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Porous Organic Polymers and it's application in CO_2 fixation reactions

Nishi Bipin Maru*, Vishal Shivaji Shelke .
Ramnarain Ruia Autonomous College, Matung, Mumbai .

1. ABSTRACT:

Porous organic polymers (POPs) are organic marcomolecules and are considered emerging functional organic materials. Owing to high specific surface areas, tunable porosities, low densities, high chemical and thermal stabilities, variable compositions, extended pi- conjugations and high content of carbon, oxygen, nitrogen and other non-metallic atoms, POPs have potential applications in CO_2 uptake, energy storage, H2 evolution, photocatalysis and photovoltaics. A wide range of POPs can be synthesized using multidentate amines, aldehydes or triazine monomers via polycondensation reactions. They are ideal adsorbents for CO_2 storage and CO_2 fixation reactions. This review presents a comprehensive summary of the developments in designand synthesis of Porous Organic Polymers (POPs) with regard to fix carbon dioxide synthetically. It provides promising research activities and their prospects in the areas of carbon capture and storage and chemical fixation of carbon dioxide in constructing a future low-carbon global economy.

Key words: Porous organic polymers, CO_2 fixation, natural pathways.

2. INTRODUCTION

The natural sequestration of CO_2 happens mainly by photosynthetic organisms present in the terrestrial as well as aquatic environments and this helps in maintaining the global carbon cycle. The major metabolic pathway through which CO_2 is sequestered is the Calvin–Benson cycle which is the light independent reaction of photosynthesis. Today, six natural pathways for fixing CO_2 is known to the mankind. But these have low efficiency and cannot meet with the demands imposed due to pollution and increasing CO_2 in atmosphere. With a view of implementation of green chemistry concepts and to establish a sustainable society, a large scale research has been devoted to reduce carbon footprint. An attractive and promising pathway to effectively reduce anthropogenic CO_2 emissions and produce fine chemicals is the Carbon Capture and Utilization Technique (CCU)[1]. CO2 being inexpensive and abundantly available, acts a C1, non toxic source for synthetic chemistry. Since CO_2 possesses inherent thermodynamic stability and kinetic inertness, the reaction pathways for CO_2 fixation often requires harsh reaction conditions. The challenging part is to overcome the thermodynamic

constraints and to achieve the activation of inert CO_2 under relatively less drastic conditions[2].

A large number of homogenous catalysts (metal complexes, quaternary ammonium or phosphine salts, organic bases, ionic liquids) to heterogeneous catalysts (metal oxides, porous inorganic materials, metal-organic frameworks (MOFs), covalent organic polymers (COFs), porous organic polymers (POPs)) have been exploited to achieve efficient, atom-economic and environment benign processes for catalytic CO_2 fixation. With the significant development in covalent chemistry, Organic functional materials offer an unparalleled advantage of being able to design according to the requirements of functional groups on a molecular level. Any desired functionality can be introduced into porous materials through atomic level control over the structures and compositions. Organic functional materials have the capability of regulating the synergistic interactions among reactant molecules for achieving high efficiency catalysis. These organic macromolecule polymer possess very high molecular weight, nearly-perfect heterogeneity and fascinating architectural stability as well as exceptional designability which is undoubtedly considered as an ideal heterogeneous catalyst[3].

Out of these, POPs are the most appealing and promising purely organic forms which have low density, high surface areas, tunable pore sizes, designable catalytic active site and satisfactory physicochemical stability. POPs frameworks include subclasses like porous aromatic frameworks (PAFs), covalent triazine frameworks (CTFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), hypercrosslinked polymers (HCPs), and conjugated microporous polymers (CMPs)[3]. These have many potential applications because of their high surface areas and uniform pore sizes, with large numbers of channels and active sites available for chemical reactions. POPs have thereby attracted a lot of attention for their use in the degradation of organic pollutants, energy storage, photocatalysis, H2 evolution, etc. POPs are insoluble in organic solvents due to their rigid chemical bonds and high degree of polymerizations and therefore can easily be separated and recycled. Herein, the six natural pathways for CO_2 fixation are explored followed by synthesis of POPs and it's application in CO_2 fixation reactions.

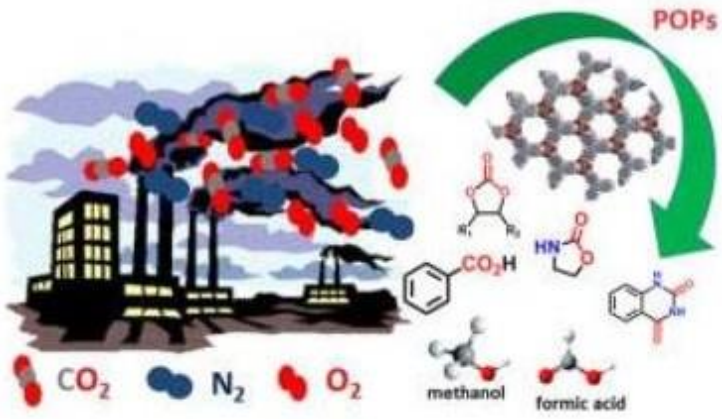


Fig. 1. : Illustration of use of POPs in CO2 fixation

Source: *Piyali Bhanja AM, and Asim Bhaumik. Porous organic polymers for CO2 storage and conversion reactions.*

ChemCatChem. 11 August, 2018 2018;11(1):244-257

3. Autotrophic CO_2 fixation

Autotrophs use photosynthesis to convert CO_2 to useful products. They inhale CO_2 as C1 carbonsource and most of them exhale O_2 as byproduct. The CO_2 molecules are introduced in chlorophyll via CO_2 acceptors. The assimilation of CO_2 into cellular carbon needs reducing equivalents. Since CO_2 (+4) state has to be reduced to carbohydrates (oxidation state of C is 0), 4reducing equivalents are needed. The reductive conversion of CO_2 to cell carbon also needs energy which is provided by the hydrolysis of ATP [4]. Anaerobes generally use a low potential electron donor like reduced ferredoxin whereas aerobes use NAD(P)H as a reductant. A carboxylating enzyme attaches to CO_2 or HCO3- with an organic receptor molecule. This receptor molecule is regenerated in the following steps of pathway. The inorganic carbon speciesare pH-dependent. The product of the autotrophic pathway is a central metabolite from which other carbohydrates, proteins, nucleic acids and lipids can be derived. The enzymes catalyzing the difficult steps of the pathways evolved during the evolution and are conserved till date, making them key enzymes. Ribulose-1,5-bisphosphate carboxylase, CO dehydrogenase/ acetyl CoA synthase are such enzymes. Today, 6 autotrophic CO_2 fixation mechanisms are known. Let us have a brief overview of them.

3. 1. CALVIN CYCLE

The Calvin- Benson Cycle, also known as reductive pentose phosphate cycle, is the most important pathway of autotrophic CO_2 fixation in nature. This pathway converts 3 molecules of CO2 into sugar via three distinct phases (carboxylation, reduction and regeneration). 3 CO_2 molecules are added to ribulose-1,5-bisphosphate to form 6 molecules of 3-phosphoglycerate (3-PGA) in the carboxylation step. The enzyme ribulose bisphosphate carboxylate/oxygenase (RuBisCO) facilitates the reaction.

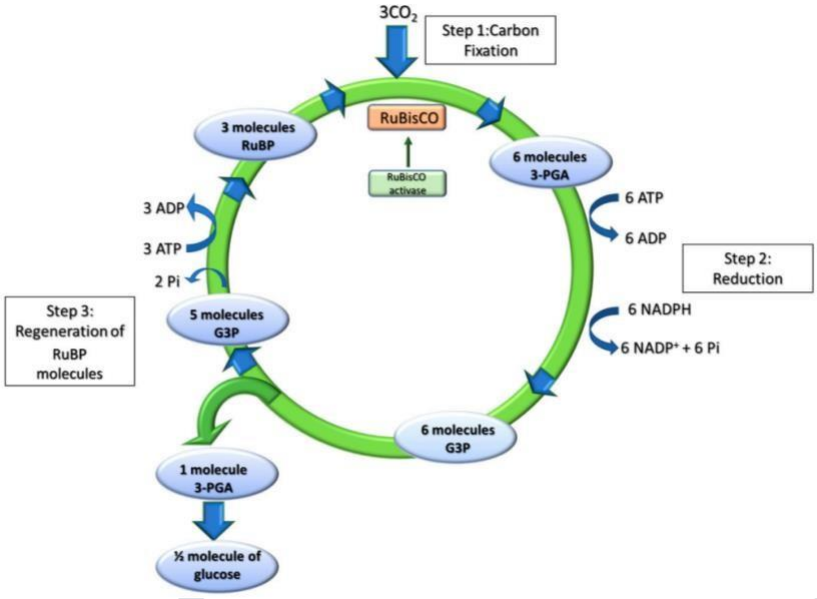


Fig.2: The Calvin-Benson Cycle

Source: Valeria Vechhi, S. B., Roberto Bassi and Luca Dall'Osto (2020). "Potential and Challenges of Improving Photosynthesis in Algae." Plants ***9****(1)* [5]

6 molecules of 3-PGA are converted to 6 molecules of Glyceraldehyde-3-P (G3P) by consuming the energy of ATP and reducing power of NADPH in the reduction phase. In regeneration phase, ribulose-1,5-bisphosphate is regenerated so that the cycle continues. This step involves many complex series of reactions yielding carbon sugar phosphates. Out of the 3 PGA molecules, one 3-PGA molecule is converted to half molecule of glucose. Almost all the evolved plants use this pathway to fix CO2.

3.2. REDUCTIVE CITRIC ACID CYCLE (ARNON-BUCHANAN CYCLE)

The reductive citric acid cycle, also known as reductive tricarboxylic acid (rTCA) cycle, was introduced in 1966 by Arnon and his coworkers. They proposed that the carbon assimilation in bacterium *Chlorobium limicola* (a green sulphur bacteria) proceeds via a reductive citric acid cycle and not the standard Calvin-Benson cycle [6]. The pathway provides synthesis of organic acids from CO_2 which inturn becomes the carbon skeleton for amino acid biosynthesis which areprimarily the main products of bacterial photosynthesis [6]. The decarboxylation of pyruvate to

acetyl-CoA and CO; the decarboxylation of alpha ketoglutarate to succinyl-CoA and CO_2 are irreversible reactions in aerobic cells whereas in rTCA, these are reversible.

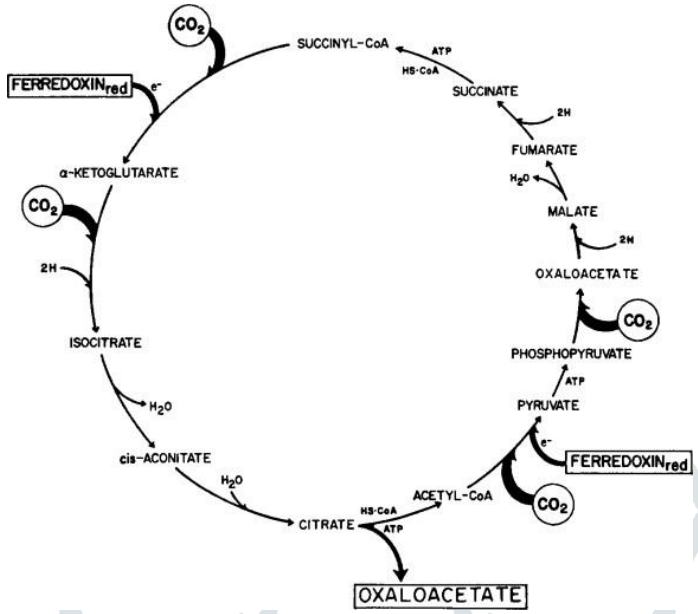


Fig. 3: The Reductive Carboxylic Acid Cycle (rTCA)

Source: Bob. B. Buchanan DIA. The reductive carboxylic acid cycle Methods in enzymology. 1696;13:170-181.

In rTCA, the acetyl-CoA is formed from 2 molecules of CO_2. This CO_2 fixation product of the cycle is further converted to other intermediates of the carbon metabolism via conversion of acetyl-CoA to phosphenol pyruvate, to oxaloacetate and 2-oxoglutrate. For such conversion and acetyl-CoA assimilation, this pathway requires additional enzymes. Ferredoxin-dependent pyruvate synthase is used to reductively carboxylate acetyl-Co-A to pyruvate which can further be converted to phosphoenol pyruvate. The reducing power of ferredoxin also helps in formationof alpha ketogulatarate from succinyl-CoA and CO_2. One complete reductive carboxylic acid cycle results in fixation of four molecules of CO_2 and formation of one oxaloacetate [6].

3.3. REDUCTIVE ACETYL-CoA (WOOD-LJUNGDAHL) PATHWAY

The Wood-Ljungdahl pathway is a non-cylic pathway and a major CO_2 fixation pathway under anaerobic conditions [7], preferred by prokaryotes which live close to the thermodynamic limit, like acetogenic bacteria and methanogenic archaea [4]. Wood and his co-workers proposed the

fixation of atmospheric carbon dioxide into reduced organic compounds by the heterotrophic propionic acid bacteria. The fixation in this pathway is a simple process where 2 molecules ofCO_2 are used to form two-carbon compound. It leads to formation of acetyl-CoA using a coenzyme and an enzyme metal center as CO_2 acceptors.

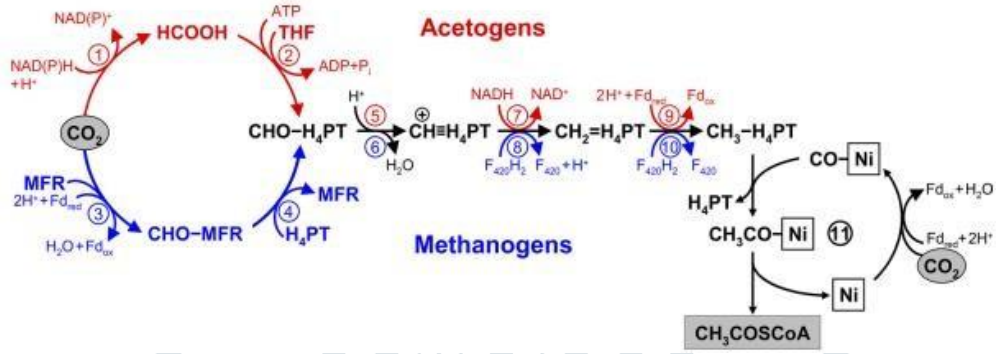


Fig.4: The Wood-Ljundahl Pathway

Source: Berg IA. Ecological Aspects of the Distribution of Different Autotrophic CO2 fixation pathways. Applied and Environmental Microbiology. 10th March, 2011 2011;77(6):1925-1936.

In the first step, carbon dioxide is reduced to a methyl group, which binds itself to tetrahydropterin coenzyme. Another CO_2 molecule binds to the reaction centre of CO dehydrogenase which contains Ni, and reduces it to carbon monoxide[4]. The pterin binds to CoASH and forms acetyl-CoA via the carboxylic donor ie. Carbon monoxide dehydrogenase [4,7].The acetyl-CoA is assimilated via pyruvate synthase as in rTCA cycle.

3.4. The Hydroxypropionate (Fuchs-Holo) Bi-cycle / 3-Hydroxypropionate cycle

Helge Holo designed the 3-hydroxypropionate cycle in *Chloroflexus aurantiacus* and George Fuchs did it's elucidation and hence the name 'Fuchs-Holo (bi)cycle'. The primary CO_2 fixationproduct is glyoxylate. But it is not a precussor metabolite and needs a second cycle for it's conversion to the cellular building block. And hence it is named as a bi-cycle. It occurs in strain of thermophilic, non sulphur green bacteria. This pathway uses biocarbonate as their active inorganic carbon species. Since these bacteria are present in environments which are neutrophilicand alkaliphilic, the dissolved CO2 in water as bicarbonate is advantageous.

The first cycle involves synthesis of glyoxylate where in the acetyl-CoA is carboxylated to malonyl-CoA. This is further reduced to propionyl-CoA via 3-Hydroxypropionate as intermediate. Subsequent carboxylation of propionyl-CoA yields succinyl-CoA which is converted to S-malyl-CoA. The S-malyl-CoA cleaves are regenerates acetyl-CoA and releases glyoxylate. The second cycle involves assimilation of glyoxylate and it begins with the addition of glyoxylate to propionyl-CoA which via subsequent reactions is converted to citramalyl-CoA.This is cleaved into pyruvate and acetyl-CoA

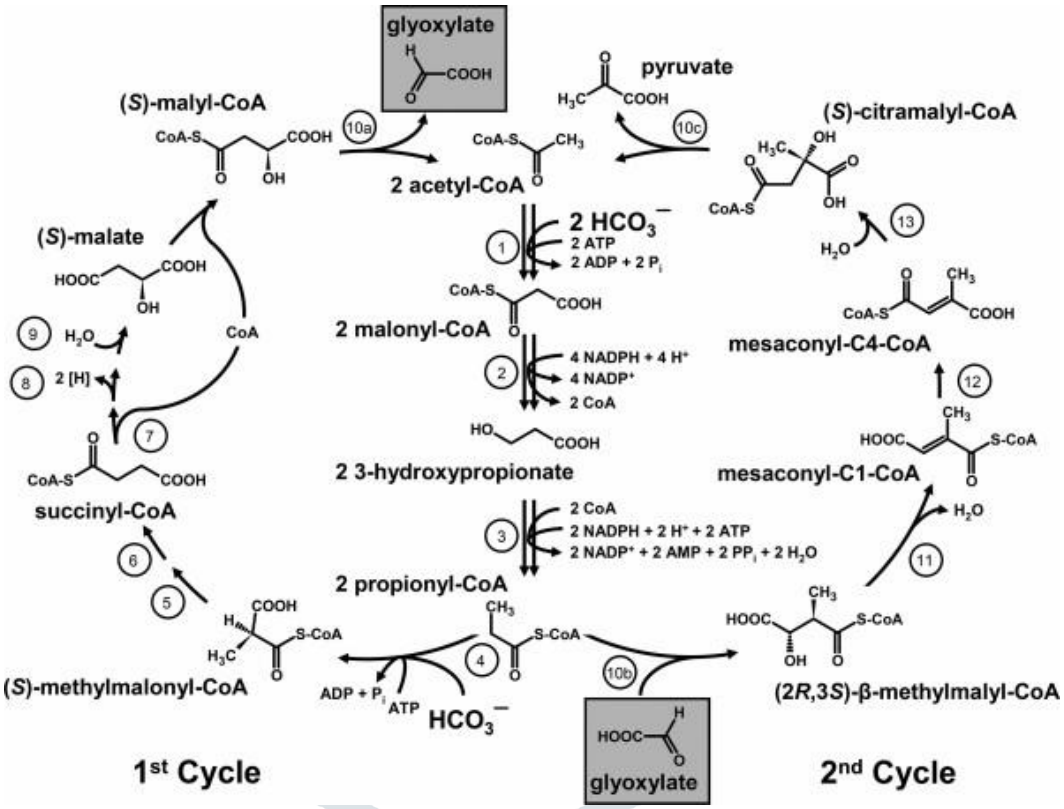


Fig. 5: The Fuchs-Holo (bi)-Cycle

Source: Berg IA. Ecological Aspects of the Distribution of Different Autotrophic CO2 fixation pathways. Applied and Environmental Microbiology. 10th March, 2011 2011;77(6):1925-1936.

3.5. The 4-Hydroxybutyrate cycles

The 3-Hydroxypropionate/4-hydroxybutyrate (HP/HB) and the dicarboxylate/4-hydroxybutyrate (DC/HB) are two CO_2 fixation cycles observed in *Crenarchaeota.* These two cycles are

collectively referred as the 4-Hydroxybutyrate cycles. In HP/HB cycle, acetyl-CoA carboxylase fixes two molecules of bicarbonate and the DC/HB cycle uses pyruvate synthase and PEP carboxylase as carboxylating enzymes. These cycles differ in their sensitivities to oxygen. The HP/HB (fig. 6. A)cycle functions in aerobic Sulfolobales whereas the DC/HB cycle (Fig 6. B). is observed in anaerobic autotrophic representatives of *Thermoprotealses* and *Desulfurocccales*.

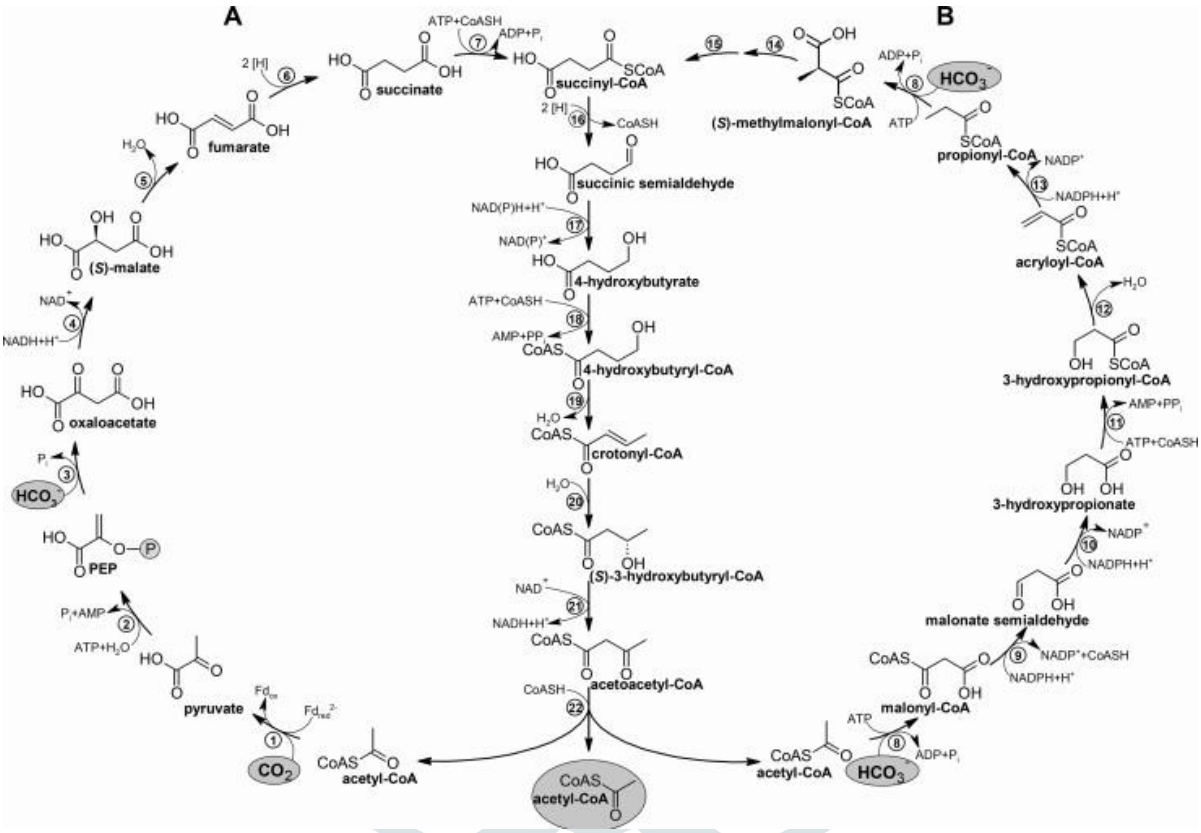


Fig. 6: The 4-Hydroxybutyrate cycles

Source: Berg IA. Ecological Aspects of the Distribution of Different Autotrophic CO2 fixation pathways. Applied and Environmental Microbiology. 10th March, 2011 2011;77(6):1925-1936.

4. Challenges facing biological carbon fixation

In the past eighty years, six natural pathways have been discovered to biological fix carbon. More pathways are expected to be known with the increase in development genome, metagenome and microbiome projects[8]. But these pathways do not meet industrial demands asthey have low efficiency and limited capacity for genetic modifications. The carbon fixating enzymes have low activity. There are many reactions steps involved which make the entire system less productive. Researchers are on a conquest to construct more efficient and effective synthetic methods.

5. Design and Synthesis of Porous Organic Polymers

The extended polymerization of one or more monomeric moieties is the essential key in the planning of POP materials. POPs do not as such have periodicity of pores but due to extended 3D-structure of organic units, they possess high specific surface area. High surface area is quite beneficial as support for loading small, reactive nanoparticles. Many polycondensation reactionshave been exploited to obtain a wide range of POP materials. To name a few, free-radical polymerization, Schiff-base condensation, thermal/chemical substitution reactions, Friedal-craft reactions, Diazo-coupling, metal-catalysed C-C homo/cross coupling reactions, thermal/solvothermal condensations [1]. Herein, few synthesis have been discussed.

5.1. POPs synthesized via free radical polymerization

Feifei Xie. et al. reported an alternating radical polymerization technique to form hypercrosslinked organic porous polymers (HCPNs)[9]. Fumaronitrile (FN) and divinylbenzene (DVB) lead to the production of a microporous organic polymer. These MOPs have intrinsic alternating copolymerization properties and hence possess defined molecular structure. The MOPs built by this method demonstrat a high surface area and amazing thermochemical stability. Due to high surface area, CO_2 uptake is also commendable. In this method, no catalystare needed. During polymerization, no byproducts are formed. Hence, this method is atom economic and green.

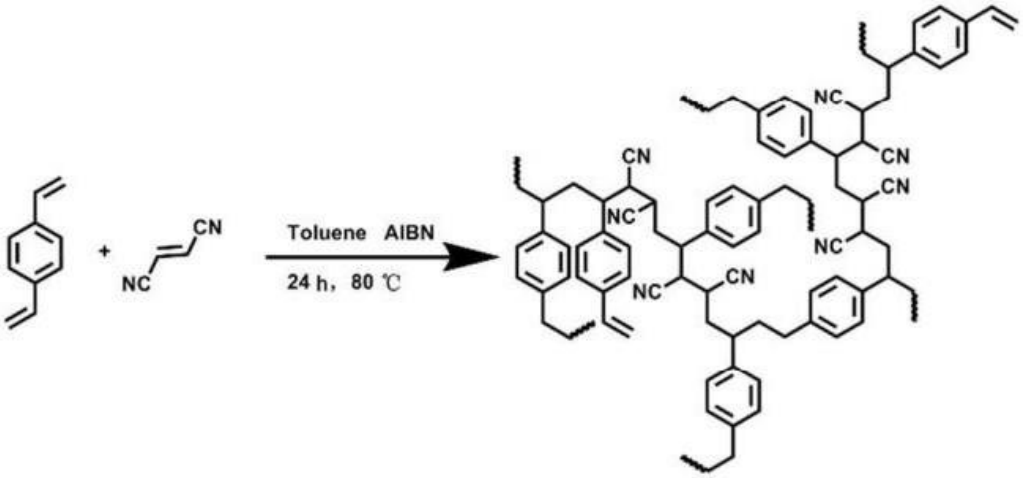


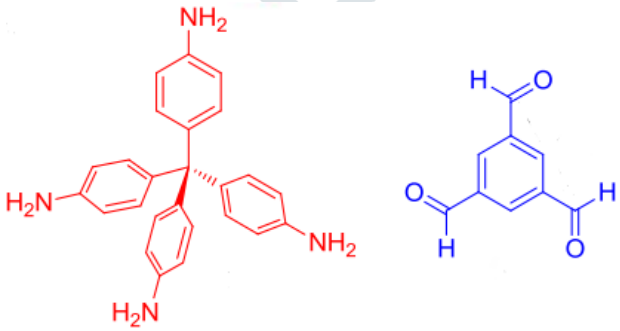
Fig. 7: Illustration of the radical polymerization of FN with DVB

Source: Feifei Xie WH, Lei Ding, Ke Tian, Zhengchen Wu and Lei L. Synthesis of microporousorganic polymers via radical polymerization of fumaronitrile with divinylbenzene. Polymer Chemistry.

In presence of azobisisobutyronitrile (AIBN) as a radical initiator, fumaronitrile reacts with divinylbenzene via free radical polymerization. On varying the mole ratio of FN to DVB, tunableporosity can be obtained along with high surface area, chemical and thermal stability. It can significantly adsorb CO_2 and act as promising material for CO_2 capture and energy storage.

5.2. POPs synthesized via Schiff base reaction

A polycondensation reaction between an aldehyde containing two or more –CHO groups and an amine having two or more primary amine site results in formation of organic framework. The synthesis of this polycondensation reaction proceeds via formation of multiple imine bonds. Wei Zhang and his group reported synthesis of [3+4] structure motifs from readily accessible buildingblocks via imine condensation[3].



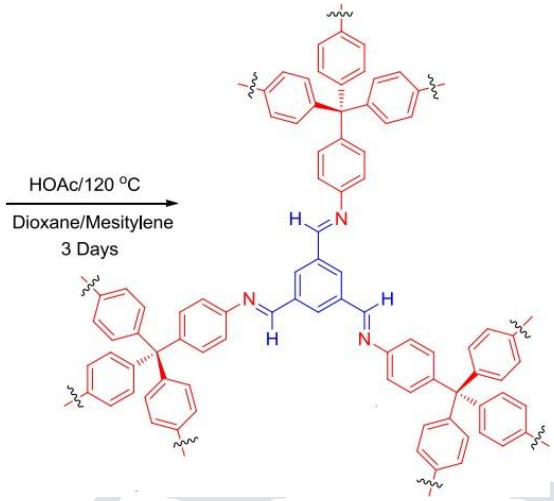


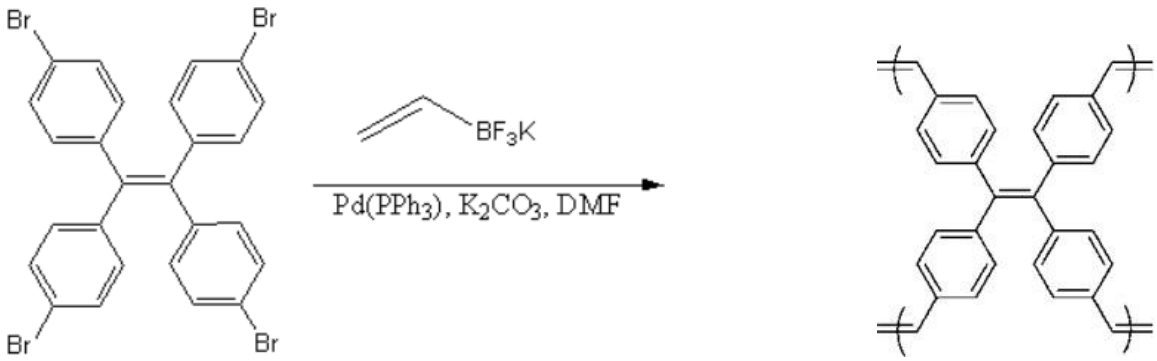
Fig. 8: tetra-(4-anilyl)-methane as the amine building block with triformyl benzene as the aldehyde monomer.

Source: Youlong Zhu HL, Wei Zhang. Imine-linked Porous Polymer Frameworks with HighSmall Gas (H2, CO2, CH4, C2H2) Uptake and CO2/N2 Selectivity. Chemistry of Materials2013;25(9):1630-1635

Amorphous POPs are formed due to unsymmetrical molecules bearing multiple amines and aldehydes and C3symmetric monomers yield crystalline COF under high vacuum conditions[1].

5.3. POPs synthesized via homo/cross-coupling reactions

C-C homo or cross coupling reactions is one of the common methods employed for designing ofPOPs. Sun et al. used Suzuki-Heck coupling reactions between aromatic halides with potassium vinyltrifluoroborate inorder to obtain microporous organic polymers. These possess fluorescent properties[10].



TBPE Microporous Organic Polymers

Fig. 8: Suzuki-Heck coupling reactions

Bohra and Wang exploited C-C cross coupling strategy for designing pi-conjugated POPs using linear and hyper-branched aromatics via C-H activation in presence of Pd catalysts. These are demanding in the optoelectronic field due to extensive pi-conjugation[11].

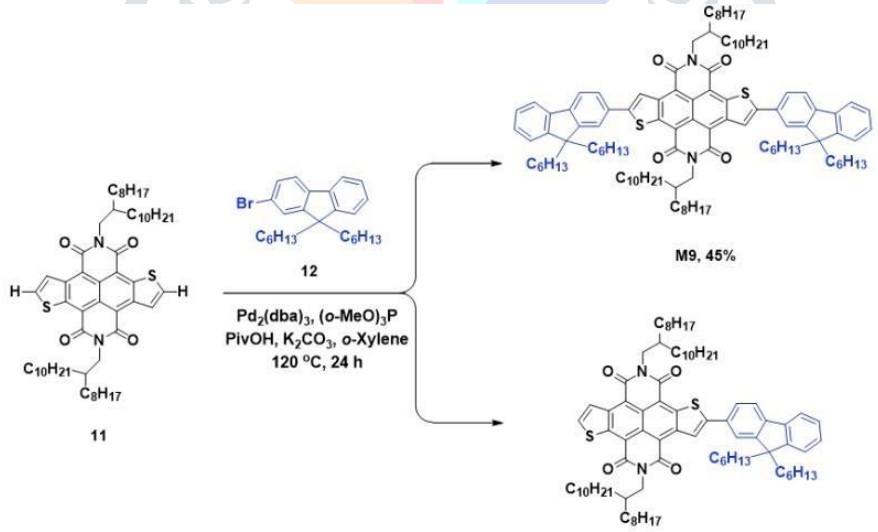


Fig. 9: Synthesis of napthodithiophenediimide (NDTI) by direct arylation coupling

Source: Wang HBaM. Direct C-H Arylation: A "Greener" Approach Towards Facile Synthesis of Organic Semiconducting Molecules and Polymers. Journal of Materials Chemistry. 2017;5:11550-11571.

5.4 POPs synthesized via Friedel-Craft polycondensation reactions

Cross linked polymers constitute a group of porous organic materials where in more than one aromatic monomers are formed through lewis catalysed polycondensation reaction. These act as heterogeneous catalysts for formation of organic fine chemicals and biofuels as these possess reactive functional groups. Microporous polycarbazoles are also a group of POPs which are generally synthesized through oxidative coupling and friedel-crafts reaction of carbazole based monomers. Tan and his group has reported a synthesis of hypercrosslinked polymer by using oxidative polymerization of different heterocyclic compounds in presence of dimethoxymethane as a cross-linker and $FeCl_3$ as a lewis acid catalyst [12]. Thiophene, Furan and pyrrole are employed as monomers which results in formation of porous polymers Th-1, Fu-1, Py-1 with microporous nature of organic framework. As these contain large amount of heteroelement, they display high CO_2 selectivity together with large number of catalytic sites/ binding sites at the pore surfaces.

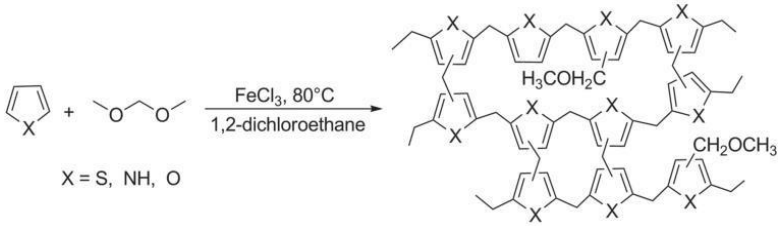


Fig. 10: Schematic representation of the synthesis of aromatic heterocyclic microporouspolymers.

Source: Yali Luo BL, Wei Wang, Kangbing Wu, Ben Tan. Hypercrosslinked Aromatic Heterocyclic Microporous Polymers: A New Class of Highly Selective CO2 Capturing Materials.

Advanced Materiald. 2012;24(42):5703-5707

5.5. POPs synthesized via solvothermal/thermal polycondensation reactions

Inter connected macrocyclic rings are formed by polycondensation reactions via aromatic substitution reaction. Modak et al. reported the use of triazine containing trialdehyde and pyrroleto obtain a POP named PPOP-1 via polycondensation reaction[13]. This consisted of triazine as well as porphyrin moieties in the polymeric network. The extended electrophilic aromatic

substitution at 2 and 5 positions of the pyrrole ring, under strong acidic pH conditions in presence of Fe(III) is stabalised by the porphyrin based polymer network. Since there is N-richporphyrin network present along with Fe(III), these show good CO_2 adsorption property.

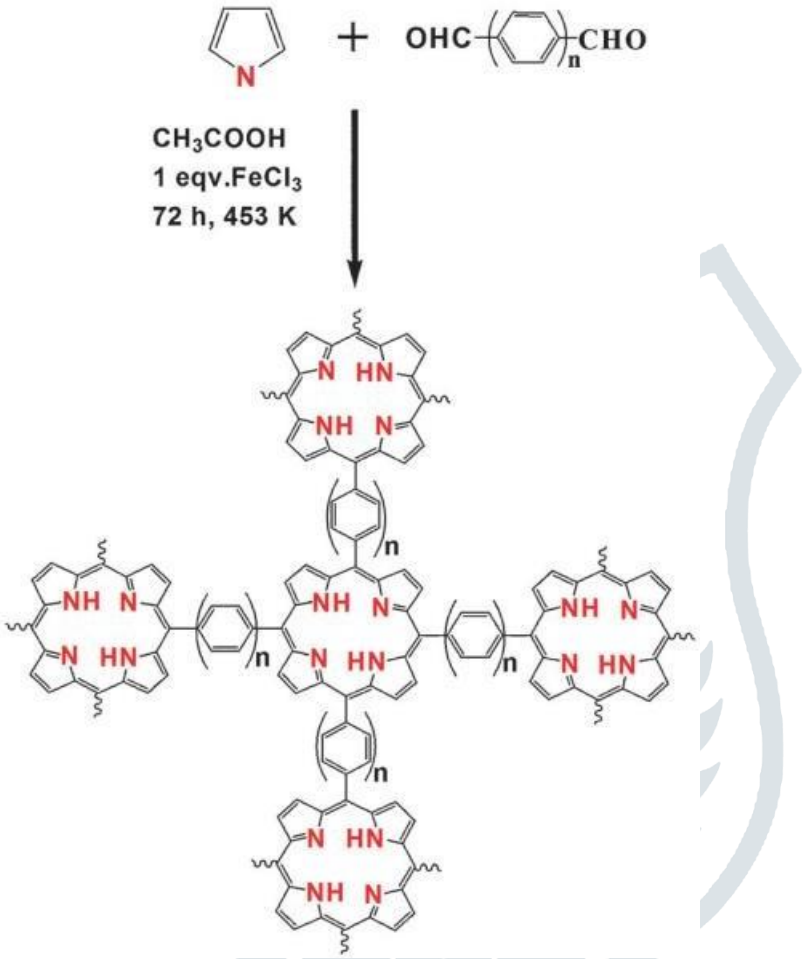


Fig. 11: Formation of molecular building blocks of Fe-POPs

Source: Arindam Modak MN, John Mondal, Asim Bhaumik. Porphyrin based porous organic polymers: novel synthetic strategy and exceptionally high CO2adsorption capacity. Chemical Communications. 2012;48(2):248-250

6. CO_2 Fixation Reactions

6. 1. CO_2 fixation over inbuilt metal centres in POPs

The Co_2-philic nature of POPs bearing inbuilt metal centres like Fe, Mn, Co, Zn can be very useful as heterogeneous catalyst for CO_2 conversion reactions. They form rigid cross-linked polymers of large molecular dimensions which are responsible for generation of large microspores and mesopores in organic frameworks[1]. Porphyrin moieties also add up as buildingblock bearing unique macrocyclic structure by introducing porosity in the organic framework.

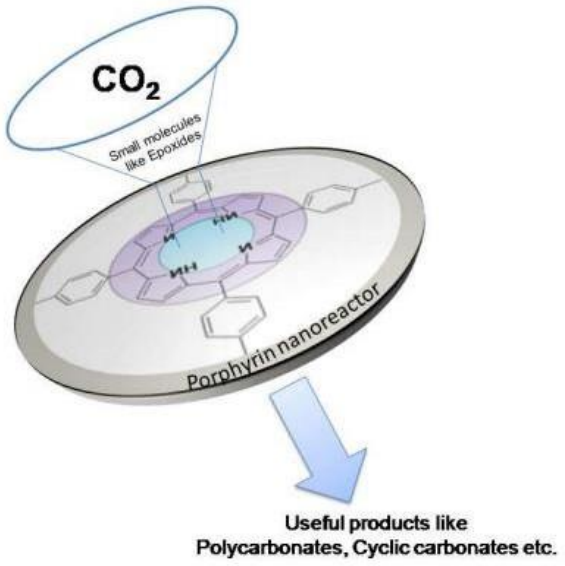


Fig. 12: Metalloporphyrin based POPs used for cycloaddition of CO_2 into epoxides.

Source: Santosh Kumar MYW, Cláudia T. Arranja, Joana de A. e Silva, B. Avula, Abilio J. F., N. Sobral. Porphyrins as nanoreactors in the carbon dioxide capture and conversion: a review. Journal of Materials Chemistry. 2015;3(39):19615-19637

Metalloporphyrins are particularly found useful for formation of epoxides via CO_2 cycloaddition (fig 12). Low amounts of metal ions are loaded in porphyrin based POPs and the turn over frequencies are very high. The robustness of the framework also offer recyclability. The CO_2 molecules interact with multiple pore surfaces simultaneously in a porphyrin nanoreactor[14].

In 1986, Inoue et al. developed first porphyrin bases homogeneous single site catalyst with an aluminium center (fig 13). CO_2 and epoxides can be converted to cyclic carbonates under solvent free conditions using a bifunctional Mg porphyrin catalyst[15](fig 14) and fig 15 gives it's plausible mechanism.

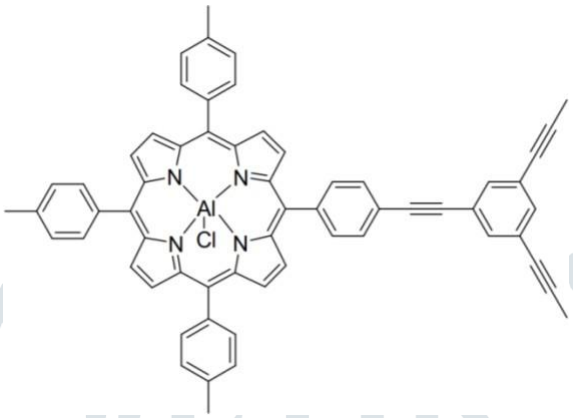


Fig. 13: Al metalloporphyrin based conjugated microporous polymer

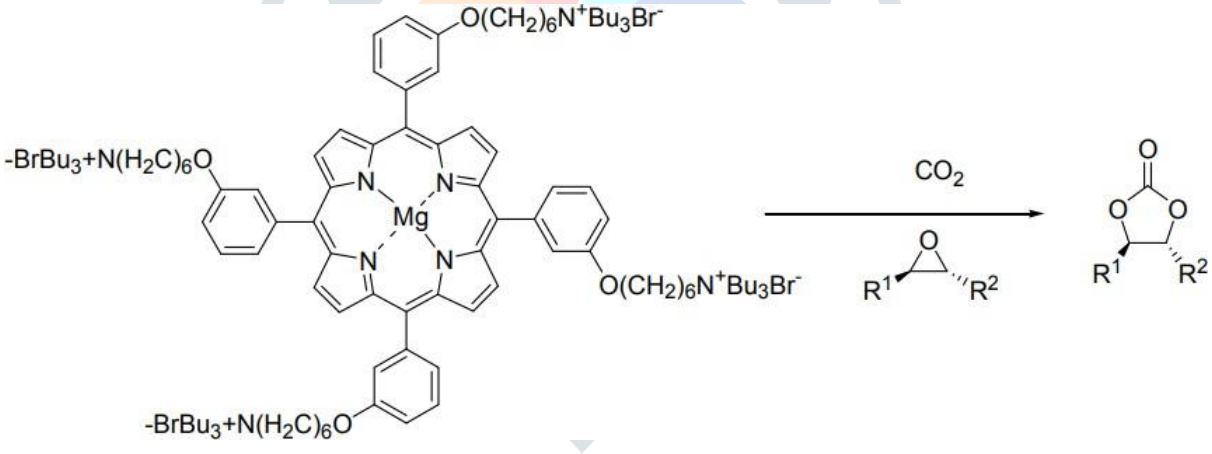


Fig. 14: Synthesis of cyclic carbonates from epoxides and CO_2

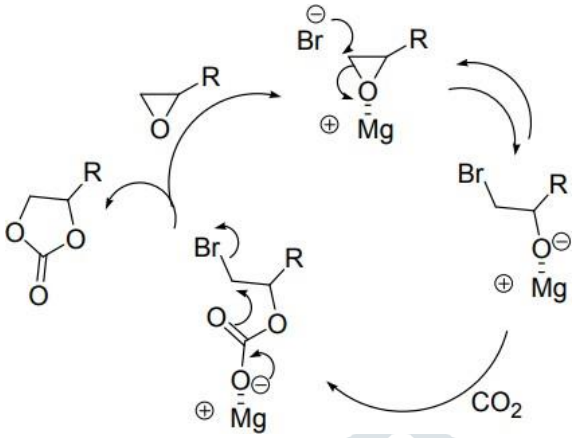


Fig. 15: Plausible mechanism

Source: Tadashi Ema YM, Shohei Koyama, Yuya Yano, Takashi Saka. A bifunctional catalyst for carbon dioxide fixation: cooperative double activation of epoxides for the synthesis of cyclic carbonates. *Chemical Communications*. 2012;48(37)

A zinc coordinated conjugated microporous polymer, referred to as Zn-CMP (fig 16) is synthesized by attaching salen zinc with 1,3,5-triethynylbenzene. It exhibits extraordinary catalytic activity towards formation of cyclic carbonates and hence is a highly efficient heterogeneous catalyst[16].

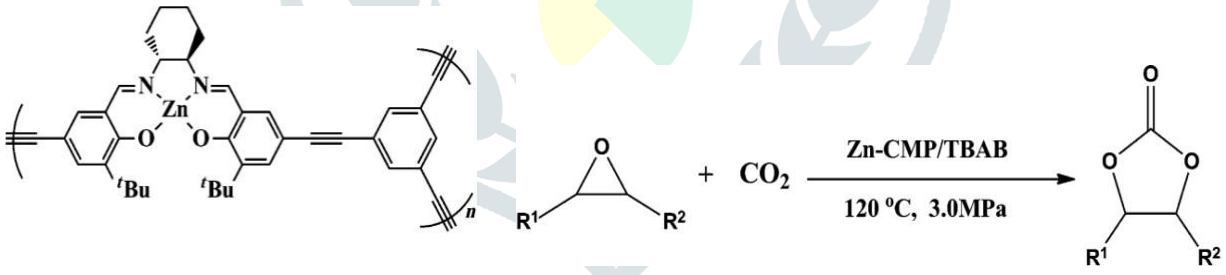


Fig. 16: Zn-CMP and it's use in synthesis of functional organic carbonates from epoxidesand CO_2

6.2. CO_2 Fixation over metal-free POPs

CO_2 is thermodynamically stable and exists in gas phase. It is a non-reactive species. It requires harsh conditions like high temperatures, pressure and catalysts to activate and react to give

organic molecules. To activate the CO_2, catalysts need to have basic sites where as to activate the substrates, the catalyst needs to have acidic, basic or reactive metal site. Cao et al. reported the synthesis of porous cationic covalent triazine frameworks (CCTFs) (fig 17) by employing cyano funtionalized imidazolium moiety in the porous organic framework[17]. The positive charge of the imidazolium ion helps in adsorption of CO_2 at the pore surface via dipole-quadruple interactions.

Guanidine, ionic liquids and N-heterocyclic carbenes are highly CO_2-Philic in nature and can easily be incorporated in POP network using respective monomers. In presence of CO_2, guanidine based organocatalyst can efficiently catalyse the synthesis of imidazolidin-2-ones and oxazolidinones from primary and secondary propargylamines. These offer synthesis of linear and cyclic urea via CO_2 fixation in amines. Ionic liquids, as homogeneous organocatalyst can effectively catalyse the synthesis of quinazoline-2,4-dione via fixation of CO_2 in 2- aminobenzonitrile.

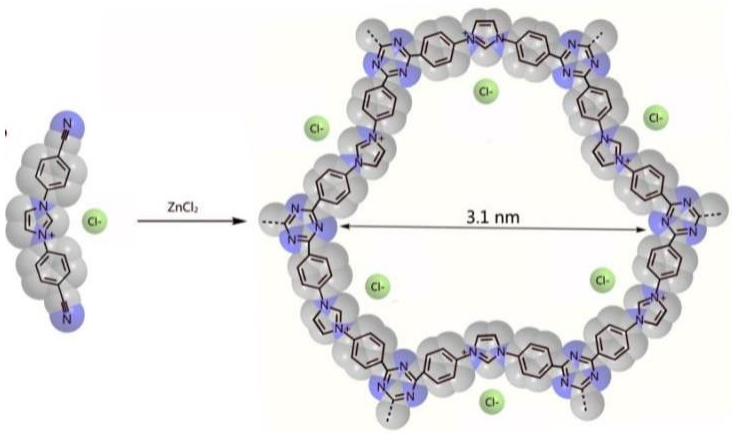


Fig. 17: Synthesis of CCTFs

Source: Tao-TAo Liu J-DY, Jung Xu-Sheng Wang, Peng-Chao Shi, Yuan Biao Huang, Rong Cao. Imidazolium-Based Cationic Covalent Triazine Frameworks for Highly Efficient Cycloaddition of Carbon Dioxide. ChemCatChem. 2018;10(9):2036-2040

6. 3. CO_2 fixation reactions over supported POPs

Reactive metal nanoparticles are stabilized effectively in POPs containing N-rich centres. Liu and his group reported synthesis of CarPy which has tubular morphology[18]. It is formed by using

pyridine-containing carbazole, 2,6-di(9H-carbazol-9-yl-pryridine) (Fig. 18) . It is formed via freeradical oxidative coupling polymerization and is catalysed by $FeCl_3$ in presence of Chlorofrom. On this, with the help of reductive deposition, CarPy-CMP@Ru (supported Ru nanocatalyst) is synthesized. CarPy-CMP@Ru is employed in N-formylation reaction via CO2 fixation on amines in presence of H2 under pressure (Fig. 19)

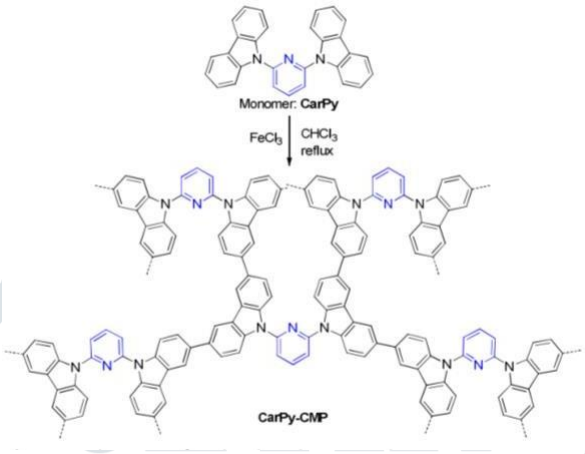


Fig. 18: Synthesis of CarPy-CMP

Source: Zhenzhen Yang HW, Guiping Ji, Xiaoxiao Yu, Yu Chen, Xienwie Liu, Cailing wu, Zhimin Li. Pyridine-functionalized organic porous polymers: applications in efficient CO2 adsorption and conversion. New Journal of Chemistry. 2017;(8):2869-2872

Fig. 19: Formylation of piperazine with CO2 , H2 catalysed by CarPy-CMP@Ru

NPs supported POPs are also seen to enhance the electrochemical reduction of CO_2 to methane, methanol and ethylene. Alkordi and co workers have studied the interaction of POP and carbon nanotubes. These improve the catalytic activity of the material enormously as they induce rigidity (fig 20)[19]. These are quite useful in electrochemical reduction of CO_2.

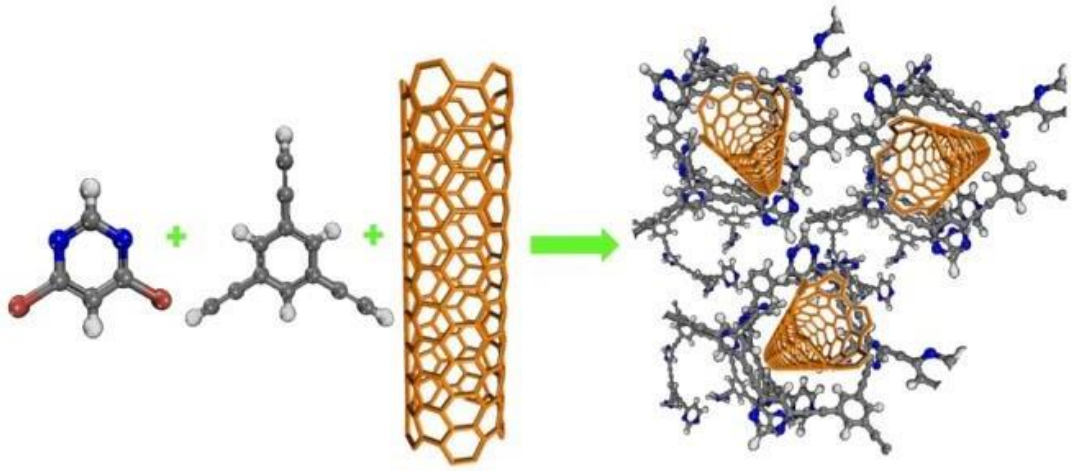


Fig. 20: POPs with multi-walled carbon nanotubes

Source: Rana R. Haikal ABS, Muhamed Amin, Stavros G. Karakalos, Youssef S. Hassan, Ahmed M. Elmansi, Inas H Hafez, Mohammed R. Berber, Abdou Hassanien, Mohammed Alkordi. Synergism of Carbon Nanotubes and Porous-Organic Polymers (POPs) in CO2 Fixation: One-pot Approach for Bottom-up Assembly of Tunable Heterogeneous Catalyst. Applied catalysis b-Environmental. 2017;207:347-357.

Conclusion

All the synthetic routes discussed above for designing POPs have multiple possibilities to tune the surface properties depending on the nature of functional group, shape, size and symmetry of the building molecular units. POP framework can be synthesized with introduction of highly reactive metal centres, fluorescent building blocks, pi-conjugated networks and post surface functionalization; these make them ideal candidate as catalyst to carry out chemical, photochemical and electrochemical reduction of CO2. The aromatic moieties in the organic framework can be functionalized such that the reactive functional groups help in yielding materials with enhanced CO2 capture property and its subsequent conversion reactions. POPs result in new materials with interesting properties which can be employed to explore frontline applications of energy, environment. The heteroelements in POP not only enhance the CO2 uptake but also help to promote the CO2 fixation reactions for the synthesis of value added organic fine chemicals and fuels in atom economic, green and facile way. These POPs can therefore act as adsorbent and C1 source in CO2 fixation reactions and contribute significantly in constructing a future low-carbon global economy. As for future perspectives, the study of decomposition of these

polymers would help to reflect on it's sustainability. More efforts should be made to design metal free organic polymers which would be cost efficient and green.

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