Iranian Journal of Catalysis Spotlight 11(4), 2021, 417-424

IRANIAN JOURNAL OF CATALYSIS

Catalytic applications of porous organic polymers

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

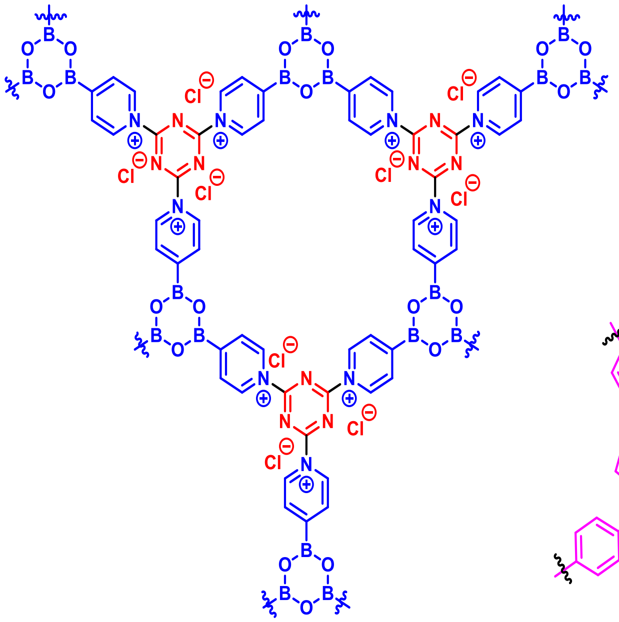
Porous organic polymers (POPs) as one of the major domains of porous materials have apivotal role in modern sciences and technologies. POPs have the advantages of both polymers and porous matrials [1-3]. Due to the excellent properties, such as large accessible surface areas, tunability of pores, designability and excellent thermal stability, POPs have found many privileges and tremendous applications in the different areas including catalysis, gas storage, gas separation, charge carriers, sensors, and optoelectronic [4-6]. Generally, POPs are devided into covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), ionic porous organic polymers, hypercrosslinked polymers (HCPs), conjugated microporous polymers (CMPs), etc. [7-11]. COFs due to reversible chemical synthesis and subsequently repair of structural defects have a good crystalline framework. These reactions include Schiff base reaction, Knoevenagel condensation, Ullmann reaction, spiro-borane condensation, imide condensation, and trimerization of nitrile or borazine. For the synthesis of other subset of POPs, Suzuki cross-coupling reaction, Yamamoto reaction, Sonogashira–Hagihara reaction, oxidative coupling, Schiff base reaction, cyclotrimerization, phenazine ring fusion reaction, and Friedel-Crafts arylation can be named [12-16].

There are different methods for the synthesis of POPs. The most prominent methods for the synthesis of POPs include the solvothermal, microwave, ionothermal, mechanochemical, interfacial and ambient conditions synthetic manners [17-19].

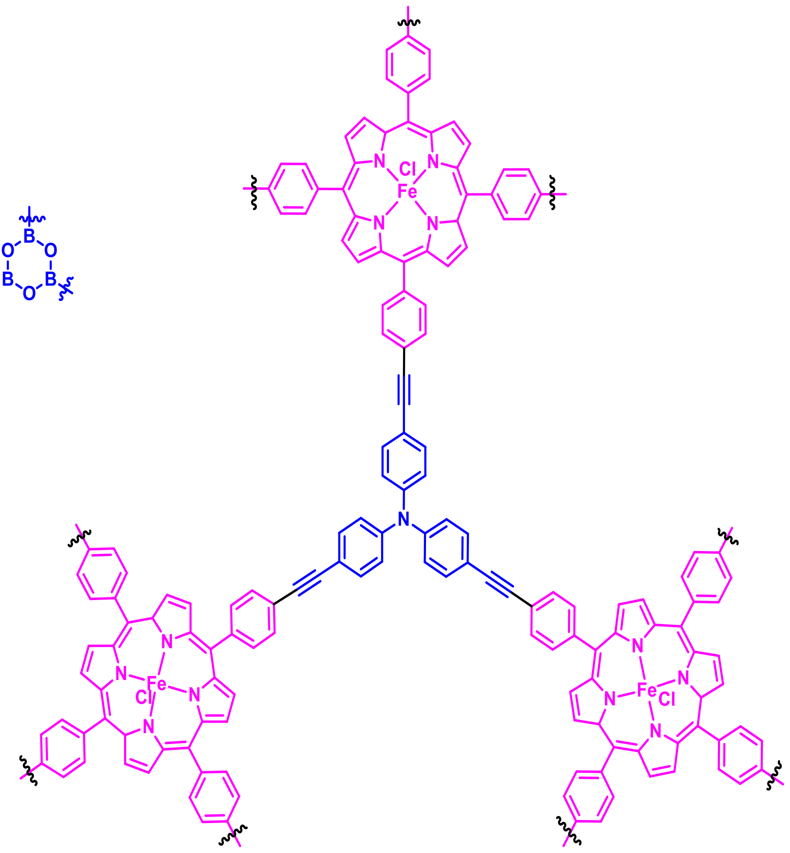
Despite suitable immobilizability and stabilizability of MOFs and COFs, their reversible attributes and physicochemical instability against environmental conditions limit their applications compared to POPs [20-21]. Nevertheless, POPs can be a robust tool in the chemistry of catalyst and have attracted the attention of many scientists. POPs, due to high designability, can be functionalized with organocatalyst groups, acidic/basic groups, ionic groups, chiral ligands and organic ligands. Moreover, POPs with catalytically active metal centers are a bridge between homogeneous and heterogeneous catalysts [22-25].

POPs have both potential of homogeneous and heterogeneous catalysts. They have a good activity similar to classic homogeneous catalyst and they are easily separated from the reaction mixture and can be recycled several times similar to classic heterogenous catalyst [22].

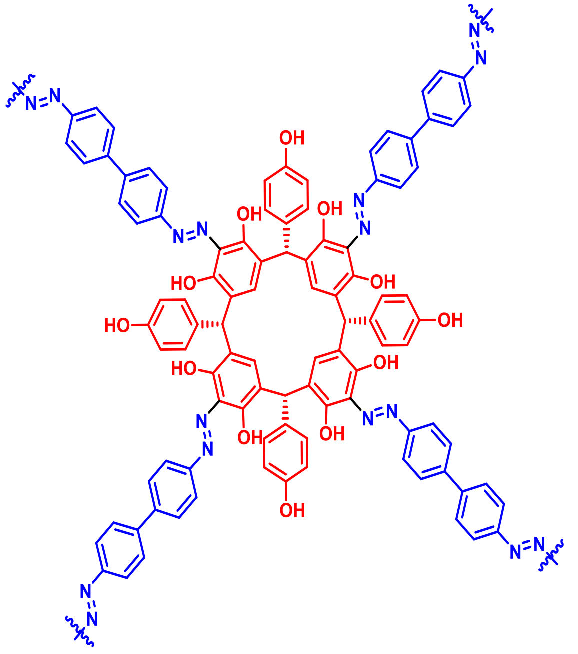
Some of the applications of POPs are shown in the **Scheme 1**. In this spotlight, I am going to highlight the catalytic applications of POPs.



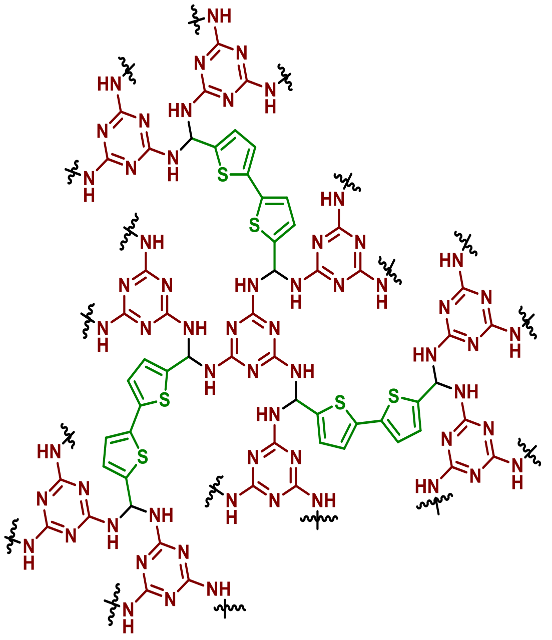
Antibacterial material



Peroxidase mimics for sulfide ion colorimetric sensing



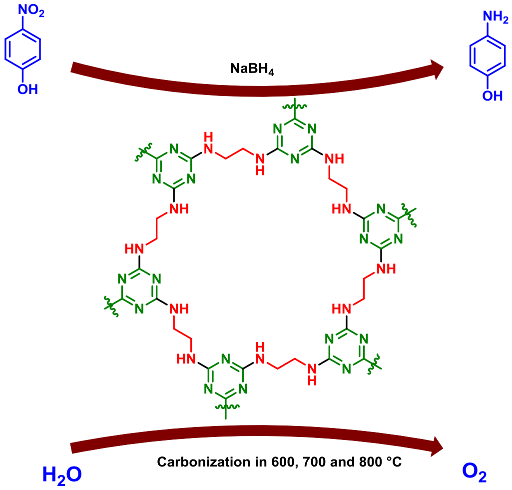
As catalyst in CO_2fixation



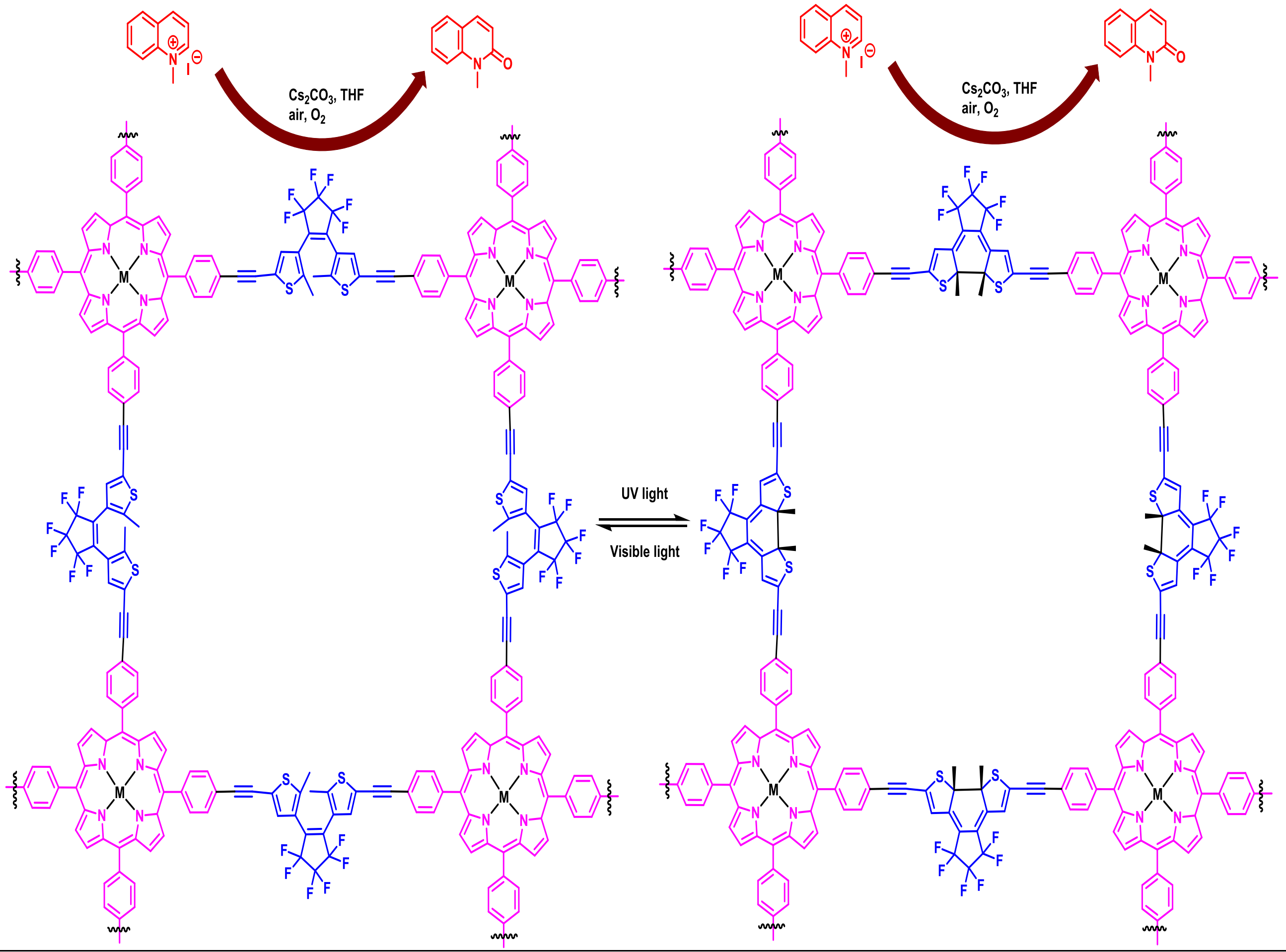
Capture of CO_2 and iodine

Abstracts

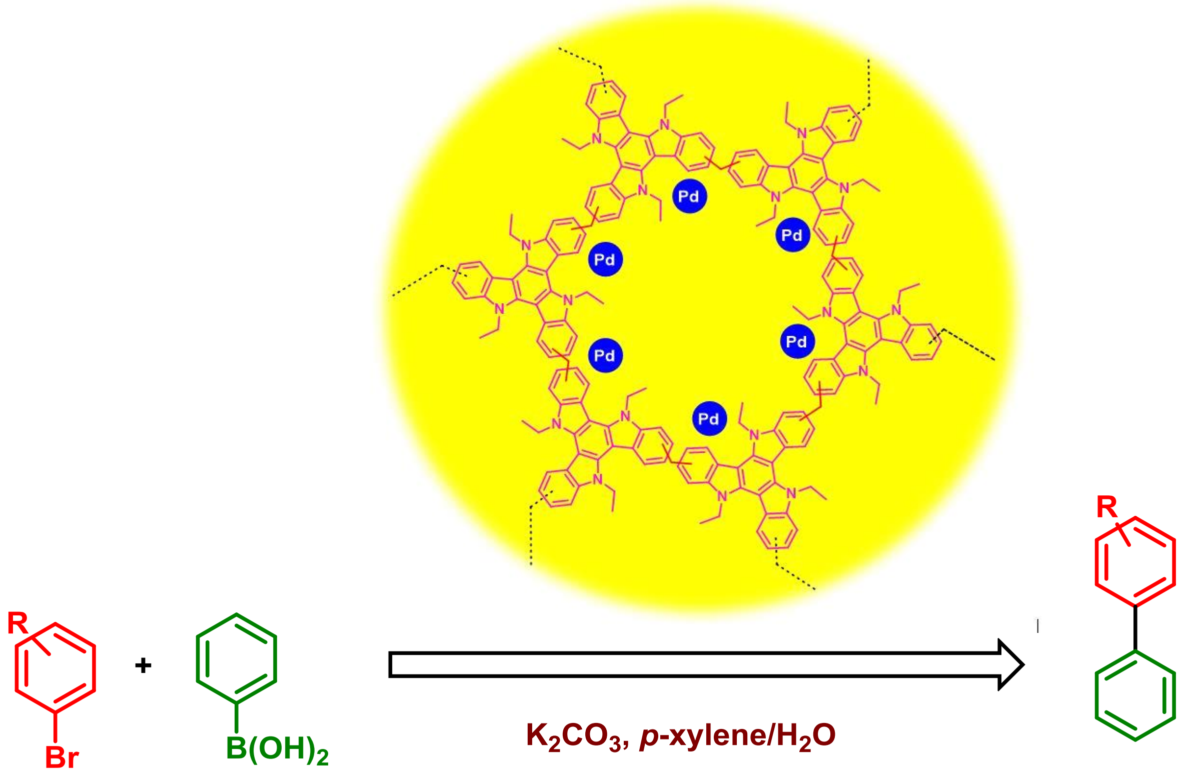
(A) In 2018, Kathiresan et al. reported POP based on triazine and ethylene diamine as an effective catalyst for evolution of oxygen and reduction of nitrophenol. They carbonized the mentioned POP at different temperatures, and carbonation at 700 °C had the best results for oxygen evolution reaction (OER). This system has an excellent stability with an overpotential of 580 mV and the current density was 300 mA/cm^2 for oxygen evolution reaction and it is better than metal-free catalysts and other metal-based OER catalysts. Moreover, the reported POPs have excellent catalytic activity in the reduction of nitrophenol and the reaction was relatively performed in less time compared to other reported mehods [26].



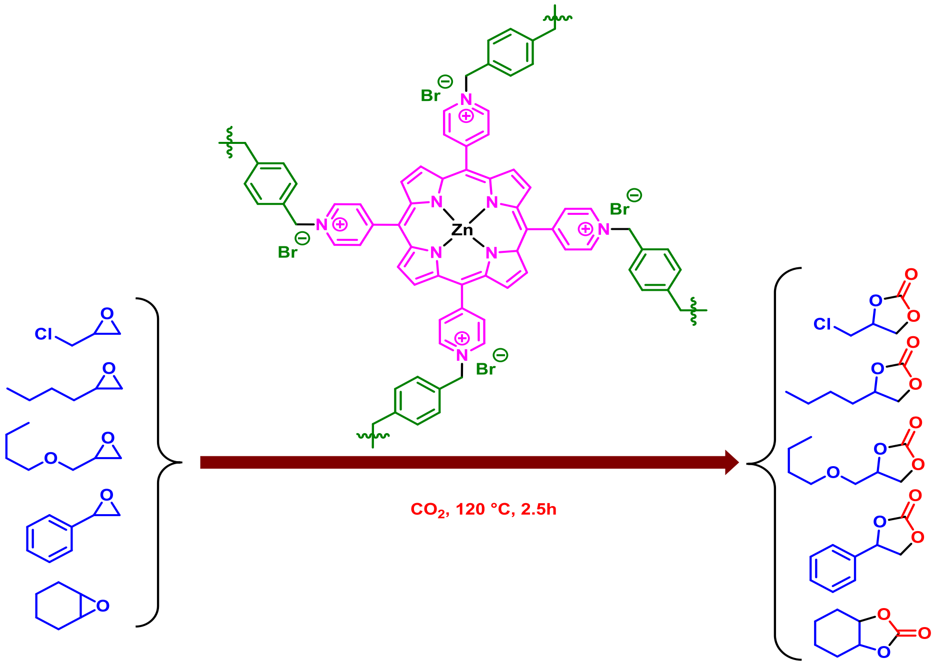
(B) Sonogashira-Hagihara coupling reaction was applied for the synthesis of new series of POPs. Wang and coworkers described a photoswitchable dithienylethene with metal-free 5,10,15,20-tetrakis(4-iodophenyl)porphyrin and its metal derivatives based photoswitchable catalyst for the oxidation of *N*-methylpyridinium salts with visible light conditions. This system, due to high specific surface area and controlling the behavior of the catalyst in different light irradiations, has a prominent role in photocatalytic reactions [3].



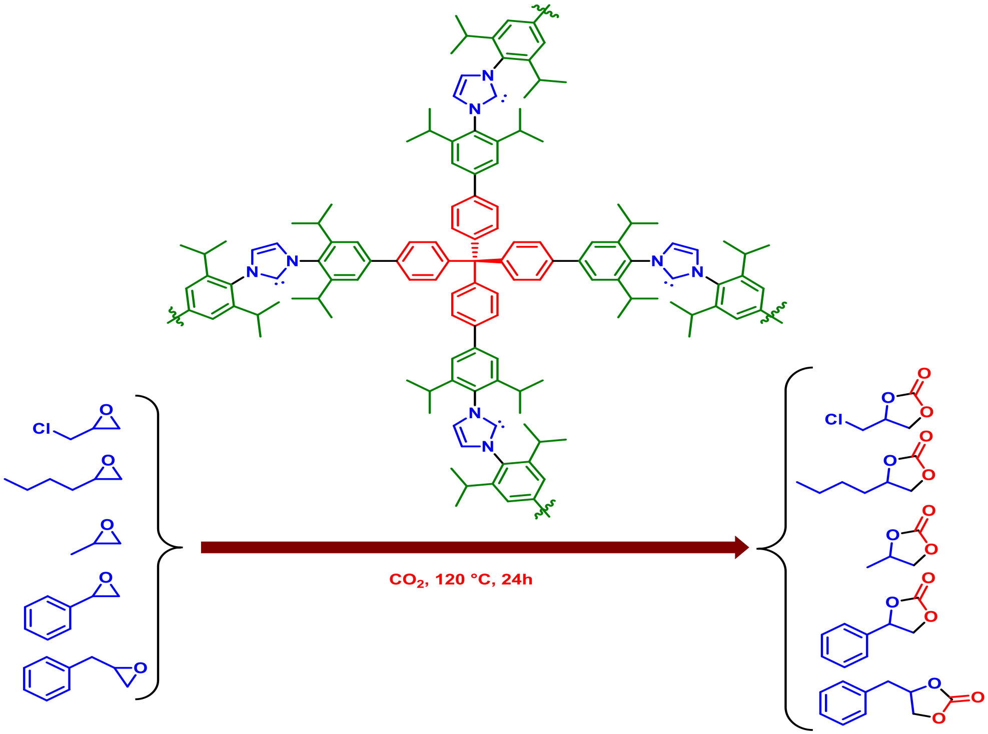
(C) In 2020, Sadak and coworkers reported a new hypercrosslinked microporous organic polymer network with a trimer indole building block using Friedel–Crafts alkylation reaction. This POP has a robust potential in gas adsorptions and catalytic application in Suzuki-Miyaura coupling reaction and also has a good stability in a different chemical and thermal conditions [27].



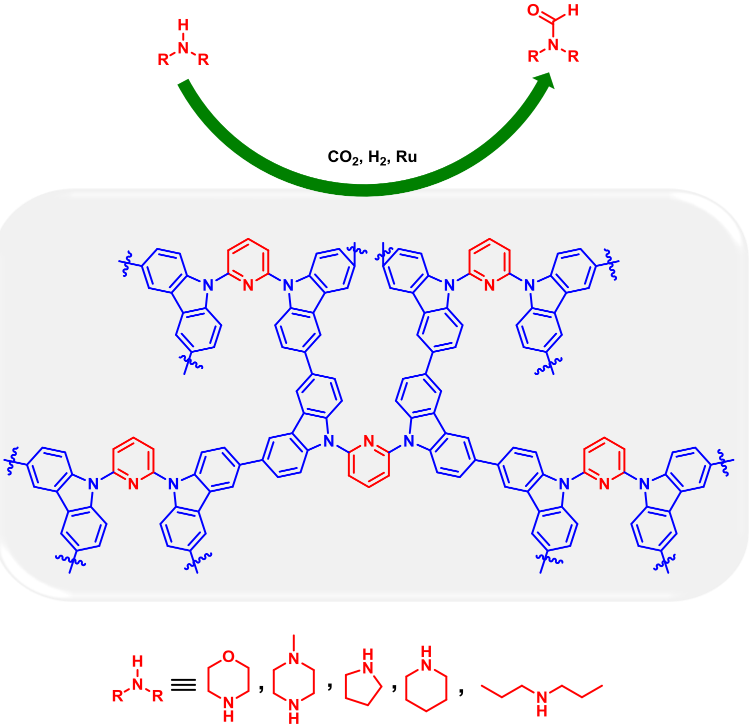
(D) Ionic porous organic polymers (IPOPs) as one of the most important subsets of POPs have multiple active sites in their structure. Nonetheless, these systems have an extraordinary potential in areas of catalyst. In 2017, Yang and coworkers developed a cationic porphyrin-based polymers supported on carbon nanotubes as heterogeneous catalyst and desired catalyst was used in CO_2 fixation reaction under solvent free conditions [28].



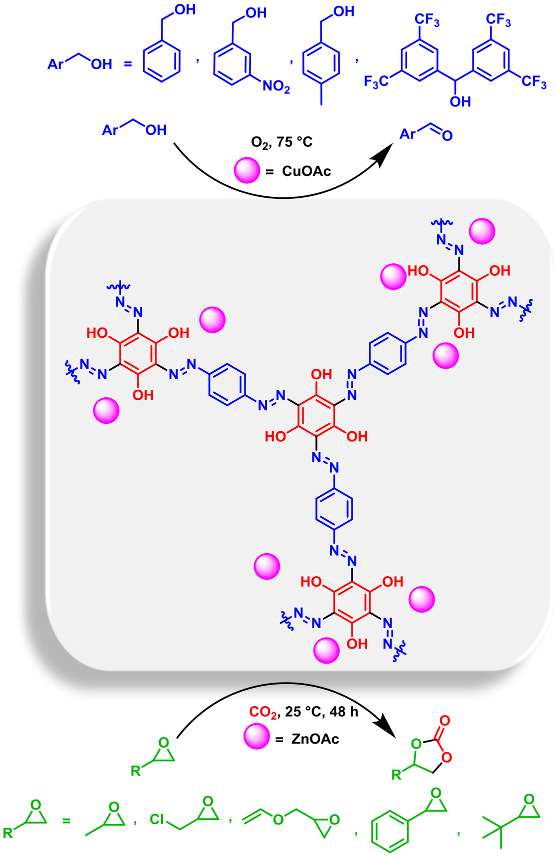
(E) Trapping of CO_2 and conversion of it into valuable chemical product always attract more attention of environmental and industry areas. Sterically-confined *N*-heterocyclic carbenes were extensively used for CO_2 fixation. It is demonstrated that *N*-heterocyclic carbene based nanoporous polymer showed exceptional CO_2 fixation up to 97% at room temperature. This result is better than all previous reports on carbene based materials measured in the solid state [29].



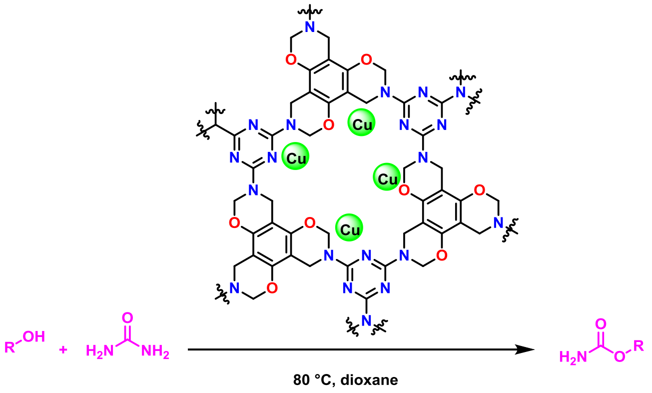
(F) Pyridine-functionalized POPs have excellent properties for CO_2 capture. In 2013, Liu used the pyridine-functionalized POPs as an efficient CO_2 absorbent catalyst and formylation of amines. This system has good CO_2 uptake capacity (up to 63 and 171 mg g^{-1} at 0.1 bar and 1 bar at 273 K) and is a good support for Ru(0) nanoparticles. Moreover, amine groups were activated through hydrogen bonding interactions with pyridine cores [30].



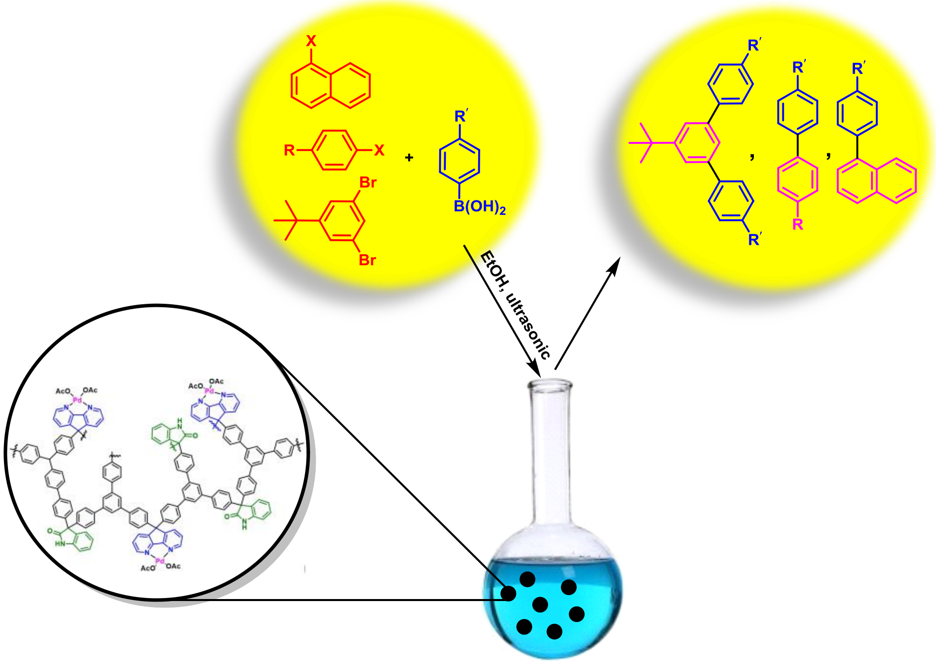
(G) Synthesis of the phenolic azopolymers based on diazocoupling reactions is one of the most important synthetic routes for design and synthesis of novel POPs. Nevertheless, this strategy deserves more attention. In 2016, Liu synthesized phenolic azopolymers based on diazocoupling reaction in an aqueous solution under mild conditions. These systems have a high ability to form Cu^{2+}, Zn^{2+} and Ni^{2+} complexes. These catalysts have a fantastic performance for CO_2 fixation and oxidation of alcohol with high efficiency [31].



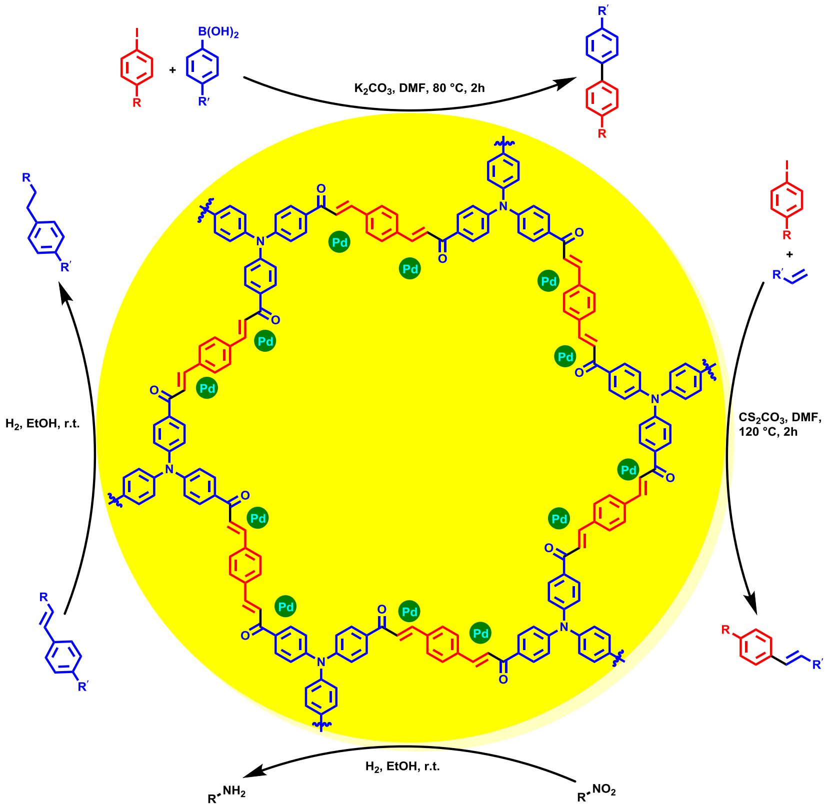
(H) Carbamates were synthesized from amines and alcohols using phosgene ($COCl_2$) as the carbonyl source. Nevertheless, this method has low atom economy, large amount of toxic waste production and harmful reagent such as phosgene which was applied for the synthesis of carbamates. Islam et al. introduced an essential and drastic method for the synthesis of carbamates. They used organic polymer-based (Cu-NPs@TzTa-POP) material as a catalyst for the synthesis of carbamate derivatives. Different benzylic alcohols, phenols and heterocyclic alcohols were used as alcohol sources. Recyclability and reusability of the catalyst without substantial loss of active Cu metal are undeniable [32].



(I) In 2020, Miguel and coworkers designed new microporous POPs anchored palladium(II) that was synthesized by the reaction of 1,3,5-triphenylbenzene and ketones with electron-withdrawing groups, 4,5-diazafluoren-9-one and isatin. Catalytic application of this POP was investigated in Suzuki−Miyaura reactions. The main benefits of this catalyst are performing the reaction in green solvent under aerobic conditions, using low amount of metal and good recoverability of catalyst by washing in EtOH [33].



(J) Synthesis of POPs based on aldol condensation between aldehyde and ketones is almost unknown. In 2020, Moorthy et al. synthesized new series of POPs by aldol condensation reaction of dialdehydes and tri or tetraacetyl ketones that have tolerable gas sorption properties and stabilized remarkably Pd akin to the manner of Pd(0). This catalyst was successfully applied in different reactions such as Suzuki, Heck reactions and reduction reactions such as nitro-to-amine and hydrogenation of olefins. All of reactions have a good yield and were performed in mild conditions. [34].



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