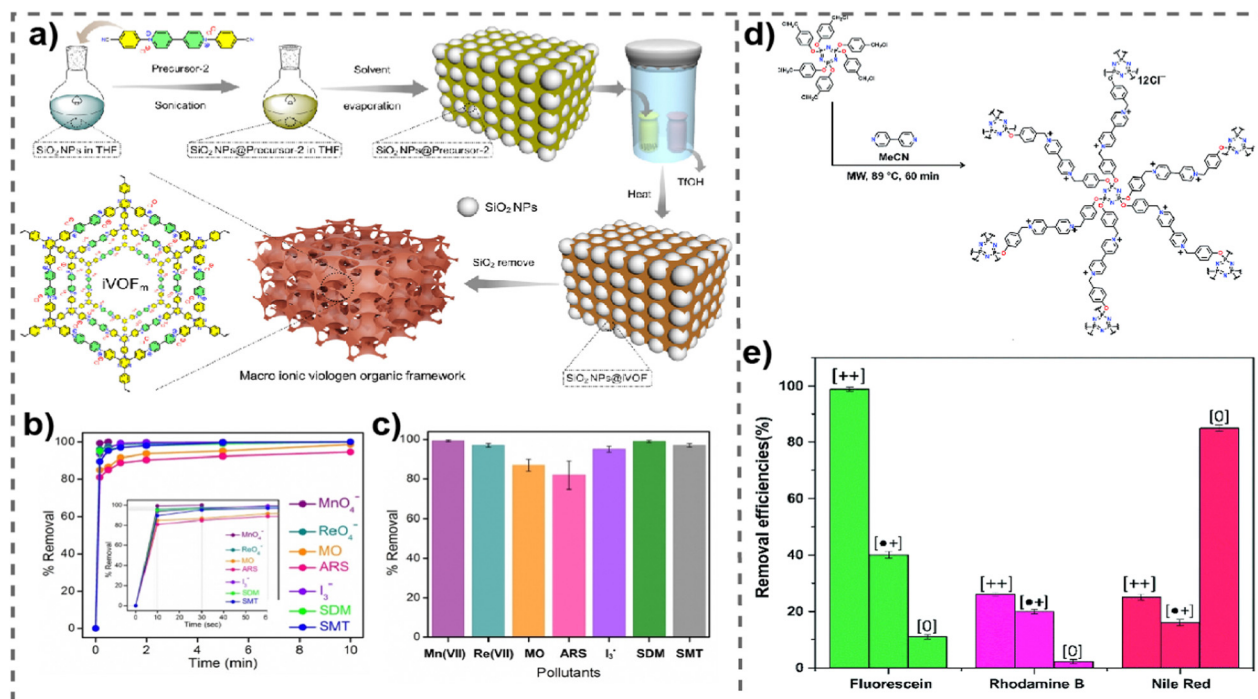


Fig. 2 (a) Synthetic route for iVOFm. (b) and (c) Removal kinetics and % removal of all pollutants through iVOFm. Reproduced with permission from ref. 58. Copyright 2022 Wiley-VCH. (d) Schematic representation of the synthesis of COP₁⁺. (e) Bar graphs of adsorption capacities of the cationic, radical-cationic and neutral forms of COP₁ for fluorescein, rhodamine B, and Nile Red. Reproduced with permission from ref. 59. Copyright 2014 the Royal Society of Chemistry.

(COP₁⁰) vPOPs. Similarly, the neutral COP₁⁰ demonstrated significant capability, eliminating approximately 85% of Nile red within an hour. The effectiveness of this removal is likely due to the potential occurrence of hydrophobic interactions between the COP₁⁰ and Nile red. Dicationic (COP₁⁺⁺) and radical cationic (COP₁^{•+}) conjugated organic polymers displayed a maximum removal efficiency of 25% for Nile red. The study's findings suggest that the specificity of vPOPs may be customized for a particular pollutant by altering the redox phase of the viologen moiety. Li *et al.* explained these anionic dye adsorption phenomena through viologen-based cationic POPs (PC-COF) by the concept of soft and hard acid-base theorem (Fig. 3(a)).⁶⁰ Anionic dyes are generally considered as soft bases, which will be paired up with viologen-based POPs, and act as soft acids, whereas the Cl⁻ anions are considered as hard bases, paired up with cations from dye considered as hard acids. They synthesized crystalline imine-based vPOPs (PC-COF) and further conducted adsorption studies, examining a range of anionic dyes such as acid green, acid red 27, indigo carmine, methyl orange, and Direct Fast Brown M. Remarkably, this material demonstrated an uptake exceeding 97% for these diverse dyes even at very low concentrations (Fig. 3(b)). The authors attribute the enhanced absorption capacity to the implementation of the hard and soft acid/base approach. In this context, anionic dyes, serving as soft bases, create pairs with the softly acidic vPOPs (PC-COF), while hard Cl⁻ ions form pairs with hard Na⁺ ions and these lead to efficient adsorption of toxic dyes. Several vPOPs are reported for this particular removal study, which are documented in Table 2.



Fig. 3 (a) Schematic of the synthetic route for PC-COF. (b) The plots of absorbance of dyes by PC-COF versus concentration of the dyes in water. Reproduced with permission from ref. 60. Copyright 2014 the Royal Society of Chemistry. (c) Synthetic strategy for ACA-COF through the Zincke reaction. (d) Removal percentage (%) of uric acid and creatinine via ACA-COF. Reproduced with permission from ref. 44. Copyright 2022, American Chemical Society.

The recent advancement of research has led to the utilization of these vPOPs in the adsorption of uric acid and



Table 2 Tabular representation of vPOPs used as an adsorbent material for removal of toxic organic dyes from water

S. no.	Name of vPOPs	Organic dye	Organic dye capture capacity (mg g ⁻¹)	Equilibrium times	Cycle	Ref.
T2.1	iVOFm	Alzarine red S	—	5 min	—	58
		Methyl orange	—	5 min	—	
T2.2	COP ₁ ⁺⁺	Fluorescein	—	4 min	—	59
T2.3	COP ₁ ^{•+}	Rhodamine B	—	60 min	—	
T2.4	COP ₁ ⁰	Nile red	—	60 min	—	69
T2.5	COP ₁ ⁺⁺	Congo red	928 mg g ⁻¹	15 min	—	
T2.6	C-NSA _{Naph} HCP@Br	Methyl orange	1010 mg g ⁻¹	60 min	5	90
T2.7	QUST-iPOP-1	Congo red	1074.9 mg g ⁻¹	90 min	—	92
		Methyl orange	300 mg g ⁻¹	90 min	—	
T2.8	V-CDP	Congo red	323 mg g ⁻¹	425 min	5	94
		Methyl orange	370 mg g ⁻¹	425 min	5	

creatinine which are present in water used for dialysis. Trabolsi *et al.*⁴⁴ synthesized an azacalix[4] arene-based vPOP (ACA-COF) under microwave irradiation (Fig. 3(c)).⁴⁴ This is an exceptional instance where a synthetic approach is used to chemically modify an organic macrocycle to limit its ability to change shape and create an ordered substance. The ACA-COF was further used for the removal of uric acid and creatinine from dialyzed water. This application has the capability to save 400 L of water per patient per week. Although it has just gained recognition in the last decade, it has the potential to successfully tackle the issue of water shortage in arid regions worldwide. Their COF exhibited very fast adsorption rates, surpassing previously documented values by many orders of magnitude (Fig. 3(d)).

Inorganic pollutant removal from water. Among the primary inorganic pollutants, the well-known categories include metal cations, oxoanions based on metals or metalloids, and radioactive species. These substances, despite being below the Environmental Protection Agency (EPA) and World Health Organization (WHO) thresholds, are still highly toxic and hazardous to the environment and human health. As a result, there is a strong research focus on selectively removing certain metal species from water-based systems. Although many efficient adsorbent substances have been devised, the existing materials have some restrictions, necessitating the development of new, more dependable alternatives.⁶¹ These replacements should inhibit swelling, contain readily available chelating or ion exchange sites, offer a high capacity for saturation or exchange, and have rapid kinetics. In this context, vPOPs have demonstrated outstanding performance in efficiently extracting these pollutants from contaminated water systems. This is attributed to their tunable nature, regulated pore sizes, exchangeable anions and impressive chemical stability.⁶²

Oxoanion removal from water

The escalating phenomenon of urbanization and rapid industrial growth is leading to an increased influx of harmful contaminants into freshwater reservoirs. The Environment Protection Agency (EPA) has identified specific metal or metalloid-based oxoanions, such as chromate (CrO₄²⁻), pertechnetate (TcO₄⁻), perrhenate (ReO₄⁻), arsenate (AsO₄²⁻), among others, classifying them as potential hazardous

inorganic pollutants in wastewater and placing them on a priority list.⁶³ The Environmental Protection Agency (EPA) has recognized metalloid-derived oxoanions (CrO₄²⁻, TcO₄⁻, ReO₄⁻, AsO₄²⁻) as harmful inorganic pollutants in wastewater, leading to an increasing need for clean water. Hence, wastewater remediation is crucial, and purification methods such as adsorption and ion exchange are emerging as promising alternatives to conventional approaches. In this context, vPOPs are also considered as very promising adsorbent materials to remove metalloid contaminants from water bodies due to their chelating or ion-exchange properties, and are quite favoured because of their cost, user-friendly nature, and ability to minimize the production of dangerous secondary species.⁶⁴ In this regard, vPOPs have been specifically investigated for their efficacy in selectively capturing oxoanions. It is worth noting that due to the robust electrostatic attraction between the mesoporous structure of cationic vPOPs and free replaceable counter anions, various vPOPs have been reported for effectively capturing anionic oxo-pollutants, which are mentioned in Table 3. Among them, triazine-based vPOPs were very efficient for oxoanion removal. Ghosh *et al.* successfully detoxified wastewater by selectively eliminating various metal-based oxoanions by using triazine based vPOPs (compound-1) (Fig. 4(a)).⁴⁶ Compound-1, which was synthesized through the solvothermal assisted Zincke reaction, showed remarkable chemical stability. The vPOPs included mobile exchangeable chloride ions, creating an optimal platform for removing toxic oxoanions from water. Compound-1 exhibited strong adsorption capabilities by selectively extracting the carcinogenic ReO₄⁻ ions from water (Fig. 4(b)–(g)). Additionally, to assess real-time effectiveness, an experiment capturing oxoanions through column exchange was conducted. Recently the same group reported the same viologen compound but in the macroporous form, which is discussed in the organic pollutants removal from water section.⁵⁸ In the same paper, they also checked oxoanion removal through iVOFm and demonstrated exceptionally rapid removal rates for oxoanions (approximately 99% for KMnO₄ and around 97% for KReO₄ within a 30 s timeframe) (Fig. 3(b) and (c)).

In a very recent report, the tetra aza macrocycle containing vPOP was considered as a very potential adsorbent material for separating TcO₄⁻ and ReO₄⁻ from wastewater.⁹⁹Tc is a radioactive element that releases beta particles. It has a significant



Table 3 Tabular representation of vPOPs used as an adsorbent material for removal of toxic oxoanions from water

S. no.	Name of vPOPs	Kinetic study		Oxoanion capture capacity (mg g ⁻¹)	Selectivity	Ref.
		Time for oxoanion removal	% of oxoanion removal			
Cr₂O₇²⁻ removal						
T3a.1	C-NSA _{Naph} HCP@Br	60 min	95%	745	F ⁻ , Cl ⁻ , Br ⁻ , ClO ₃ ⁻ , NO ₃ , CO ₃ ²⁻ and PO ₄ ³⁻	90
T3a.2.	IISERP-POF9	60 min	77%	128.10	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	83
T3a.3.	IISERP-POF10	60 min	78%	125.21	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	
T3a.4.	IISERP-POF11	60 min	81%	131.22	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	
T3a.5.	COP ₁ ⁺⁺	15 min	95%	—	—	70
T3a.6.	CON-1	60 min	98%	293	—	93
CrO₄²⁻ removal						
T3b.1.	Compound-1	30 min	98.25%	133	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻	46
T3b.2.	iCOF-2	60 min	99%	253	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻	91
MnO₄⁻ removal						
T3c.1	Compound-1	5 min	99.9%	297.3	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻	46
T3c.2	IISERP-POF9	60 min	99%	110.53	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	83
T3c.3	IISERP-POF10	60 min	97%	103.11	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	
T3c.4	IISERP-POF11	60 min	98%	113.81	Cl ⁻ , ClO ₄ ⁻ , and SO ₄ ²⁻	
T3c.5	iVOFm	30 s	99%	—	—	58
T3c.6	COP ₁ ⁺⁺	< 1 min	99%	—	—	70
T3c.7	iCOF-2	60 min	99%	334	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻	91
T3c.8	QUST-iPOP-1	8 min	99%	514	—	92
ReO₄⁻ removal						
T3d.1	Compound-1	60 min	> 80%	517	Cl ⁻ , NO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻	46
T3d.2	TFPM-BDNP	1 min	90%	998.26	NO ₃ ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , CO ₃ ²⁻	67
T3d.3	TZ-PAF	—	—	982	NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , H ₂ PO ₄	66
T3d.4	VBCOP	5 min	98%	444	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	65
T3d.5	iVOFm	30 s	97%	—	—	58
T3d.6	COP ₁ ⁺⁺	30 min	99%	—	—	70
T3d.7	SCU-COF-1	1 min	99%	367	NO ₃ ⁻ and SO ₄ ²⁻	86

fission output and a lengthy half-life. The prompt removal of ⁹⁹Tc from liquefied radioactive waste is essential due to its intrinsic potential for causing harm to humans. On the other hand, Re is also considered as a carcinogenic material. In this report, Xia *et al.* synthesized a tetraaza macrocycle containing vPOP through the solvothermal-assisted Zincke reaction, named VBCOP (Fig. 4(h)).⁶⁵ This material has great potential as an adsorbent for the absorption of ReO₄⁻/TcO₄⁻, demonstrating exceptional adsorption properties such as fast adsorption rate, high adsorption capacity, excellent selectivity, and efficient regeneration (Fig. 4(i) and (j)). This efficient adsorption process is primarily governed by ion-exchange mechanisms. In addition, they demonstrated the new sequestration of Re(IV) by including a malleable tetraaza macrocycle ligand inside the framework architecture for the first time. The use of EXAFS and XPS analysis reveals that VBCOP⁰ has the ability to create a compound with Re(IV), indicating its potential use in eliminating soluble low-valent Tc species from radioactive wastewater. In summary, VBCOP showed promise in effectively treating both high-valent and low-valent Tc in nuclear effluent. The same group reported a diamond-like topological vPOP named TZ-PAF, for efficient remediation of radioactive TcO₄⁻ from wastewater. TZ-PAF was solvothermally synthesized *via* the Zincke reaction (Fig. 4(k)).⁶⁶

The TZ-PAF that was synthesized had exceptional resistance to acids and high thermal environment. The material showed rapid anion-exchange kinetics and a high capacity for adsorption (982 mg g⁻¹ for ReO₄⁻), which may be ascribed to its low-

density structure and the presence of many cationic pyridinium rings that act as sites for anion exchange (Fig. 4(k)-(m)). In addition, TZ-PAF had the greatest capacity for removing TcO₄⁻, with a *K_d* value of 5.02 × 10⁶ mL g⁻¹. It also exhibited exceptional reusability for extracting TcO₄⁻ from both extremely acidic media and low-activity wastewater streams. Hence, the dia-topology TZ-PAF has successfully addressed the drawbacks of vPOPs, including their susceptibility to acid damage and limited ability to absorb TcO₄⁻/ReO₄⁻. As a result, it has emerged as a promising option for efficiently and completely eliminating ReO₄⁻ from nuclear wastes. This paper presents a novel method for creating very stable sorbents, which are very efficient for TcO₄⁻ adsorption.

Qui *et al.* recently documented, for the first time, the synthesis of three-dimensional viologen-based covalent organic frameworks (Fig. 4(n)).⁶⁷ They have successfully produced a novel 3D ionic covalent organic framework (iCOF), named TFAM-BDNP, through the microwave-assisted Zincke reaction. TFAM-BDNP demonstrates exceptionally rapid response times, a high adsorption rate, superior selectivity, and impressive resistance to changes in pH, along with the ability to be reused for the removal of TcO₄⁻/ReO₄⁻. Owing to its outstanding stability, open hydrophobic channels, and high charge density, TFAM-BDNP presents itself as a promising candidate for the removal of TcO₄⁻/ReO₄⁻ (Fig. 4(o) and (p)). This research not only diversifies the structural variations of 3D covalent organic frameworks but also broadens their applications in processes related to the disposal of nuclear waste.





Fig. 4 (a) Schematic representation of the oxo-anion capture by compound-1. (b)–(g) Kinetic studies of removal of all oxoanions by compound-1. Reproduced with permission from ref. 46. Copyright 2014 the Royal Society of Chemistry. (h) Schematic representation of the synthesis of VBCOP. (i) Effect of contact time on the removal efficiency of $\text{Re}(\text{VII})$ by VBCOP ($C_0 = 45 \text{ mg L}^{-1}$, $\text{pH} = 7$). (j) Effect of contact time on the removal efficiency of $^{99}\text{Tc}(\text{VII})$ by VBCOP. Reproduced with permission from ref. 65. Copyright 2018, Elsevier. (k) Schematic of the synthetic route for TZ-PAF. (l) and (m) Sorption kinetic investigations of TZ-PAF for ReO_4^- uptake. Reproduced with permission from ref. 66 Copyright 2018, Elsevier. (n) Synthetic pathway of 3D iCOF (TFAM-BDNP). (o) and (p) Adsorption kinetics and adsorption isotherm of TFAM-BDNP for ReO_4^- capture. Reproduced with permission from ref. 67. Copyright 2018, Elsevier.

I₂ uptake. Iodine is considered one of the most hazardous elements and can cause very serious health issues due to its radioactive decay.²⁸ So, the removal of iodine from water bodies is one of the most important considerations for healthy

mankind. Over the years, iodine removal has become one of the extensively researched areas. Among all the iodine-adsorption materials, vPOPs possess extremely strong iodine-capturing capabilities due to their redox switch and



quaternized nitrogen atoms.⁶⁸ The researchers investigated the impact of various redox states of viologen on iodine absorption in many vPOPs with distinct core structures, including phosphazene, calixarene, 1,3,5-tris(4-aminophenyl)benzene (TAPB), *etc.* The findings are impacted by several factors, such as the basic features, presence of viologen counterions, porosity, redox state, and the presence of existing iodine sorption sites. The inclusion of large counterions like PF_6^- limits the available surface area for iodine interaction, leading to a reduction in absorption efficiency of up to 30%. vPOPs (COP_1^{++} and COP_2^{++}) that are fully reduced and neutral possess a significant capacity to absorb iodine, resulting in a maximum increase in mass of up to 380% (Fig. 5(g)).⁶⁹ The radical cationic vPOPs act as Lewis bases and are likely responsible for the enhanced interactions with Lewis acids I_2 and I_3^- . Additionally, neutral vPOPs (COP_1 and COP_2) lack counterions, perhaps increasing the available surface area for iodine to engage with the framework (Fig. 5(a) and (d)).⁷⁰ Highly stable radical cationic vPOPs ($\text{COP}_1^{\bullet+}$ and $\text{COP}_2^{\bullet+}$) have the potential to engage in a series of reduction-oxidation reactions with polyiodides and formed dicationic vPOP and I_3^- (Fig. 5(h)). This process provides vPOPs a substantial ability for absorbing iodine vapor.⁶⁹ The enduring nature of the radical cationic viologen is crucial for facilitating these reactions.

The above-mentioned discussion is a common overview of how the redox-active behaviour of vPOPs affected the iodine adsorption process. The 1st synthesized vPOPs gel (COGF), through the solvothermal assisted Zincke reaction, exhibited remarkable iodine adsorption efficiency (Fig. 5(e)).⁴³ The same research group reported viologen and pyrene-based covalent organic nanosheets (CONs) and covalent organic tubes (COTs) for iodine adsorption in the solution phase as well as the vapor phase (Fig. 5(i)). COTs exhibited high efficiency in iodine adsorption in both phases, as the presence of triple bonds and more cationic surface leads to fast iodine capture in COTs (Fig. 5(j) and (k)).⁸⁹

Gas storage and separation

The proliferation of modern industrial processes has resulted in the substantial emission of greenhouse gases, most notably carbon dioxide (CO_2), which presents a considerable peril to the state of the environment.⁷¹ Therefore, it is crucial to prioritize the development of renewable energy sources and implement efficient strategies for storing and converting greenhouse gases. The high surface areas of vPOPs, which are essential for gas adsorption materials that interact with gas molecules *via* non-covalent means, have prompted investigations into their potential as CO_2 adsorbents.⁷² vPOPs frequently distinguish themselves due to their exceptional stability, economical nature, and straightforward synthesis. Nevertheless, the adsorption capabilities of vPOPs have been predominantly evaluated in less severe environments, and they have been widely employed in the storage and conversion of greenhouse gases. Although there have been conjectures regarding the cationic charge of viologen and the potential pore-blocking effect of

counterions restricting the porosity of viologen-based POPs, there have been numerous reports of materials with considerable surface areas.⁷³ Dicationic viologens, in conjunction with their corresponding counterions in vPOPs, are capable of forming electrostatic interactions with CO_2 by virtue of their polar functional groups which enhances the affinity of the material for CO_2 . Coskun *et al.* reported a vPOP (PCPs) synthesized *via* the Sonogashira–Hagihara coupling reaction to examine the effect of exchangeable counterions on the adsorption of CO_2 (Fig. 6(a)).⁷⁴ The incorporation of bulkier counterions such as BF_4^- or PF_6^- resulted in a reduction in the material's surface area. However, BF_4^- and PF_6^- may function as Lewis bases, which somewhat compensates for their CO_2 absorption capability, although at the expense of having comparatively lower surface areas (Fig. 6(b) and (c)). Recent observations from the same research group indicate that substituting a bromide counterion for chloride improves CO_2 uptake in a vPOP (cCTF) containing a Zincke reaction-fabricated polyhedral oligomeric silsesquioxane core.⁷⁵ At elevated temperatures, gas adsorption diminishes, irrespective of the type of counterion. For CO_2 adsorption, a covalent triazine framework (cCTF) was utilized, which consisted of a porous viologen substituted with cyanophenyl, as illustrated in Fig. 6(d). The reaction temperature during the synthesis process had a significant impact on the surface areas of these frameworks, with the highest value of $1247 \text{ m}^2 \text{ g}^{-1}$ occurring at 500°C . The compound exhibited highest CO_2 adsorption capacity (133 mg g^{-1}) among all other vPOPs. (Fig. 6(e)–(h)). The authors hypothesized that the cationic groups attached to viologen groups increased the CO_2 absorption capacity of vPOPs by as much as fivefold, in comparison with other triazine framework-based materials that possess comparable surface areas. D'Alessandro *et al.* studied the effect of the redox behavior of the viologen moiety on CO_2 uptake experimentally as well as theoretically.⁷⁶ After the two-electron reduction of dicationic viologen, the gas uptake capacity decreases, from 0.92 mmol g^{-1} (approximately 40.5 mg g^{-1}) to 0.67 mmol g^{-1} (approximately 29.5 mg g^{-1}) in POP-V1, and from 1.27 mmol g^{-1} (approximately 55.9 mg g^{-1}) to 1.09 mmol g^{-1} (approximately 48.0 mg g^{-1}) in POP-V2 (Table 4). The authors posit (based on their theoretical modelling) that Cl^- counterions have paramount importance in enhancing the interactions with CO_2 molecules. The decrease in CO_2 absorption is a direct consequence of the elimination of the counterion during reduction from dicationic state to its neutral state. As a result of these investigations as a whole, it is clear that the charge on viologen and its chloride counterions is vital for covalent materials based on viologen to maximize their CO_2 adsorption capacity. Nowadays, researchers are finding several innovative ways or concepts to improve the catalytic efficiency of vPOPs for CO_2 fixation (Table 4).

The incorporation of halogen bond donors (HBDs) in the frame of vPOPs leads to a new class of materials that can be used as a catalyst for CO_2 fixation. Utilizing this new concept Chen *et al.* synthesized HBD-incorporated hybrid vPOPs, named V-iPHPs (Fig. 7(c)), and used these materials for catalytic CO_2 fixation.⁷⁷ V-iPHPs were synthesized through the





Fig. 5 (a) Synthesis of COP₁¹⁺ and COP₂²⁺. (b) Real images of iodine vapor adsorption in COP₁ and COP₂ at 60 °C. (c) Iodine vapor capture capacities of COP₁ and COP₂ in three different redox states. (d) Schematic representation of anion removal (MnO₄⁻, Cr₂O₇²⁻) by anion exchange, where yellow spheres represent polymer particles (COP₁ and COP₂). Reproduced with permission from ref. 70. Copyright 2014 the Royal Society of Chemistry. (e) Synthesis of the hollow sphere (HS) and hollow tube (HT) via the solvothermal synthesis approach and the covalent organic gel framework (COGF) via the microwave synthesis approach. (f) Graph of % removal of I₂ from a 1 mM solution in cyclohexane over time by HT, HS and COGF. Reproduced with permission from ref. 43. Copyright 2022, American Chemical Society. (g) Synthesis of COP₁¹⁺ and COP₂²⁺. (h) Solution-phase iodine adsorption by the three redox states of COP₁ and COP₂. Reproduced with permission from ref. 69. Copyright 2022 Wiley-VCH. (i) Synthesis of CONs and COTs, (j) and (k) iodine adsorption experiments. Reproduced with permission from ref. 89. Copyright 2022 Wiley-VCH.



storage and conversion technologies. In recent years, attention has shifted towards new energy devices like batteries and supercapacitors. Viologens and their derivatives are frequently employed in these devices due to their optimal electron accepting capability and favorable redox behavior.^{31,79}

Very recently our group reported a series of viologen-based covalent organic networks (vCONS) as metal-free bifunctional

electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).⁸⁰

Here, we synthesized four vCONS through the solvothermal-assisted Zincke reaction, denoted as vGC, vGAC, vMEL and vBPDP, based on triamines used as reactants (Fig. 8(a)). The incorporation of redox-active viologen groups into the extended covalent organic framework was essential for achieving

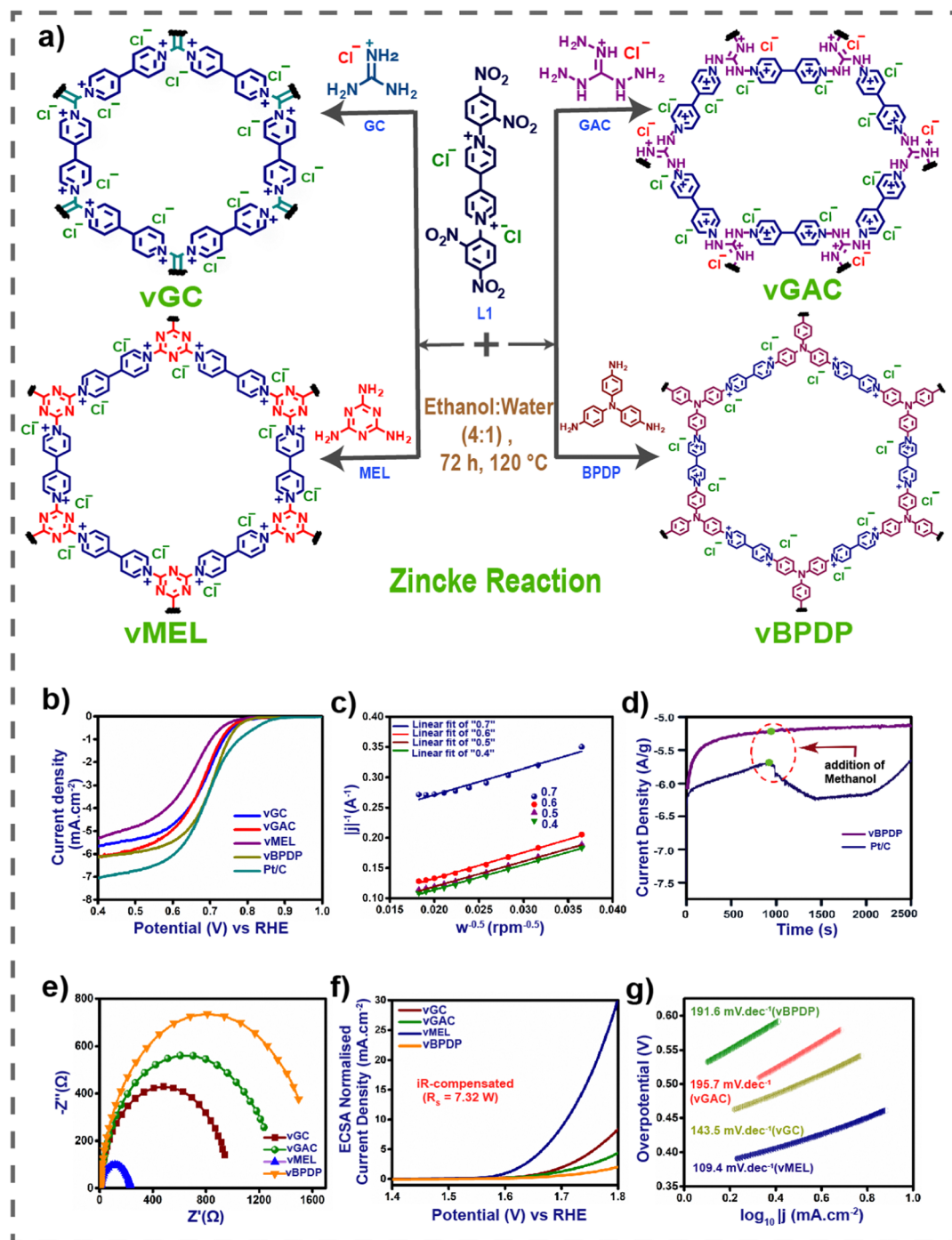


Fig. 8 (a) Synthesis of vGC, vGAC, vMEL and vBPDP. (b) LSV curves of all vCONS. (c) K–L plot of vBPDP. (d) Methanol stability of vBPDP. (e) EIS spectra of all vCONS. (f) LSV curves for the OER of all vCONS. (g) Tafel plots of all vCONS. Reproduced with permission from ref. 80. Copyright 2014 the Royal Society of Chemistry.



exceptional stability in both acidic and basic environments, as well as for demonstrating dual functionality in the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The verification was conducted using cyclic voltammetry (CV) curves. Significantly, vBPDP exhibited a remarkable oxygen reduction reaction (ORR) efficiency, achieving a half-wave potential of 0.72 V relative to a reversible hydrogen electrode (RHE) in a 1 M KOH electrolyte (Fig. 8(b)–(e)). However, vMEL demonstrated impressive OER (oxygen evolution reaction) performance, achieving an overpotential of 320 mV at a current density of 10 mA cm⁻² and a Tafel slope of 109.4 mV dec⁻¹ in a 1 M KOH electrolyte solution (Fig. 8(f) and (g)). This research is notable for using unadulterated viologen-based covalent organic networks as bifunctional electrocatalysts (for ORR and OER) without the inclusion of any metallic elements or conductive substances. There is a firm conviction that these particular varieties of vCONs possess the capability and efficiency to function as bifunctional electrocatalysts for ORR and OER. Consequently, these vCONs will be extremely useful in energy storage devices of the upcoming generation.

Wen *et al.* have effectively synthesized a two-dimensional redox-active cationic covalent triazine network (cCTN) utilizing the solvothermal-assisted Zincke reaction.⁴⁵ This network acts as a metal-free electrocatalyst for ORR in order to generate H₂O₂ (Fig. 9(a)). The cCTN electrocatalyst was synthesized with a mesoporous structure, characterized by a pore width ranging from 2 to 10 nm. It has a total nitrogen concentration of 13.3 wt%. This polymer has a reversible two-electron redox mechanism, which is thought to enhance the ORR efficiency for the generation of H₂O₂. The cCTN electrocatalyst exhibits excellent ORR performance and impressive specificity (over 85%) for H₂O₂ production across a broad potential range (0.1–0.7 V) (Fig. 9(b)–(e)). Electron paramagnetic resonance (EPR) tests showed that the viologen units in the cCTN electrocatalysts may initiate the activation of molecular oxygen, resulting in the production of superoxide radicals (O²⁻), which support the 2e⁻ pathway of the ORR for the electrochemical synthesis of H₂O₂. This work presents a novel method for developing metal free electrocatalysts that are extremely specific to producing H₂O₂ from O₂. Current research is dedicated to improving the efficiency and specificity of the cCTN electrocatalyst.

These ionic vPOPs are also recognized as remarkable cathode materials for Li-ion batteries. Recently, Li *et al.* reported a series of novel cationic vPOPs, denoted as TpVXs (where X = Cl, Br, or I), used as cathode materials in Li-ion batteries (Fig. 9(f)). Halogens which are used in Li-ion batteries serve as efficient cathodic materials but exhibit significantly very poor cycling efficacy.⁸¹ The vPOPs (TpVXs) are specifically engineered to feature numerous pores and ionic redox-active components to effectively and durably trap halogen anions accurately and appropriately. The TpVBr and TpVI electrodes demonstrate a notable initial specific capacity of 116 and 132 mA h g⁻¹ at 0.2C, respectively, along with an elevated discharge voltage of around 3.0 V (Fig. 9(g)–(i)). Remarkably, due to their permeable and ionic composition, TpVBr and TpVI exhibit exceptional durability over extended periods of use (86% and 98% capacity preservation after 600 cycles at 0.5C), surpassing the performance of the most advanced halogen electrodes (Fig. 9(j)).⁸¹

Viologens recognized as a crucial optoelectronic material have found application in solar cells either as the active chromophore or as materials modified for electrodes. Feng *et al.* showcase a highly crystalline 2D polymer film with immobilized viologen (V2DP),⁴⁷ characterized by a dense array of inherent pores and well-defined channels that facilitate the efficient utilization of viologen moieties and ion transport (Fig. 9(k)). Leveraging this, they constructed V2DP-based electrochromic devices (ECDs) demonstrating swift switching speeds (2.8 s for coloration, 1.2 s for bleaching), a high Coulombic efficiency (989 cm² C⁻¹ at 90% of the full switch), and low energy consumption (21.1 μW cm⁻²) (Fig. 9(l)–(n)). Additionally, the researchers illustrated the integration of these ECDs with transparent solar cells (TSCs), creating energy-efficient electrochromic window systems capable of dynamically adjusting light automatically (Fig. 9(o) and (p)). This innovation aligns with intelligent solar spectrum management. Their findings lay the foundation for designing and synthesizing electroactive 2D polymer films for superior smart windows, broadening the possibilities for energy-efficient building applications in the future.

Catalysis

Catalysis is important to facilitate chemical reactions. Catalytic reactions hold considerable importance in the production of numerous industrial compounds and minerals, in addition to their utilization in a diverse array of applications such as pharmaceutical synthesis, environmental remediation, energy generation, and food manufacturing.^{97,98} Catalysis may be classified into two primary categories: homogeneous catalysis and heterogeneous catalysis. Homogeneous catalysts are characterized by their ability to stay in the same phase as the reactants, whereas heterogeneous catalysts are distinguished by their ability to remain in a separate phase. Homogeneous catalysts, despite their superior activity and selectivity, encounter some constraints such as stability and separation challenges. Consequently, substantial scientific efforts have been dedicated to the creation of heterogeneous catalysts.⁹⁹ In this regard, vPOPs are one of the most ideal materials for heterogeneous catalysts due to their insolubility in water and organic solvents along with exceptional durability and longevity, hence facilitating advantageous chemical reactions under the conditions of reduced temperatures and pressures. vPOPs exhibit redox chemistry, enabling the transfer of electrons, and forming robust complexes with metal nanoparticles that have a negative charge. Moreover, the counterions of the viologen moiety function as nucleophiles and leaving groups, which helps in enhancing their catalytic efficiency.¹⁰⁰ These insoluble and stable vPOPs were used as heterogeneous catalysts for several reactions such as cycloaddition of CO₂ or CO₂ fixation, debromination, Michael addition of thiols, *etc.*

In the year of 2019, Li *et al.* reported an exceptionally stable vPOP, known as bipy-POP (Fig. 10(a)), which was synthesized by reacting 4,4'-bipyridine with tetrakis(4-(bromomethyl)phenyl)methane in *N*-methylpyrrolidone at a temperature of 110 °C and which was further employed as a heterogeneous catalyst for





Fig. 9 (a) Synthesis of cCTN:Cl⁻, (b) CVs of cCTN:Cl⁻, (c) CV of cCTN:Cl⁻ in 0.1 M KOH solution, (d) LSVs of the ORR of cCTN:Cl⁻, and (e) Koutecky-Levich plots at different potentials. Reproduced with permission from ref. 45. Copyright 2014 The Royal Society of Chemistry. (f) Proposed mechanism of TpVXs, electrochemical characterization of TpVXs as cathode materials. (g) CV curves of TpVXs, (h) charge/discharge curves at indicated current densities of TpVXs, and (i) rate performance and (j) cycling stability of TpVXs cathodes. Reproduced with permission from ref. 81. Copyright 2022 Wiley-VCH. (k) Synthesis of the V2DP film. Electrochemical characterization of the V2DP film. (l) CV curves of the V2DP electrode at different scan rates from 10 to 100 mV s⁻¹. (m) Real time images of reversible color changing of the V2DP film. (n) Schematic presentation of the *in situ* spectroelectrochemical measurement. UV-vis spectral changes of the V2DP electrode recorded during (o) reductive and (p) oxidative processes. Reproduced with permission from ref. 47. Copyright 2022 Wiley-VCH.

the debromination coupling reaction.¹⁰¹ The bipy-POP catalyst has shown significant efficacy in facilitating the reductive debromination of several benzyl bromides in *N,N*-dimethylformamide, using dithionite as the reductive reagent. The reactions preferentially produced dibenzyl sulfone derivatives for substrates that had an electron-donating group on the benzene ring (Fig. 10(b)). In general, the presence of an electron-withdrawing group on the benzene ring in substrates has been seen to result in the formation of coupling products, namely ethane derivatives. In some cases, substrates containing F,

Cl, or CF₃ were seen to have a preference for the production of sulfone derivatives. The study investigated the recyclability of bipy-POP in the catalysis of the reaction between (4-fluorophenyl) methyl bromide and diphenylmethyl bromide, resulting in the formation of sulfone or ethane derivatives. The results indicated that, even after 40 cycles of repeated use, the heterogeneous catalysis did not demonstrate a significant decrease in activity. Recently, a novel vPOP named IPOPOP was employed as a heterogeneous catalyst for the Michael addition of thiols to α,β -unsaturated carbonyl compounds (Fig. 10(c)).¹⁰² IPOPOP was





Fig. 10 (a) Synthesis of bipy-POP, (b) catalyst bipy-POP used for debromination coupling reaction for formation of sulfone. Reproduced with permission from ref. 101. Copyright 2022 Wiley-VCH. (c) Synthesis of IPOP, (d) IPOP-catalysed Michael addition of thiols to α,β -unsaturated carbonyl compounds. Reproduced with permission from ref. 102. Copyright 2018, Elsevier. (e) Schematic diagram of the synthesis route for HVPOP-Cl, (f) performance of comparative materials in the cycloaddition of CO₂. Reproduced with permission from ref. 103. Copyright 2014 the Royal Society of Chemistry.

synthesized through the Menshutkin reaction by using a twisted biaryl (TMBB) as the monomer (Fig. 10(c)). IPOP exhibits thermal stability and lacks solubility in water as well as in commonly used organic solvents such as MeOH, MeCN, EtOH, DCM, and others. IPOP has capabilities similar to the phase-transfer quaternary ammonium salt tetra-*n*-butylammonium bromide (TBAB), due to the inclusion of cationic sites and counter bromide anions in its polymeric matrix. This characteristic enables IPOP to be used as a reusable heterogeneous catalyst for organic transformations. IPOP is a very effective catalyst for the Michael addition of thiols to α,β -unsaturated carbonyl compounds (Fig. 10(d)). This process allows for the production of organosulfur compounds, namely *b*-arylthioketones, with high yields in isolation. Comparably, it has been demonstrated that IPOP can serve as a recyclable heterogeneous catalyst for the easy production of biscoumarins. These compounds belong to a significant category of molecular systems that demonstrate diverse biological properties, including anti-coagulant, anti-anthelmintic, anti-HIV, anti-bacterial, anti-oxidant, anti-cancer,

and so on. Therefore, a new, effective, and environmentally friendly method has been created to synthesize *b*-arylthioketones and biscoumarins by imitating the phase transfer of quaternary ammonium salts. IPOP can be used as a heterogeneous catalyst for a minimum of 10 catalytic cycles without any decrease in catalytic activity.

It has also been reported that vPOPs can play a direct catalytic role in fixing CO₂ into cyclic carbonates from a variety of epoxide-starting materials. The mechanisms by which these reactions occur are as follows: at the very first step, the epoxide is activated *via* hydrogen bonding with the α -protons of viologen and the epoxide ring is then exposed by a nucleophilic attack of Cl⁻ ions. The resulting intermediate undergoes cyclization upon reaction with CO₂, whereas Cl⁻ functions as a leaving group.⁷² Based on this mechanism, using the Sonogashira-Hagihara cross-coupling reaction, a viologen-based porous organic polymer featuring a hollow structure and active anions was synthesized (named VPOP-Cl) from two basic monomers (Fig. 10(e)).¹⁰³ This material exhibited exceptional



performance in the catalytic cycloaddition of CO₂. The pore properties of pristine VPOP-Cl were modified by alterations in micromorphology, and the exchange of anions enhanced its catalytic performance. Additionally, the modified HVPOP-Br demonstrated excellent reusability and catalytic performance in a solvent-free, metal-free reaction system devoid of cocatalysts. A substantial enhancement in the catalytic efficiency of CO₂ cycloaddition was achieved through the modification of the microscopic structure and the exchange of anions (Fig. 10(f)). This approach may offer suggestions for enhancing the catalytic performance of POPs utilizing polymers with a basic structure. Similarly, Chen *et al.* reported a series of crystalline vPOPs (designated VIP-X, X = Cl or Br) that have acted as the metal-free heterogeneous catalyst for the degradation of CO₂. In the synthesis of cyclic carbonate *via* CO₂ cycloaddition with epichlorohydrin at atmospheric pressure (1 bar) and a low temperature (40 °C), the optimal catalyst VIP-Br produced a high yield of 99%.⁸⁸ Furthermore, under mild conditions, other diverse epoxides could also be converted into cyclic carbonates. Additionally, the catalyst VIP-Br exhibited favorable stability and could be readily isolated for reuse. The exceptional catalytic performance may be ascribed to the synergistic influence of the enriched bromine anion species and the accessible hydroxyl

(OH) groups that originate from water molecules that are H-bonded. The same group reported HBD-incorporated hybrid vPOPs, named V-iPHPs (Fig. 7(c)), that were used for catalytic CO₂ fixation.⁷⁷ The V-iPHP-1 catalyst has exceptional metal-free heterogeneous catalytic properties in the process of CO₂ fixation using various epoxide substrates, even under very gentle circumstances. Moreover, the heterogeneous catalyst V-iPHP-1 exhibits a high degree of recoverability and impressive reusability. The exceptional catalytic performance may be attributed to the synergistic catalytic effects resulting from the presence of hydrogen bond donors, namely Si–OH groups and Br[−] anions, as well as the abundance of mesopores and the hydrophobic reaction microenvironment.

Photocatalyst. Photocatalysis is the process by which substances that are classified as photocatalysts modify the rate of chemical reactions when exposed to light or sunlight. Visible-light-driven photocatalytic technology, which converts solar energy to chemical energy, offers the potential for chemical transformations such as pollutant removal, water splitting, and hydrogen evolution. Therefore, creating effective photocatalysts with high catalytic activity is crucial.^{104,105} Eventually, vPOPs are considered as an ideal photocatalyst for the photocatalysis phenomenon due to the redox-active nature of the viologen



Fig. 11 (a) Schematic diagram of the dual-module COF (System I) and the mixture of single-module COF with unembedded ETM (System II). (b) The hydrogen evolution test of the integrated Tp-2C/BPy²⁺-COF (19.10%) and the bare Tp-BPy-COF mixed with additional 2C/BPy²⁺ used as an ETM under visible-light irradiation. The orange integral area roughly reflects the hydrogen evolution difference between the two photocatalytic systems. (c) HERs of Tp-2CPBy²⁺-COF (10 mg) with different quaternization conversions. Reproduced with permission from ref. 107. Copyright 2022 Wiley-VCH. (d) Schematic representation of photocatalytic oxidative coupling of benzylamine through VCR-POP-1. (e) Photocatalytic performance in white-light-driven photocatalytic oxidative coupling of benzylamine into imine over different catalysts VCR-POP-1, VIL-CN, and V-POP-1. Reproduced with permission from ref. 110. Copyright 2022, American Chemical Society. (f) Schematic representation of TPCBP X-COF [X = ethyl (E), butyl (B), and hexyl (H)] structures. (g) Photocatalytic hydrogen evolution activities of TPCBP X-COFs. (h) pH effect of TEOA. (i) Photocatalytic stability test of TPCBP X-COFs. Reproduced with permission from ref. 108. Copyright 2022, American Chemical Society.



moiety and radical formation tendency. Recently, radical porous organic polymers (RPOPs)¹⁰⁶ are emerging as potential materials for photocatalysis and vPOPs are considered as one kind of RPOP because vPOPs form easily stable radical cations by undergoing one electron reduction (Scheme 1). Viologen and its derivatives facilitate the rapid transfer of electrons from photosensitizers to active sites by functioning as electron-transfer mediators (ETMs). However, the electron-transfer capability is frequently impeded by the formation of a stable dipole structure due to the coupling between viologen-derived ETMs that contain cationic radicals; this results in the restriction of the electron-transfer process. To address this issue, Guo *et al.* installed a cyclic diquat in a 2,2'-bipyridinium covalent organic framework *via* a quaternization reaction (Fig. 11(a)).¹⁰⁷ Cyclic diquats are known for viologen-derived ETMs.¹⁰⁸ By the synergistic influence of steric hindrance and electrostatic repulsion, these entities are selectively immobilized on distinct sites and kept apart. This prevents the development of stable p-stacked cationic radicals throughout the electron transfer procedure. The conductivity and electron-transfer capability of quaternized COFs are significantly enhanced in comparison to pristine COFs. These properties can be further modified through adjustments to the dimension of cyclic alkyl chain length and quaternization transformations. At 420 nm, the Tp-2C/BPy²⁺-COF containing 19.10 mol% of 2C/BPy²⁺ demonstrates the highest hydrogen evolution reaction (HER) (34560 $\mu\text{mol h}^{-1} \text{g}^{-1}$, utilizing 10 mg COFs) along with a high apparent quantum efficiency (AQE) of 6.93% (Fig. 11(b) and (c)). Moreover, these exceptional results persisted throughout a 48 h photocatalytic cycle, surpassing the performance of the COF/ETM mixture system. Their approach was to maximize the utilization of 2D COFs, as a customizable platform utilized to incorporate various fundamental functions and improve photocatalytic performance synergistically *via* pre-designed ordering frameworks.

Recently, Koyuncu and co-workers reported novel vPOPs [(TPCBP X-COF) [X = ethyl (E), butyl (B), and hexyl (H)]] where the frameworks containing a viologen moiety act as an acceptor structure and a biphenyl-bridged dicarbazole acts as an electroactive donor skeleton (Fig. 11(f)).¹⁰⁹ Further, TPCBP X-COF is used as a photocatalyst for the photocatalytic HER. When subjected to visible light illumination for a duration of 8 h, the H₂ evolution rate of the TPCBP B-COF (12.276 mmol g^{-1}) is 2.15 and 2.38 times greater than that of the TPCBP H-COF (5.697 mmol h^{-1}) and TPCBP E-COF (5.165 mmol h^{-1}), respectively (Fig. 11(g)). The TPCBP B-COF structure is regarded as one of the most effective catalysts described in the literature for photocatalytic HER; it generates 1.029 $\text{mmol g}^{-1} \text{h}^{-1}$ of hydrogen and has an apparent quantum capacity of 79.69% at 470 nm (Fig. 11(h) and (i)). This approach offers fresh perspectives on the development of innovative vCOFs for the future evolution of metal-free hydrogen through solar energy conversion.

vPOPs were also considered as a remarkable heterogeneous photocatalyst for the coupling reaction but this area of research is explored very rarely. Very recently, Chen *et al.* reported radical cationic vPOPs (named VCR-POPs) which are intended

to facilitate metal-free photoredox catalysis of oxidative coupling of amines in the presence of visible light (Fig. 11(d)). These acetonitrile-based radical cationic vPOPs (VCR-POPs) are synthesized through a one-pot Knoevenagel condensation reaction involving 1,3,5-tris(*p*-formylphenyl)benzene and an acetonitrile-functionalized viologen-based ionic monomer (VIL-CN). It is noteworthy that the VCR-POPs obtained a stable viologen cationic radical, which likely underwent *in situ* single-electron reduction of the dicationic monomer VIL-CN during the Knoevenagel condensation reaction facilitated by the base catalyst Cs₂CO₃. The electron paramagnetic resonance spectrum and X-ray photoelectron spectroscopy were employed to validate the radical nature of the prototypical porous organic polymer VCR-POP-1. Compared to the ionic monomer VIL-CN, the optical and electrochemical properties of VCR-POP-1 demonstrate its semiconductor nature, exceptional light-harvesting capability, and enhanced charge separation and transfer efficiency due to its well-designed cationic radical polymer structure (Fig. 11(e)). Hence, by virtue of the predominant reactive oxygen species of singlet oxygen, the polymer VCR-POP-1 featuring π -conjugated structures and viologen-based cationic radicals may be considered a metal-free heterogeneous photocatalyst that exhibits exceptional efficiency in facilitating the oxidative coupling of amines in air driven by visible light.

Outlook and summary

In this review, we have provided a comprehensive overview of the synthesis of vPOPs through several synthetic methods and their various potential applications for energy and environmental remediation. Diverse methodologies were deliberated about the synthesis of vPOPs, including solvothermal, microwave, and room temperature approaches, as well as name reactions including Zincke, Schiff base, Menshutkin, and others. vPOPs possess excellent chemical stability with reversible redox state characteristics and have been extensively utilized in the fields such as energy storage/conversion, gas absorption/storage, toxic pollutant removal, iodine uptake and catalysis reaction. Recent years have witnessed a substantial increase in the structural diversity of vPOPs, which has also resulted in an expansion of the energy and environmental remediation applications of vPOPs. Due to their exceptional chemical stability and redox activity, vPOPs are more promising materials for employment in environmental and energy restoration.

The strategies employed for the synthesis of vPOPs are antiquated and devoid of progress in this domain. The majority of crystalline vPOPs were synthesized through the microwave method. However, solvothermal or room temperature synthetic approaches ended up with amorphous or semi-crystalline vPOPs. Surprisingly, synthesis of vPOPs at room temperature is very rare and less attempted. Room temperature synthesis offers several advantages over solvothermal synthesis or microwave synthesis. Synthesizing crystalline vPOPs at room



temperature is a significant challenge as the reaction follows sluggish kinetics of crystallization. Therefore, researchers should explore innovative strategies, such as the use of tailored molecular precursors or novel templating agents, to overcome these barriers and develop efficient room-temperature synthesis protocols for crystalline vPOPs. Such advancements could revolutionize the field by enabling highly scalable and sustainable production of these materials for a wide range of applications.

We believe that significant studies have been achieved in energy and environmental remediation with the advent of vPOPs; however, there remain unresolved obstacles and challenges that necessitate attention. A significant obstacle is the presence of clogged surface regions on vPOPs, which arise from the occlusion of pores by counter anions. This occlusion hinders the uniform distribution of active sites with the desired porosity. To address these challenges, it is strongly encouraged that researchers prioritize template synthesis of vPOPs to achieve surface and pore size homogeneity; synthesize template-assisted thin layers; or implement 3D architectures onto vPOPs to enhance the likelihood of achieving uniform pore distribution. Limited research has been conducted on hybrid materials and vPOPs such as the implementation of macrocycle inside the vPOPs, or metal composite vPOPs, *etc.* Integrating viologens and other functional molecules into polymers holds significant promise and can significantly expand the range of applications for materials based on viologens. Fine-tuning mechanical properties through the selection of axle and macrocycle structures could yield valuable insights for optimizing applications, such as the utilization of resilient materials in flow experiments to remove pollutants through membranes. Presently, researchers have focused predominantly on the synthesis of vPOPs at laboratory-based small scale and showcasing their application in different directions. However, vPOPs exhibit immense potential for industrial-scale applications due to their unique combination of properties, including redox molecular switches and chemical stability. These materials offer solutions to a wide range of challenges in sectors such as gas storage, separation, catalysis, wastewater treatment, *etc.* In the future, transitioning vPOPs from laboratory-scale synthesis to industrial production could revolutionize various industries by providing efficient and cost-effective solutions. Scaling up production processes requires addressing challenges related to reproducibility, scalability, and cost-effectiveness. However, with continued research and development efforts, along with advancements in synthesis methodologies and manufacturing techniques, vPOPs have the opportunity to make a significant impact on industrial processes, leading to sustainable and innovative solutions for energy and environmental remediation. Regarding this matter, vPOPs' structures can be strategically designed when particular applications are identified by analysing the correlations between functionality, performance, and pore structure. Notwithstanding these obstacles, the immense capacity of vPOPs as adsorbents and catalysts is substantial in terms of environmental remediation and energy conversion, and will likely inspire additional developments in structural chemistry and practical implementations. The unique coordinated sites, donor-acceptor structure, and electrostatic interactions within vPOPs

make them a promising framework for resource recycling and energy conversion.

Abbreviation

EtOH	Ethanol
MeOH	Methanol
DCM	Dichloromethane
DMF	<i>N,N'</i> -dimethylformamide
MeCN	Acetonitrile
THF	Tetrahydrofuran
AcOH	Acetic acid
BuOH	Butanol
<i>o</i> -DCB	<i>Ortho</i> dichlorobenzene

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

PJ acknowledges VIT Vellore for the teaching and research assistant (TRA) fellowship. TP acknowledges the financial assistance of Council of Scientific & Industrial Research (CSIR, India) (sanction no: 01/3130/23 EMR-II) and SERB start-up research grant SRG/2020/001108 from the Government of India.

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