

# Chapter 1

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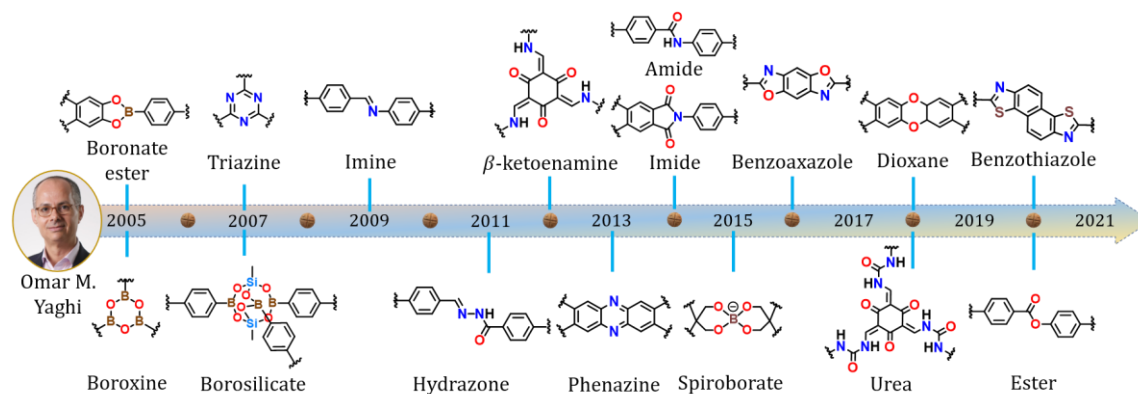
Introduction

## 1.1 Overview

Materials with permanent pores or voids are widely found in nature for centuries. Complex systems such as plants' seeds, eggshells of birds and biological tissues like bones, wood, cork, etc. have natural pores that prevent themselves from outside inundation of water, cracks and helps in improving the properties like permeability, physical and chemical stability, etc [1, 2]. Inspired from nature's creation of complex molecules, researchers have invented various artificial porous materials including zeolites, mesoporous materials, or metal organic frameworks (MOFs). Permanent pores or voids define the utility of such materials in numbers of domains including water treatment, biogas upgrading, CO<sub>2</sub> sequestration, energy applications, sensor, catalysis, and various biological applications, etc. A survey from "*Web of Science*" suggests more than 6000 publications are reported on porosity behaviour in past two decades. In this growing field of research, porous organic polymers (POPs) being an emerging organic material that follows the principles of reticular chemistry gain special attention since 2005 [3]. Reticular chemistry concerns with the assembling of rigid building units periodically across the crystal lattice *via* strong interaction affording predesigned structural skeleton [4]. This approach of chemistry has revolutionized many branches of material science offering industrial applications and is epitomized by the recent reports/articles/books on POPs.

POPs are the network solids constructed by linking organic nodes and linkers *via* strong covalent bonds [3-8]. By sophisticated selection of the building blocks, as well as the underlying network topology, the shape and size of the pores in POPs can be predesigned and tuned. But the choice of appropriate building units with reactive functionalities to trigger the formation of dynamic covalent bond is a vital and challenging aspect in POPs synthesis. Indeed, manipulating the direction of building unit to construct discrete bond is extremely difficult and hence at the initial stages, Yaghi and coworkers demonstrated only boronate ester and boroxine linkage. Later on, other linkages like inime, hydrazone, azine, imide, amide, urea, ester, etc. have been modified with time (Figure 1.1) [9]. Since the entire structural architecture is composed of lighter element such as C, B, N, O, S, or Si etc., such materials are having enough porous space and low density, whereas the strong covalent bond provides high chemical and thermal stability. Attaining the precise control over the reaction is crucial. This is due to the multiple possible ways of extension of covalent bonds at

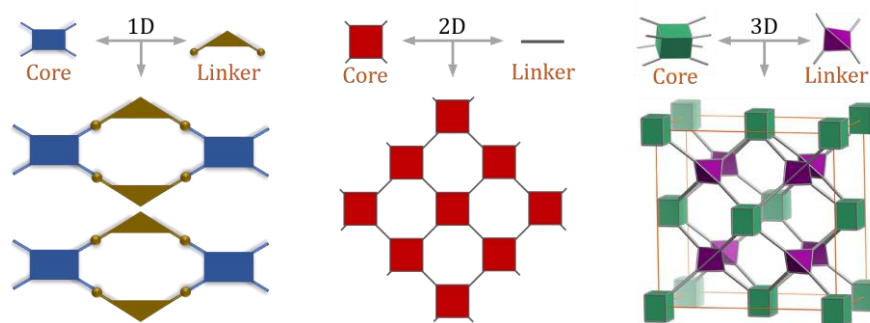
higher dimensions [10]. The irreversibility of strong covalent bond resists the crystallinity correction that could lead to irregular linking of building units affording poor crystalline networks. But the tunable pore size, shape, volume, connectivity, and the functionality make POPs an emerging platform for designing multifunctional porous materials with pre-designed skeleton having diverse potential applications. The versatile applications of POPs that includes catalysis, optoelectronic devices, environmental applications, gas separation, energy storage, sensing, nanoreactor, biomedicine, etc. evidence its potency in various industries [11-20]. Despite being providing foundation for the reformation of many branches of industry POPs also shape us to advance our philosophy of the functional materials. Growing attention to academic research POPs are owing to their persistent porous cages solely constructed by covalent bonds with varied functionalities. Design and synthesis of such porous system with desired properties is expected to serve as implants of new generation.



**Figure 1.1** Evolution of various linkages over the time since 2005

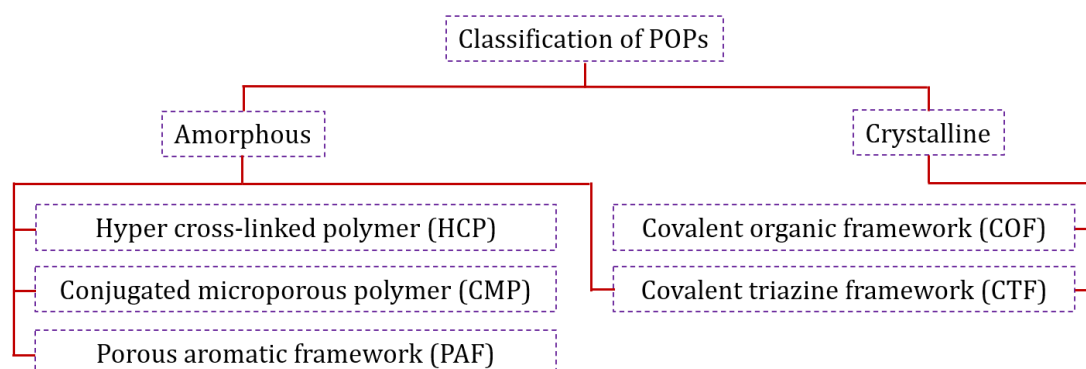
## 1.2 Classification of POPs

POPs, in general, are classified based on various factors such as size, shape, chemical environment and morphology, etc. POPs are structurally pre-designed precise integration of building units producing desired shape and pore size. The pore size ranges from micro to macro based on the size of the building unit and the linker associated in the construction of POPs. Based on pore diameter, IUPAC classification refers POPs to be microporous (<2 nm), mesoporous (>2 nm to <50 nm) and macroporous (>50 nm) [21-26]. Depending on the shape of the core/secondary building units and the linkers, the extended network achieves 1D, 2D or 3D architecture (Figure 1.2).



**Figure 1.2** Pictorial representation of 1D, 2D and 3D POPs based on the symmetry of the chosen building units and the linkers

Synthesis of POPs experiences structural irregularities because of the possible pathways of the extended covalent bonds in higher dimension. As a result, morphology control in POPs at ambient conditions is proven to be an impossible task. Based on the degree of orderness of this extended network, POPs can be classified into crystalline and amorphous solids and be further majorly sub divided into the following categories (Figure 1.3) *viz.* hyper cross-linked polymer (HCP), Conjugated microporous polymer (CMP), porous aromatic framework (PAF), covalent organic framework (COF), covalent triazine framework (CTF) [27-30]. Apart from COFs and few of the CTFs, almost all other POPs exist as amorphous material. Due to the high reactivity of building units and lack of the directing sites to react, kinetically disordered polymeric structure dominates at ambient condition. Whereas additional treatment is needed to reach the reversible equilibrium to heal such irregularities in the structural skeleton to obtain thermodynamically ordered crystalline networks.

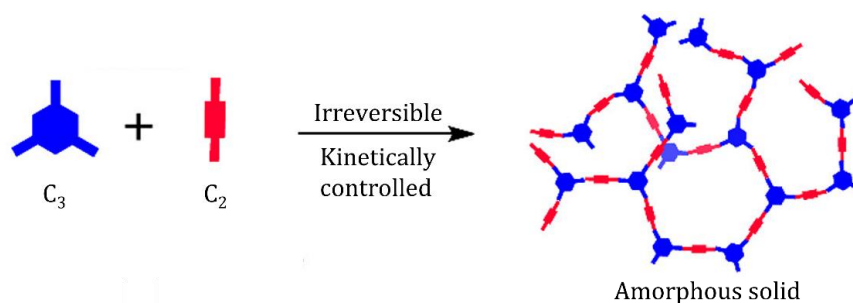


**Figure 1.3** Classifications of POPs based on their crystalline behaviour

Polymers with intrinsic microporosity (PIM) is usually considered under the class of POPs which is actually a rare class of one-dimensional polymer, where porosity is achieved through inefficient packing of the twisted polymer backbone [31,32].

### 1.2.1 Amorphous POPs

In general, amorphous POPs holds lower degree of orderness in their extended network structures. These are comparatively easy to prepare but possesses random pores and raises difficulties to control the pre-sketched structural skeleton. In fact, the process demands a high activation barrier to make the overall reaction reversible for error correction in their multidimensional network. Hence it is difficult to obtain an ordered structure at low temperature. As a result, kinetically controlled polymeric network is seen to dominate the overall product formation at ambient temperature (Figure 1.4) [10]. However, owing to its ease for the inclusion of functionality, POPs behave as potent candidate towards sensing, proton conduction, and specially a heterogeneous catalyst [33].

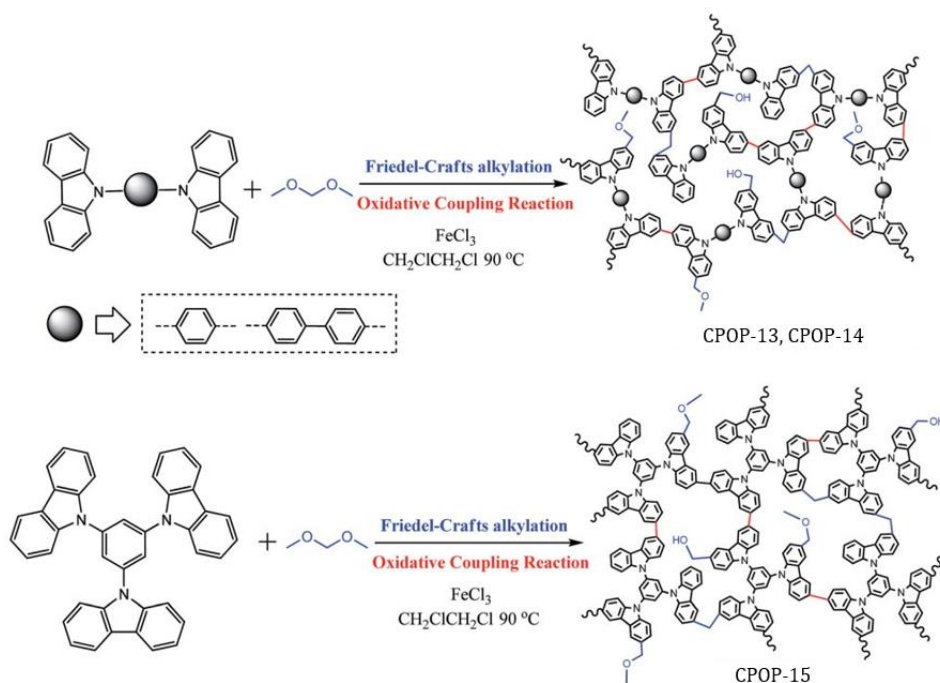


**Figure 1.4** Formation of kinetically controlled amorphous POPs

Based on the irreversibility, kinetically controlled product, nature of functional linkages and building units, amorphous POPs are further sub-classified into HCPs, CMPs, PAFs, and a very few of the CTFs etc [34].

#### 1.2.1.1 Hyper cross-linked polymers (HCPs)

HCPs do not appear to be new porous polymers. However, they have experienced remarkable expansion in recent years. HCP is mostly synthesised using Friedel-Crafts chemistry, which enables quick kinetics for establishing strong bonds, resulting in materials with strongly cross-linked networks and substantial porosity [35]. Han and coworkers reported a series of carbazole based HCPs (Figure 1.5) *via* one step oxidative coupling and Friedel-Crafts alkylation reactions in one pot [36]. Due to the adaptable and simple synthetic process, a wide variety of aromatic monomers can either add specialised functionalities that enhance the materials' high surface area and distinctive properties or form polymer networks with various pore shapes.



**Figure 1.5** Preparation of hyper cross-linked carbazole-based porous organic polymers *via* Friedel-Craft alkylation [36]

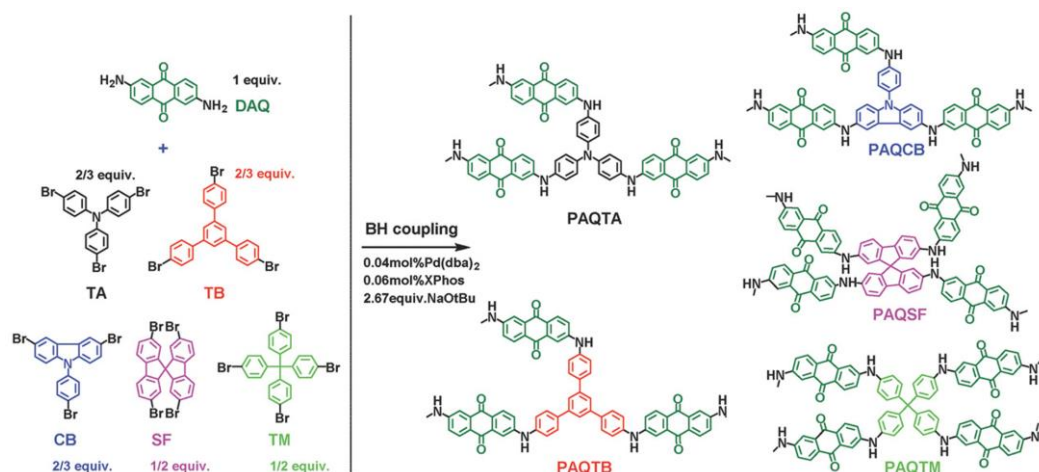
Additionally, conventional synthetic HCP processes use the least expensive reagents such as monomer, reaction medium, and catalyst, as well as straightforward-to-manage and -monitor reaction conditions, to produce high yield products that are microporous materials. HCPs are typically synthesized using one of the following three synthetic techniques: (i) direct one-step functional monomer polycondensation, (ii) post-crosslinking of polymer precursors, and (iii) knitting together of aromatic and rigid building blocks utilising an external crosslinker. The range of building blocks combined with improved synthetic techniques make HCPs useful testing grounds for novel organic porous materials with great promise to address complex energy storage, separation and catalysis [37-40]. In many cases metal incorporation on HCPs results excellent catalytic behaviour for many catalytic reactions. HCP with substantial porosity prepared from knitting *N*-heterocyclic carbene with benzene monomers adopted to incorporate palladium and copper afford outstanding catalytic performance in oxidative condensation reaction of indole, 1,3-cyclohexandione and phenylglyoxal monohydrate as well as three-component click, Ullmann C–N coupling, and Glaser coupling reactions [41,42].

HCPs are often prepared with massive amounts of polymerization catalyst, commonly Lewis acids such as  $\text{FeCl}_3$  or  $\text{AlCl}_3$ . Despite its low cost, this process

generates enormous waste since catalysts are seldom collected for reuse. Ongoing research is being conducted to improve the efficiency of hyper cross-linking.

### 1.2.1.2 Conjugated microporous polymers (CMPs)

CMPs are conjugated amorphous porous extended solids, first reported in 2007, usually formed from combining  $\pi$ -conjugated building units causing rigid porosity. Most common way of constructing CMPs are *via* C–C coupling reactions such as Suzuki-Miyaura, Sonogashira-Hagihara, Yamamoto, Heck coupling, etc and *via* other methods such as schiff-base condensations, Buchwald-Hartwig amination, alkyne metathesis, cyclotrimerization reaction, etc. Most building blocks have rigid components such as alkynes that cause the microporosity [43]. The presence of  $\pi$ -conjugation defines extra stability and opens for variety of functionality into the walls. It possesses similar properties of conductivity, mechanical rigidity, and insolubility. Thomas and coworker first reported the application of poly(*p*-phenylene) CMP in organic light-emitting-diode (OLED). The study opens the exploration of the optoelectronic properties of CMPs [44]. Indeed, the extended  $\pi$ -conjugation responds to the luminescent properties of CMPs as various chemicals' sensors by quenching of the fluorescence [30]. Dichtel and coworker reported several Sonogashira-Hagihara cross-coupling synthesized CMPs, with BET surface area up to  $259 \text{ m}^2\text{g}^{-1}$ , as sensor giving highest sensitivity for detection of 2,4,6-trinitrotoluene (TNT) at vapor state [45]. The inherent tuning property in CMP plays important role determining its applicability. In 2018, five CMPs had been synthesized using Buchwald-Hartwig cross coupling reactions (Figure 1.6) that possessed potent applicability as supercapacitors [46].



**Figure 1.6** Synthetic route for CMPs *via* Buchwald-Hartwig coupling [46]

Large numbers of reports already available furnishing variable applications of CMPs. However, their utility in industrial scale is limited due to the two prime challenges: (a) synthesis of required pre-functionalized monomer needed for targeted functionality and (b) the use of expensive metal/metal ion catalyst for C–C coupling reaction. The amorphous CTFs may be regarded as a subclass of CMPs since they are microporous and have extensive  $\pi$ -conjugation, despite the fact that they were synthesized separately and their formation chemistry was initially relatively different.

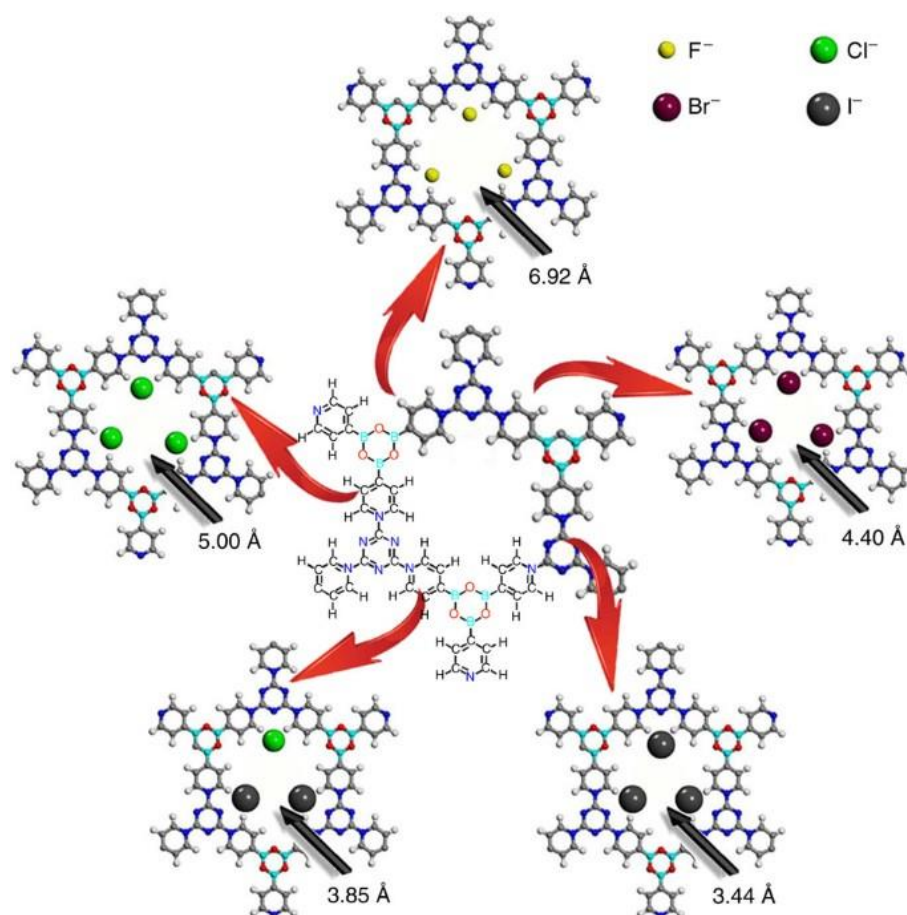
### 1.2.1.3 Porous aromatic frameworks (PAFs)

Regardless the similar coupling chemistry of formation of PAFs with CMPs, they do not possess extended  $\pi$ -conjugation [47]. These are 3D rigid frameworks with exceptionally high surface areas, constructed from C–C bond linked aromatic-based building units. The strong C–C bond in PAFs render them being tolerant of severe environments by harsh chemical treatments. Other terminology used to describe PAFs, based on the selection of building units, are porous polymer networks (PPNs) and element-organic frameworks (EOFs). EOFs are formed through organo-metallic coupling routes of silane-containing analogues [48,49].

The first long range PAF-1 was reported by Zhu and coworker in 2009 with diamond topology having record BET surface area of  $5640 \text{ m}^2\text{g}^{-1}$  [50]. The 3D array of Ni(0)-catalysed Yamamoto-type Ullmann coupled PAF-1 showed very high  $\text{CO}_2$  uptake of  $1.3 \text{ gg}^{-1}$  at 40 bar and 298 K. This new type of 3D dimensional rigid open-network structure became a new generation material that opens scope for several unusual, even peculiar properties.

Interestingly in the 3D arrangement, the central tetrahedral carbon can be substituted by other elements from group 13 or group 15 that lead to the formation of ionic PAFs [51]. Such modification enriches the applications of PAFs to include greenhouse gas storage and radioactive element capture [52]. Ionic PAFs of quaternary pyridinium centre with tuned pore size ranging 3.4 to 7 Å by adjusting the sterically hindered counter ions demonstrated as polymeric sieves that efficiently separate a five-component ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ) gas mixture (Figure 1.7) [53].





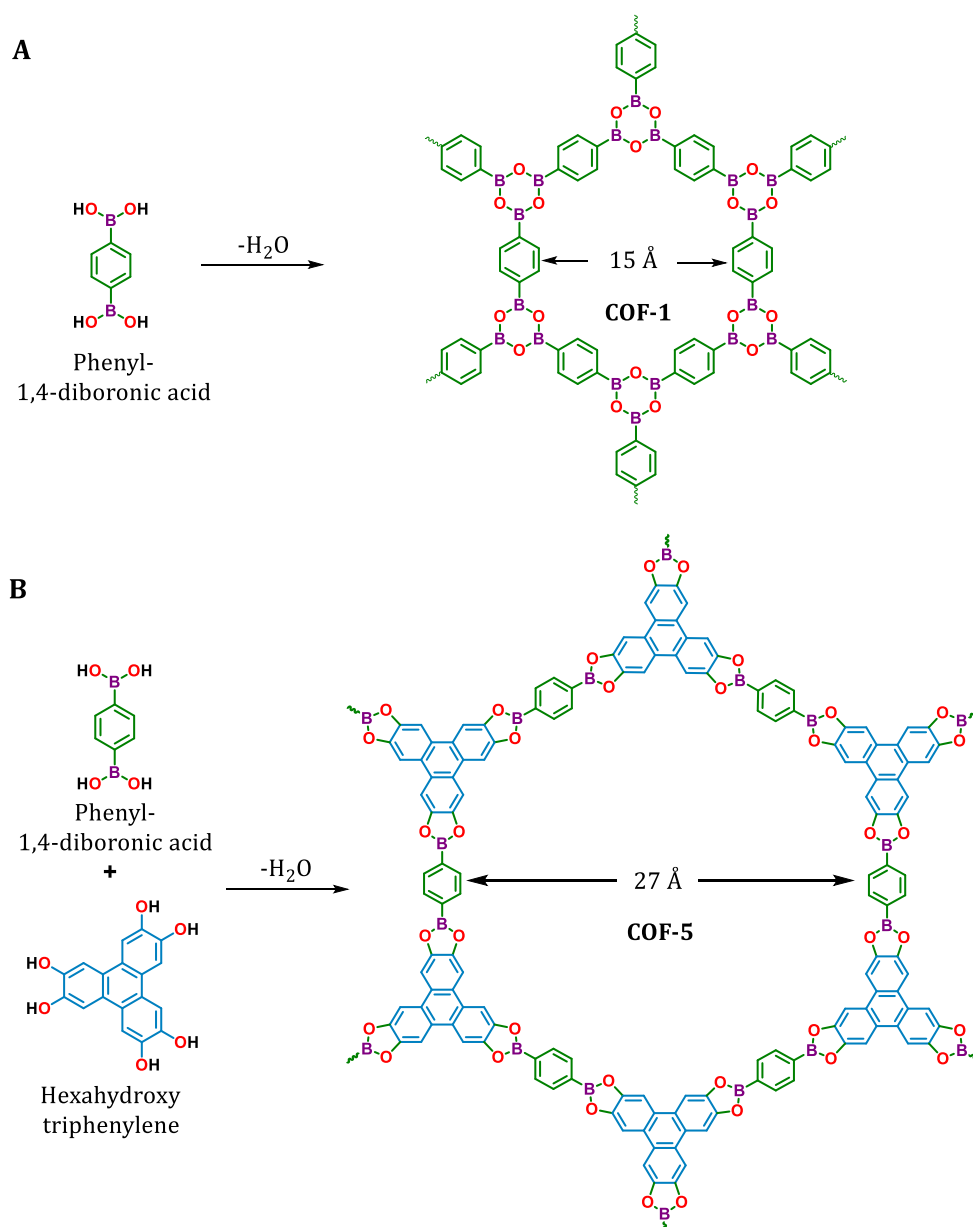
**Figure 1.7** Representation of anion template PAF with tuned pore sizes for gas mixture separation [53]

### 1.2.2 Crystalline POPs

Compared to amorphous POPs, synthesis of crystalline POPs is somewhat difficult to attain as controlling the multidimensional growth of extended network is a crucial step. Control over crystallization has always been a matter of concern. Leaving few of the boronate ester and imine linked POPs, almost all the other POPs exist as amorphous in nature. Hence imposing the conditions of reversibility in a reaction is an essential step to get crystalline POPs [54]. It prevents the degree of disorderness in the product and gives thermodynamically the most stable form. However, the conditions of reversibility can be achieved only at high temperature and pressure owing to the higher covalent bond energies ( $50\text{--}110\text{ kcal mol}^{-1}$ ) [10]. It imparts self-healing and error correction during the crystallization. Such materials experience structural regularity with uniform pore sizes. In general, crystalline POPs are referred to divide into covalent organic frameworks (COFs) and few of the covalent triazine frameworks (CTFs).

### 1.2.2.1 Covalent organic frameworks (COFs)

Covalent Organic Frameworks (COFs) are sub-class of crystalline POP. The synthesis of COF falls under dynamic covalent chemistry that direct such materials having well-defined pore structure.

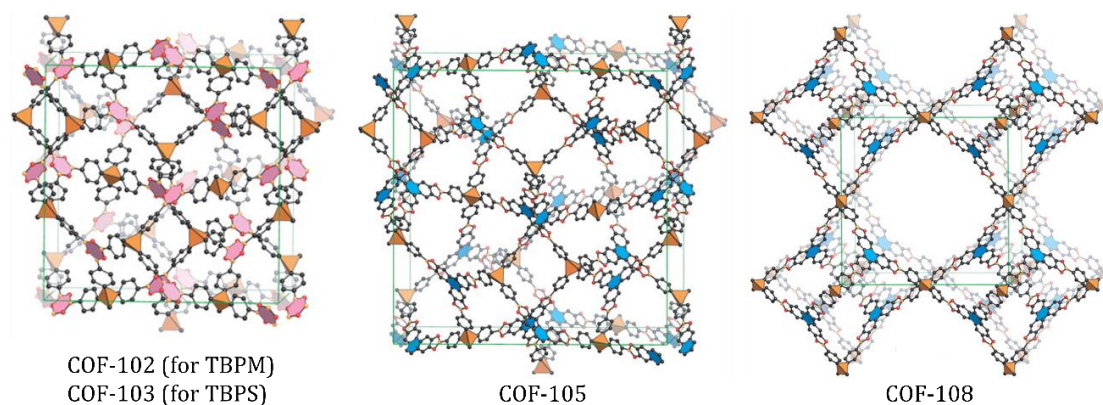


**Figure 1.8** Synthesis of first two COFs by (A) self-condensation of 1,4-diboronic acid (COF-1), and (B) with hexahydroxytriphenylene (COF-5) [3]

The first reported crystalline POPs that pave the way were the synthesis of two 2D COFs namely COF-1 and COF-5 [3]. The former was synthesized by self-condensation of phenyl-1,4-diboronic acid while the later was synthesized by hetero-condensation with hexahydroxytriphenylene respectively (Figure 1.8).

COFs are often called as “organic zeolites” [55]. The shape and size of the building units and the linkers regulate the pore size, volume and structural dimensions associated with the COF materials. However, lengthening the linkers may affect the crystallinity due to their propensity to extend outgrowth arms irregularly during the reticulation. The highly ordered extended networks of COFs usually provide better thermal/chemical stability and higher specific surface area compared to any other amorphous POPs.

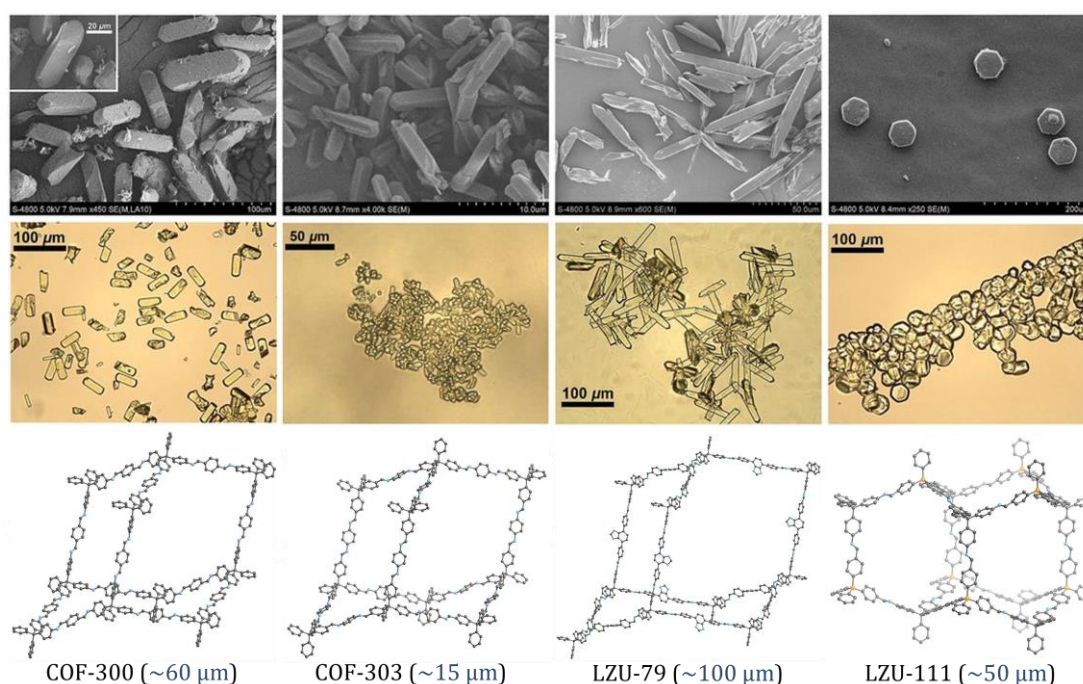
Following successful establishment of 2D COFs, four novel 3D COFs namely COF-102, COF-3, COF-105 and COF-108 have been synthesized for the first time in 2007 *via* boroxine and boronate ester linkages using Self-condensation and co-condensation of the tetrahedral *tetra*-(4-dihydroxyborylphenyl)methane (TBPM), *tetra*(4-dihydroxyborylphenyl)silane (TBPS) and planar hexahydroxytriphenylene (HHTP) [6]. Perhaps, getting monocrystalline structure was another drawback of such materials as these are insoluble polycrystalline or microcrystalline substances in most of the common organic or inorganic solvents. Thus, based on the PXRD pattern obtained during molecular modelling revealed the 3D extended network and their geometry of all the four reported COFs as shown in Figure 1.9.



**Figure 1.9** Crystalline structures of COF-102, COF-103, COF-105 and COF-108 based on molecular modelling. C (or Si), B and O atoms are represented as grey, orange, and red spheres, respectively. Hydrogen atoms are omitted for clarity [6]

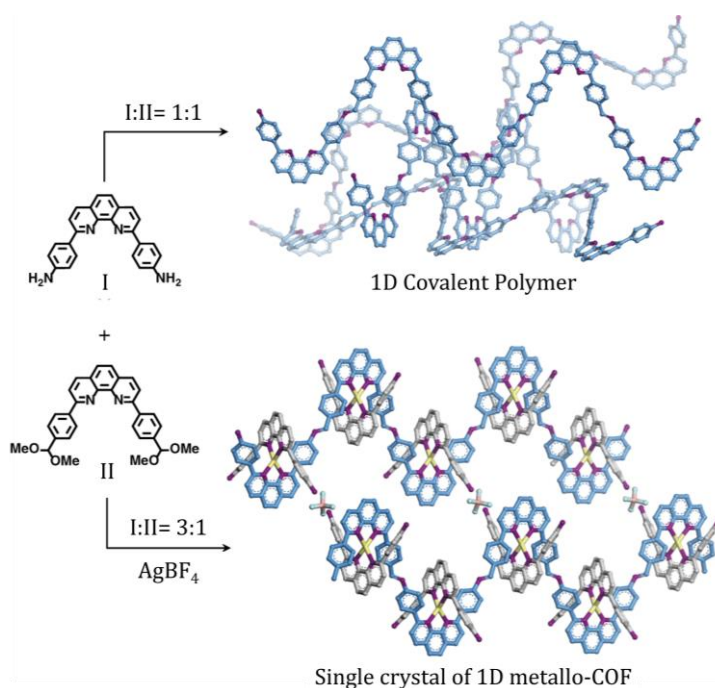
All the synthesized crystalline 3D structures possess high thermal stability of 400-500 °C and extraordinarily low densities: COF-102 ( $0.41 \text{ g cm}^{-3}$ ), COF-103 ( $0.38 \text{ g cm}^{-3}$ ), COF-105 ( $0.18 \text{ g cm}^{-3}$ ), and COF-108 ( $0.17 \text{ g cm}^{-3}$ ). The high surface area and low density together naturally impart their exceptional porosity towards gas sorption/separation or energy storage, etc.

Revisiting the reported synthetic procedure, another 3D monocrystalline COF in the form of membrane has been reported by growing the crystals supported over surface functionalized porous ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate [55]. Later, reversible connectivity protocol was employed on reported imine-based COFs for error correction resulting size controlled monocrystalline COFs [56]. Here addition of excess aniline in the reaction solution behaves as a modulator and inhibit the nucleation. As a result, higher concentration of aniline enhances the reversibility of imine bond formation for error corrections, and ultimately, crystallization. Notably, adjusting the amount of aniline control crystal size of various imine based COF-300, COF-303, LZU-79, and LZU-111 (Figure 1.10).



**Figure 1.10** SEM, microscopic images, and crystal structures of COF-300, COF-303, LZU-79 and LZU-111. Hydrogen atoms are omitted in the crystal structure for clarity. Size of the crystallites are represented in blue [56]

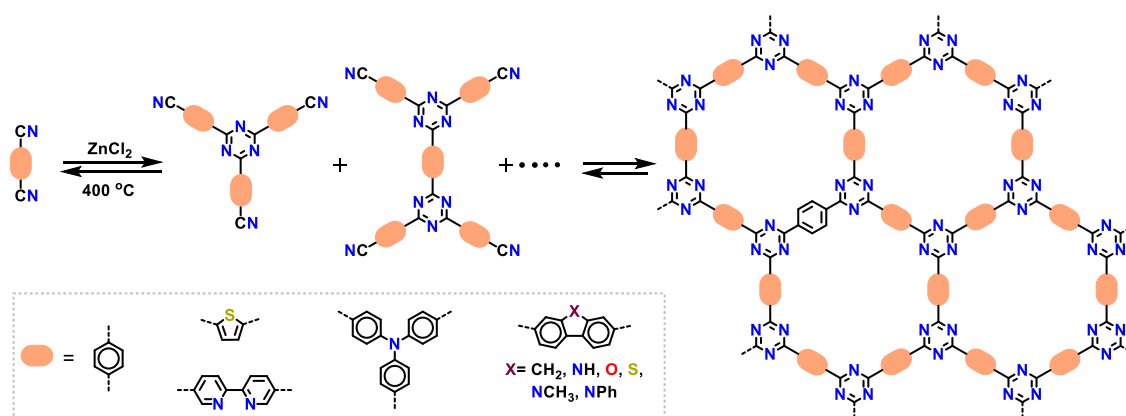
Even though all the crystalline topological POPs reside in 2D and 3D array, very recently crystalline 1D POPs has also been designed, synthesized and are emerged as efficient candidate for various applications such as sensing, fluorescence enhancer, conduction, etc [57,58]. In fact, 1D infinite covalent polymer has also been transformed to 1D monocrystalline metallo-COF combining labile metal coordination and dynamic covalent chemistry (Figure 1.11) [59].



**Figure 1.11** Strategy of synthesizing single-crystalline 1D metallo-COF [59]

### 1.2.2.2 Covalent triazine frameworks (CTFs)

These are another class of crystalline POPs having triazine moiety as their basic building unit in the framework. In particular, the strong C=N endow CTFs with high stability and interesting heteroatom effect that bring great value for many practical applications such as separation and storage, energy storage, photocatalysis, heterogeneous catalysis, etc. Thomas and coworkers first reported the trimerization of 1,4-dicyanobenzene under ionothermal method where molten  $\text{ZnCl}_2$  salt was used as solvent medium at  $400\text{ }^\circ\text{C}$  affording 2D sheet like structure of CTF-1 with BET surface area of  $791\text{ m}^2\text{ g}^{-1}$  (Figure 1.12) [60].



**Figure 1.12** Schematic representation of CTF synthesis under ionothermal synthesis with molten  $\text{ZnCl}_2$  having crystalline columnar array

Being a medium, molten  $\text{ZnCl}_2$  also acts as good catalyst for the trimerization reaction which enables the reversible reaction easily. Unfortunately, this protocol was found to be size and symmetry specific along with planar nitrile derivatives results amorphous POPs [61]. In addition, the optimal temperature and the  $\text{ZnCl}_2$  stoichiometry plays a crucial role in determining the crystallinity of CTFs [62]. Complete removal of  $\text{ZnCl}_2$  after completion of the reaction is another issue of the protocol. The necessity of the high temperature destroys the structure and cause partial carbonization. Therefore, modified synthetic methodology at comparatively lower temperature has been developed later to restrict the carbonization during the CTFs synthesis. These modifications include high temperature  $\text{P}_2\text{O}_5$ -catalysed method by Baek and coworkers, amidine based polycondensation methods by Tan and coworkers, superacid catalysed method by Cooper and coworkers, Friedel-Crafts reaction method by Ahn's and Borchardt's group, etc [63-68]. However, controlling the crystallinity with such modifications was still not generalized as most of them produces amorphous CTFs. Therefore, having enormous potential for various applications, designing proper synthetic protocol for crystalline CTFs synthesis is needful to promote the development of the CTF field.

### **1.3 Synthesis of POPs**

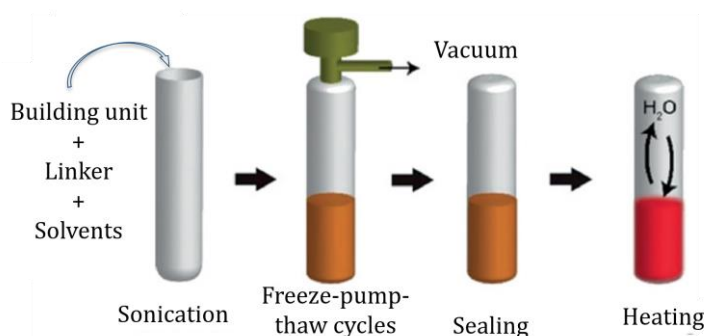
In the past decade and half, POPs have been aroused as great interest due to their pre-set architecture of shape, pore size, and network type by adjusting the ratio, size, and symmetry of the structural units [69]. Since the advent of the POPs, the synthesis has been dominated by the solvothermal method for a long time. But for better crystallinity, the reactions were carried out at very low concentration. Meanwhile the abundant solvent is difficult to recycle. Therefore, efforts in finding cost effective and green synthetic methods have attracted extensive attention. A lot of literatures available claiming different synthetic routes for the synthesis of POPs. Meanwhile based on reaction medium, synthetic methods can be classified as follows.

#### **1.3.1 Solvent-based methods**

##### **1.3.1.1 Solvothermal approach**

Traditional solvothermal process is implemented in sealed degassed tubes with elevated temperature and consists of organic solvents, such as dioxane, mesitylene,

*n*-BuOH, etc. As per the literature report, 150 mTorr is the optimum pressure for a vessel of 10 cm<sup>3</sup> (Figure 1.13) [3]. This high temperature reaction usually takes days to occur. The high temperature and pressure are the essential needs of solvothermal process to have precise control over shape, size, and crystallinity behaviour. Unfortunately, apart from few boroxine, boronate ester and imine linked POPs that undergo condensation reaction, others occur as powdery material.



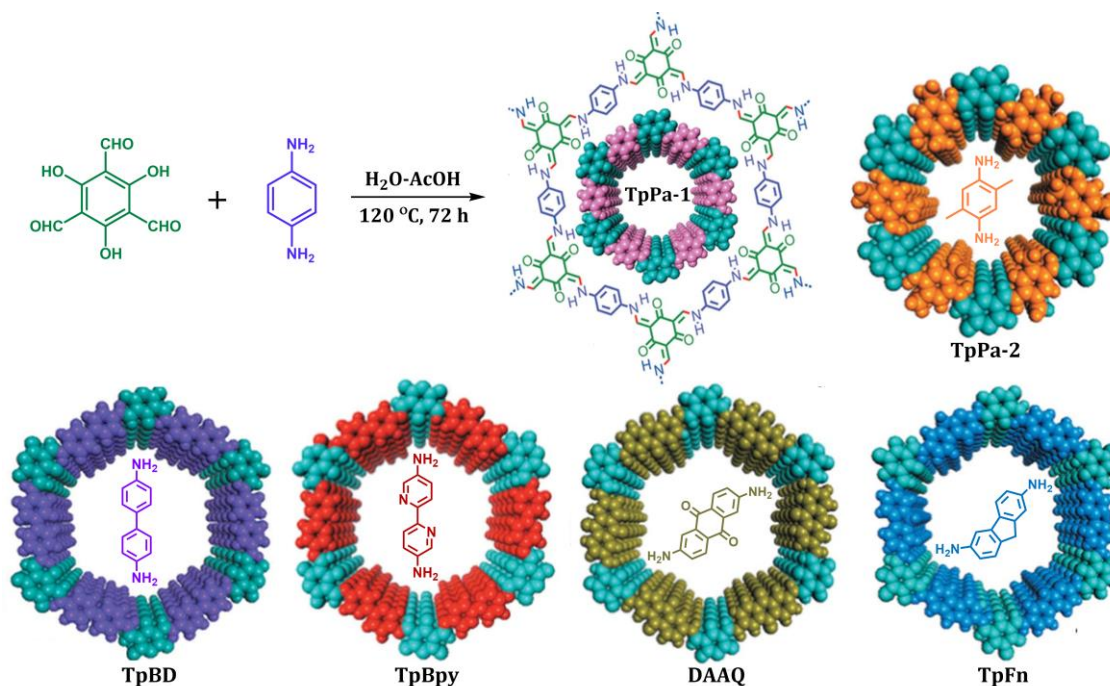
**Figure 1.13** Schematic diagram of traditional solvothermal method for POPs synthesis

In context, Dichtel and coworker developed a single-layered graphene sheet supported method under solid-liquid interfaces solvothermal process to synthesize better crystalline 2D COF-5 films in 2011 demonstrated by synchrotron X-ray diffraction (XRD) pattern analysis and scanning electron microscope (SEM) analysis [70]. Some other POPs have also been synthesized using a supporting layer and in addition exhibits some unique properties, especially strong absorption ability of visible light. The strong light absorption capacity raises the applications of POPs to optoelectronic devices.

### 1.3.1.2 Hydrothermal approach

Water is considered as universal green solvent for enormous organic reaction synthesis. However, miscibility principle does not prefer water as solvent in organic synthesis due to polarity difference. Reports suggest that breaking the sufficient hydrogen bond at higher temperature increases the non-polarity nature of water [71]. Notably, Banerjee and coworkers synthesized six keto-enamine-based POPs from different aromatic amines using water as medium with catalytic amount of acetic acid at 120 °C for 72 days (Figure 1.14). The acid-water mixture promotes the hydrogen bonding environment around the amine and hence provide better crystallinity in POPs. However lower solubility of the carbonyl compounds in

aqueous media lowers the surface area than that of the traditional solvothermal process [72].



**Figure 1.14** Hydrothermal synthesis of six different keto-enamine-based POPs from 1,3,5-triformylphloroglucinol (TFP) [72]

Fang and coworker first demonstrated the industrial scale azine-linked POP (HCOF-1) under hydrothermal method without any catalyst but with excellent productivity up to 97%. In fact, the large-scale synthesis of as prepared POP has better surface area of  $617\text{ m}^2\text{g}^{-1}$  than that found in traditional method and breaks down the bottleneck of the solvothermal method [73,74]. So far, hydrothermally generated linkers are generally limited to azines, imides and amides but more types will certainly appear in the future [71].

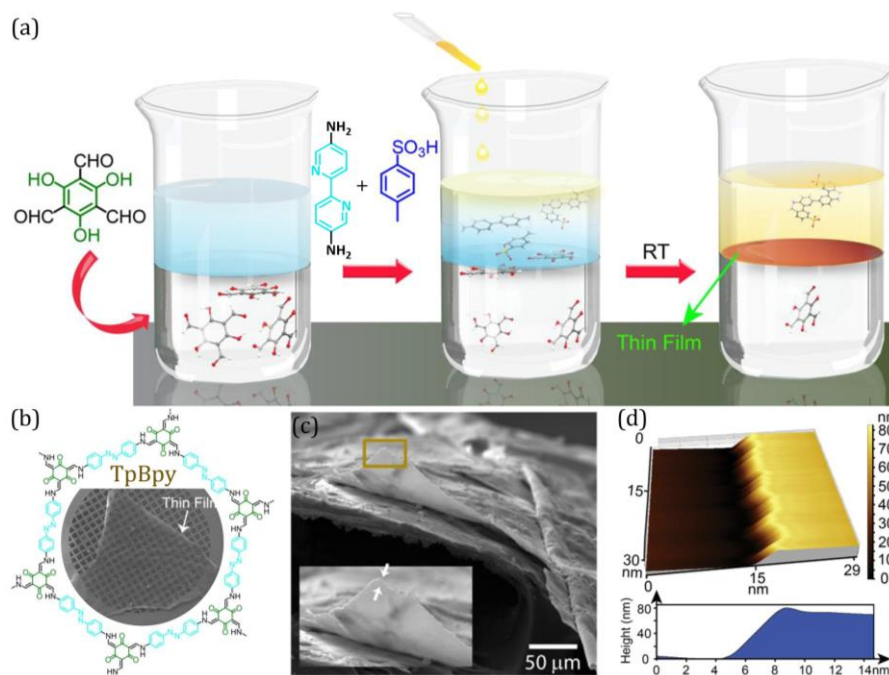
### 1.3.1.3 Microwave approach

This particular methodology has been developed over solvothermal/hydrothermal for the rapid preparation of POPs. A mixture of monomers in a suitable solvent is vacuum sealed in a microwave tube and heated for 60 min at a designated temperature. The product obtained were found to have better porosity than other methods. Unfortunately, this approach has a very limited scope selectivity. Until now, only six POPs have been reported; two of them are boronate ester linked, one imine linked and three are CTFs [75,76].



### 1.3.1.4 Interfacial approach

Interfacial strategy is a novel and efficient method for fabricating thickness-controlled POP thin films [77]. Initiation of this strategy was led by the synthesis of four crystalline POPs, namely TpBpy, Tp-Azo, Tp-Ttba, and Tp-Tta, using TFP as counterpart of different aromatic amines (Figure 1.15).



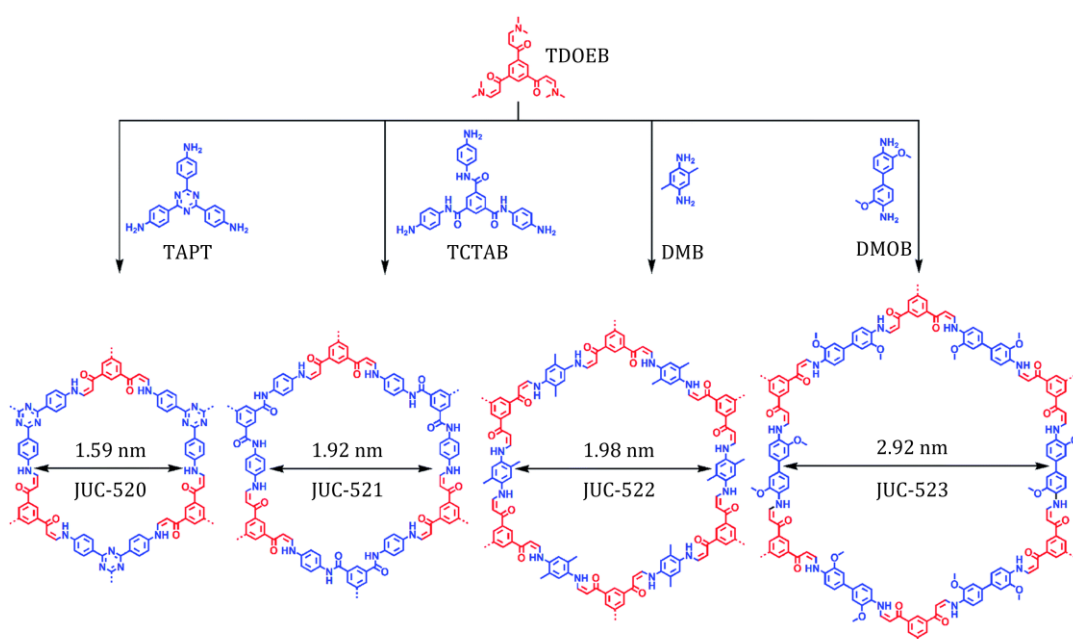
**Figure 1.15** (a) Schematic representation for the liquid-liquid interfacial preparation of TpBpy thin film. (b) Chemical structure of TpBpy and SEM image on TEM grid (inset). (c) Thin film SEM image of TpBpy. (d) AFM image of the thin film and height profile [77]

TFP was first dissolved in dichloromethane (DCM) followed by the corresponding dissolved amine salts of *p*-toluenesulfonic acid (PTSA) in aqueous-acetonitrile mixture solution paved on the DCM layer. Slow condensation at the interface of the solvent afforded subjected thin films in the thickness range of 45-90 nm. Recently, Suzuki coupling reaction has been performed to synthesize two C-C linked crystalline POPs at toluene-water interface under inert condition. At low temperature ( $\sim 2$  °C), the Pd source added on the top of aqueous solution of  $K_2CO_3$  afforded stable POPs after one month [78].

### 1.3.1.5 Ambient temperature approach

The synthesis of POPs at room temperature is indeed attractive. Several room temperature synthesized POPs have been reported till now. For example, mixing

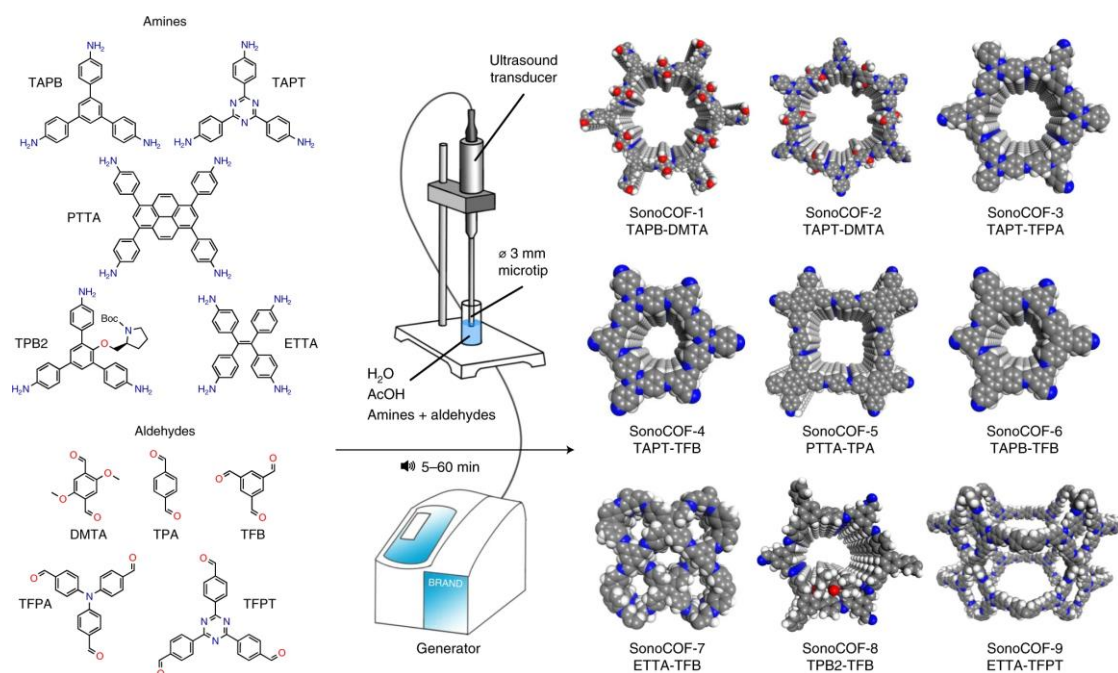
1,3,5-tris(4-aminophenyl)benzene (TAPB) and benzene tricarbaldehyde (BTCA) monomers with acetic acid forms yellow gels (RT-COF-1) in *m*-cresol or DMSO which transforms to crystalline POP when washed with methanol and THF [79]. This strategy, in fact, offers a way to make POPs processable. The high temperature and long reaction time necessity for the synthesis of TAPB-PDA is replaceable with Sc(OTf)<sub>3</sub> catalysed room temperature condensation of the monomers in the 4:1 (v/v) mixtures of 1,4-dioxane and mesitylene only in 10 min [80]. On the other hand, aqueous phase synthesis of  $\beta$ -ketoenamine linked POPs are known with 1,3,5-tris(3-dimethylamino-1-oxoprop-2-en-yl)benzene (TDOEB) as monomeric precursor at room temperature without using any catalytic pathway (Figure 1.16) [73].



**Figure 1.16** Aqueous phase condensation of TDOEB with different amines to give microporous JUC-520, JUC-521, JUC-522 or mesoporous JUC-523 [73]

On a contrary note, special care has to be taken while dealing with carbonyl chloride as a POP precursor. In the synthesis of amide linked POPs from carbonyl chloride and amines, it is mandatory to provide an inert atmosphere to avoid the residual water or moisture as it can directly convert highly reactive carbonyl site into inactive carboxylic acid [81-83].

Ultrasonication is another recent modification in the ambient temperature synthesis of POPs. Under the aqueous-acetic acid media, several imine linked rapid (<60 min) synthesized crystalline POPs from their precursors have been reported very recently using sonochemistry at room temperature (Figure 1.17).



**Figure 1.17** Sonochemical synthesis of crystalline POPs [84]

The overall materials' property has been found comparable to or better than those in traditional solvothermal routes. This ultrasonication strategy even works in food-grade vinegar [84].

### 1.3.2 Ionothermal method

In this synthetic strategy, the POP precursors are, in general, mixed with metal salts that usually behave both as catalyst and solvent media at high temperature in the form of molten salts. CTFs are the first examples of obtained material under ionothermal synthesis where molten  $\text{ZnCl}_2$  had been used as the trimerization catalyst as well as solvent [60]. However, this process of synthesis suffers for appreciation at many stages because of its harsh reaction condition, limited scope, and difficulties in purification.

In 2018, ionic liquid was established as a competing agent for molten salts in ionothermal synthesis. A series of both 2D and 3D crystalline POPs have been reported using ionic liquids at ambient temperature and pressure [85,86]. In fact, ionic liquid assisted synthesis offers green an extremely time efficient strategy.

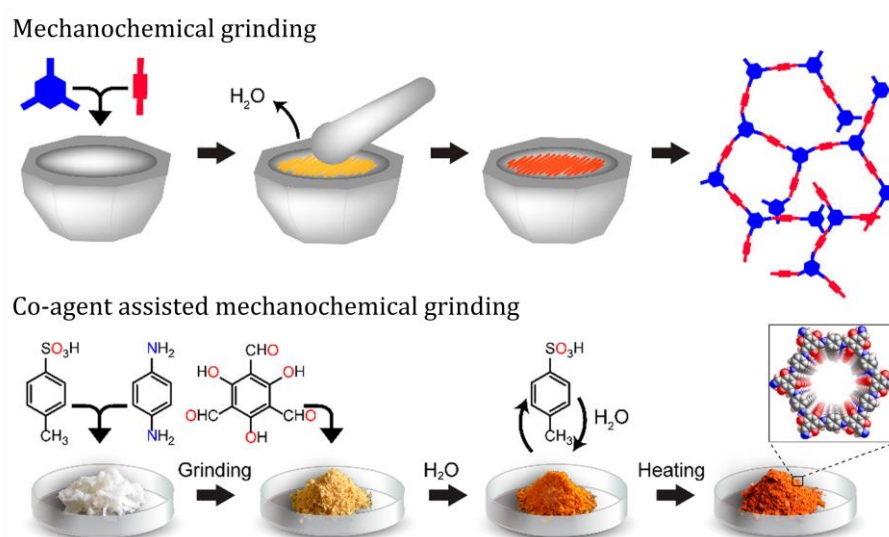
The major disadvantage associated with the use of ionic liquid is its occupancy inside the POPs. Although its presence offers good affinity towards  $\text{CO}_2$  selectively, but the porous channel blockage may interrupt its applications in other fields. But

interestingly at the same time inclusion of the ionic liquid act as structure directing agents during nucleation of the POP by reducing the structural degrees of freedom of adducts and results preorganized network form [87].

### 1.3.3 Solvent-free method

#### 1.3.3.1 Mechanochemical approach

Mechanochemical route for the synthesis of POPs was first introduced in 2013 and it possessed mild conditions, easy operation and environmental friendliness [88]. Poor crystalline imine-based POP was first detected when the precursors were ground at room temperature without the addition of any promoter. The formation of the POP was clearly visible from the changes in the colour within 40 min. Soon found that the co-agent assisted grinding enhanced the materials' property by many folds [89].



**Figure 1.18** Mechanochemical/co-agent assisted grinding for the room temperature synthesis of imine based POP

Specifically, PTSA is mixed with the amine precursor for 5-10 min followed by the addition of aldehyde precursor and a small amount of water with continuous grinding of another 10-15 min. The mixture is then subjected to heat at high temperature ( $\sim 170$  °C) for 60 s that affords high surface area POPs (Figure 1.18). PTSA and water together regulates the reaction reversibility by inducing a salt-mediated crystallization approach. Besides the advantages outcomes of mechanochemical synthesis, this protocol has notable additional merit of reacting highly polar POP precursors those cannot be synthesized in traditional solvothermal

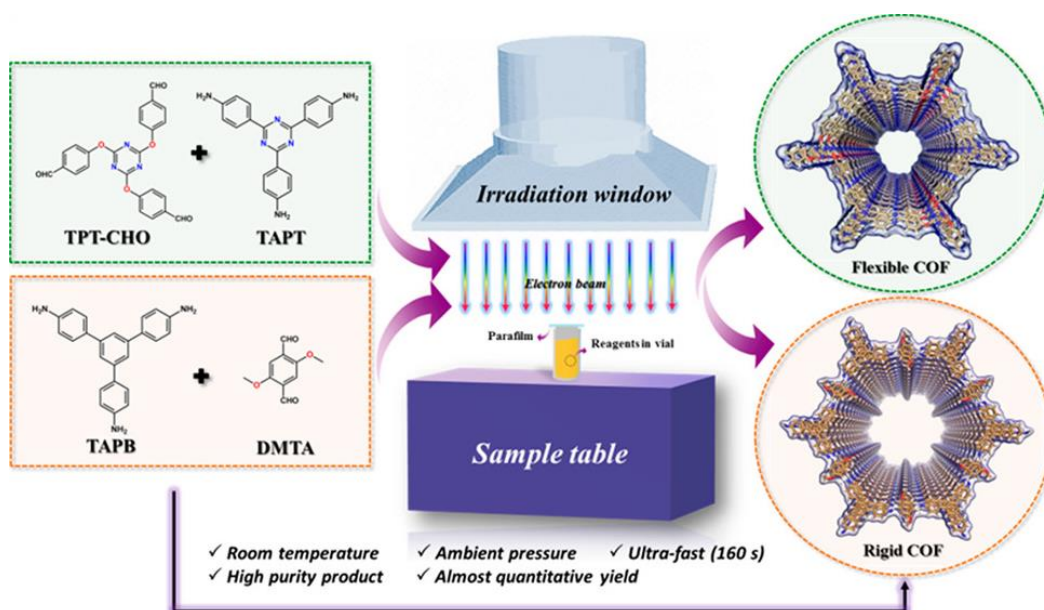
strategy solubility issues. Reported sulfonated POPs namely NUS-9 and NUS-10 synthesized by Zhao and coworker is the example of one of such kind [90]. This work demonstrated the indispensable role of mechanochemical synthesis.

### **1.3.3.2 Vapour-assisted approach**

Oligomer formation in some POPs is another drawback in solid phase mechanochemical grinding. Vapour-assisted synthesis method provides additional morphology control in synthesizing crystalline POPs. In a typical synthesis, a mixture of monomers was ground for 1 h and put in a glass beaker placed inside a closed container that had already contained another small beaker with solvent mixture (ethanol : mesitylene : 6 M AcOH = 5 : 5 : 1). The closed container was then heated to 120 °C for 48 h to get uniform nanofibrous morphology of POPs [91]. Although organic solvent was used in the described process, but the amount is more than 50 folds less than that of traditional solvothermal method. Synthesized thin films under vapour assisted protocol show great affinity towards conductance. The surface area obtained under this approach is slightly lower than that of the solvothermal method, but it greatly reduces the use of organic solvents. Indeed, the POPs thin film obtained have the thickness ranging from 300 nm to 7.5 mm. Furthermore, the method gained great significance for fragile building blocks, those usually not appropriate for solvothermal synthesis [92].

### **1.3.3.3 Electron beam irradiation or direct heating approach**

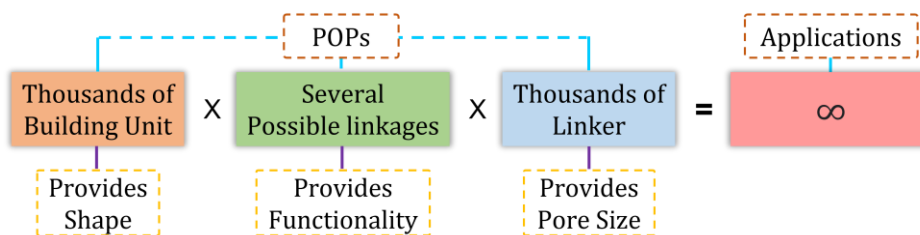
In traditional solvent based thermal treatment, a large part of the energy is consumed by thermal motion of the reagents and solvents. To overcome this inefficiency, Wang and coworker modified an energy-saving solvent free synthetic strategy where the POPs precursors are exposed to direct irradiation by electron beam that afforded crystalline POP at room temperature (Figure 1.19) [93]. A small amount of a mixed solvent of dichlorobenzene, butanol and aqueous acetic acid has been used as medium and was irradiated by an electron beam for 160 s; a yellow product powders were obtained. The as-synthesized POPs exhibited excellent stability, and a large BET surface area ( $738 \text{ m}^2 \text{ g}^{-1}$ ). As a result, its energy consumption is decreased by 2 orders of magnitude. This is a universal method for different POPs including new ones that cannot be synthesized by traditional method.



**Figure 1.19** Rapid synthesis of COFs by electron beam irradiation [93]

#### 1.4 Applications of POPs

Although there is no hard-and-fast rule to differ the monomer molecules as the building unit and the linker, but a conventional way is to consider the more rigid/bigger/highly symmetric one as building unit that usually responsible for determining the shape of the extended network. While the less symmetric portion can be considered as the linker molecule which provides the direction of the extended network and determines the shape/size of the pores or channels. Opulent with varied functionalities, applications of POPs skyrocketed from laboratory to industrial scale since the beginning (Figure 1.20).



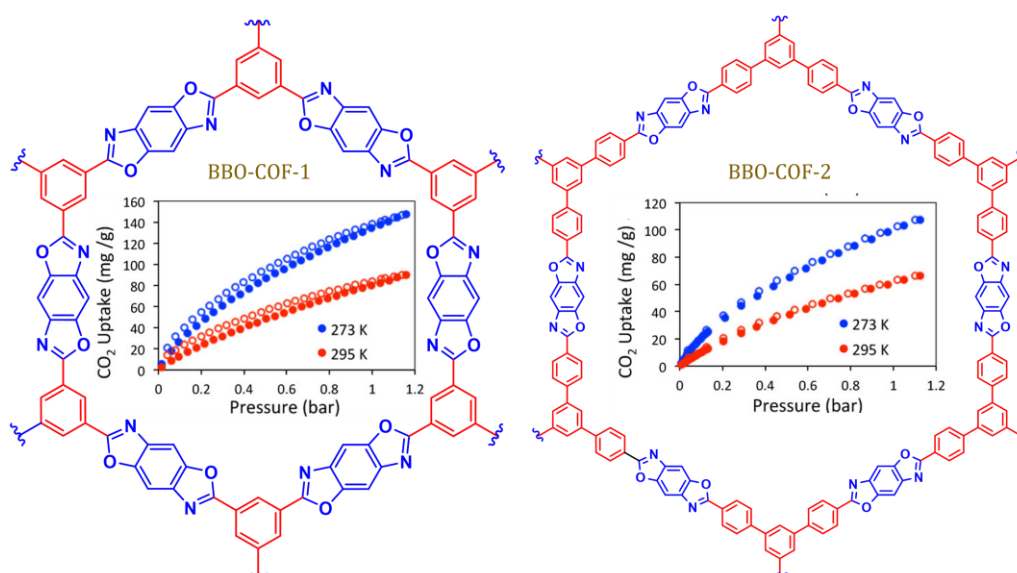
**Figure 1.20** Schematic representation of the practical importance of POPs

As previously mentioned, the high thermal and chemical stability, varied functionality, tunable pores/surface area of POPs exhibit efficient applications in starting from gas adsorption/separation to medicinal sciences. Amongst these broad utilities, a few remarkable bids relevant to the objectives the thesis and future scope have been quoted below. Perhaps there lies enormous scope to design and synthesis

of such materials and applications in the form of academic and industrial development.

### 1.4.1 Gas adsorption and separation

Limited existence of fossil fuel in the earth crust is forcing us to look for an alternate source of energy. Also burning of fossil fuel exerts a large amount of  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$  etc. to the atmosphere. Increasing level of  $CO_2$  which is the predominant component of flue gas is becoming a major threat to the universe and is responsible for global warming. In this context,  $CO_2$  capture, and storage is of vital necessity to mitigate the problem of global warming. On the contrary,  $H_2$  and  $CH_4$  have been being used as a source of greener energy. In few years, world will be in need of enormous amount of greener sources for energy once the fossil fuel will no more exist. Intriguing fact about POP materials in this context is that these can be utilized as a potent adsorbent over other known porous materials. Extremely good for suitably capturing and storing of  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $N_2$  etc. gases exerted by fossil fuel on burning or by any other means as the shape, size, porosity, functionalities, etc. of these materials can be tailor made [52-54]. Psaras L. McGrier and coworker have recently in 2016 reported cyanide catalysed two benzobisoxazole (BBO) linked COFs (BBO-COF 1 and BBO-COF 2) (Figure 1.21) that shows a good  $CO_2$  uptake of approximately 150.6 mg/g and 112.3 mg/g at 273 K while 91.9 mg/g and 69.9 mg/g at 295 K [94].



**Figure 1.21** Schematic representation of benzobisoxazole (BBO) linked COFs synthesis that has been used for  $CO_2$  uptake [94]

POP materials containing boroxine ring or boronate ester and imine linkage are good at storing high amount of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. Depending on the channel wall functionalities and surface area, storage capacity of gases varies from POPs to POPs. It is not necessary for these types of porous materials to limit its applications on storage ability only to the above-mentioned gases. Depending on the nature of the interaction between the host and the guest molecule, it is expected to capture and separate any types of gases as one wants. Apart from its ability to adsorb and separate gas molecules, POPs with continuous  $\pi$ -conjugation in it also exhibits excellent candidature for the selective adsorption of hydrocarbons. Shengqian Ma and his colleagues for the first time reported the adsorption of hydrocarbons by POP introducing  $\pi$ -complexation to POP [95]. The Ag(I) functionalized porous aromatic framework (PAF) by formation  $\pi$ -complexation shows remarkable selectivity towards adsorption of ethylene over ethane. To surprise, this PAF reveals high ethylene selectivity thereby surpassing the so far reported zeolites, MOFs and POPs.

#### 1.4.2 Energy storage/conversion and conduction

A severe energy crisis and environmental problems have resulted from aggressive fossil fuel use, and the threat of global warming is growing as a result of excessive greenhouse gas emissions. As a result, there is a huge need for clean and sustainable energy conversion systems and energy storage technologies to help with the dramatically rising global energy needs and environmental problems. With their large surface area, porosity, and highly conjugated modifiable structures, crystalline POPs or COFs have demonstrated promising potential in the field of energy applications including supercapacitors, rechargeable batteries, etc. The  $\pi$ - $\pi$  stacking of 2D sheets create 3D porous channels with low density that provides efficient electron and ion transport. Dichtel and coworkers were the first to apply crystalline POPs to supercapacitors and have since led the trend of such materials for supercapacitors [96]. The Schiff base reaction between 1,3,5-triformylphloroglucinol and 2,6-diaminoanthraquinone yielded anthraquinone-based-ketoenamine crystalline POP (DAAQ-TFP COF) with a specific capacitance of 409 Fg<sup>-1</sup> after 5000 cycles. Tang and coworkers demonstrated a pyridine functionalized TaPa-Py COF that exhibits pyridine group redox activity with a specific capacitance value of 209 Fg<sup>-1</sup> and high capacitance retention of 92% after 6000 cycles [97]. Recently, ultralight

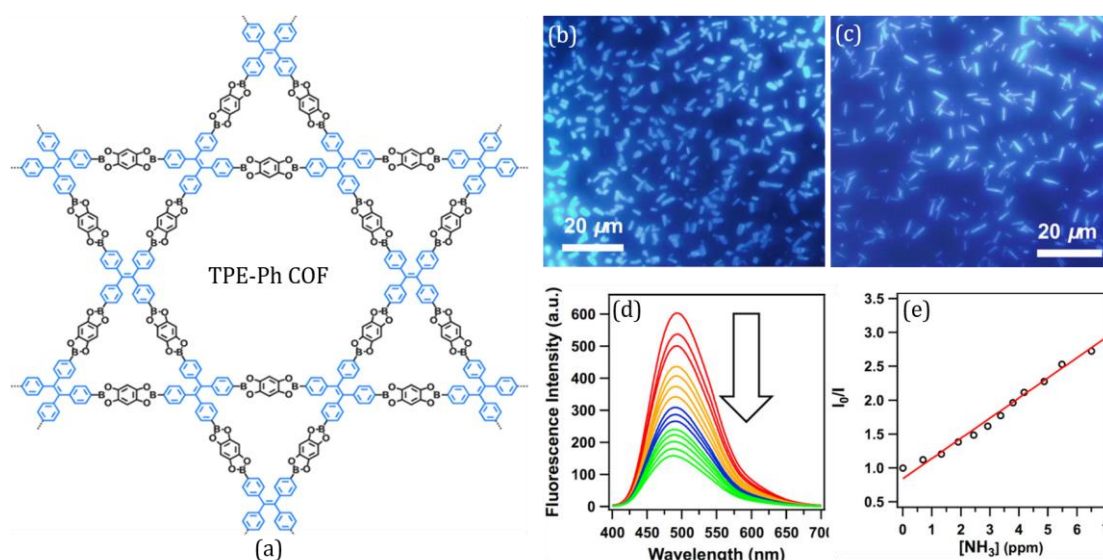


COF/rGO aerogels with hierarchical porosity were reported where the COF was synthesized in the presence of graphene oxide using hydrothermal treatment. The specific capacitance found for the synthesized aerogel delivered high capacitance of  $269 \text{ Fg}^{-1}$  at  $0.5 \text{ Ag}^{-1}$  and enhanced cycling stability higher than most of the reported POP-based electrodes [98].

POPs have recently been demonstrated as potential candidate for the use in the field of proton conduction by incorporating amphoteric molecules into the cavity of polymers [99]. Banerjee and coworkers reported the proton conducting POP for the first time by immobilising the phosphoric acid group in the azo-linked crystalline material to display moderate conduction behaviour [99]. Sulfonic acid-incorporated POP recently shown conductivity ( $1.59 \times 10^{-1} \text{ S cm}^{-1}$ ) that was even greater than Nafion ( $10^{-1} \text{ S cm}^{-1}$ ), a typical polymer electrolyte for proton conduction in fuel cells [100].

### 1.4.3 Sensors

These structures' exceptional quality amplifies the generated luminescence signal within their conjugated framework, increasing the luminescence intensity [98]. Additionally, a series of polymers with varied functional groups have been explored as probes for different anions, cations, and small organic molecules detection due to the unique properties of POP-based fluorescence sensors, such as their high quantum efficiency, signal amplification effect, quick response time, and long luminescent lifetime [101]. The columnar  $\pi$ - $\pi$  stacking array in 2D crystalline POPs prevent them from entering a photoexcited state, effectively freezing their emission behaviour. It is owing to the aggregation-caused quenching (ACQ) mechanism, which exists in such materials and checks their luminous nature despite the presence of luminescent units [102]. Jiang and coworkers used the aggregation-induced-emission (AIE) process to create a solvothermally synthesised crystalline 2D POP (TPE-PH COF) with dual pore size of both micro- and meso- that exhibits the strongest emission observed to date (Figure 1.22) [102]. AIE is a phenomenon where the scaffolds that make up the chromophores are prevented from freely rotating, causing them to become emissive when they are aggregated. The Lewis acid-base interaction mechanism has been used to quickly detect ammonia down to sub ppb level using TPE-Ph COF.

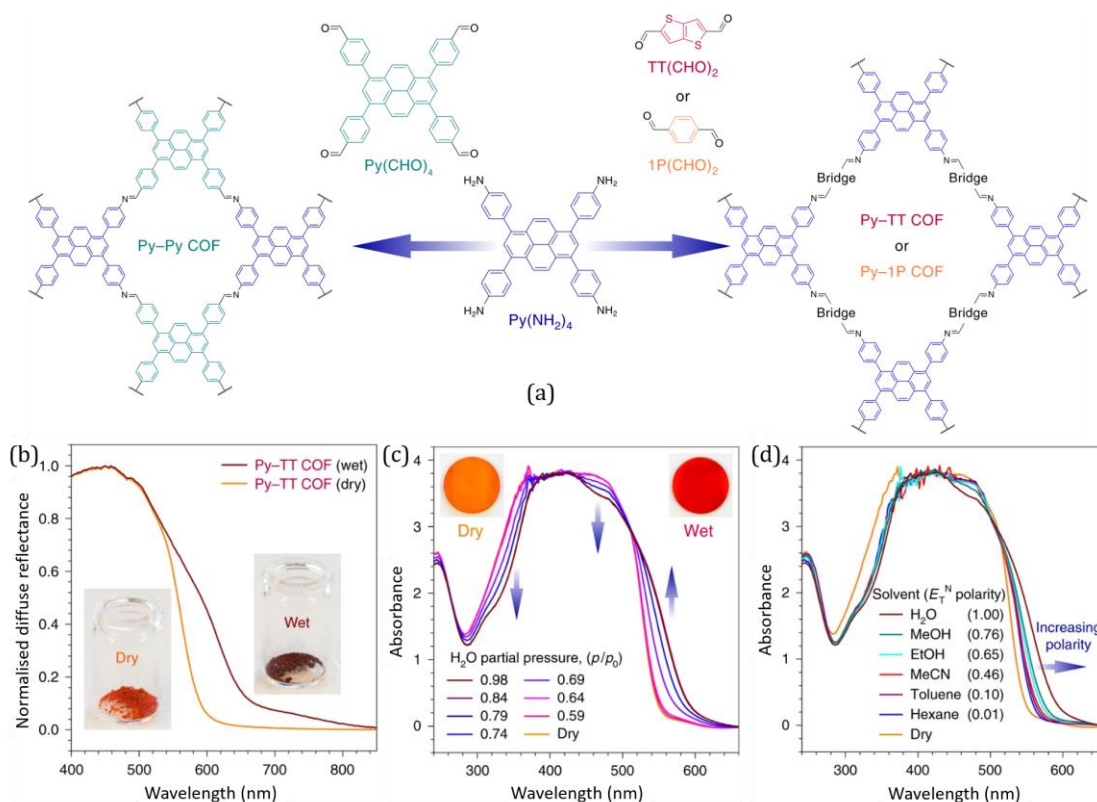


**Figure 1.22** (a) Schematic representation of TPE-Ph COF having dual pore frame. Fluorescence microscopy images of TPE-Ph COF samples prepared at different reaction times of (b) 3 days, and (c) 10 days. (d) Fluorescence spectral change of the TPE-Ph COF upon addition of ammonia. (e) Stern-Volmer plot of the fluorescence quenching by ammonia [102]

Auras and coworkers demonstrated two pyrene-based crystalline 2D POPs (Py-Py COF and Py-TT COF) can function as solid-state supramolecular solvatochromic sensors, changing colour when exposed to humidity or solvent vapours depending on vapour concentration and solvent polarity (Figure 1.23). They show a fast humidity sensor that is fully reversible and stable over at least 4000 cycles [103].

Another report describes a dynamic 3D crystalline POP (dynaCOF-330) made of an environmentally sensitive fluorophore that can undergo concerted and adaptive structural transitions upon varied volatile organic compounds (VOCs) quickly under humid conditions. It is reliable even in non-polar hydrocarbon gas with enhancing host-guest interactions based on polarity and size/shape. The findings pave the way for molecular-specific multiplex fluorescence sensing of various VOCs [104]. These also broaden the range of possible applications for such materials in optoelectronics.

The use of POPs chemistry in the detection of heavy metals, which are typically extremely toxic and are also thought to be environmental pollutants, is another success. By interacting with the thioether groups, which are an effective mercury receptor, a fluorescent COF with a thioether base called COF-LZU8 is able to detect and remove  $\text{Hg}^{2+}$  from water with efficiency [105].



**Figure 1.23** (a) Schematic synthesis of Py-Py COF and Py-TT COF. (b) Diffuse reflectance spectra of the dry (orange) and wet (brown) Py-TT COF showing a strong solvatochromic red-shift. (c) UV-Vis absorption spectra of the Py-TT COF at different concentration of H<sub>2</sub>O and (d) saturated atmospheres of various solvents with their corresponding polarity [103]

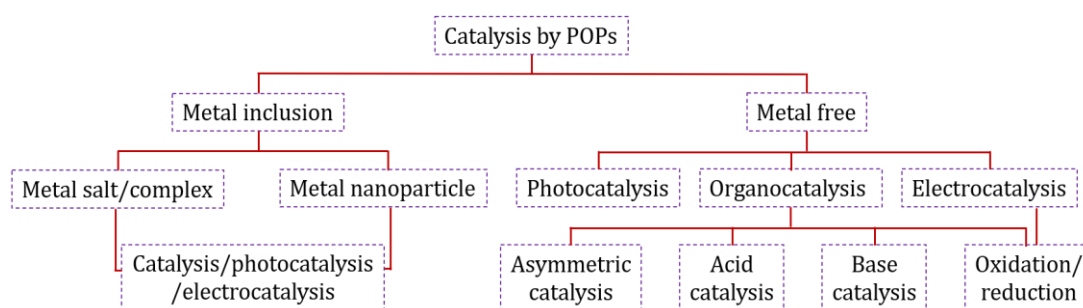
#### 1.4.4 Biomedical applications

POPs with easily tunable features such as adjustable architectures, minimal cytotoxicity, ease of introducing chosen functions, and biocompatibility have sparked unprecedented interest and attention in biological applications [11]. Yan and coworkers synthesized two imide connected 3D POPs with diamondoid structure for the first time by imidizing pyromellitic dianhydride with 1,3,5,7-tetraaminoadamantane and tetra(4-aminophenyl)methane [11]. In-vitro loading and releasing of three pharmacological molecules, namely ibuprofen, captopril, and caffeine, in these POPs has been demonstrated. Zhao and coworkers recently created nanoporous crystalline POPs by condensation of amine and aldehyde functionalized building blocks, which perform as a smart carrier for the anticancer medication 5-fluorouracil with high biocompatibility and stability [20]. A major platform for POPs was also found in phototherapy. A nanometal integrated on pores that functions as a photothermal agent to destroy the cancer cell has been developed [106]. After being

treated with the polymer and then being exposed to 808 nm of near-infrared (NIR) light, the murine hepatocarcinoma (H22) infected tumour shrank by 93% in size, demonstrating the photothermal efficacy of POPs.

### 1.4.5 Catalysis

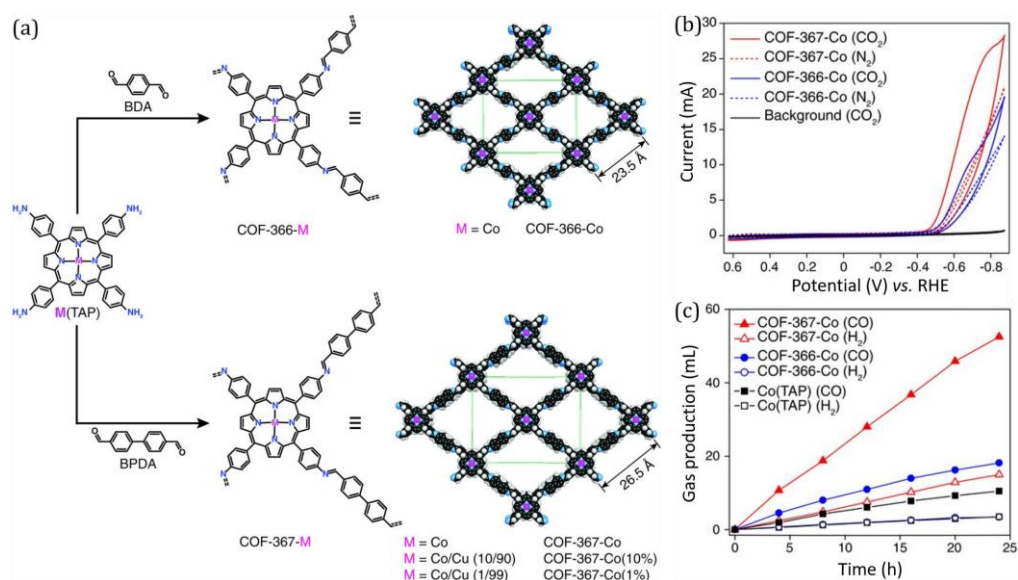
The high thermal and chemical stability, insolubility in most of the common organic and inorganic solvents makes POPs an excellent candidate for heterogeneous catalysis, including greater access to active sites. However, in comparison to other classes of porous materials, the use of POPs in heterogeneous catalysis remains largely unexplored, despite their high porosity and tunability. Below flow chart represents the way POPs have been explored in the field of catalysis till date (Figure 1.24).



**Figure 1.24** Schematic representation of different catalytic systems by POPs

The catalytic potency of such materials was first introduced by Wang and coworkers in Suzuki-Miyaura coupling using Pd supported over imine based porous organic material [107]. The superiority of the material in catalysis was elucidated by the broad scope of the reactants in excellent productivity of 96–98% together with the high stability and easy recyclability of the catalyst. This strategy opens up a new window for heterogeneous metal catalysis as well as photo/electrocatalysis [108,109].

Beyond organic transformation reactions, Chang and coworkers took the cobalt embedded porphyrin based crystalline framework a step ahead by reporting electrochemical reduction of CO<sub>2</sub> to clean energy in water (Figure 1.25). The Cobalt porphyrin ring linked by the organic struts *via* imine condensation possessed a high Faradaic efficiency upto 90% and resulted a TON and TOF upto 2,90,000 and 9,400 h<sup>-1</sup> respectively at pH 7. These values are 26-fold improved while compared to molecular cobalt complex without any degradation over 24 h.

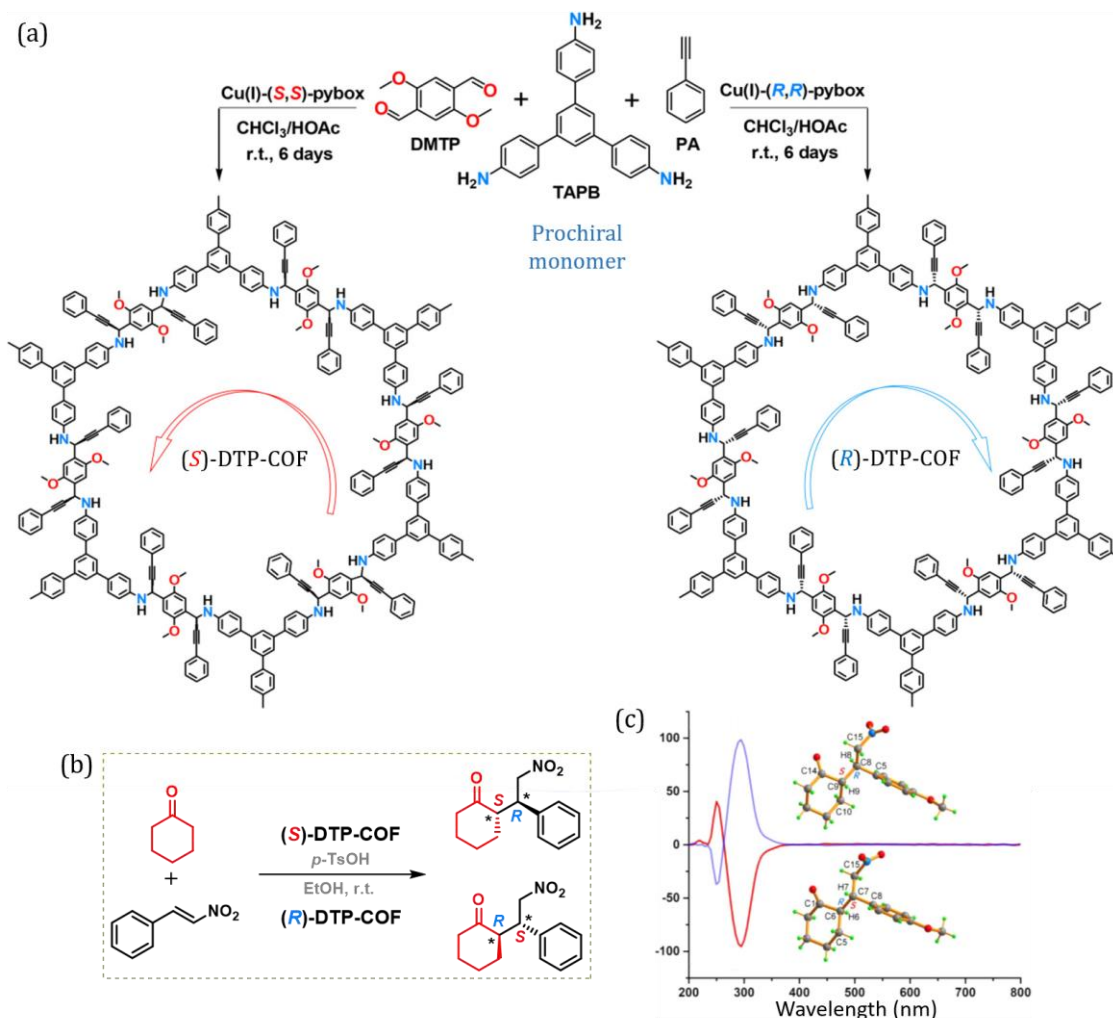


**Figure 1.25** (a) Synthesis of metalloporphyrin-derived 2D COFs. (b) Cyclic voltammograms of COF-366-Co and COF-367-Co in carbon dioxide-saturated medium (blue and red solid lines, respectively) or nitrogen-saturated medium (blue and red dotted lines, respectively). The black solid line shows background (bare carbon electrode) CV responses in carbon dioxide-saturated medium. (c) Volume of carbon monoxide produced [109]

Later on, numerous such examples of metal supported porous materials were reported. However, metal free POPs in catalysis are yet to be explored especially when it has the ability to enter the industrial scale of applications.

The key to creating crystalline POPs is to take advantage of their structural potency. Even better than the most advanced metal-free photocatalyst, g-C<sub>3</sub>N<sub>4</sub>, highly conjugated pyrene based porous organic material has been investigated as an efficient metal free photocatalyst for C-3 functionalization of indole [110]. Such a development draws attention to the use of heterogeneous supports free of metals in organic transformation reactions. The majority of columnar  $\pi$ -arrays and/or conjugated  $\pi$ -electrons are used to drive known POP accomplished catalytic reactions like the Diels-Elder adduct, Cascade reactions, etc [111,112]. The lone pair on nitrogen serves as the site of interaction to modify the reaction in nearly all cases, and POPs with imine functionality are used to carry out these types of transformations. The important role of embedded quaternary heteroatom in metal-free triazine framework in producing active hydrogen species through charge delocalization was recently demonstrated by Van Der Voort and coworkers [113].

Catalytic asymmetric methodology is widely recognised as the most important and effective synthetic approach for obtaining chiral organics. Dong and coworkers reported the chiral crystalline POPs ((*S*)-DTP-COF and (*R*)-DTP-COF) synthesised from prochiral monomers using catalytic asymmetric polymerization (Figure 1.26).



**Figure 1.26** (a) Schematic representation of the synthesis of (*S*)- and (*R*)-DTP-COFs via Catalytic Asymmetric Polymerization. (b) Asymmetric chiral catalytic Michael addition reaction and (c) CD spectra indicating the products are mirror images of each other; Single-crystal structures of the Michael addition products (insets) [114]

The obtained propargylamine-linked chiral crystalline POPs were highlighted as reusable chiral catalysts to promote asymmetric Michael addition reactions. This concept of catalytic asymmetric polymerization could pave the way for the creation of chiral POPs that are currently not possible using existing synthetic methods [114].

Few reported examples of the important POPs that demonstrated tremendous activity in catalysis are exemplified in Table 1.1.

**Table 1.1** Tabulated POPs in catalysis

<i>POPs</i>	<i>Applications in</i>	<i>Reference</i>
<b><i>Organocatalysis</i></b>		
Pd/COF-LZU1	Suzuki-Miyaura coupling	[107]
Pd/TPA-TCIF	Cyanation of haloarene	[115]
Au(0)@TpPa-1	Nitro reduction	[13]
COF-Am	Benzyl alcohol oxidation	[81]
( <i>S,R</i> )-DTP-COF	Asymmetric Michael-addition	[114]
LZU-76	Asymmetric aldol condensation	[115]
CCOFs	Asymmetric amination of $\beta$ -ketoesters	[115]
BF-COFs	Knoevenagel condensation	[115]
Py-An COF	Diels-Alder	[115]
COF-SQ	Michael-addition	[115]
<b><i>Photocatalysis</i></b>		
OH-TFP-TTA, TzTz-CMP-3	Selective sulfide oxidation	[117]
Cz-POF-1, LZU-190, BBO-COF	Hydroxylation of arylboronic acid	[117]
COF-JLU5, DA-CMP3	Aza-Henry reaction	[117]
C-CMP, PyTz-COF	Oxidative amine coupling	[117]
CoNi-COF-3, Ni-TpBpy	CO <sub>2</sub> reduction	[115]
TFB-COF	Cross-dehydrogenative coupling	[115]
g-C <sub>3</sub> N <sub>4</sub>	C-3 functionalization of indole	[110]
NH <sub>2</sub> -MIL-68@TPA-COF	Degradation of Rh B	[116]
<b><i>Electrocatalysis</i></b>		
COF-366-Co, COF-367-Co	CO <sub>2</sub> reduction	[109]
Co-TpBpy	OER	[116]
COF-C <sub>4</sub> N	OER	[117]
SB-PORPy-COF	HER	[116]
CTF@MoS <sub>2</sub>	HER	[117]
COF <sub>BTC</sub>	ORR	[116]

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## 1.5 Importance of Nitrogen Enrichment in POPs

Investigation suggests that the replace or addition of heteroatom in the backbone of the POPs lead to structural defects which enhances the catalytic activity by modulating multiple active sites. Among the other heteroatoms (B, N, S, F, P), nitrogen integrating POP shows higher activity due to a shift in electronic distribution in the material [113]. Besides the atomic radius of nitrogen is similar to that of carbon, which minimises the lattice mismatch greatly. Furthermore, nitrogen has a strong chelating ability for various metal ions, which is important for stabilising diverse metal nanoparticles and forming uniform particle distribution throughout the material. The addition of nitrogen to the material improves its overall thermal stability. Because nitrogen is basic, it absorbs more acidic gases (CO<sub>2</sub>) and allows for selective gas separation *via* the membrane. Furthermore, this material can be used to extract acidic protons, which aids in proton conduction, or as a helpful membrane in a fuel cell. Because nitrogen has a higher electronegativity than carbon, doping the material with nitrogen makes the neighbouring carbon atoms more electron deficient. As a result, it promotes increased oxygen adsorption into the catalyst and is useful for the oxygen reduction reaction (ORR) in fuel cells as well as an energy storage material (EDLC supercapacitor). The main disadvantage of this procedure is that determining the precise site of the nitrogen after doping is more difficult due to restricted instrumental technique and significant material flaws. As a result, nitrogen-rich porous crystalline material design and synthesis from nitrogen-containing precursors will be the most viable solution to the challenge [118-121].

## 1.6 Summary

POPs are comprised of lighter components with strong covalent bonds (C-C, C-N, B-O, C-S, etc.) and a pre-designed skeleton with excellent thermal/chemical stability and low density. Herein is presented a brief overview of porous organic polymers (POPs), their classifications, the strategic design synthesis method, and a few applications pertaining to their structurally induced features. Integrating several functionalities into POPs might drastically modify their interactional behaviour, hence enhancing their catalytic properties. With such customised properties, these materials have extensive applications in the sectors of gas storage/separation, conduction, biorefinery, biomedicine, and others. It has recently found widespread



application as an organocatalyst and/or as a support matrix for metal ion as a heterogeneous catalyst for a variety of organic transformation processes. Particularly in the realm of catalysis, an exhaustive literature review of POPs and their customised functionality has been utilised. In fact, the efficiency of these POPs in catalysing organic reactions prompted the invention of a porous polymeric network containing enriched nitrogen, which showed excellent use as heterogeneous catalysts.

In light of the importance of nitrogen enrichment systems in the field of catalysis, objectives are set forth to design and synthesis *N*-rich POPs for a handful of cutting-edge organic transformation reactions under both added metal and metal-free conditions.

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