

# Chapter 6

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Conclusion & Future Prospects

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## 6.1 Conclusion

The overarching goal of this research was to develop and manufacture porous organic polymers (POPs) with high nitrogen content in backbone as well as linker in the framework. POPs are often constructed of lighter components with strong covalent bonding (C–C, C–N, B–O, etc.) and a pre-designed skeleton with good thermal stability and low density [1-3]. The characteristics of the synthesised POPs toward catalytic conversion were investigated further. More significantly, integrating different functions into POPs might alter the interaction behaviour, hence improving catalytic property. With such tailored features, these materials also have numerous applications in gas storage/separation, conduction, biorefinery, catalysis, biomedicine, and other fields [4-17]. It has lately found broad usage as an organic catalyst and/or as a support matrix for metal ion as a heterogeneous catalyst for a number of organic transformation processes. Nitrogen rich POPs with a two-dimensional covalent network and a  $\pi$ -wall architecture are capable of building organised one-dimensional channels and episodic columnar arrays in a predetermined manner. Indeed, the efficacy of these POPs in carrying out organic reactions spurred the development of a porous polymeric network containing enrich electrons, which demonstrates effective applicability as heterogeneous catalysts.

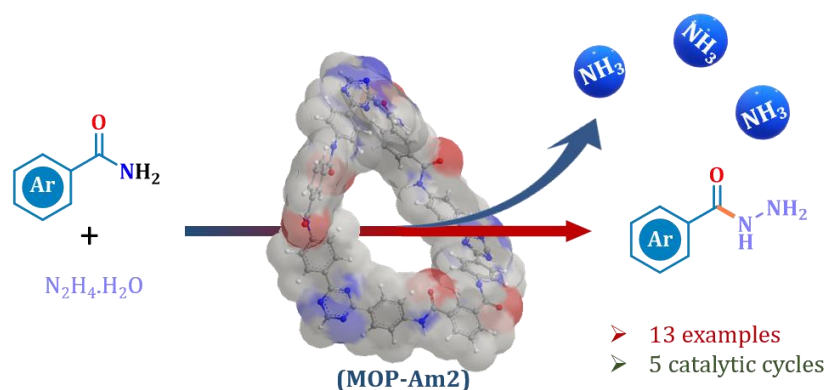
The thesis comprises of six chapters, the first of which is introductory and the last of which is conclusion. Working chapters established the impacts of enrich electron cloud delocalization in triazine POPs promoted by amide functionality and its influence as organocatalysts or as a catalytic scaffold for heterogeneous catalysis in executing forefront organic transformation reactions. Finally, the entire scientific effort carried out throughout the PhD programme in designing *N*-rich POPs and its powerful applications in the realm of catalysis was set forth.

Chapter 1 described a brief background about the porous organic polymers (POPs), their classifications, strategic design synthesis process, and a few quoted applications related to their structural induced property. Immense literature survey on POPs and their tailored functionality has been exploited especially in the field of catalysis. Evidenced by the relevance of nitrogen enrich systems in the realm of catalysis, objectives have been established to prepare nitrogen rich POPs to perform few

cutting-edge organic transformation reactions under both metal and metal-free condition.

Chapter 2 illustrated the strategic design and synthesis of amide functionalized triazine based 2D porous organic polymer (MOP-Am2). The MOP-Am2 is synthesized from [C3+C3] condensation of 2,4,6-tris-(4-aminophenyl)-1,3,5-triazine (TAPT) and 1,3,5-benzenetricarbonylchloride (BTCl) in 1,4-dioxane at ambient temperature. Special care had been taken care to avoid the discharge of corrosive and reactive HCl gas in the solution. The structural integrity of the obtained the MOP-Am2 was investigated with various thermal, microscopic, and spectroscopic techniques such as FT-IR, TG,  $^{13}\text{C}$  CP/MAS NMR, PXRD, BET, FESEM, TEM and TEM-EDX analyses.

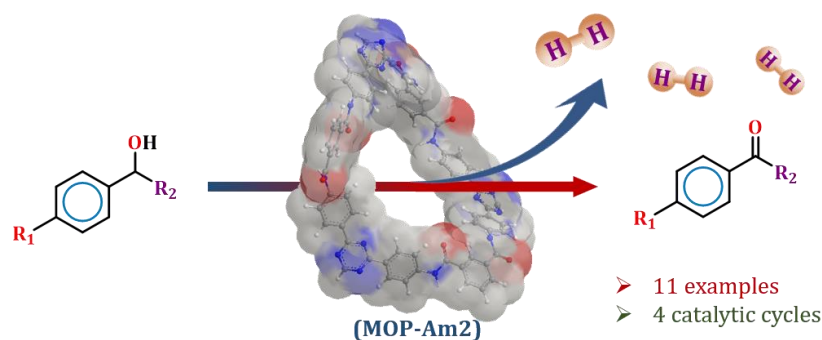
The amide moiety is a well-known synthon as for both H-bond donor and acceptor. Highly stable MOP-Am2 was explored as heterogeneous catalyst for deamination reaction during hydrazide synthesis from benzamide derivatives or also called as transamidation of benzamide. Thirteen substrate molecules with varied substituents have been demonstrated with good recyclability. The experimental and computational support evidenced MOP-Am2 to be an excellent facilitator to convert  $-\text{NH}_2$  to a good leaving group *via* weak H-bonding through amide moiety without using any external activating agent.



**Figure 6.1** Transamidation of benzamide to benzhydrazide over MOP-Am2

Chapter 3 emphasized the role of  $\pi$ -cloud of MOP-Am2 as facilitator for the anaerobic oxidation of benzyl alcohols under basic medium. The solid-state UV-Vis DRS analysis revealed the presence of low band gap of 1.95 eV in MOP-Am2 that trigger the electronic interaction of the substrate molecule over the catalyst to get oxidized. The charge transfer from MOP-Am2 enhanced the natural electronic charge on benzylic

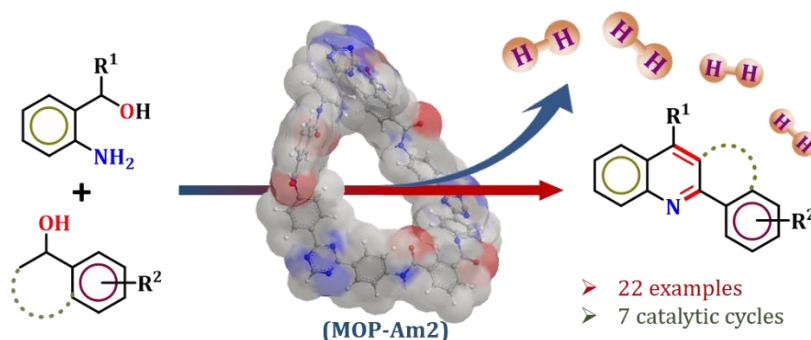
carbon and hence weakening the benzylic C–H bond. DFT study, taking BP86-D3BJ/6-311++G\*\* level of theory, supported the findings of the protocol where the weak interaction from MOP-Am2 behaves as the driving force for forming of the labile C–H bond. As a result, hydride is eliminated in the form of H<sub>2</sub> confirmed by *in-situ* reduction of diphenyl acetylene.



**Figure 6.2** Base mediated anaerobic oxidation of benzyl alcohols to benzaldehydes over MOP-Am2

Substrate scope study with diverse benzyl alcohols was performed and characterized with GCMS analysis. Carbon balance analysis using modified Walkley-Black method has also been demonstrated to record the carbon emission to the atmosphere during the protocol suggesting it as environmentally benign.

Chapter 4 revealed the morphological alteration of MOP-Am2 to gain stronger surface contacts, promoting it as a metal-free organocatalyst for base-mediated multicomponent oxidative annulation reactions, specifically medicinally valued quinolines, without the need of an external oxidant. The protocol was determined to be anaerobic in nature, with three reaction steps, *viz*, alcohol oxidation, imine condensation, and cyclization.

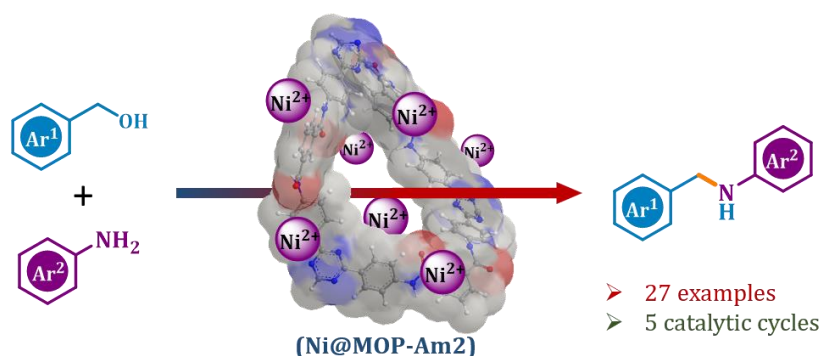


**Figure 6.3** Base mediated oxidative annulation of alcohols to quinolines facilitated by MOP-Am2

While performing this reaction with approximately twenty two substituted alcohols, hydride removal in the form of H<sub>2</sub> gas was also evidenced, providing good to excellent conversion with excellent catalyst recovery. The <sup>1</sup>H NMR titration approach was used to dig into the mechanistic insight. Green matrices for scale-up synthesis are evaluated for industrial feasibility.

Chapter 5 emphasized the utility of evolved H<sub>2</sub> from Chapter 3 and 4 in C–N bond formation reaction. The presence of excess nitrogen on MOP-Am2 made itself a catalytic scaffold for metal immobilization. Accordingly, NiCl<sub>2</sub>.6H<sub>2</sub>O has been incorporated on it making Ni@MOP-Am2 and characterized with PXRD, BET, AAS, FESEM, SEM-EDX, TEM and XPS analyses.

The catalytic potency of Ni@MOP-Am2 was summarized with base mediated *N*-alkylation reaction from diverse alcohols and amines. The protocol affirmed good to excellent yield and easy catalyst recovery. Computational study with B3LYP/6-31G(d) level of theory suggested a three-step mechanism with the alcohol being first oxidized to its corresponding carbonyl compound under anaerobic condition leaving H<sub>2</sub> which was trapped by Ni@MOP-Am2 in the reaction media; followed by the Schiff-base condensation of the carbonyl compound and amine to form imine intermediate. The third step is the *in-situ* reduction of C=N by the captured H<sub>2</sub> on the catalyst. This process of transfer of H<sub>2</sub> is known as “hydrogen autotransfer” or “borrowing hydrogen”. Nearly twenty seven substrate molecules with diverse functionality have been exploited characterized with NMR analysis and demonstrated.



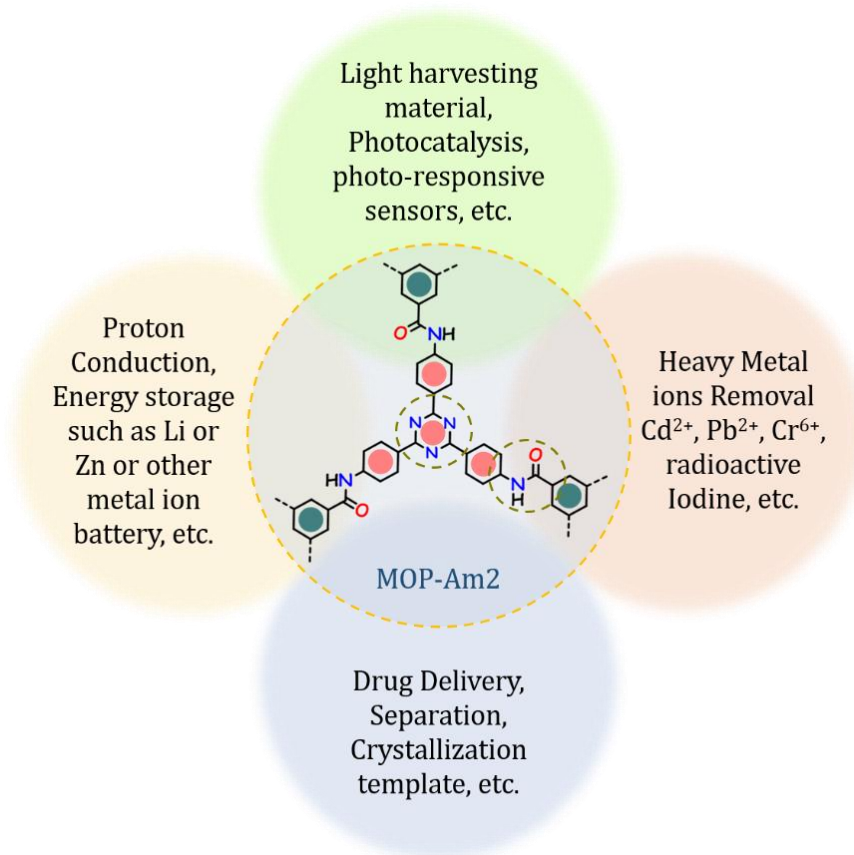
**Figure 6.4** Base mediated *N*-alkylation of amines over Ni@MOP-Am2 via “Borrowing Hydrogen” or “Hydrogen Auto-transfer” strategy

The thesis represents a summary of all the significant findings from the series of experiments carried out to meet the objectives. The material was exclusively explored

for its potential in catalysis emphasizing the role of hydrogen bonding motifs, electron rich units, surface electronic environment, and its ability to store liberated  $H_2$  opening a scope for numerous applications in catalytic transformation reactions.

## 6.2 Future Scope of the Work

Although MOP-Am2 is utilised in heterogeneous catalysis summarized in the thesis, its high nitrogen content and  $\pi$ -electron abundance open the door for a variety of additional uses. Numerous applications, including the adsorption of photo-responsive molecules for light harvesting materials, photocatalysis, photolytic sensors, proton conduction, energy/gas storage, batteries, purification processes, toxic metal ion detection/removal, radioactive iodine detection, etc., are greatly expected to facilitate by the simple access to nitrogen lone pair and polar amide functionality. The use of the synthesised POP is also anticipated in the newly increasing momentum pharmaceutical research fields such as drug delivery, separation technology, etc. A pictorial representation of the future prospects of the synthesized POP is demonstrated in Figure 6.5.



**Figure 6.5** Pictorial representation of the possible future aspects of MOP-Am2

Due to the presence of polar amide functionality, homogeneous dispersion of MOP-Am2 in water is an added feature. Based on that efficiency we have been looking into the efficiency of the synthesized POP in removing metal toxicity from contaminated water. The material is showing excellent activity in removing  $\text{Cr}^{6+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  for now. Further investigation to explore its efficiency in soil and air is yet to achieve.

While these prospective applications appear promising, it is crucial to emphasise that more work needs to be done in order to improve the characteristics and functionality of amide functionalized triazine-based porous organic polymers and investigate their potential applications in a variety of sectors.

### 6.3 Bibliography

- [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] Katsoulidis, A. P. and Kanatzidis, M. G. Mesoporous hydrophobic polymeric organic frameworks with bound surfactants. Selective adsorption of  $\text{C}_2\text{H}_6$  versus  $\text{CH}_4$ . *Chemistry of Materials*, 24(3):471-479, 2012.
- [5] 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.
- [6] Chandra, S., Kundu, T., Kandambeth, S., BabaRao, R., Marathe, Y., Kunjir, S. M., and Banerjee, R. Phosphoric acid loaded azo ( $-\text{N}=\text{N}-$ ) based covalent organic framework for proton conduction. *Journal of the American Chemical Society*, 136(18):6570-6573, 2014.
- [7] 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.

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- [8] Zhao, Y., Liu, X., and Han, Y. Microporous carbonaceous adsorbents for CO<sub>2</sub> separation *via* selective adsorption. *RSC Advances*, 5(38):30310-30330, 2015.
- [9] Xu, H., Tao, S., and Jiang, D. Proton conduction in crystalline and porous covalent organic frameworks. *Nature Materials*, 15(7):722-727, 2016.
- [10] Kaur, P., Hupp, J. T., and Nguyen, S. T. Porous organic polymers in catalysis: Opportunities and challenges. *ACS Catalysis*, 1(7):819-835, 2011.
- [11] Zhang, Y. and Riduan, S. N. Functional porous organic polymers for heterogeneous catalysis. *Chemical Society Reviews*, 41(6):2083-2094, 2012.
- [12] 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.
- [13] Pathak, D., Khatioda, R., Sharma, H., Guha, A. K., Saikia, L., and Sarma, B. Endorsing organic porous polymers in regioselective and unusual oxidative C=C bond cleavage of styrenes into aldehydes and anaerobic benzyl alcohol oxidation *via* hydride elimination. *ACS Applied Materials & Interfaces*, 13(13):15353-15365, 2021.
- [14] 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.
- [15] 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.
- [16] Li, Z. and Yang, Y. W. Creation and bioapplications of porous organic polymer materials. *Journal of Materials Chemistry B*, 5(47):9278-9290, 2017.
- [17] 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.