Porous organic polymers

1.1 Introduction

Porous organic polymers (POPs) which is an emerging class of organic materials with desired pores, functionality and surfaces have recently attracted attention of researchers in the area of organic chemistry and materials science. These materials are composed of lighter elements such as B, C, N, O, etc. and constructed by forming covalent bonds between B–O, C–C, C–N etc. These organic network solids exhibit low densities and high physical and chemical stability [1-7]. They are important because of the promise to develop a new robust material for a purpose evidenced by number of recent research articles published in lavish journals/books. Moreover the novelty, utility and synthesis can make these solids a patentable stuff, from the perspective of intellectual property as well as emerged and viable alternative materials. They are synthesized by connecting various organic building units based on simple condensation reactions following the principles of reticular chemistry [8]. Reticular chemistry deals with linking and/or assembling of rigid molecules or building blocks/units by strong bonds (preferably covalent bonds) affording predetermined network structures. The resulting materials provide the basis for revolutionizing many branches of industry from catalysis to optoelectronic devices. It also improves our understanding of the functional materials. Designing such porous system with desired properties will transform new composite biocompatible materials for precise applications viz. in gas storage and energy applications, in heterogeneous catalysis, making optoelectronic devices, in environmental applications, as nanoreactor, as material carriers, etc. from material industries to drug delivery purpose in pharmaceutical which will serve as implants of new generation [9-20]. Very recently an important goal has also been achieved in the applications of POPs which is the detection and removal of heavy metal (Hg and Pb) both in liquid and gaseous phase [21].

Growing interest of academic researchers towards this field is owing to its persistent porous cage solely constructed by covalent bonds with varied functionalities. These materials can be classified into three major types/categories: (i) POPs that incorporate rigid well-defined homogeneous catalysts as building blocks, (ii) POPs that can be tuned post synthesis, and (iii) POPs that could successfully incorporate metals [22]. Selection of suitable building blocks containing reactive functionalities that trigger dynamic covalent bond formation is an important and challenging aspect in production of organic network solids with permanent porosity. Precisely, directing building blocks to construct discrete bonds is extremely difficult. In general, POPs are referred by various nomenclatures depending on the chemical environment of the structural integrity, pore size ranging from micro to meso and the crystallinity of the networks. POPs are atomically precise integration of building units with pre-designed skeleton giving desired shape to the porous materials. Depending on the shape of the core/secondary building blocks and the linkers associated in the construction of POPs the polymeric network may have either two dimensional (2D) or three dimensional (3D) in architecture (Figure 1.1). More intriguingly, advantage of POPs relies on the fact that their pore size, pore shape, pore volume, structural diversity, connectivity and functionalities are tunable. By virtue of the diversity of topologies and ease of functionalization, POPs have emerged as an excellent platform for designing multi-functional porous materials with pre-designed skeleton having diverse potential applications.

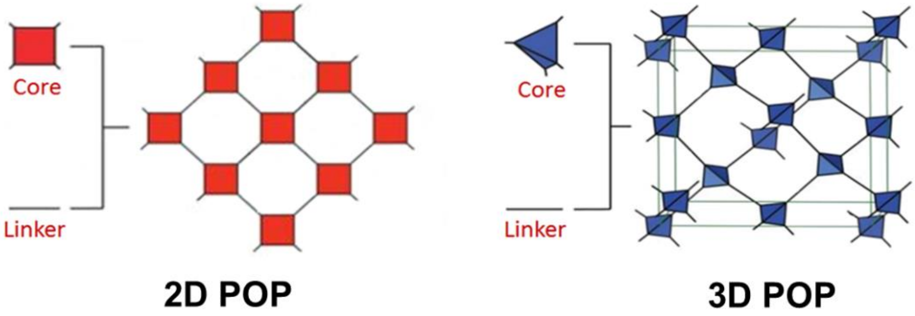


Figure 1.1 Pictorial representations of 2D and 3D porous polymeric networks.

1.2 Classification of POPs

On the basis of morphology, POPs are classified into crystalline and amorphous in nature. Crystalline POPs experiences structural regularity with uniform pore sizes and includes covalent organic frameworks (COFs) and covalent triazine frameworks (CTFs). However, during the COFs/CTFs synthesis attaining control over the reaction i.e. the concentration of reactants, allowance of prolongs reaction time is crucial. Failure in it could lead for irregular linking of building units affording amorphous POPs. The synthesis is comparatively easier since it is difficult to maintain the high ordered symmetry throughout the reaction process to achieve or yield the crystalline POPs.

1.2.1 Crystalline POPs

COFs are the first class of crystalline periodic porous organic polymers ingeniously constructed with building units extended with a multidirectional linker. The pioneer work of Omar Yaghi and co-workers in 2005 paves the way for COF synthesis [1]. The first reported COF materials, COF-1 and COF-5 having 2D crystalline structure have been synthesized by self-condensation of phenyl 1,4-diboronic acid and hetero-condensation with hexahydroxytriphenylene respectively (Figure 1.2) [1]. His seminal contribution in the development of such materials spreads very rapidly in organic and materials chemistry research divisions. The well-defined porous structure with simple but desired functionalities made the COF materials industrially potential. But the synthesis is generally associated with number of challenges. For example, it requires building blocks with high symmetry, reversible reaction pathway and more importantly requires extremely slow crystallization process. Control over crystallization and solving its problem has always been a matter of concern for structure activity relationship.

COFs are often known as “organic zeolites” [23]. The shape of the building units connected by robust covalent bond determines whether the desire synthesized COFs experience predicted 2D or 3D crystalline structure. Figure 1.3 displays the types of widely reported linkages associated with COF synthesis. The shape and length of the building unit determines the pore size, pore volume and pore shape of the COF materials. However, controlling the regularity in size of the pores is quite difficult due to its propensity to extend outgrowth arms irregularly. For example, in case of tetrahedral building block, the extension linked arm below or above the plane can interrupt in the formation of the desired shape selective cavities, hence losses regularity.

The first 3D COF (COF-102 and COF-103) has also been reported in 2007 via boronate anhydride and boronate ester formation between the building units. The units are linked by condensation reactions of tetrahedral tetra(4-dihydroxyborylphenyl)methane or tetra(4-dihydroxyborylphenyl)silane and by co-condensation of triangular 2,3,6,7,10,11-hexahydroxytriphenylene (Figure 1.3). COFs synthesized have high thermal stability up to 500 ºC and high surface area (4210 m^2g^{-1} for COF-103) [24].

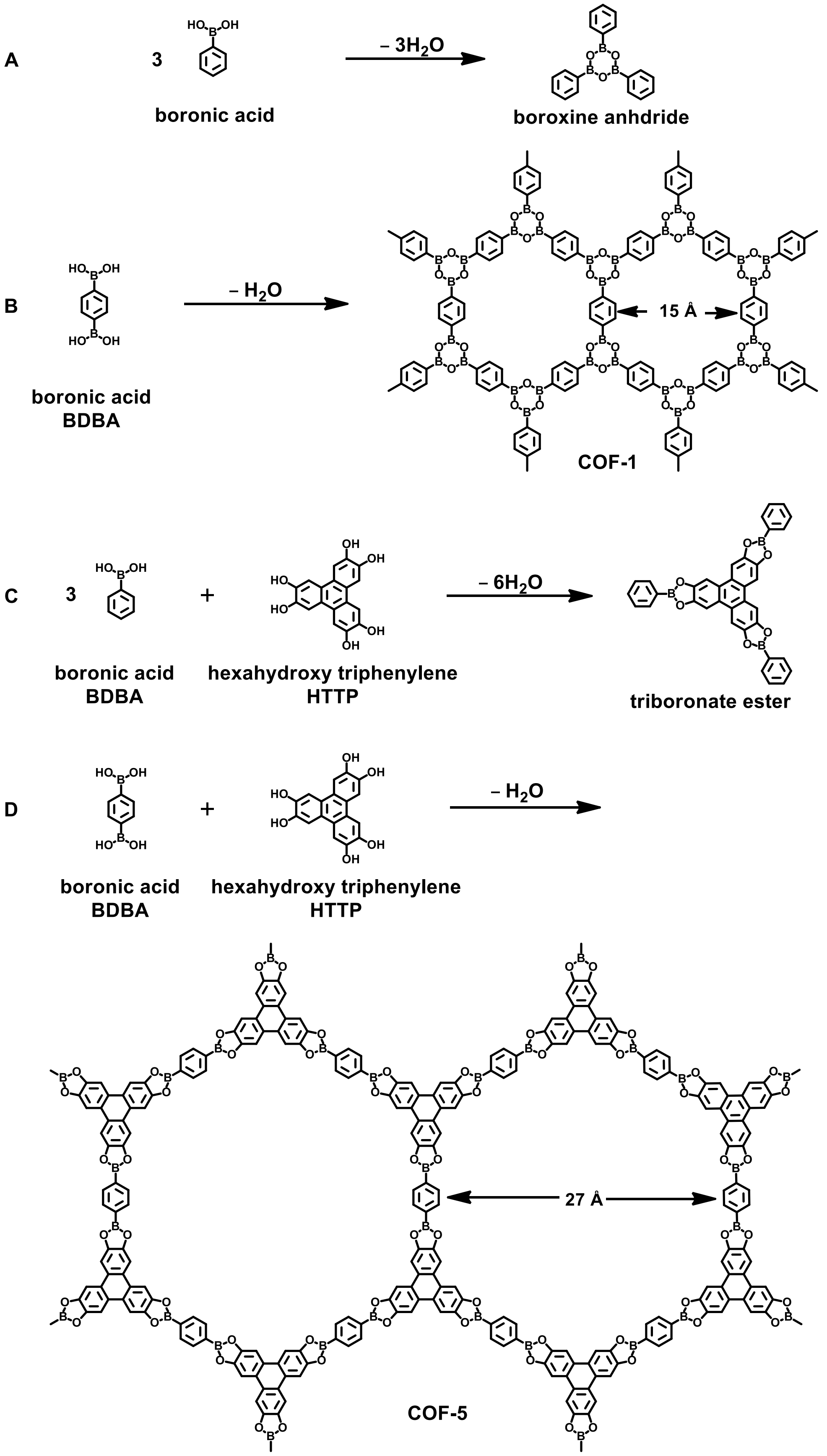


Figure 1.2 Synthesis of first two COFs (COF-1 and COF-5) by condensation of 1,4-diboronic acid [1].

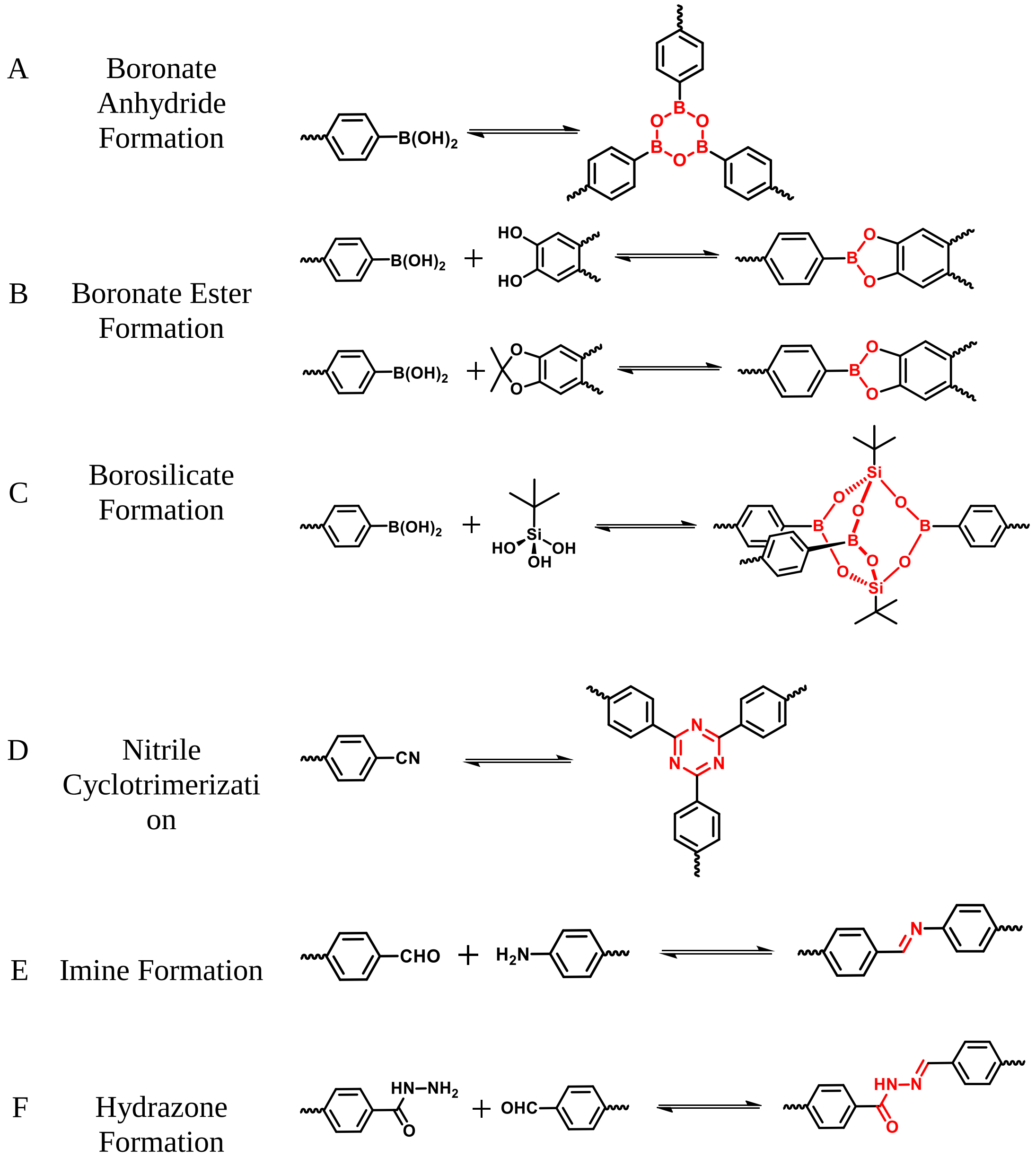


Figure 1.3 Different type of covalent linkages (in red) associated in the reversible reactions between building units during COF synthesis.

Synthesis of another 3D COF is recently reported under solvothermal condition on the surface of the functionalized porous ceramic α-Al_2O_3 substrate. The COF is associated with imine formation between the tetrahedral building block, tetra(4-anilyl)methane and the linear linker 4,4′-biphenyldicarboxaldehyde (Figure 1.4) [25]. Related issues associated with COF synthesis are that majority of COFs are poly- or microcrystalline and insoluble in common organic solvents for crystallization. Wuest et al. perhaps successfully synthesized monocrystalline COF by reversible polymerization of pre-designed monomeric units. Suitable crystals were generated and determined the structure using single crystal X-ray diffraction technique [26].

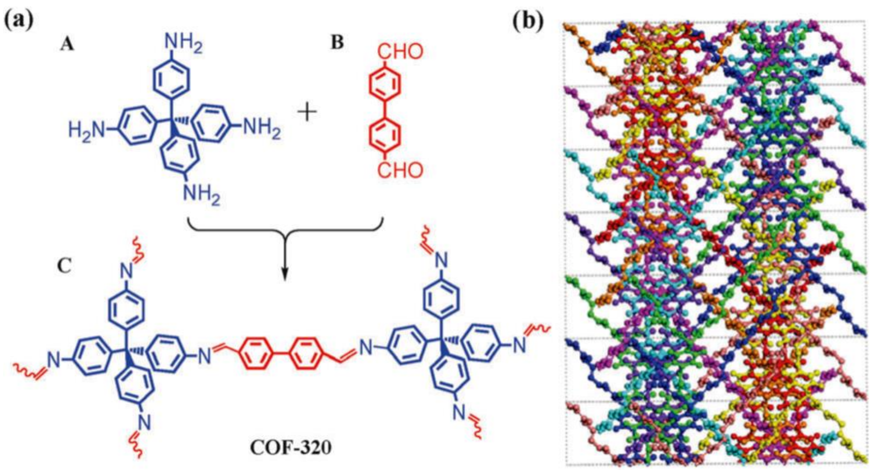
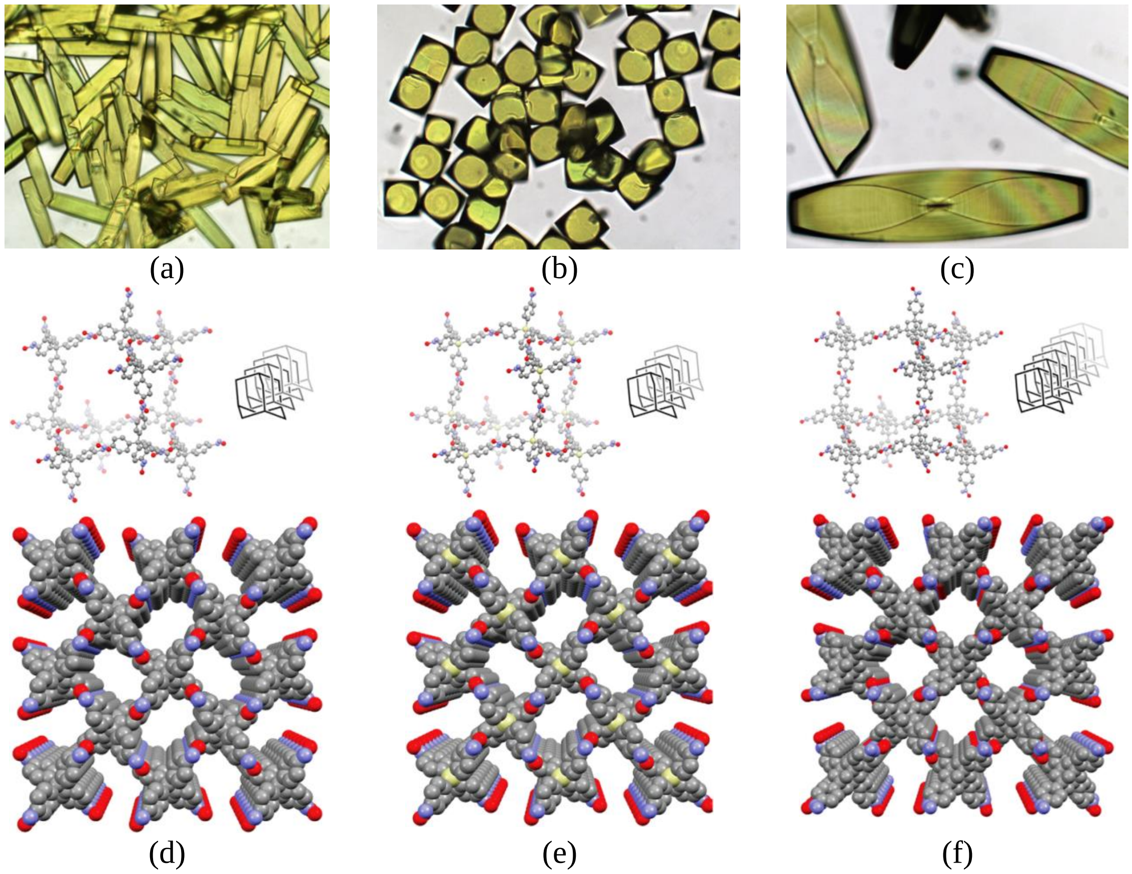


Figure 1.4 3D COF-320 constructed on the surface of functionalized ceramic α-Al_2O_3 (a) and the interpenetration of the diamondoid net (b) of COF synthesized [25].


(a) (b) (c)

(d) (e) (f)

Figure 1.5 Single crystals of three covalent nitroso polymer networks obtained by polymerization of tetrakis(4-nitrosophenyl)methane (a), tetrakis(4-nitrosophenyl)silane (b) and 1,3,5,7-tetrakis(4-nitrosophenyl)adamantane (c) building units and the corresponding crystal structures (d, e, f) [26].

Considering the tetrahedrally oriented nitroso group containing monomer and their self-addition polymerization produces the yellow colored monocrystalline covalently linked nitroso polymeric network (Figure 1.5).

Covalent triazine frameworks (CTFs) are another class of crystalline POPs containing triazine ring as the basic building unit in the frameworks. Thomas and co-workers first synthesized CTF by trimerization reaction of 1,4-dicyanobenzene using the molten $ZnCl_2$ affording 2D sheet like structure (Figure 1.6) with hexagonal pores [27]. The high nitrogen content and higher surface area in CTF-type network solids present them as a potent adsorbent for gas molecules, as fluorescent and also an excellent support for metallation in heterogeneous catalysis.

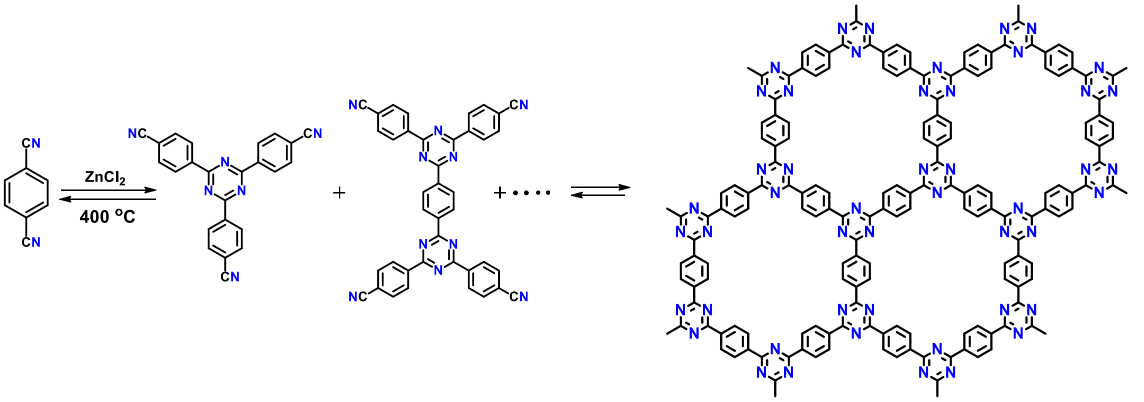


Figure 1.6 Synthesis of first CTF with the hexagonal columnar pores [27].

Cooper and coworkers have illustrated the synthesis of CTF-typed porous polymers that exhibited remarkable fluorescent behavior under the UV-light [28]. An ultramicroporous triazine based framework has recently been synthesized that possesses high chemical and thermal stability having potent ability to selectively capture CO_2 over N_2 and CH_4 [29]. A triazine based non-crystalline POP with amide functionality is developed and illustrated in chapter 4. The synthesized POP is employed as organic catalyst in performing organic transformation reaction.

1.2.2 Amorphous POPs

Analogous to COFs and CTFs, the amorphous POPs also have garnered considerable attention of scientific community owing to its potent applications alike COFs in the varied field ranging from gas adsorption to catalysis and in biomedicine. In general, amorphous POPs are a class of crosslinked amorphous polymers holding micro porous cavity, emerging as a material of interest especially as a heterogeneous catalyst [22]. However, owing to its ease for the inclusion of functionality, POPs represent as a potent candidate deploying excellent activity towards sensing, proton conduction, adsorption of small molecules, etc. Relates to COFs/CTFs, amorphous POPs are comparatively easy to synthesize but possesses irregular pores that raises difficulties to control the pre-sketched structural skeleton. Thus there prevail challenges in the synthesis of regular structure. Depending on the varying pore sizes, building units and the network formation between the building units in POPs, the amorphous POPs are also referred by various nomenclatures. To mention a few are conjugated microporous polymers (CMPs), polymeric organic frameworks (POFs), covalent organic polymers (COPs), porous aromatic frameworks (PAFs), microporous polymer networks (MPNs), microporous organic polymers (MOPs), nanoporous aromatic networks (NANs), porous polymer networks (PPNs), anionic microporous polymer networks (ABNs), hyper cross-linked polymers (HCPs) etc. [30-39].

1.2.2.1 Porous Aromatic Frameworks (PAFs)

PAF represents the rigid and open-network porous structure in the family of porous organic network solids. This new porous material replicates structure of diamond in general with tailored porosity by the replacement of C–C bond in diamond by rigid phenyl ring retaining its structural identity and stability. Synthetic procedure for PAFs follows the well-established coupling reactions such as Yamamoto-type Ullmann cross-coupling. PAF-1, the first PAF has been synthesized by coupling the tetrahedral building unit, tetrakis(4-bromophenyl)methane with phenyl ring [40].

Interestingly, PAF-1 shows remarkable surface area of 7100 m^2g^{-1} and is unprecedented. Very recently, researchers from USA successfully synthesized a porous polymer PAF-1-CH_2AO by functionalizing PAF-1 with amidoxime to employ as an adsorbent for uranium with uptake of more than 300 mgg^{-1} [42]. In an another report, an organic positive charged PAF, Cl-PAF-50 with tuned pore size ranging from 3.4 to 7 Å (Figure 1.7) added in-depth towards PAF chemistry [41]. It is demonstrated as potent application as sieves in separation of small gas molecules from the mixture.

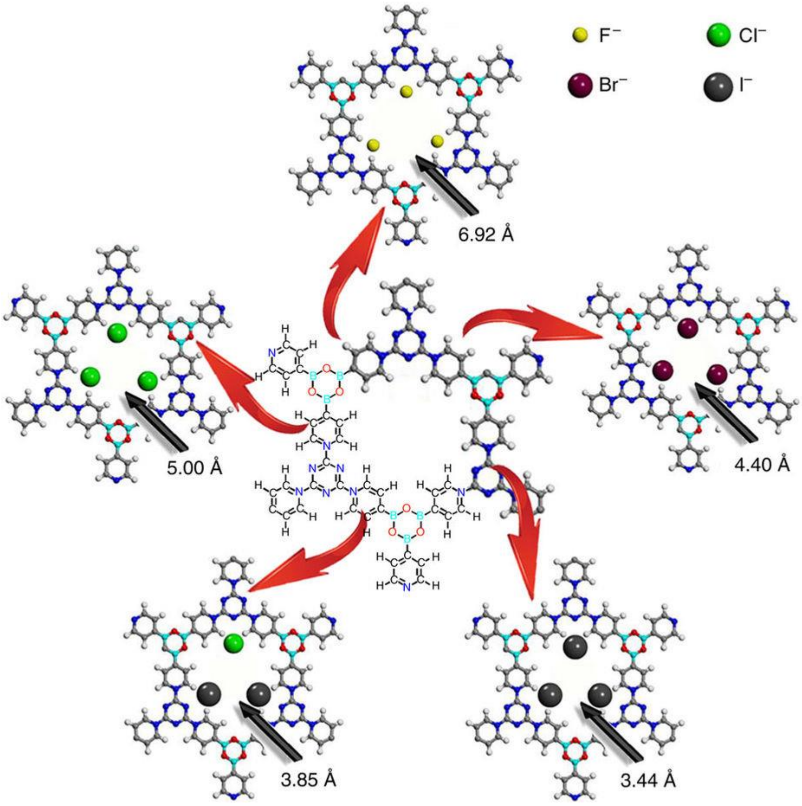


Figure 1.7 Representation of anion template PAF with tuned pore sizes [41].

1.2.2.2 Microporous Organic Polymers (MOPs)

MOPs with pore size less than 2 nm are a class of POPs that exhibit potent applications especially in the absorption of CO_2 gas owing to its intrinsic properties. They also exhibit large specific surface area, fine pore size distribution and low density with high chemical and thermal stability [43,44]. The MOPs are formed by assembling different monomeric building units with varied functionalities and groups by the rigid linkages (Figure 1.8) amongst them [45].

Based on these linkages and by “Click Chemistry” several MOPs have been developed such as hyper cross linked polymers (HCPs), polymers of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), etc. In recent past a novel indole based MOP that parades a significant selectivity and uptake of CO_2 over N_2 and CH_4 gases has been exploited [44]. The specific adsorption of CO_2 is facilitated by the existence of dipole–π interaction between the polarizable CO_2 and the MOP. Apart from gas adsorption, noted examples of MOPs persist in other potential applications such as in conduction and in catalysis. A synthesized porous material has been sulfonated to encapsulate water molecules executing proton conduction behavior [46]. Maji et al. reported an amide linked MOP proving the catalytic activity of it towards Knoevenagel condensation reaction [35].

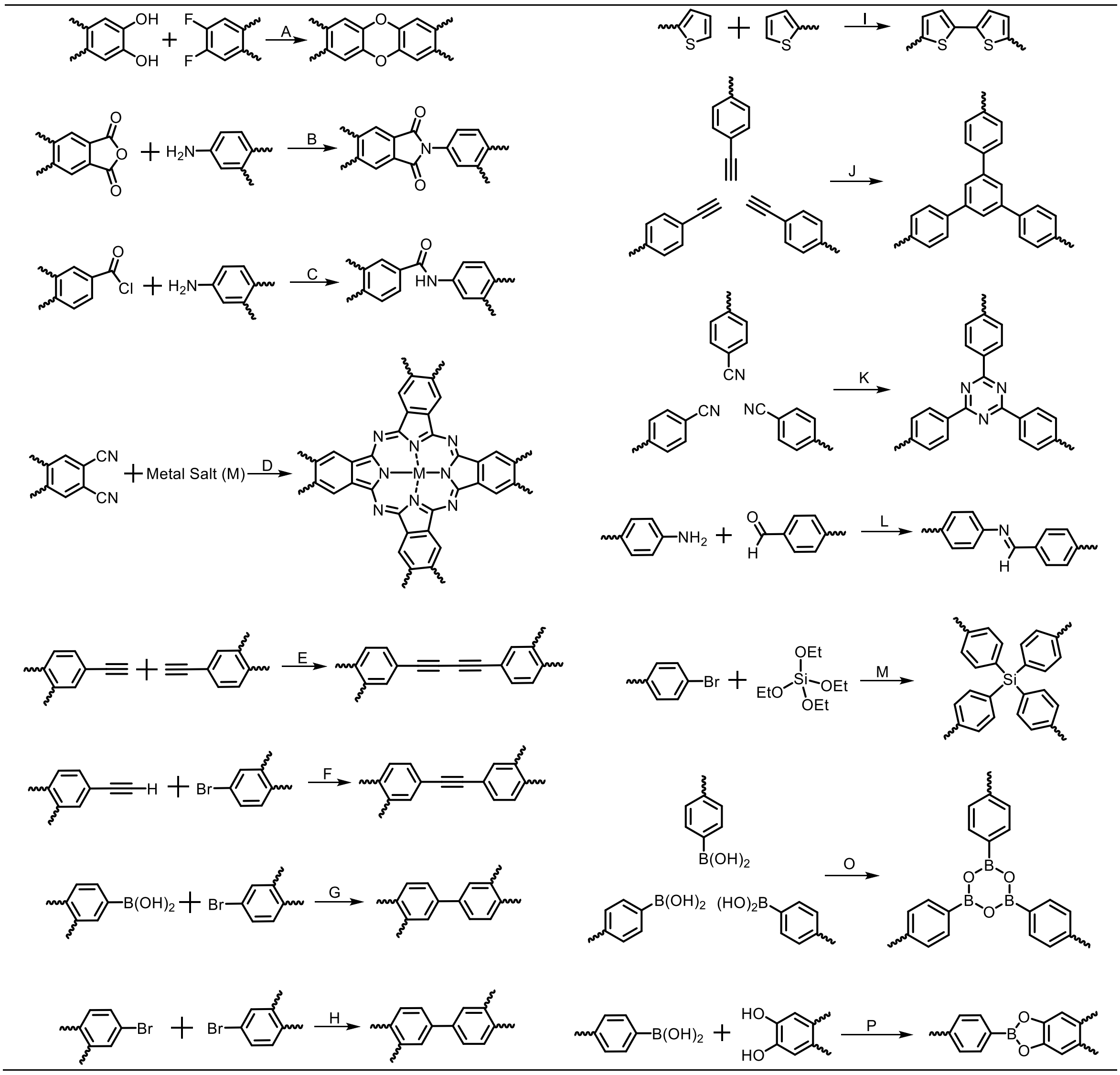


Figure 1.8 Various types of linkages and/or building units used in the preparation of MOPs [45].

1.2.2.3 Conjugated Microporous Polymers (CMPs)

CMPs a member of MOPs have drawn significant attention of scientific community in materials division due to its inimitable structure with continuous π-conjugation. The π-conjugation provides extra stability and opportunity to introduce varied functionalities into the pore walls. Although large number of articles are available in the literature establishing the potential applications of CMPs in various fields, especially in gas adsorption and separation, in heterogeneous catalysis [47] and in luminescence; its wide range applications at industrial scale is still limited. “This is because of the two prime challenges: (i) the design and synthesis of functional monomers to introduce the required functionality and microporous structure in the CMPs (ii) the use of expensive and rare transition/noble metal catalysts in C–C coupling methods, e.g., Sonogashira–Hagihara coupling," restricts the large scale applications of CMPs [48].

Thomas and his coworkers reported five different CMPs (Figure 1.9) following Buchwald–Hartwig reaction mechanism through C–C coupling while illustrating the potent application of CMPs as supercapacitors [49]. Metal coordinated CMPs with outstanding application in the catalytic conversion of captured atmospheric CO_2 had added further depth towards the advantage and importance of synthesizing CMPs amongst other member of MOPs [47].

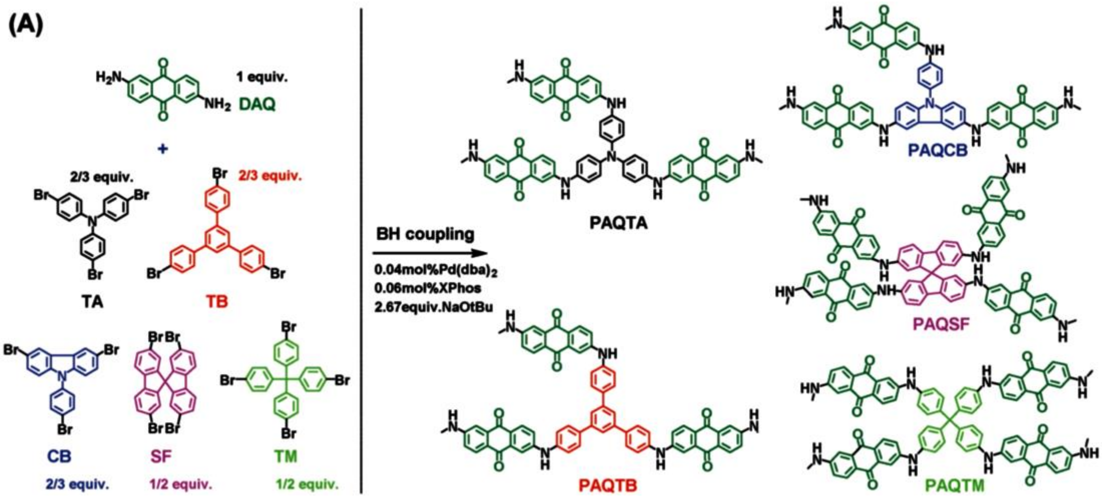


Figure 1.9 Synthesis of different CMPs via Buchwald-Hartwig (BH) C–N coupling reaction [49].

1.3 Synthesis of POPs

Crystalline POPs i.e., COFs and CTFs are highly reversible in nature. Reversibility condition makes the synthetic pathway of COFs/CTFs not to be an easy task. Hence the successful synthesis of those frameworks with the intact pre designed skeleton remains as a great challenge. Though difficult, there are mainly four different types of synthetic methods for preparation, (i) Ionothermal, (ii) Solvothermal, (iii) Microwave and (iv) Mechanochemical grinding techniques. Nearly identical methodologies have been adopted for the design-synthesis of amorphous POPs which are irreversible in nature.

1.3.1 Ionothermal process

This method provides opportunity to get better crystalline framework materials. Thomas and his group used molten $ZnCl_2$ as catalyst as well as solvent at 400 ºC to form a triazine based cyclotrimerized covalent organic framework from 1,4-benzenedinitrile [27]. The POP material in this process shows excellent thermal stability. However this process is extremely limited due to its inability to form regular ordered structure. Harsh conditions do not allow formation of crystalline material due to the reversibility criteria of the cyclotrimerization reaction. Therefore successful synthesis of POPs following this method is not very common as only two such materials are reported so far using ionothermal process.

1.3.2 Microwave process

Microwave process is newly introduced by Cooper and co-workers that is realized to be fast, efficient and greener. The COF-5 can be obtained only in 20 minutes by this process which is nearly 200 times faster than that of solvothermal process [50]. The surface area of COF-5 is found to be more in case of microwave assisted synthesis than that of solvothermal process. The microwave solvent extraction method eliminates impurities and residues from the framework materials causing better porosity. BET calculation of the surface area of COF-5 synthesized through microwave process was found to be 2019 m^2g^{-1}. Whereas synthesized from solvothermal process it was found to be 1590 m^2g^{-1}. Now-a-days, room temperature method is being practiced for the preparation of POPs and only imine based POPs was prepared till now. Further improvement in this direction is in progress.

1.3.3 Mechanochemical grinding

Mechanochemical (MC) grinding for the preparation of POP material takes an advantageous step not only towards green chemistry but also provides an effective catalytic material. Mechanochemical grinding is an ancient idea having importance because it can rapidly promote solid state reaction only by using nominal amounts. The required mass and energy transport without solvent can be made feasible with ball milling or grinding [51]. Banerjee and coworkers reported three isoreticular COFs synthesized by mechanochemical grinding and solvothermal processes (Figure 1.10) [51,52].

Figure 1.10 Schematic representation of COF synthesized using mechanochemical grinding techniques [51].

1.3.4 Solvothermal process

In solvothermal process, reactants are allowed to react in a sealed vessel such as autoclave made-up of stainless steel at 80−120 ºC (in general) for few days under high pressure. As per the literature report, 150 mTorr is the optimum pressure for a vessel of 10 cm^3 [1]. Solvothermal process allows precise control over shape, size and crystallinity behavior of the material. Later on Lavinge developed a condensation process in presence of crucial solvents under ambient pressure [53]. This method is considerably easier to carry without using a sealed vessel. Major disadvantage of this process is to lead powdery material and thereby limits its applications under certain circumstances. In context Dichtel et al. developed a new solvothermal process where the 2D COF is crystallized on a single-layered graphene sheet (Figure 1.11) [54]. Few POPs were also synthesized using a supporting layer that show unique properties like strong absorption ability of visible light. The strong light absorption capacity opens up its applications towards optoelectronic device designing.

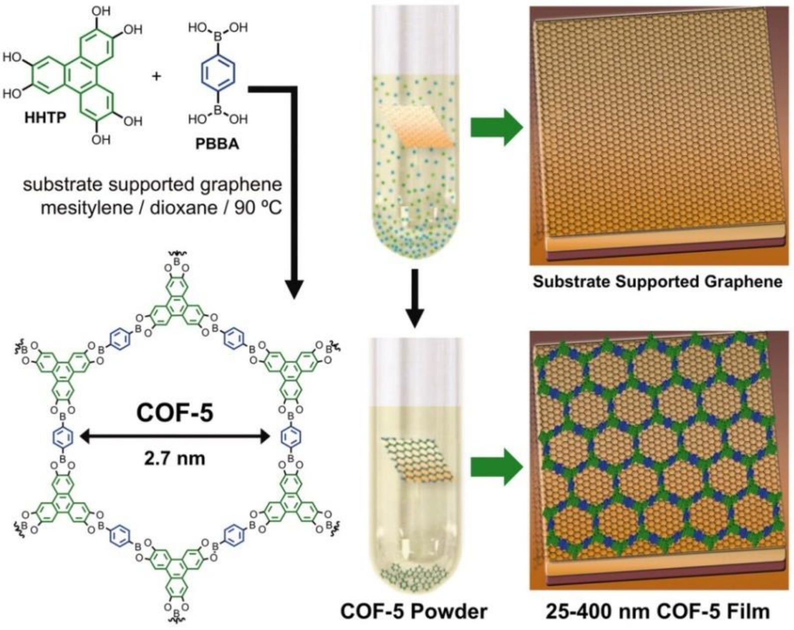


Figure 1.11 Synthesis of COF-5 on the surface of graphene sheet employing solvothermal technique [54].

1.4 Characterization of POPs

POPs are primarily characterized using usual techniques such as fourier-transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, thermal gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface area analysis etc. Apart from all these techniques, other sophisticated methods are also available for the structural and functional determination of the porous materials. These sophisticated methods usually include transmission electron microscopy (TEM) and scanning electron microscopy (SEM) imaging, energy dispersive X-ray spectroscopy (EDS or EDX), X-ray diffraction (XRD) analysis, etc.

At a very primary level, formations of new covalent bonds are characterized with FT-IR spectroscopy. For example, in case of an imine linked POP, the building block and the linker must be a primary amine and an aldehyde. Comparing the measured FT-IR spectrum of both the building units with that of the newly formed POP, the formation of imine linkage can be distinctly observed. The two broad N─H stretching signals at a frequency range of 3500-3400 cm^{-1} and the aldehyde carbonyl stretching at around 1710 cm^{-1} disappears and a new signal at a stretching frequency of 1690-1640 cm^{-1} appears corresponding to the formation of imine (C=N) linkage (Figure 1.12a). Similarly, in case of amide bond formation, the strong signal for the carbonyl stretching at 1710 cm^{-1}

would shift to a relatively lower frequency. This change in the stretching frequency is due to the conversion of isolated carbonyl group to a conjugated amide bond. During conjugation, the π-electron density of carbonyl group (C=O) delocalize over the –NHCO group by weakening C=O bond. Hence IR spectroscopy can provide valuable information about the formation of a covalent bond between the building block and the linker. Similarly we can recognize the formation of borate ester, boronic anhydride linkages etc.

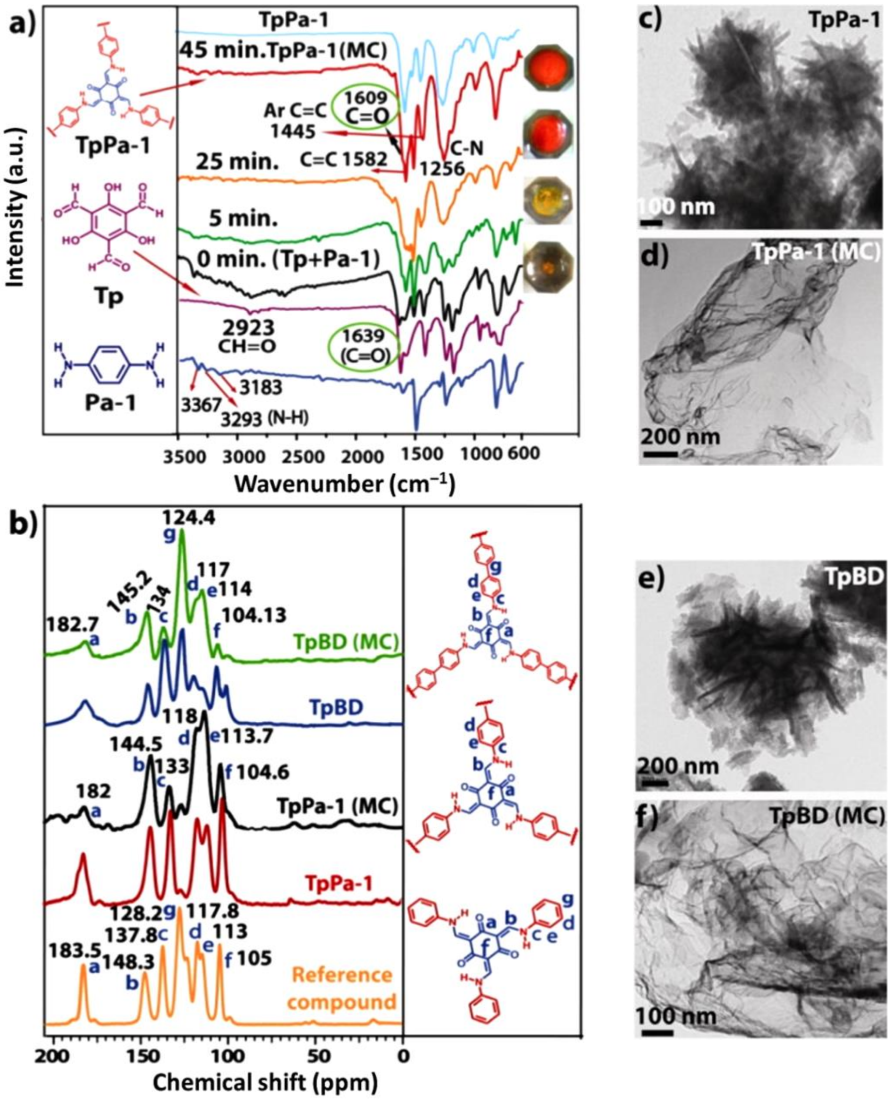
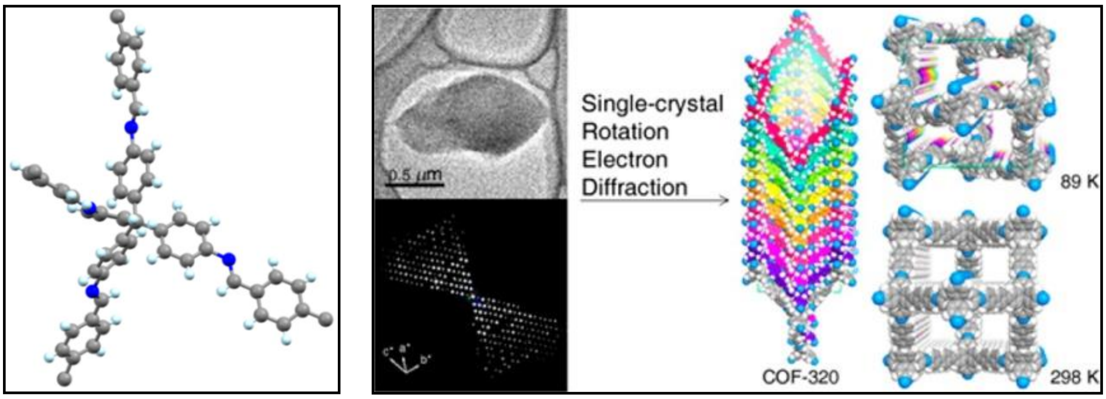


Figure 1.12 FT-IR spectra of building units and synthesized COF (a), ^{13}C ssNMR spectrum of monomeric unit (b) and the high resolution TEM images (c to f) of COF synthesized mechanochemically [53].

Nuclear magnetic resonance (NMR) technique allows us to determine the chemical environment of molecular structure with the help of a radio-wave frequency. In general, POPs/COFs are insoluble in normal NMR solvents. As a consequence, ^{13}C cross polarization magic angle spinning (^{13}C CPMAS) solid state NMR (ssNMR) spectroscopy is employed to determine the monomeric unit in polymeric network. For example, the ssNMR spectrum with resonance signal of monomeric unit in 2D COFs with imine functionality has been depicted in Figure 1.12b.

The thermal stability of a molecule depends on the molecular size, shape, polarity, packing pattern, intermolecular interactions etc. Based on the mentioned properties, the porous polymers get high thermal stability. Also the thermal stability is enhanced by various molecular interactions such as π-π or van der Waals interactions extinct within the polymer. The stable temperature of POPs is determined by differential scanning calorimetry (DSC) or thermal gravimetric nalysis (TGA) characterization tools. However in between these two, later one is more preferable. As the porous materials are good absorber, TGA allows us to understand not only the thermal stability but also the amounts of content present either as solvent or as impurity inside the pore or on surface of the porous materials.

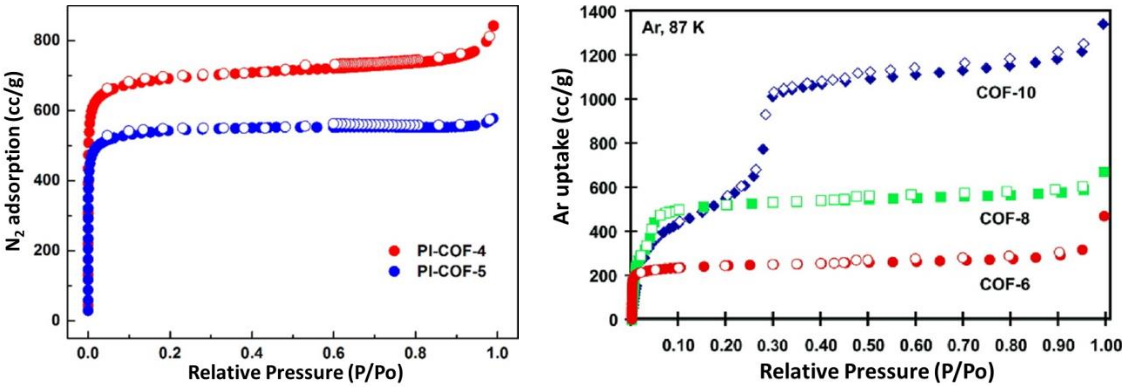
X-ray diffraction pattern of the powder sample of POP reveal its crystallinity thereby showing whether it is crystalline or amorphous in nature. Two types of X-ray diffraction viz. Powder X-ray diffraction (PXRD) and Single Crystal X-ray diffraction (SCXRD) is employed. The use of SCXRD is very limited as POPs are generally insoluble in common organic solvents and is difficult to generate a suitable single crystal for diffraction. However, the single crystal structure could be determined by employing rotation electron diffraction (RED) technique. Exploiting the similar technique, a diamondoid net structure of COF-320 with rectangular channel (Figure 1.13) has been determined successfully [55]. The PXRD pattern has been an alternative to SCXRD in most of the cases while determining the structure and crystallinity of materials. Structure modeling in material studio and thereby comparing thus generated PXRD pattern with the experimentally obtained pattern provides additional evidences for the characterization of POPs. Depending on the PXRD pattern of the material one can also distinguish crystalline and amorphous POPs. In addition the existence of stacking between the sheets of frameworks could also be attributed from the PXRD pattern.



(a) (b)

Figure 1.13 Single crystal structure of the molecular unit in COF-320 (a) and the diamondoid network with columnar rectangular channel in it (b) obtained by employing RED technique [55].

The porous polymeric network consists of both regular porous polymer and irregular porous polymer. The permanent porosity of the material can be obtained from BET isotherm, first introduced by Brunauer, Emmett and Teller. This is basically a method that includes adsorption-desorption mechanism where liquid nitrogen in general is first adsorbed on the surface of the porous material at 77 K by increasing the relative pressure of liquid nitrogen. The volume of adsorbed/desorbed liquid nitrogen in cc/g is plotted against the partial pressure to get the BET isotherm. Amongst the different types (type I - type V) of adsorption isotherm, type-I, II and IV are quite common in both crystalline and amorphous POPs. But in some rare examples type VI isotherms were also observed.



(a) (b)

Figure 1.14 (a) Nitrogen adsorption-desorption isotherm, type-I and (b) argon adsorption desorption isotherm (type-I and type-IV) exhibited by COFs [17,56].

Figure 1.14 displays the two different types of nitrogen adsorption-desorption isotherm. From the isotherm the porosity nature of the polymer is observed. Depending on the size of pores in the polymer and the type of adsorption isotherm revealed by POPs, these materials are classified as nano to macroporous structure in architecture. BET analysis is an imperative characterization technique characterizing porous materials. It provides the average diameter of pores, pore volume and surface area of these materials. In addition, an idea about the uniformity in pore size can be made from the BJH pore size distribution plot.

The electron microscopy imaging that includes scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images are also important tools that provide crucial information for characterization of porous materials. These images show the type of morphology and structure exhibited by the POPs. In addition, TEM image also displays the interlayer distances and stacking between the layers sheet apart from revealing the shape and calculating particle size of these materials.

1.5 Applications of POPs

Constituted by varied functionalities with high stability and tunable pore size, pore volume and surface area with tailor made properties, POPs exhibit efficient applications in the field ranging from gas adsorption and separation to medical sciences. Amongst these broad utilities, a few remarkable bids in the various fields have been quoted below. Perhaps there lies enormous scope to design and synthesis of such materials and applications in form of academic and industrial development.

1.5.1 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 flu 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. Moreover, H_2 and CH_4 are being used as a source of greener energy. As per prediction, world will be in need of huge amount of greener sources for energy after the fossil fuel extinct. Intriguing these facts about POP materials, they can act as a potent adsorbent over other known porous materials for suitably capturing and storing of H_2,

CO_2, CO, CH_4, N_2 etc. gases exerted by fossil fuel on burning [57-59]. McGrier and his group in 2016 reported cyanide catalyzed two benzobisoxazole (BBO) linked COFs (BBO-COF 1 and BBO-COF 2, Figure 1.15) that shows good CO_2 uptake of approximately 150.6 $mgg^{-1}$and 112.3 mgg^{-1} at 273 K [60]. POP materials containing boroxine ring or boronate ester and imine linkage are good at storing high amount of H_2, CH_4 and CO_2 [61]. 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 molecules, one can aim to capture and separate of any type of gases as desire.

Apart from its ability to adsorb and separate gas molecules, POPs with continuous π-conjugation in it also exhibits excellent candidature for the selective adsorption of hydrocarbons. Ma and his coworkers reported the adsorption of hydrocarbons by POP introducing π-complexation to POP [62]. The Ag(I) functionalized porous aromatic framework (PAF) by formation π-complexation shows remarkable selectivity towards adsorption of ethylene over ethane (Figure 1.16). Surprisingly this PAF reveals high ethylene selectivity thereby surpassing the so far reported zeolites, MOFs and POPs.

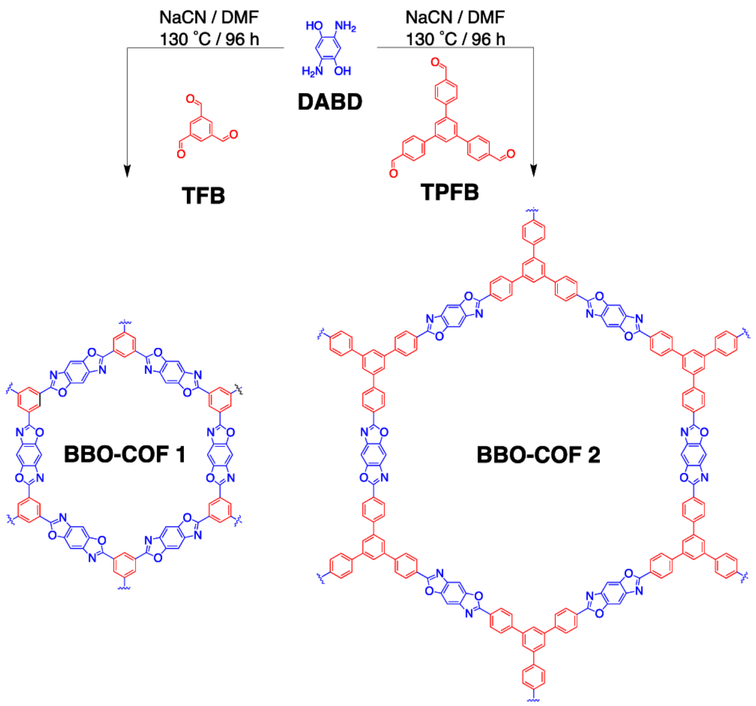


Figure 1.15 Schematic representation of benzobisoxazole (BBO) that exhibits excellent activity toward CO_2 absorption [60].

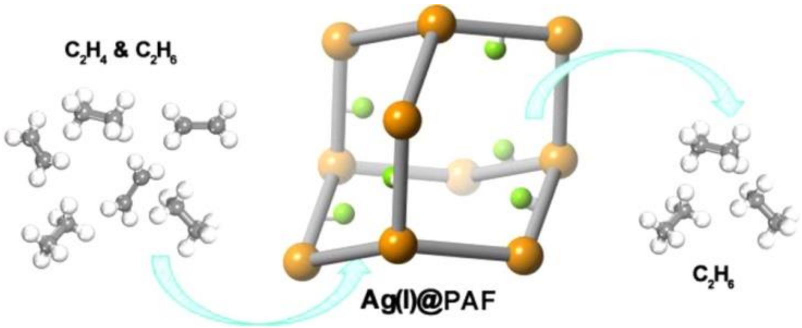
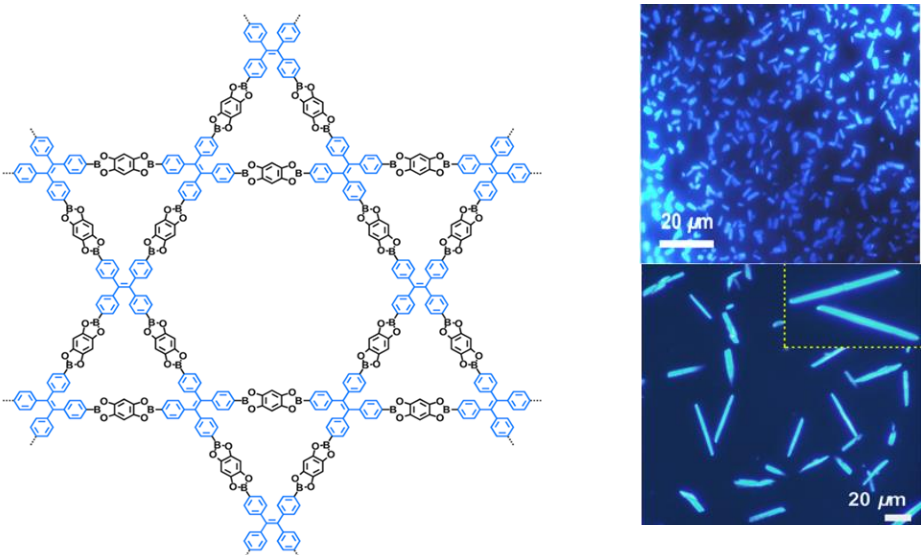


Figure 1.16 Selective adsorption of ethylene over ethane by PAF through π-complexation between ethylene and the framework [62].

1.5.2 Ion and/or Chemical Sensing

Even though applications of POPs range from gas adsorption to sensing, these materials high emission capacity are still scarce. Crystalline POPs such as COFs are the amalgamation of building units into periodic columnar π-arrays. Presence of this π···π stacked structure precludes the photoexcitation state of COFs, consequently freezing their emission behavior. It is due to the aggregation-caused quenching (ACQ) mechanism existing in COFs which checks their luminescent nature despite of the presence of luminescent π-units in COFs [63,64]. Donglin Jiang and co-workers solvothermally synthesized COF (TPE-PH COF, Figure 1.17) having dual pores (micro- and meso-pores) that shows highest emission reported till date by employing aggregation-induced-emission (AIE) mechanism [63].



(a) (b)

Figure 1.17 Schematic representation of TPE-Ph COF having dual pore frame (a) and its fluorescence image (b) that acts as robust sensor for NH_3 detection [63].

AIE is a phenomenon where the chromophores become emissive in aggregated state due to prevention of free rotation of these groups. TPE-PH COF with boronate linkage has been exploited as a rapid sensor for ammonia via Lewis acid-base interaction mechanism. They also designed a highly stable crystalline POP based on azine linkage from 1,3,6,8-tetrakis(4-formylphenyl)pyrene and hydrazine having ordered pyrene columnar channels in the framework displaying fluorescence. Interestingly, this POP acts as a chemical sensor to detect nitrophenol explosives [65]. Another achievement in POPs chemistry is its application in detecting the heavy metals which are generally highly toxic and also regarded as environment pollutant. A π-conjugated thioether based fluorescent COF, COF-LZU8 efficiently sense and removes Hg^{2+} from water by interacting with the thioether groups which is a good receptor of mercury [66]. Addition to it there are reports available in the literature disclosing the utility of COFs for sensitive and selective applications in identification of Cu^{2+} and iodine in water [67,68].

Similar to COFs, amorphous POPs with π-conjugation also serves as fascinating porous materials for chemical sensing [69,70]. Intriguing fact about such materials is that the band gap as well as specific active sites for interaction with the targeted molecule in the POPs can be tuned. Cooper and his group demonstrated the doping technology to control the photophysical properties of CMPs [71]. They were able to successfully tune the optical band gap and emission property of polyphenylene network CMPs by the inclusion of comonomer dopant (Figure 1.18) and thereby able to control the fluorescence behavior of CMPs. Thus, dopant CMPs finds potent applications as fluorescent sensors to detect volatile organic compounds.

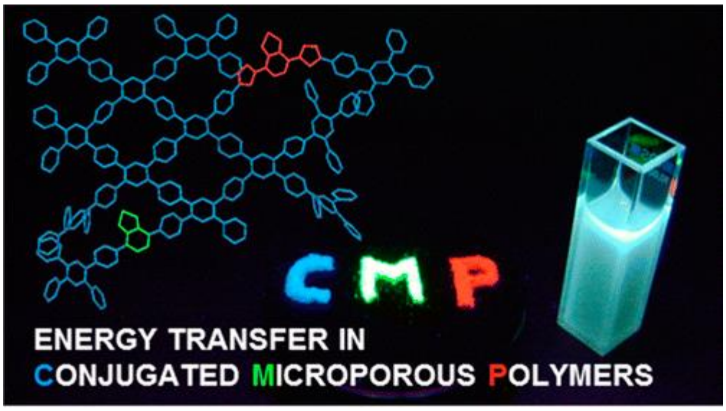


Figure 1.18 Inclusion of comonomer dopant to tune the photophysical properties of CMPs acting as fluorescence sensor for volatile organic compounds [71].

1.5.3 Conduction

Over half a century, extensive research had been conducted in search for materials with various skeletal and functionalities that could exhibit good conductivities [72]. Relates to it, the well-order structured polymeric materials with ionic channel are of highly desired. In recent years, porous polymers with well-defined and stable channel have been emerging as effective materials for the purpose. Liu and co-workers synthesized a 2D COF by condensing tetrathiafulvalene tetraaldehyde with 1,4-diaminobenzene and demonstrated conductivity of 0.28 S m^{-1} which is known to be the highest among the COFs [73].

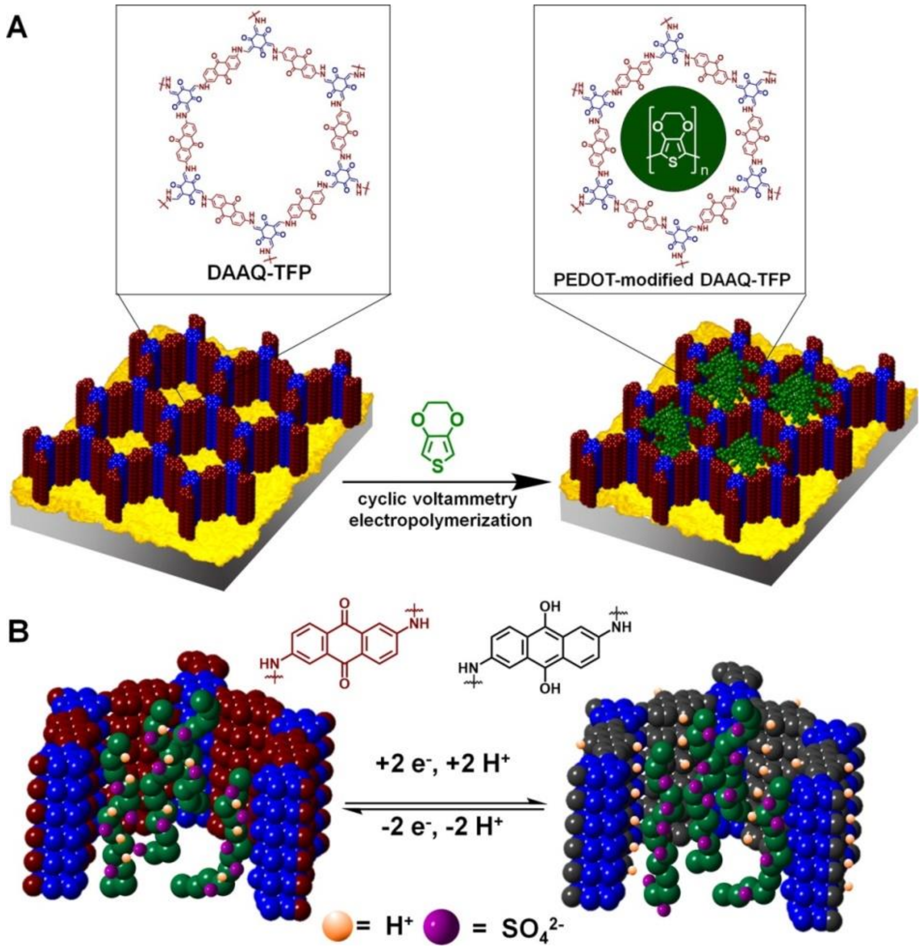


Figure 1.19 Displaying electropolymerization of poly(3,4-ethylenedioxythiophene), (PEDOT) into the pores of 2D COF 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol (DAAQ-TFP) [74].

A newer technique termed electropolymerization is adopted in present days to enhance the conductivity of COFs. A two dimensional COF, DAAQ-TFP, obtained from 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol was electropolymerized (Figure

1.19) within it pores with poly(3,4-ethylenedioxythiophene) (PEDOT) [74]. This modified COF deliberates enhancement in volumetric energies and power densities with high charging rates.

Notably, 2D COF with π-conjugation and short interlayer distances are established to have a potential application as conduction materials. Two COFs from porphyrin unit have been synthesized with planar π-electron system and close intermolecular π···π interactions among the layers [75]. These materials are known to display highest charge carrier mobility amongst the organic crystalline conducting polymers.

Because of the covalently bonded network POPs show better thermal stability compared to other porous materials such as zeolites and MOFs. This allows the post synthetic modification of POPs to meet the desire applications as required by introducing the different functionality. POPs in recent times displays potential application in the field of proton conduction by the inclusion of amphoteric molecules into the cavity of polymers [74,76]. Banerjee group first reported the proton conducting POP by immobilizing phosphoric acid group in the azo linked COF to observe moderate conduction behavior [76]. Very recently sulfonic acid incorporated POP has been demonstrated as conducting POP with conductivity (1.59×10^{-1} S cm^{-1}) which is better than Nafion (10^{-1} S cm^{-1}), a standard polymer electrolyte for proton conduction in fuel cell (Figure 1.20) [77].

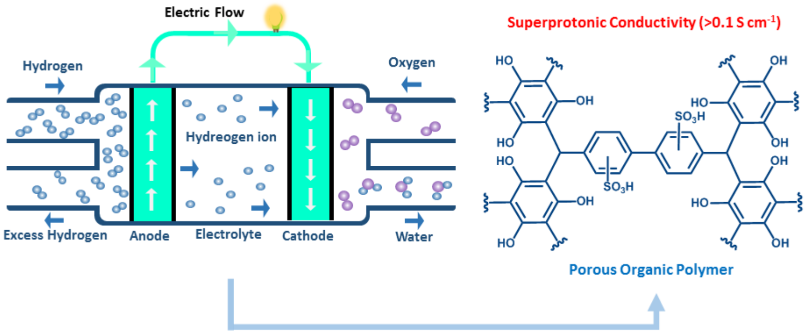


Figure 1.20 Sulfonic acid functionalized POP exhibiting proton conduction better than that exhibited by Nafion [77].

1.5.4 Biomedicine

POPs blessed with facile tailored properties including tunable structural skeleton, pore size and volume, low cytotoxicity, ease to introduce desired functionalities, high stability and biocompatibility have garnered unprecedented interest and attention towards its application in the field of biology [20,78]. In this regard, Yushan Yan and his group for the first time synthesized two imide linked 3D COFs with diamondoid topology through imidization of pyromellitic dianhydride with 1,3,5,7-tetraaminoadamantane and tetra(4-aminophenyl)methane [20]. The successful loading and releasing behavior of three drug molecules viz. ibuprofen, captopril and caffeine in these COFs have been demonstrated in-vitro. Recently, Zhao and co-workers also synthesized nanoporous COFs via condensation of amine and aldehyde functionalized building units which acts as smart carrier for anticancer drug 5-fluorouracil with good biocompatibility and stability [19].

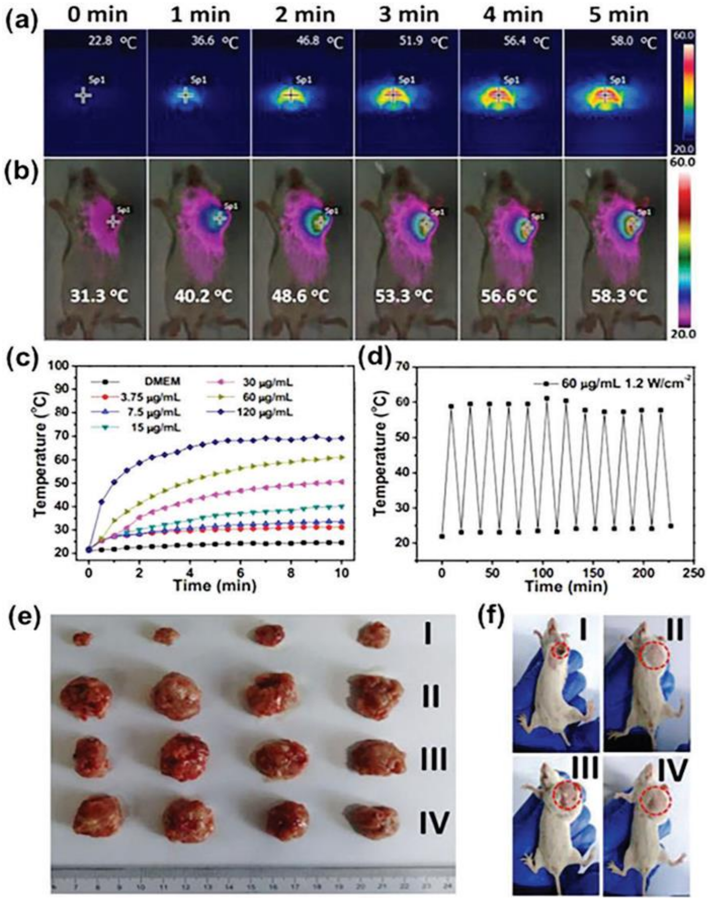


Figure 1.21 Micrographs of MCOP under irradiation with an 808 nm laser at constant time interval (a); Photothermal images of the whole mice after intratumoral injection of MCOP (b); Monitoring of temperature (c) and Representative photostability test (d) of MCOP; Photographs of tumors (e) and mice (f) under different treatment conditions [79].

POPs also discovered a significant platform in phototherapeutics. A nanometal incorporated COP (MCOP) has been designed acting as a photothermal agent in killing the cancer cell [79]. The decrease in size of the murine hepatocarcinoma (H22) infected tumor by 93 % (Figure 1.21) upon treatment with MCOP followed by post irradiation of treated tumor by 808 nm of near-infrared (NIR) light institutes the photothermal efficiency of POPs.

1.5.5 Catalysis

Built with functional moieties, POPs can be endowed with unique catalytic property. These materials can be nucleated heterogeneously to act as heterogeneous catalyst. Jiang and coworkers first demonstrated the utility of POPs in catalysis by using the Pd ion loaded imine based 2D COF (COF-LZU1) as efficient catalyst for Suzuki-Miyaura coupling [80]. The application of this Pd loaded COF (Pd/COF-LZU1, Figure 1.22) yielding 96-98% of product paves the way for COFs in catalysis.

Imine linkage COFs with considerably high surface area loaded with small amount of Pd were found to be excellent heterogeneous catalyst for phosphine free cross-coupling reaction such as Heck, Sonogashira, Suzuki-Miyaura, Heck-Matsuda reaction etc. Literature evidenced the accomplishment of organic reactions where POPs as an organocatalyst or as support matrix for incorporation of metal ions exhibit excellent catalytic activity. A catechol based COF has been introduced as organocatalyst for producing value added chemicals such as cyclic carbonates and oxazolidinones by chemical fixation of CO_2 under solvent free condition without using any transition metal. An amide linked 2D COF with extended π-conjugation has been investigated (in chapter 2) as a catalytic promoter in selective oxidation of benzyl alcohols with no metal adds-on [81]. The π-electronic COFs are further exploited as a catalytic scaffold to carry out Diels-Alder reactions [82].

Organic porous materials also provide the platform for heterogeneous, metal free, environmentally benign and sustainable pathway in performing organic transformation reactions. Zhang et al. recently made a breakthrough contribution in selective bromination of aromatic compound employing MOPs containing photoactive unit promoted by visible light using HBr as bromine source and molecular oxygen (Figure 1.23) [83]. An edge breaking application of MOP in catalysis has recently been emerged through construction of composite materials from graphene and pyrimidine based MOP [84]. The composite thus prepared acts as an excellent host for encapsulation of hemoglobin via “a ship-in-a-bottle” process. Investigation reveals its excellent electrocatalytic activity towards oxygen reduction reaction (Figure 1.24).

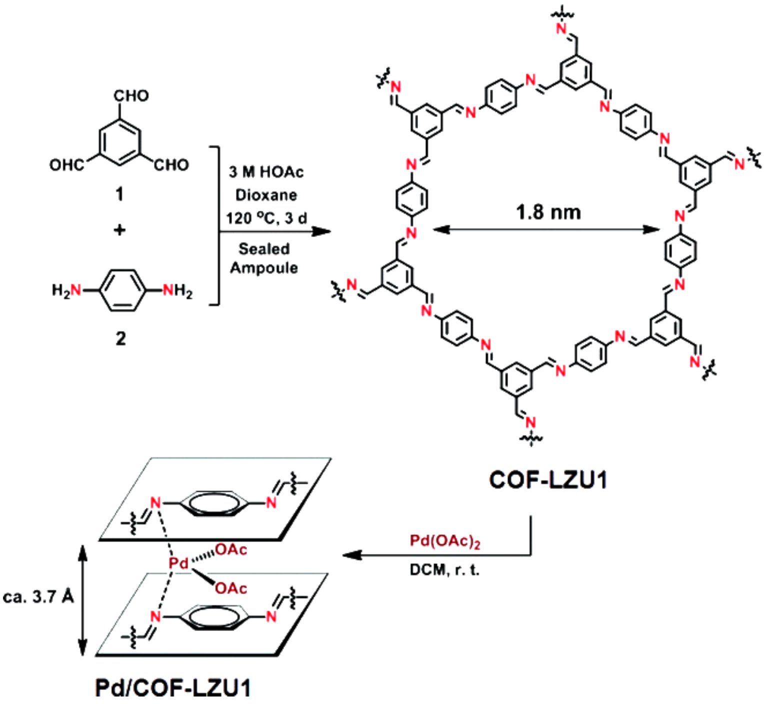


Figure 1.22 Schematic representation of Pd loaded 2D COF (Pd/COF-LZU1) as catalyst for Suzuki-Miyaura coupling [80].

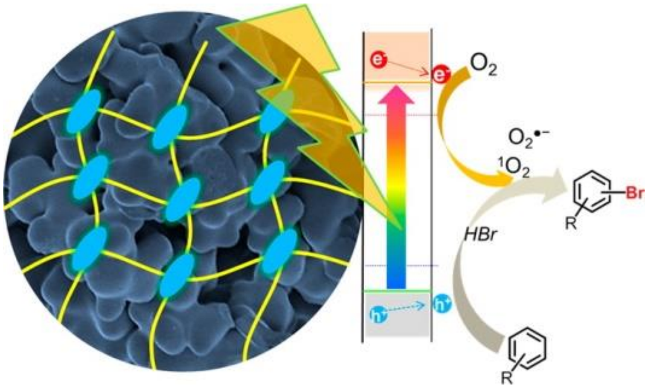


Figure 1.23 Visible light promoted photocatalytic selective bromination of electron rich aromatic compounds using MOPs [83].

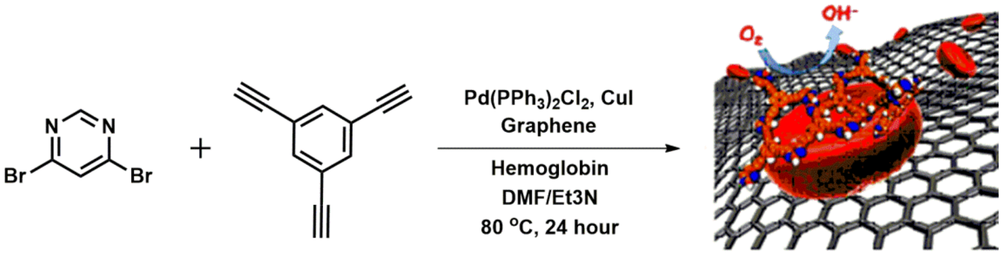


Figure 1.24 Schematic presentation of composite material from graphene and pyrimidine based POP as host for encapsulation of hemoglobin (red) and its catalytic activity toward reduction of oxygen [84].

1.6 Summary

Organic polymers with active pores and surface area have drawn extensive attention of all in the field of materials science and organic chemistry because of its potent and fascinating applications in the field of gas adsorption and separation, conduction, optoelectronics, solar fuel production, energy storage, biomedical applications, sensing, heterogeneous catalysis, etc. Even though it is an early stage of POPs, its peculiar structural features such as pre designed skeleton of structure using flexibly designed building units, tunable porosity and pore shape, ease in functionalization, tailor made engineering of overall structure of POPs, high stability and rigidity, etc. these solids gained maturity providing significant indications towards rich and broad research area of eminence in coming days. Development of newer POPs employing fresh synthetic techniques with varied functional linkages and molecular entities in its desired structure opens the door towards new POPs with potential applications. Nonetheless, the evolution of better sophisticated characterization techniques provides further boost in understanding the structure-property relationship of polymeric networks.

Stimulated by the tremendous applications of POPs, several amides linked new POPs with N-content variation have been aimed to synthesize and investigate their catalytic activity in organic transformation reactions and results are embodied in this thesis. These POPs also represent as potent candidature in adsorption of CO_2/N_2 gas in large. Chapter 2 and 4 demonstrates the role of π-electrons propagated by carboxamide functionality in the architecture of POPs acting as metal free catalyst in catalytic reactions. Whereas, chapter 3 and 5 illustrate the role of POPs as support matrix for impregnation of metal ions in performing organic transformation reactions.

1.7 References

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