Conclusion and future prospects

6.1 Conclusion

The broad objective of this research work undertaken was to design and synthesize porous organic polymers (POPs) with amide functionality and with high nitrogen content in the form of pyridine and triazine in the framework of POPs. POPs are composed generally of lighter elements via strong covalent bonding (C–C, C–N, B–O, etc.) experiencing pre-designed skeleton having high thermal stability and low density [1-5]. Synthesized POPs were further tested for their exhibited properties toward catalytic conversion in oxidation and reduction reactions. More importantly introducing varied functionalities into the POPs can change the interaction behavior to improve catalytic property. With such tailor-made properties these polymers represent as fascinating organic polymeric network. These materials have wide applications in the field of gas adsorption and separation [6,7], gas storage [8,9], conduction [10,11], biorefinery [12,13], heterogeneous catalysis [14-16], biomedicine [17,18], solar cell [19], etc. In recent days, it finds immense applications as organic catalyst and (or) as support matrix for metal catalyst as heterogeneous catalyst for various organic transformation reactions. POPs with 2D covalent network with π-wall architecture are speculated to form episodic columnar π-arrays and ordered one-dimensional (1D) channels in a predesignable manner. Thereafter acts as π-electronic bed in order to catalyze various organic transformations [20-22]. Indeed these POPs in carrying out organic reactions successfully prompted to design porous polymeric network with enrich π-electrons, which showcases as effective applications as heterogeneous catalysts.

This thesis consists of six chapters, being the first as introductory and concluding at Chapter 6. Working chapters demonstrated the effects of π-electronic cloud delocalization in POPs propagated by amide functionality and its impact as organocatalysts or as catalytic scaffold for heterogeneous catalysis in performing organic transformation reactions in an organized manner. Finally laid down the perspective of overall research works carried out during the PhD program under the domain of POPs and its potent applications in the field of catalysis.

Chapter 1 discusses the background of POPs that includes its synthetic techniques, classification and potential applications in diverse field. Evidenced by the immense applications of POPs in performing organic reactions, objectives are set to synthesis 2D POPs with continuous π-conjugation to exhibit heterogeneous catalysis.

In Chapter 2, a 2D POP with amide linked functionality has been synthesized and demonstrated. The porous framework is synthesized with [3+2] structure motif by the condensation reaction between 1,3,5-benzenetricarbonyl trichloride and *p*-phenylenediamine. The resultant mesoporous polymeric material (POP-Am) has high chemical and physical stability. It exhibits π-conjugation propagated by amide functionality with a band gap of 1.0 eV. This π-cloud delocalized POP represents as a promoter in performing the selective oxidation of benzyl alcohols. The oxidation specifically affords the corresponding benzaldehydes with 100 % selectivity as an oxidized product. Produced benzaldehydes are stabilized strongly by π···π and other intermolecular interactions with POP-Am thereby preventing its tendency of over oxidation to yield benzoic acids. From the experimental and theoretical evidences the reaction takes place through free radical pathway and is illustrated. This chapter represents the rare application of organic polymer as organocatalyst in promoting the selective oxidation of benzyl alcohols.
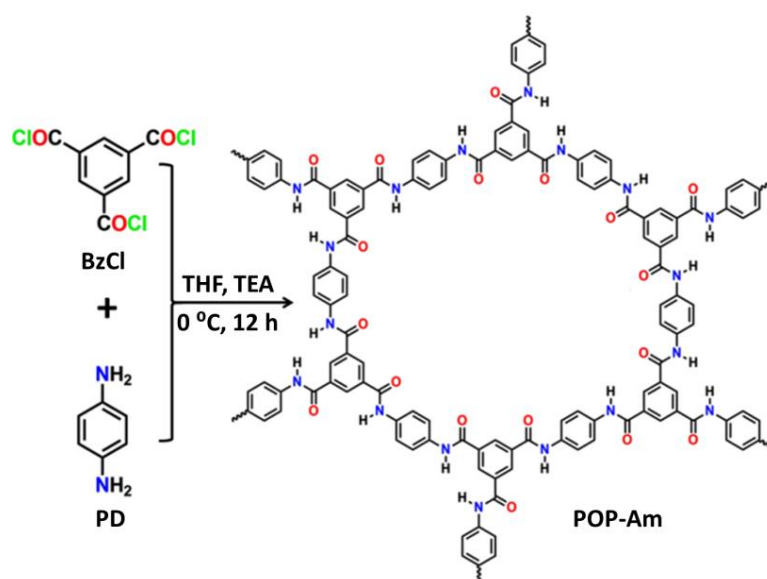

Figure 6.1 POP-Am has been used as metal free catalyst in selective oxidation of benzyl alcohols.

In Chapter 3, a pyridine based microporous organic polymer (POP-Am1) is synthesized solvothermally from 2,4,6-tris(4-aminophenyl)pyridine and 1,3,5-benzenetricarbonyl trichloride and demonstrated. POP-Am1 with extended π-cloud delocalization act as support matrix for metal sites by transferring the electrons to impregnate Cu(II) onto it. The Cu(II) impregnated POP-Am1 (Cu@POP-Am1) acts as envelop of electrons exhibiting high catalytic activity. Cu@POP-Am1 parades the hydrogenation of nitroarenes to aminoarenes using $NaBH_4$ within short span of time than those exhibited by precious metal supported polymers. Efficient reduction of 4-nitrophenol, a toxic water pollutant using atom economy and greener pathway avoiding the applications of precious and expensive metal (Pd, Au, Rh, Pt) catalyst is of prime attraction in this domain. This study definitely adds depth in the applications of porous organic polymers (POPs) in heterogeneous catalyst carrier.
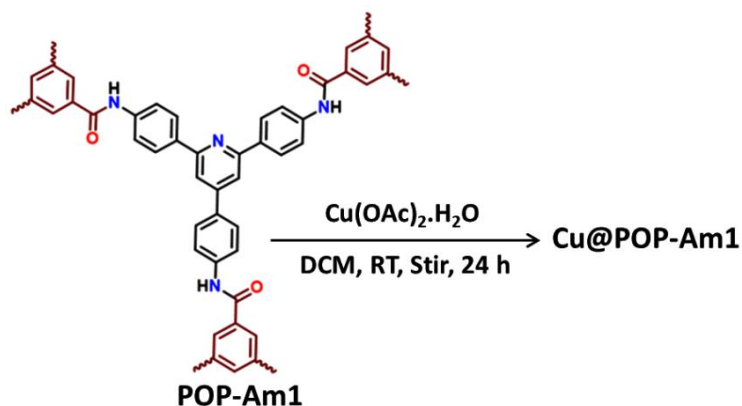

Figure 6.2 Cu@POP-Am1 used as heterogeneous catalyst in reduction of nitroarenes.

In Chapter 4, a nitrogen (N) atom rich POP with triazine ring has been pre-designed and synthesized solvothermally from 2,4,6-tris(4-aminophenyl)triazine and 1,3,5-benzenetricarbonyl trichloride. The resulted polymer (POP-Am2) with enormous number of N atom in the polymeric network solid with extended π-conjugation results enhancement in availability of π-electrons in the polymer. POP-Am2 with extended π-conjugation parades excellent catalytic activity in oxidations of α-aryl substituted olefins stabilized at catalyst surface via strong π···π interaction. Such a peculiar Wacker-type oxidation accomplishes C=C and C≡C bond cleavage to afford corresponding benzaldehydes with major selectivity and is illustrated. It is a rare outcome using metal free catalyst in olefin oxidation reactions. The Wacker-type oxidation in general is accomplished by transition metal (Pd, Rh, Cu, Pt, etc.) catalyst producing methyl ketone

as the primary product following Markovnikov rule with aldehyde in little quantity. However, with aryl alkenes such as styrene the regiospecificity is altered yielding terminal aldehyde as the major product following *anti*-Markovnikov rule. Such regiospecificity remains as a challenge since only the few reported literatures could generate it. But in either cases C=C double bond cleavage has not been accomplished. Thus POP-Am2 entertaining the cleavage of C=C and C≡C bond occupies an important space in the domain of organic catalyst performing heterogeneous catalytic reactions.
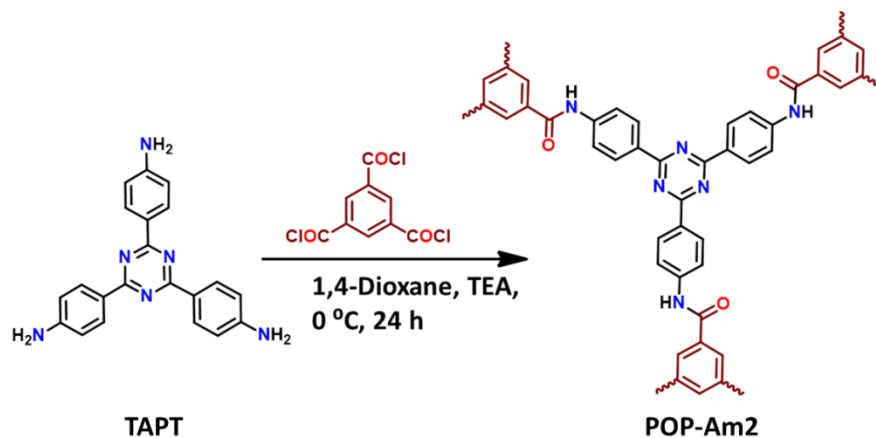

Figure 6.3 POP-Am2 with enrich π-electrons acting as organic catalyst in performing a peculiar Wacker-type oxidation of olefins accomplishing C=C bond cleavage.

In Chapter 5, the POP-Am2 rich in π-electrons enriched by N heteroatom in the polymeric framework discussed in Chapter 4 represents as catalytic scaffold for immobilization of metals onto it. Accordingly, Cu(II) ions has been immobilized to afford copper loaded POP-Am2, Cu@POP-Am2. The Cu(II) in Cu@POP-Am2 is enriched in electron density by the transfer of electrons from π-electron rich POP-Am2. Consequently, the active metal site displays excellent activity towards activation and oxidation of benzylic sp^3 C–H bond. To investigate that activity, the oxidation of benzylic C–H bond in TEXM (T= toluene, E= ethylbenzene, X= xylenes, M= mesitylene) is performed. In the process, reverse charge transfer from filled metal dπ orbital to the antibonding σ* orbital of C–H bond takes place and eventually it activates the weaker C–H bond to be broken. The oxidation of TEXM to the corresponding benzaldehydes with major selectivity takes place via free radical pathway and the mechanism is proposed
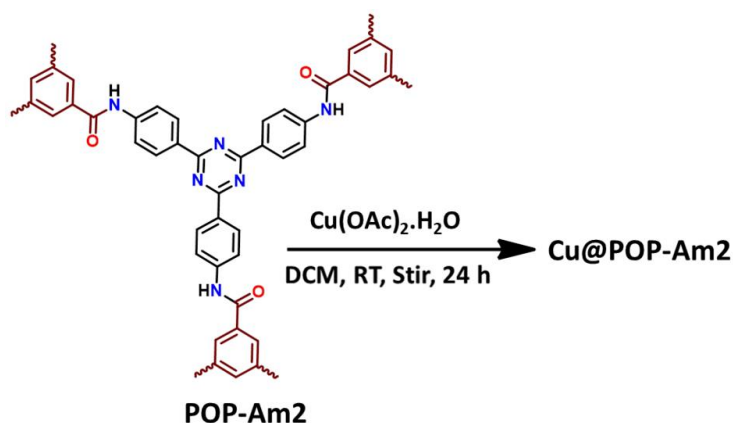
Figure 6.4 Cu@POP-Am2 as heterogeneous catalyst in nucleophilic activation and oxidation of benzylic C–H in methylarene.

The overall research work carried out in the field of amide linked POPs explained in the specific chapters is summarized below (Figure 6.5) in pictorial representation.
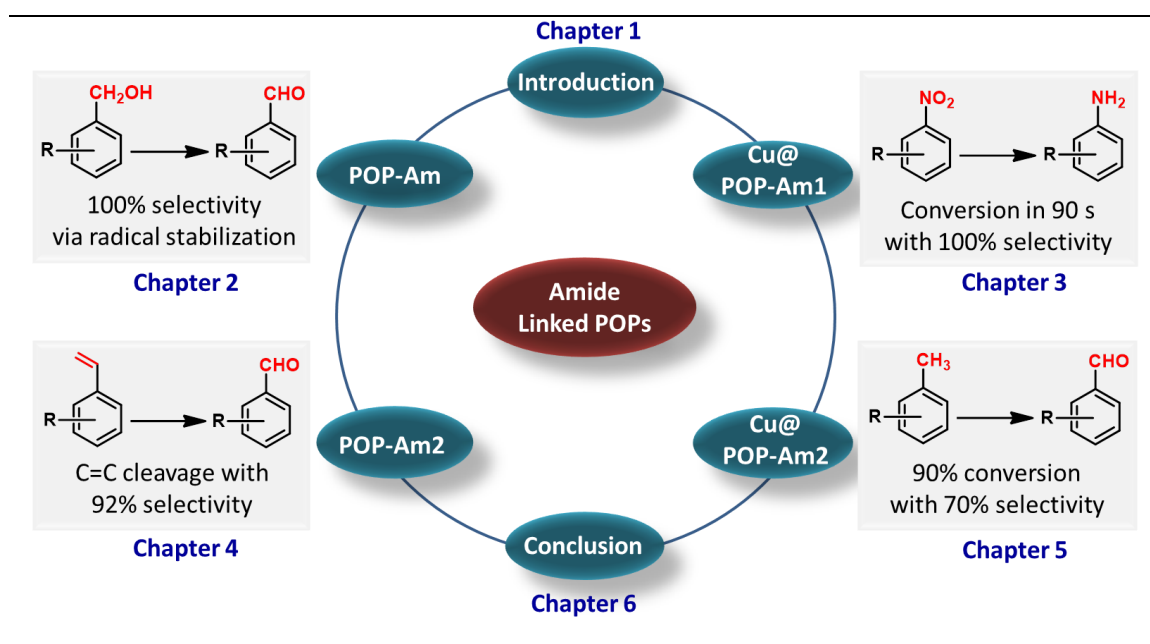

Figure 6.5 Pictorial representation of the overall thesis.

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 without using any peroxide is in progress.

6.2 Future prospects

With the experience and knowledge gained during PhD program in the field of porous organic polymers, the amide and other functionalized POPs with tuned properties is aimed to design and synthesize in the future ahead. The synthesized POPs is targeted to be used in domain of chemistry shown below (Figure 6.6) pictorially. Of the four quadrants shown in the picture, application of POP in quadrant- I is discussed in chapter 5. Quadrant-II is an important area of characterization via gas adsorption, an imperative way to verify the porosity of desired porous polymer. POPs find immense application in storage and separation of gas molecules such as CO_2, H_2S, NH_3, H_2, N_2, etc. Quadrant-IV represents POPs in performing organic transformation reactions and is presented in the working chapter of this thesis. Quadrant-III is an important area of research in pharmaceutical industries where targeted delivery of drug molecules using POPs is recently gaining acceleration.
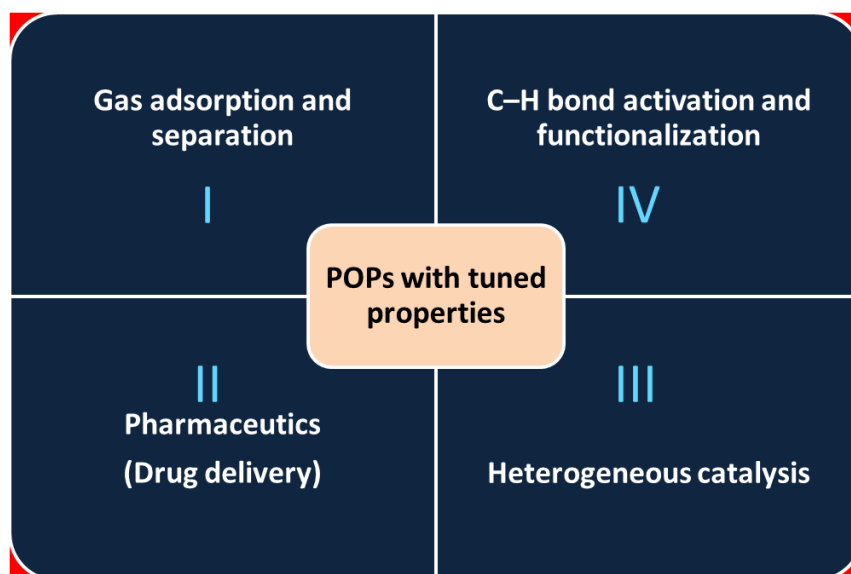

Figure 6.6 Representing the future prospects in the synthesis of POPs with tuned properties and their targeted applications in various fields.

6.3 References

[1]   Cooper, A. I. Porous molecular solids and liquids. *ACS Central Science*, 3(6):544-553, 2017.

[2] Das, S., Heasman, P., Ben, T. and Qiu, S. Porous organic materials: strategic design and structure−function correlation. *Chemical Reviews*, 117(3):1515-1563, 2017.

[3] Troschke, E., Grätz, S., Lübken, T. and Borchardt, L. Mechanochemical Friedel–Crafts alkylation—A sustainable pathway towards porous organic polymers. *Angewandte Chemie*, 129(24):6963-6967, 2017.

[4] Diercks, C. S. and Yaghi, O. M. The atom, the molecule, and the covalent organic framework. *Science*, 355(6328):eaal1585, 2017.

[5] Bisbey, R. P. and Dichtel, W. R. Covalent organic frameworks as a platform for multidimensional polymerization. *ACS Central Science*, 3(6):533-543, 2017.

[6] Zhao, Y., Liu, X. and Han, Y. Microporous carbonaceous adsorbents for CO_2 separation via selective adsorption. *RSC Advances*, 5(38):30310-30330, 2015.

[7] Katsoulidis, A. P. and Kanatzidis, M. G. Mesoporous hydrophobic polymeric organic frameworks with bound surfactants. Selective adsorption of C_2H_6 versus CH_4. *Chemistry of Materials*, 24(3):471-479, 2012.

[8] Furukawa, H. and Yaghi, O. M. Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. *Journal of the American Chemical Society*, 131(25):8875-8883, 2009.

[9] Zhang, C., Kong, R., Wang, X., Xu, Y., Wang, F., Ren, W., Wang, Y., Su, F. and Jiang, J. X. Porous carbons derived from hypercrosslinked porous polymers for gas adsorption and energy storage. *Carbon*, 114:608-618, 2017.

[10] Chandra, S., Kundu, T., Kandambeth, S., BabaRao, R., Marathe, Y., Kunjir, S. M. and Banerjee, R. Phosphoric acid loaded azo (−N=N−) based covalent organic framework for proton conduction. *Journal of the American Chemical Society*, 136(18):6570-6573, 2014.

[11] Xu, H., Tao, S. and Jiang, D. Proton conduction in crystalline and porous covalent organic frameworks. *Nature Materials*, 15(7):722-727, 2016.

[12] Bavykina, A. V., Goesten, M. G., Kapteijn, F., Makkee, M. and Gascon, J. Efficient production of hydrogen from formic acid using a covalent triazine framework supported molecular catalyst. *ChemSusChem*, 8(5):809-812, 2015.

[13] Stöcker, M. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition*, 47(48):9200-9211, 2008.

[14] Kaur, P., Hupp, J. T. and Nguyen, S. T. Porous organic polymers in catalysis: Opportunities and challenges. ACS Catalysis, 1(7):819-835, 2011.

[15] Zhang, Y. and Riduan, S. N. Functional porous organic polymers for heterogeneous catalysis. *Chemical Society Reviews*, 41(6):2083-2094, 2012.

[16] McKeown, N. B. and Budd, P. M. Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. *Chemical Society Reviews*, 35(8):675-683, 2006.

[17] Li, Z. and Yang, Y. W. Creation and bioapplications of porous organic polymer materials. *Journal of Materials Chemistry B*, 5(47):9278-9290, 2017.

[18] Zhao, H., Jin, Z., Su, H., Jing, X., Sun, F. and Zhu, G. Targeted synthesis of a 2D ordered porous organic framework for drug release. *Chemical Communications*, 47(22):6389-6391, 2011.

[19] Vyas, V. S., Lau, V. W. H. and Lotsch, B. V. Soft photocatalysis: organic polymers for solar fuel production. *Chemistry of Materials*, 28(15):5191-5204, 2016.

[20] Wu, Y., Xu, H., Chen, X., Gao, J. and Jiang, D. A π-electronic covalent organic framework catalyst: π-walls as catalytic beds for Diels–Alder reactions under ambient conditions. *Chemical communications*, 51(50):10096-10098, 2015.

[21] Khatioda, R., Talukdar, D., Saikia, B., Bania, K. K. and Sarma, B. Constructing two dimensional amide porous polymer to promote selective oxidation reactions. *Catalysis Science & Technology*, 7(14):3143-3150, 2017.

[22] Khatioda, R., Pathak, D. and Sarma, B. Cu (II) complex onto a pyridine-based porous organic polymer as a heterogeneous catalyst for nitroarene reduction. *ChemistrySelect*, 3(23):6309-6320, 2018.