

## Catalytic applications of porphyrin-based POPs

Compiled by Narges Zarei

Narges Zarei was born in 1996 in Hamedan, Iran. She received her B.Sc. in Pure Chemistry (2019) and M.Sc. in Organic Chemistry (2021) from Bu-Ali Sina University under the supervision of Professor Mohammad Ali Zolfigol. She is currently working towards her Ph.D. under the supervision of Professor Mohammad Ali Zolfigol at Bu-Ali Sina University. Her research interest is the design, synthesis and characterization of magnetic nanoparticles, porous materials and urea-based compound and their catalytic applications in organic synthesis.

*Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran  
Email: nargesza70@gmail.com*

(DOI: 10.30495/IJC.2023.1969442.1967)



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

### Introduction

Porphyrins as macromolecular heterocyclic compounds, have emerged the attention of many of researchers. Due to having a large  $\pi$ -aromatic system, they have excellent chemical and thermal stability as well as photophysical and electrochemical functions. Porphyrin-based molecular frameworks can act as a good functional receptor for various metal ions due to their strong coordination capabilities [1-5].

The history of the study of metalloporphyrin's activities began in 1747 when Menghini demonstrated the presence of iron in blood for the first time. In 1871, Hoppe and Seyler isolated porphyrins from blood and described these compounds as pyrrole derivatives [6].

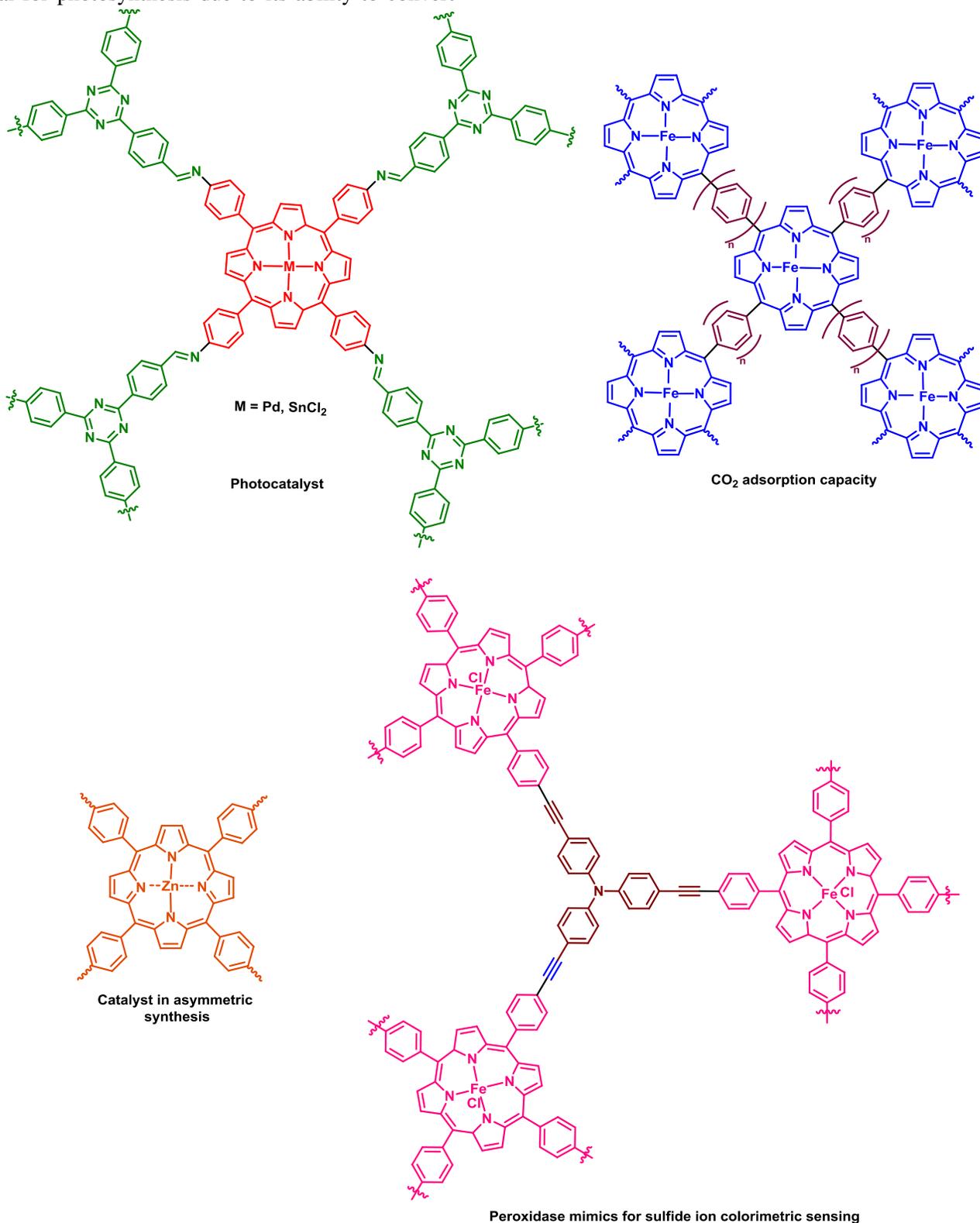
Porphyrin-based porous organic polymers (PPOPs), are a new type of porous materials which constructed from porphyrin organic building blocks and have fantastic properties *via* strong covalent bonds. These materials have been applied as photocatalysts, electrocatalysts, and oxidation and

reduction catalysts, epoxidation, functionalization of  $C(sp^3)$ -H bonds and asymmetric catalysis [7-11]. PPOPs are widely used in optical functional systems. Also, they have many applications in various fields including extraction of some aromatic compounds, chemosensors [12], materials science [13], gas adsorption and storage, light emitters, heterogeneous catalysis [6,14], redox reactions and electron transfer [12] and  $CO_2$  adsorption [15].

The rigid, robust, and multifunctional features of porphyrins, enable the construction of framework compounds such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) for use in several important applications. The facile synthesis, high chemical stability, and robust nature of these compounds has made them an appealing platform for various catalytic applications, including Lewis's acid catalysis, oxidative catalysis, photocatalysis and electrocatalysis. Porphyrin-related compounds are commonly observed in nature and function as essential catalysts for various

processes. For example, a porphyrin derivative, heme, can act as a cofactor of hemoglobin in red blood cells to transport oxygen. Another derivative, chlorophyll, which can be found in green plants, is vital for photosynthesis due to its ability to convert

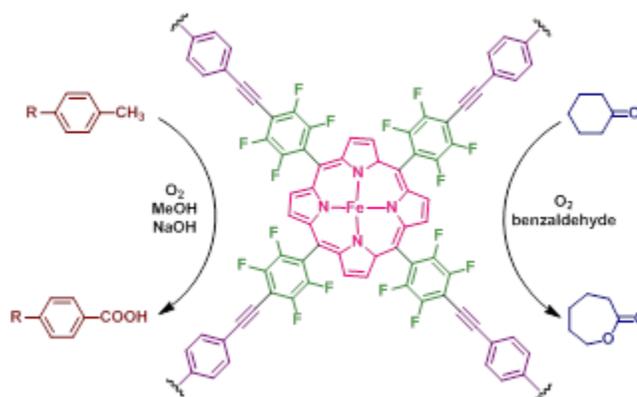
sunlight into energy [6, 14, 16]. Some of the applications of PPOPs are shown in the **Scheme 1**. In this spotlight, I am going to highlight the catalytic applications of PPOPs.



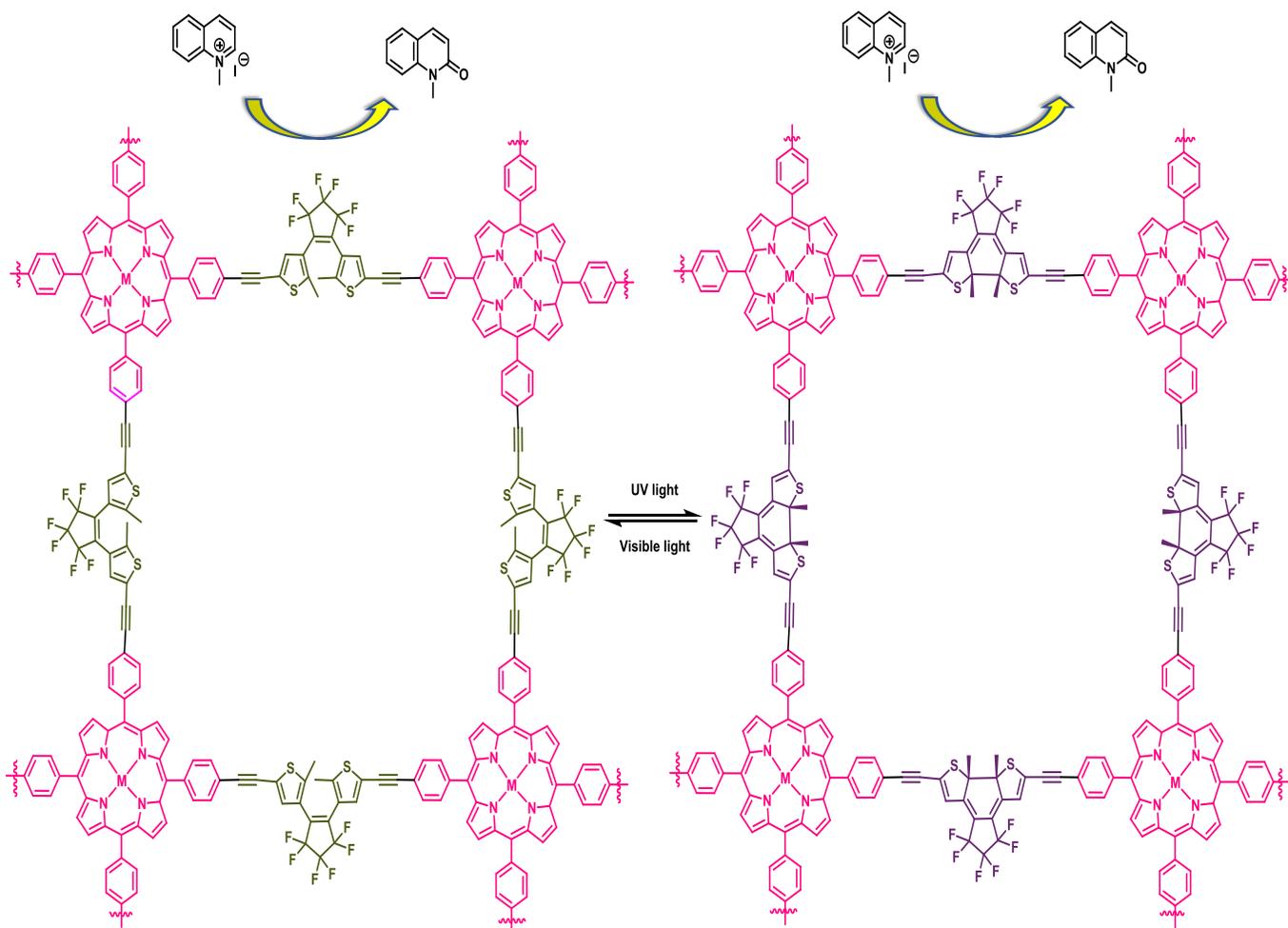
**Scheme 1.** A number of different applications of Porphyrin

## Abstracts

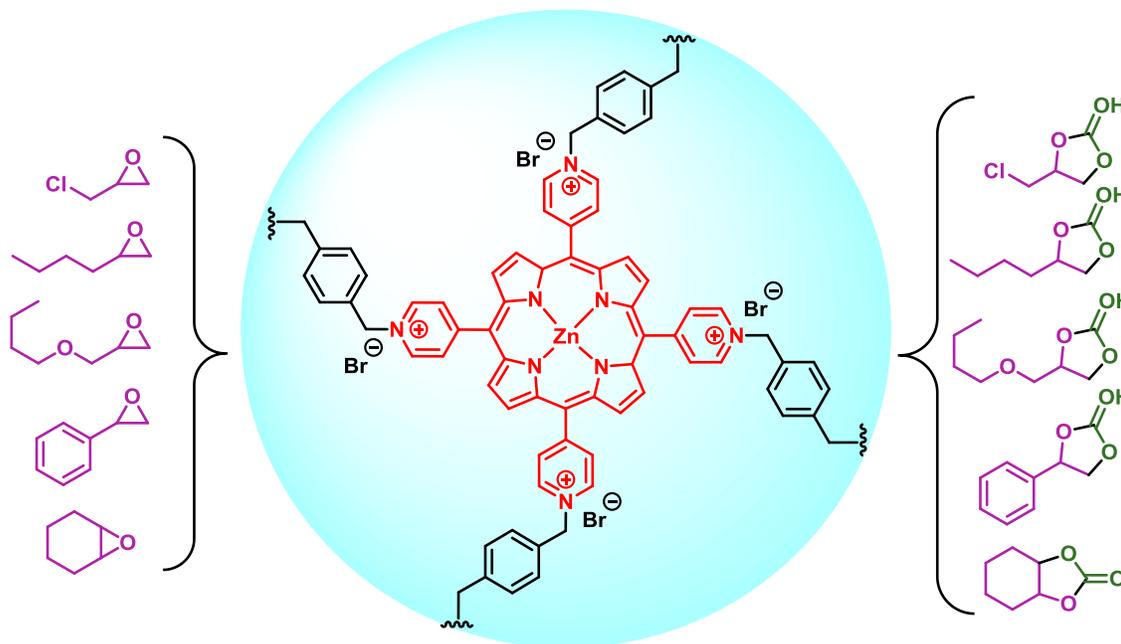
**(A)** (A) In 2018, Dong and co-workers reported a conjugated micro/mesoporous polymer based on fluorinated iron-porphyrin. FCMP-1 was prepared *via* a Sonogashira-Hagihara coupling polymerization. FCMP was used as a heterogeneous oxidative catalyst for the oxidative transformation of substituted toluene to corresponding benzoic acid as well as Baeyer–Villiger oxidation using dioxygen as an oxidant. The channels derived from the porous structure of Fe-porphyrin network are advantageous for the reactive molecules to contact the catalytic sites and accelerate the diffusion of reactant and product [17].



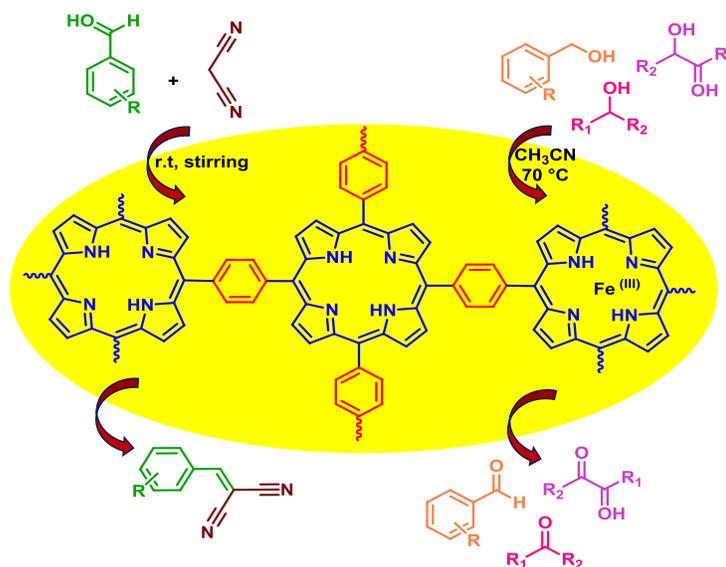
**(B)** In 2020, Wang and co-workers described a photo-switchable dithienylethene with metal-free 5,10,15,20-tetrakis(4-iodophenyl) porphyrin and its metal derivatives based photo-switchable catalyst for the oxidation of *N*-methyl pyridinium salts in visible light conditions. Due to the high specific surface area and controlling the behavior of the catalyst in different light irradiation, this system, have a prominent role in photocatalytic reactions [18].



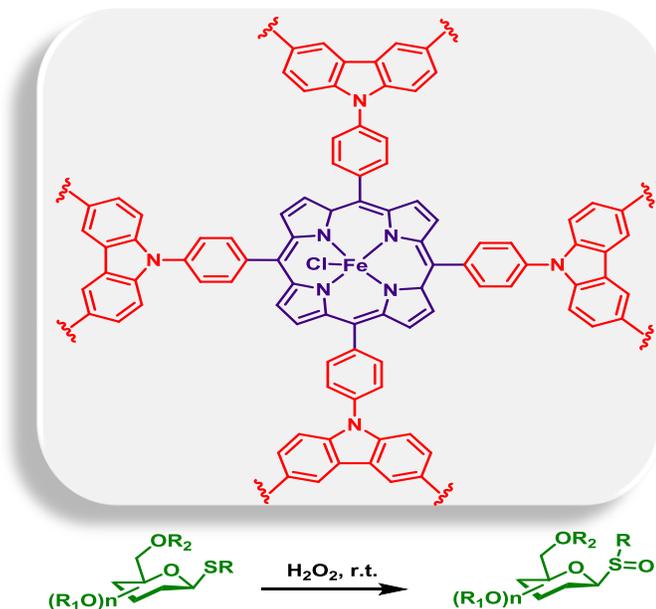
(C) Ionic porous organic polymers (IPOP)s have multiple active sites in their structures. For this reason, these systems are used as catalysts. In 2017, Yang and co-workers developed a cationic porphyrin-based polymer supported on carbon nanotubes as heterogeneous catalysts. The described catalyst was used in CO<sub>2</sub> fixation reactions under solvent-free conditions [19].



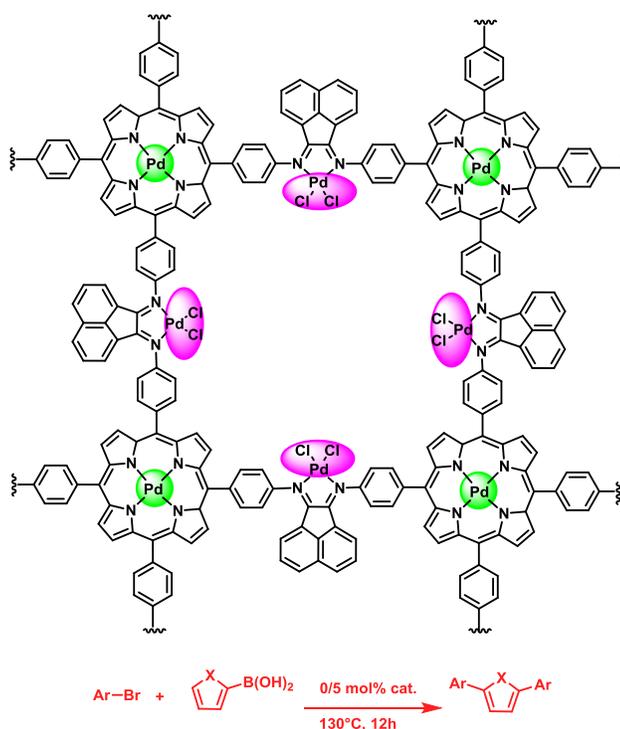
(D) In 2013, Modak and co-workers reported the synthesis of a porphyrin-based microporous organic polymer (Fe-POP-1) through a facile solvothermal method involving the extended aromatic substitution of pyrrole and terephthalaldehyde in the presence of Fe (III). This material has a very high BET surface area and exhibits two types of catalytic sites: iron-free porphyrin moieties for base catalysis as well as Fe (III)-bound sites for selective oxidation reactions. Due to the presence of a basic porphyrin macrocyclic site in Fe-POP-1, it catalyzes Knoevenagel condensation of aromatic aldehydes with malononitrile at room temperature, whereas the Fe (III)-bound site catalyzes selective oxidation of alcohols to the respective aldehyde/ketones. The catalyst has good reusability and excellent selectivity [20].



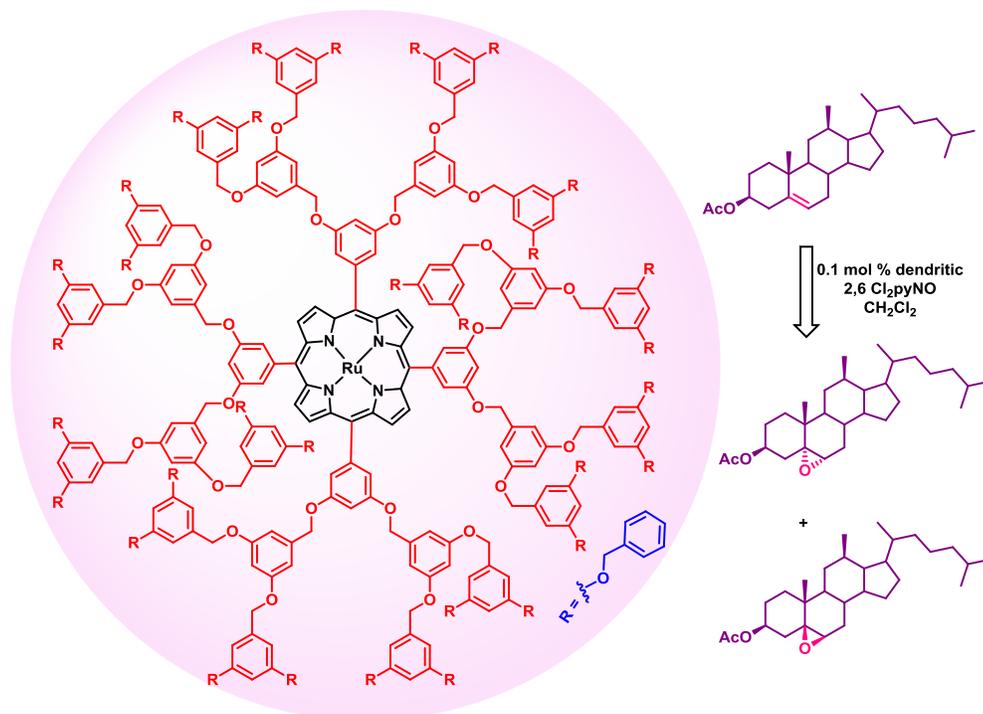
**(E)** Sulfoxide is a multifunctional intermediate for the synthesis of drugs, pesticides, and other fine chemicals. Selective oxidation of sulfides is a typical method to produce sulfoxides. Fe (II)-porphyrin complex is proved to be an effective catalyst for oxidizing sulfides to sulfoxides. Han and co-workers prepared a porous conjugated polycarbazole, CPOP-12, with Fe (II)-porphyrin units *via* the oxidative coupling reaction and applied it as catalysts for sulfoxide preparation [21-22].



**(F)** In 2019, Shen and co-workers reported a novel bifunctional porphyrin-based porous a-diimine polymer with high thermal and chemical stability synthesized by imine condensation. This porous organic polymer POP-1 (Pd) shows the ability to catalyze C-H arylation and Suzuki coupling reactions with high efficiency [7].



(G) Despite numerous studies on the metalloporphyrin-catalyzed epoxidation of olefins, the substrate types in such oxidation systems reported in the literature were rather limited and were usually confined to electron-rich alkenes such as styrenes, norbornene, cyclohexene, and cyclooctene. However, Che and co-workers investigated the catalytic application of a dendritic porphyrin for the epoxidation of unsaturated cholesteryl esters with 2, 6 Cl<sub>2</sub>pyNO in dichloromethane using just 0.1 mol % of the catalyst in high yields and turnover numbers [6].



## References

- [1] J. Chen, Y. Zhu, S. Kaskel, *Angew. Chem. Int. Ed.*, 60 (2021) 5010-5035.
- [2] J. M. Gottfried, *Surf. Sci. Rep.*, 70 (2015) 259-379.
- [3] J.-F. Longevial, S. Clément, J. A. Wytko, R. Ruppert, J. Weiss, S. Richeter, *Chem. Eur. J.*, 24 (2018) 15442-15460.
- [4] R. Fareghi-Alamdari, M. Golestanzadeh, O. Bagheri, (2016). *RSC Adv.* 6 (2016) 108755-108767.
- [5] R. Fareghi-Alamdari, M. Golestanzadeh, O. Bagheri, *Appl Organomet. Chem.* 31 (2017) e3698.
- [6] J. C. Barona-Castaño, C. C. Carmona-Vargas, T. J. Brocksom, K. T. De Oliveira, *Molecules*, 21(2016) 310.
- [7] R. Shen, W. Zhu, X. Yan, T. Li, Y. Liu, Y. Li, Z. G. Gu, *Chem. Comm.*, 55(2019) 822-825.
- [8] K. Zhang, S. Goswami, H. Noh, Z. Lu, T. Sheridan, J. Duan, J. T. Hupp, *J. Photochem. Photobiol.*, 10 (2022) 100111.
- [9] I. Ahmad, S. Rehman, *Tetrahedron*, (2022) 104, 132604.
- [10] J. Sukiennik, A. Pranowo, S. Domański, K. Hurej, *ChemComm* (2023) 59, 1149-1152.
- [11] H. H., Wang, H., Shao, G., Huang, J., Fan, W. P., To, L., Dang, & C. M. Che, *Angew. Chem.* (2023).
- [12] L. Wang, H. Li, J. Deng, D. Cao, *Curr. Org. Chem.*, 17(2013) 3078-3091.
- [13] K. Sugiyasu, S. Ogi, M. Takeuchi, *Polym. J.*, 46(2014) 674-681.
- [14] Y. Zhang, K. Ren, L. Wang, L. Wang, Z. Fan, *Chin. Chem. Lett.*, 33 (2021) 33-60.
- [15] J. Wang, C. Jiao, M. Li, X. Wang, C. Wang, Q. Wu, Z. Wang, *Microchim Acta.*, 185 (2018) 1-8.
- [16] L. Feng, Y. Wang, E. Joseph, H. C. Zhou, *Trends Chem.*, 2 (2020) 555-568.
- [17] A. Dong, D. Wang, T. Dai, Q. Chen, L. Feng, N. Wang, *Adv. Compos. Mater.*, 1(2018) 696-704.
- [18] N. Sun, C. Wang, H. Wang, X. Gao, J. Jiang, *ACS Appl. Mater. Interfaces*, 12 (2020) 56491-56498.
- [19] S. Jayakumar, H. Li, J. Chen, Q. Yang, *ACS Appl. Mater. Interfaces*, 10 (2018) 2546-2555.
- [20] A. Modak, J. Mondal, A. Bhaumik, *Appl. Catal. A-Gen.*, 459 (2013) 41-51.
- [21] W. Ji, T. X. Wang, X. Ding, S. Lei, B. H. Han, *Coord. Chem. Rev.*, 439 (2021) 213875.
- [22] L. J. Feng, Q. Chen, J. H. Zhu, D. P. Liu, Y. C. Zhao, B. H. Han, *Polym. Chem.*, 5 (2014) 3081-3088.
- [23] L. Chen, Y. Yang, Z. Guo, D. Jiang, *Adv. Mater.*, 23 (2011) 3149-3154.