

ABSTRACT

This thesis entitled “*Porous Organic Polymers with Amide Functionality: Synthesis, Characterization and Applications in Organic Transformation Reactions*” consists of six chapters.

CHAPTER 1

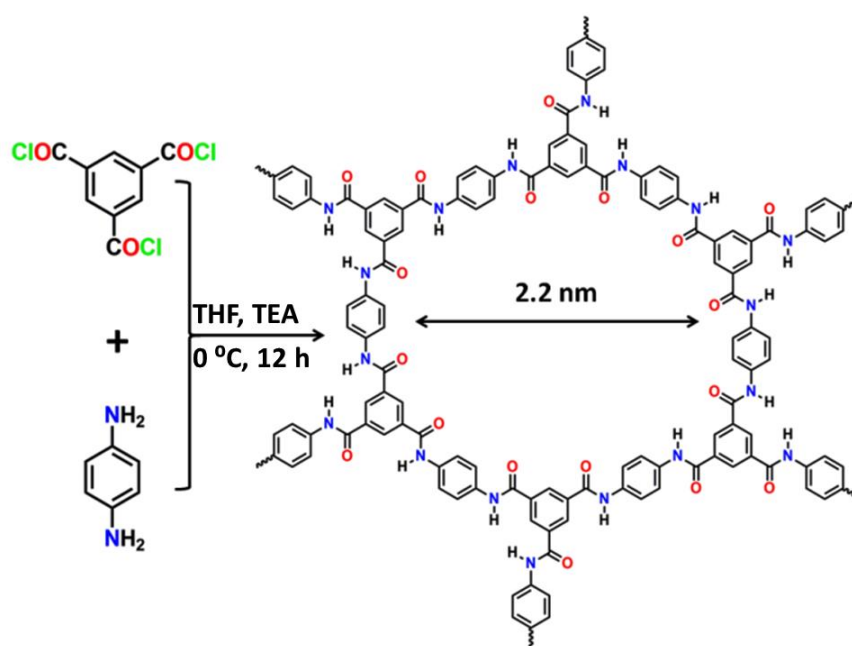
Introduction: Porous Covalent Organic Polymers

Linking organic molecules by covalent bonds into extended porous organic polymers (POPs) has become an important strategy in chemical and materials system, because these materials exhibit fantastic applications in the field of catalysis, drug delivery, gas storage/separation, conduction, energy storage and conversion, biodiesel production, biomedicine, bio-refinery etc [1-12]. In general, POPs are referred by various nomenclatures depending on the chemical environment of the structural integrity, pore size ranging from micro to macropores and the crystallinity of the networks. They are composed of light elements (i.e. B, C, N, O, Si) which can lead to formation of strong covalent bonds such as B–O, C–N, B–N, B–O–Si etc. that link the organic units. Perhaps, obtaining crystalline materials of such extended solids such as covalent organic frameworks (COFs) and covalent triazine frameworks (CTFs) draws special interest because of its precise control of the geometry and functionality [13-17]. Elsewise extended solid results in amorphous POPs which has also demonstrated recently as equally important as COFs/CTFs. Essentially these materials have become an attractive class of new promising porous materials for energy applications, solid supports for catalysis, optoelectronic devices and drug delivery. In this chapter, we summarize a succinct background of POP materials, design construction and properties with few recent examples in directing structural organization for a purpose. Chapter 1 also provides the staple information about synthesis of several novels POPs during the course of Ph.D. tenure and discussed in the subsequent chapters. The role of π -electronic clouds exhibited by them as organocatalyst in selective alcohol oxidation and in olefin cleavage is emphasized in Chapter 2 and Chapter 4 respectively. Use of these POPs as catalytic scaffold for heterogeneous catalysis in performing nitroarenes reduction and C–H activation reactions are discussed in Chapter 3 and Chapter 5. The concluding chapter, i.e. Chapter 6 briefs the summary of the work encompasses in the thesis with future prospective.

CHAPTER 2

Two Dimensional Amide Linked Porous Polymer as Organocatalyst to Promote Selective Oxidation Reactions

This chapter reports the synthesis of a novel porous polymer framework with [3+2] structure motif via the condensation of 1,3,5-benzenetricarbonyl trichloride and *p*-phenylenediamine (Scheme 1). The resulting highly stable mesoporous 2D framework material (hereafter POP-Am) was characterized using FT-IR, TGA, PXRD, BET, SEM, TEM and ^{13}C CP-MAS analytical techniques. The POP-Am exhibits continuous conjugation of π -electronic system supported by solid state UV-Vis DR spectroscopy. Apart from gas adsorption properties, this material shows remarkable catalytic activity in selective oxidation reactions manifested by low band gap of the conjugated π -cloud and presence of amide functionality (Figure 1). Utmost selectivity of the reaction that exclusively yielded aldehydes from benzyl alcohols via a free radical pathway is proposed supported by computational endorsement on Dmol3 and Gaussian09 platforms. Formation of products was monitored by NMR spectroscopy and GC-MS analysis. This POP-Am is found to be one of the rare cases of any organic polymer material acting as an outstanding organic catalyst with no metal add-ons.



Scheme 1 Schematic representation of synthesis of mesoporous POP-Am.

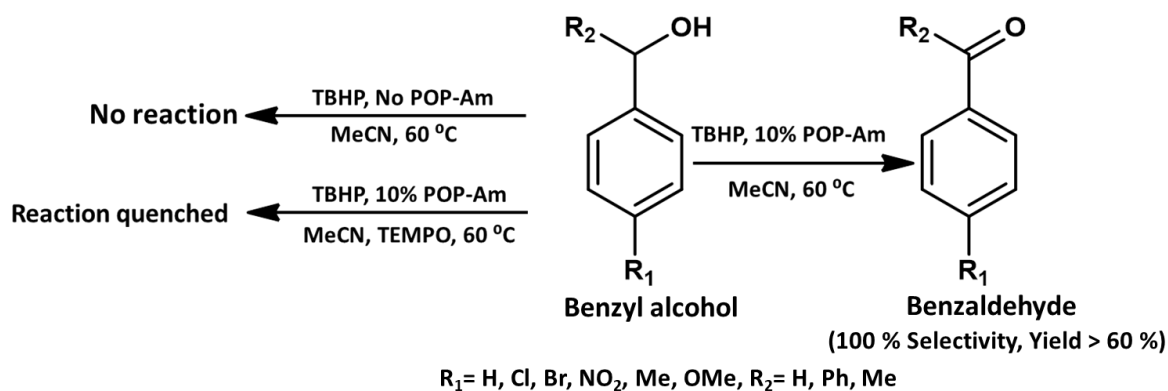
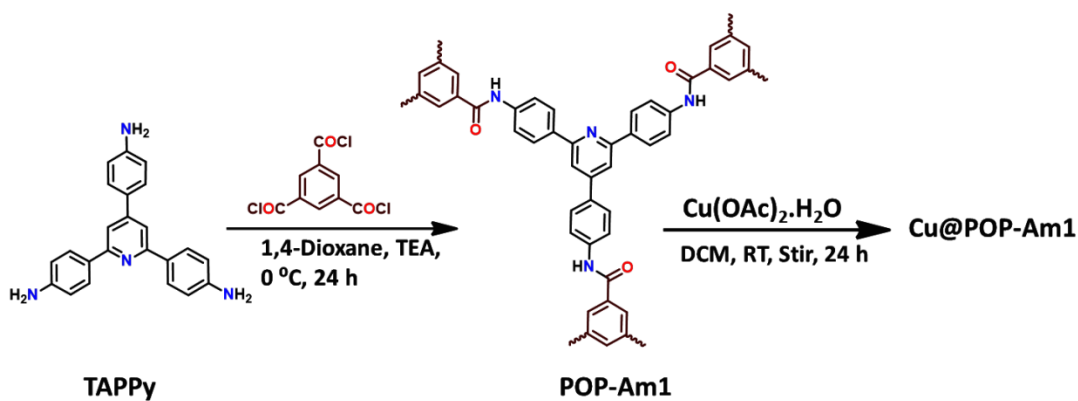


Figure 1 Oxidation of benzyl alcohols to afford benzaldehydes selectively using POP-Am.

CHAPTER 3

Impregnated Cu(II) onto a pyridine-based porous organic polymer as robust heterogeneous catalyst for nitroarenes reduction

Chapter 3 demonstrated the synthesis of pyridine based microporous organic polymer (Scheme 2) that acts as an efficient heterogeneous catalyst promoter. The porous polymeric material (hereafter POP-Am1) was synthesized from 2,4,6-tris-(4-aminophenyl)pyridine (TAPPy) and trimesoyl chloride and characterized using FT-IR, TGA, PXRD, solid state NMR, SEM, TEM and BET analytical techniques. The characterized polymer has been further subjected to impregnate Cu into the pores. The pyridine based POP loaded with copper (hereafter Cu@POP-Am1) was characterized recording SEM-EDX, AAS and ICP analysis. The Cu@POP-Am1 has been employed as a heterogeneous catalyst for nitroarenes reduction and reported as an excellent catalyst with improved performances over those reported using expensive and precious metals (like Au and Pd) immobilized on organic porous materials (Figure 2). The reaction progress was monitored by UV-Vis spectroscopy at room temperature. The oxidation state of Cu in the catalytic cycle is corroborated with XPS analysis. This study also emphasizes the role of π -electron rich organic porous polymer as promoter of electronic stature of finely dispersed Cu sites accountable for the excellent catalytic activity towards nitroarenes reduction.



Scheme 2 Schematic representation of the synthesis of pyridine based POP-Am1 followed by Cu(II) impregnation onto POP-Am1 (i.e. Cu@POP-Am1).

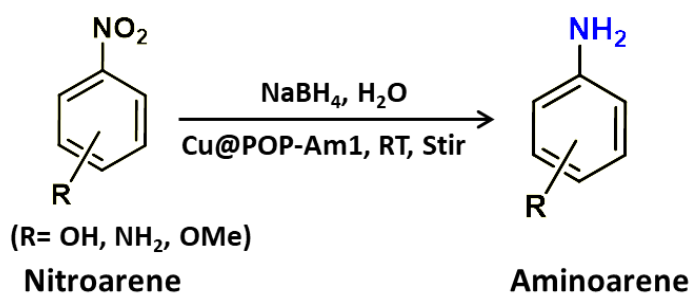


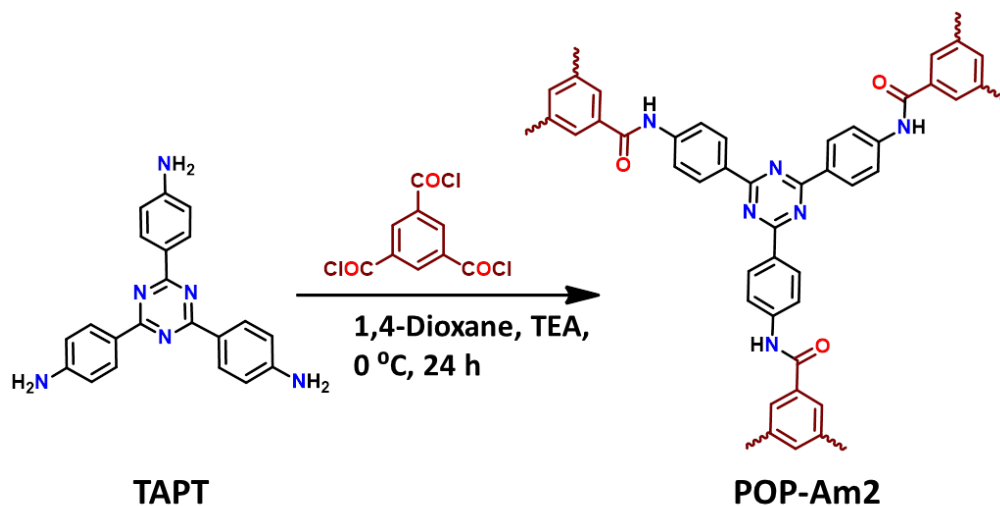
Figure 2 Cu@POP-Am1 acting as a heterogeneous catalyst carrier in nitroarenes reduction.

CHAPTER 4

Triazine-based porous organic polymer for selective oxidation of α -aryl substituted olefins cleavage into benzaldehydes

A nitrogen rich microporous organic polymer with amide linkage have been synthesized solvothermally by the condensation of 2,4,6-tris-(4-aminophenyl)triazine (TAPT) and trimesoyl chloride (Scheme 3). The triazine based porous polymer (hereafter POP-Am2) was characterized employing the thermal (TGA), microscopic (SEM and TEM), spectroscopic (FT-IR, UV-DRS, ssNMR) and powder X-ray diffraction techniques. The resulted POP-Am2 renders promising catalytic activity towards the cleavage of C=C bond in Wacker Oxidation (α -aryl substituted olefins oxidation) to produce benzaldehyde with major selectivity analyzed by GC-MS (Figure 3). Investigation of POP-Am2 over alkyne oxidation under identical conditions also delivers the cleavage of C \equiv C bond products, i.e. benzaldehyde with better selectivity. Literature reveals that the oxidation of olefin is generally performed in presence of precious metal catalysts to yield ketone as major product following Markovnikov rule or yielding aldehyde following *anti*-

Markovnikov rule. Therefore the breaking of C=C bond in absence of any metal during the reaction and formation of benzaldehyde is a rare outcome. The mechanistic insight of the exceptional behavior exhibited by this triazine based POP-Am2 in the formation of benzaldehyde as major selectivity during olefin oxidation is examined by computation and demonstrated.



Scheme 3 Synthesis of triazine based amide linked POP-Am2.

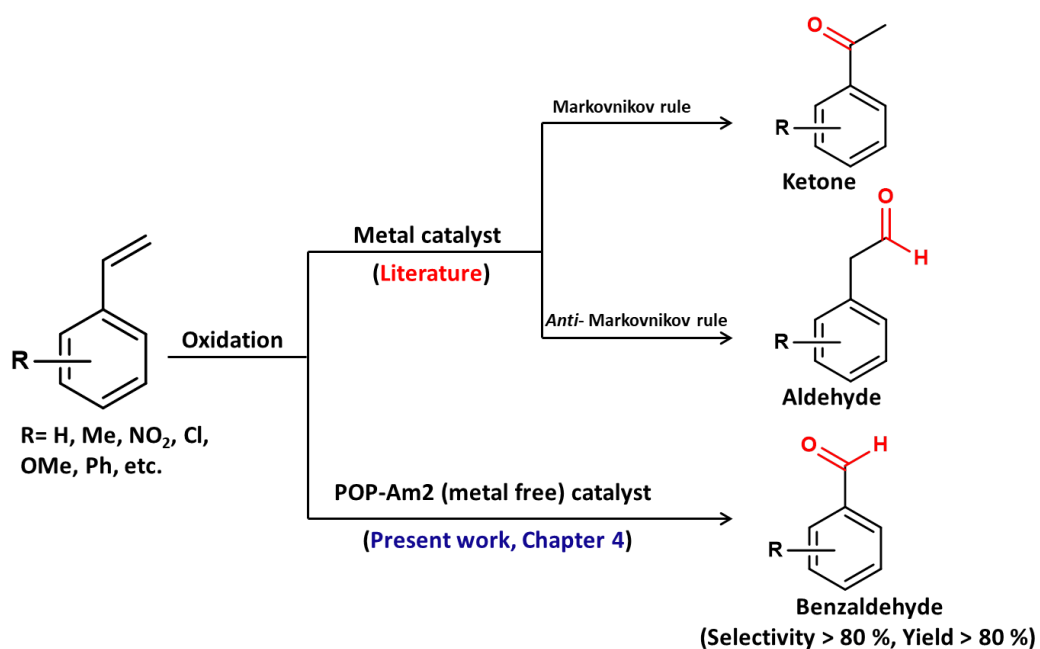
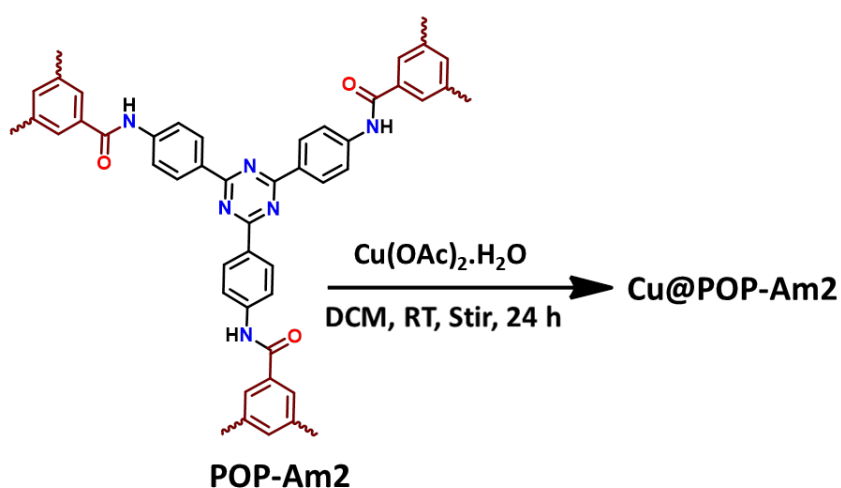


Figure 3 Wacker oxidation of olefins yielding benzaldehyde via C=C bond cleavage.

CHAPTER 5

Cu(II) complex loaded triazine-based porous organic polymer to promote benzylic C–H activation reactions

The production of benzaldehyde directly from toluene via C–H activation with high selectivity and yield has wonderful advantages. Thus we introduced Cu(II) impregnated onto POP-Am2 (discussed in chapter 4) i.e. Cu@POP-Am2 as heterogeneous catalyst for benzylic C–H activation reactions. Synthetic procedures and characterization of POP-Am2 are discussed in chapter 4. The Cu@POP-Am2 was also characterized employing the thermal, microscopic, spectroscopic, BET surface area analyzer and powder X-ray diffraction techniques. XPS analysis has been performed to investigate the oxidation state of Cu and its interaction in POP-Am2. The resulted electron rich Cu@POP-Am2 shows excellent activity in nucleophilic C–H activation during oxidations of methylarenes (TEXM, T= toluene, E= ethyl benzene, X= xylene, M= mesitylene, Figure 4) to the corresponding benzaldehyde derivatives with selectivity and stability.



Scheme 4 Impregnation of Cu(II) complex onto POP-Am2.

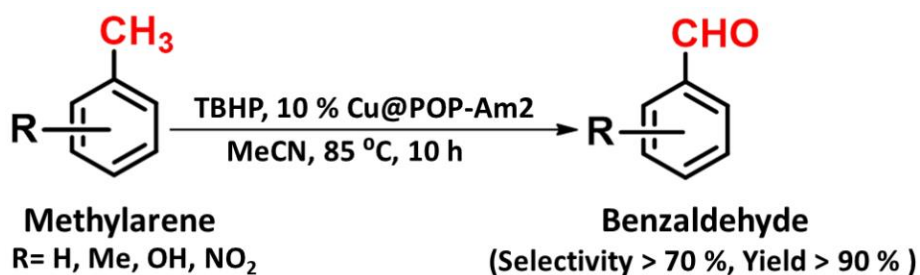


Figure 4 Cu@POP-Am2 promoted benzylic C–H activation during oxidations of methylarenes.

Chapter 6 **Conclusion and Future Prospects**

This chapter contains the perspective of overall research work carried out during the PhD program under the domain of porous organic polymers (POPs) and its potent applications in the field of organic transformation reactions. It contains the general outcome of each previously discussed chapter. Chapter 1 discusses the background of POPs that includes its synthetic techniques, classification and potential applications of POPs in diverse field ranging from adsorption and separation of gas molecules and hydrocarbons, in conduction, sensing, biomedicine, optoelectronic devices, in heterogeneous catalysis, etc.

Evidenced by the immense applications of POPs in performing organic reactions, a 2D POP with amide linked functionality (POP-Am) has been synthesized and discussed in chapter 2. The resulted POP having π -cloud delocalization propagated by carboxamide group has been employed as organocatalyst in promoting the selective oxidation of benzyl alcohols to benzaldehydes with 100 % selectivity. POPs with extended π -cloud delocalization can act as support matrix for metal sites by transferring the electrons. Subsequently, POPs could behave as heterogeneous catalyst carrier in catalytic reactions as discussed in chapter 3. A pyridine ring based POP (POP-Am1) has been synthesized and considered as support matrix for immobilization of Cu(II) onto it. The Cu(II) impregnated POP-Am1 (Cu@POP-Am1) exhibits better catalytic activity in reduction of nitroarenes to aminoarenes than those exhibited by precious metal (Au, Pd, Pt) supported polymers. Enhancement in availability of electrons in POPs could open new avenue towards effective and efficient heterogeneous catalysis. In this context a nitrogen atom rich POP (POP-Am2) having triazine ring in the porous network has been pre-designed and synthesized. With enormous number of N atom in the polymeric network solid with extended π -conjugation, POP-Am2 parades excellent catalytic activity in oxidations of α -aryl substituted olefins stabilized at catalyst surface via strong $\pi\cdots\pi$ interaction. Such organic transformation accomplishing C=C and C \equiv C bond cleavage to afford benzaldehydes with major selectivity, a rare outcome using organocatalyst has been illustrated in chapter 4. The POP-Am2 explained in chapter 4 has been utilized as catalytic scaffold for Cu(II) assisted benzylic C–H activation and is demonstrated in chapter 5. In the process, the Cu impregnated POP-Am2 (Cu@POP-Am2) displays moderate to good activity in oxidative transformation of TEXM (T= toluene, E= ethylbenzene, X= xylenes, M= mesitylene) to carbonyl compounds.

Moreover, the thesis conveys the potential application of POPs with amide functionality in performing organic transformation reactions. Furthermore, tailor made properties such as surface area, pore volume, pore size and the overall skeleton of the polymeric network with extended π -conjugation could be tuned by tuning the building units. POPs thus synthesized could be exploited in various fields such as in biorefinery, gas and/or hydrocarbons adsorption and separation, oxidations of alcohols and aliphatic alkenes, in pharmaceutical industry and in photocatalysis. The application of POP-Am2 (discussed in chapter 4) as metal free heterogeneous catalytic promoter in performing the anaerobic oxidation of benzyl alcohols to benzaldehydes assisted by KOH is in progress.

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