Iranian Journal of Catalysis Spotlight 10(3), 2020, 247-252

IRANIAN JOURNAL OF CATALYSIS

Porphyrin-based catalysts

Compiled by Mohammad Dashteh

Mohammad Dashteh was born in 1994 in Dashteh/ Hamedan, Iran. Having graduated in the field of Pure Chemistry (2016) from Bu-Ali Sina University, Hamedan, Iran, he continued his M.Sc. in 2018 in Organic Chemistry under the supervision of Professor Mohammad Ali Zolfigol. He is currently working towards his Ph.D. under the supervision of Professor Mohammad Ali Zolfigol and Professor Ardeshir Khazaei in the department of chemistry at Bu-Ali Sina University, Hamedan, Iran. His research interest is the design, synthesis, and characterization of task-specific biological-based catalysts and their applications in organic transformations.

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

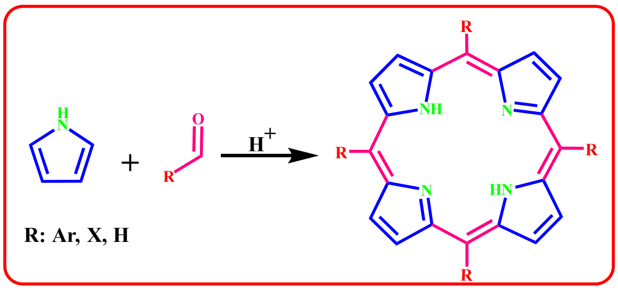
E-mail: mohammaddashteh1994@gmail.com

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

Introduction

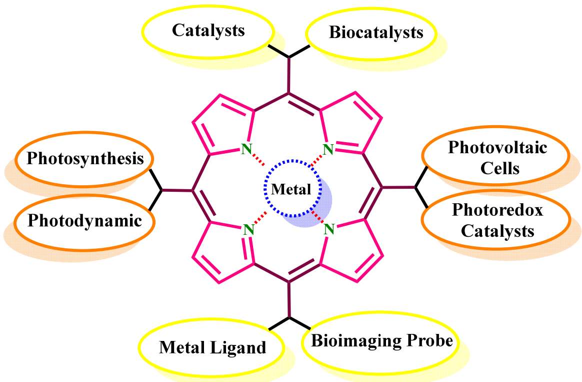
Porphyrins (Pors) are strongly believed to be one of the significant molecules playing a principle role in diverse biological relevant process [1]. The name "porphyrin" derives from the Greek word (porphyra), meaning purple [2]. The porphyrin ring structure is an 18π aromatic macrocyclic including of four pyrroles and four methine carbons. The large conjugated system leads to absorb in the visible reign of the electromagnetic spectrum, consecutively, this property affecting most of them be colored [3,4]. For example, porphyrins in numerous types of chlorophyll (green color) and heme (red color). Porphyrin investigation has long history, owning several advantageous properties and a broad range of disciplines of natural science, containing attractive absorption and emission properties, organic photovoltaic cells, strong aromaticity and rich metal coordination chemistry, structural robustness, bio-imaging probe, photodynamic therapeutic agent, P450-linked biocatalysts, photosynthesis, near infrared dye, metal ligand and so forth [5,6]. Scheme 1 show the general process for the synthesis of porphyrins. Porphyrins can be either metal central core or without metal core.

Metalloporphyrins (MPs) not only are valuable catalysts in organic chemistry but also are important in biological systems. MPs establish a type of catalysts and synthesize facile C-H oxidation with high selectivity and suitable yields to mediate [7]. Along this line, it is revealed that the enantioselective epoxidation, sulfidation and hydroxylation of styrene derivatives by using manganese and iron porphyrin as catalysts [8,9,10]. There is seen to be an obvious point about porphyrins photocatalytic action. Furthermore, porphyrins can absorb light energy resulting in an exited quantum state that can react with molecular oxygen to produce reactive oxygen species (ROS) for example singlet oxygen [11].



Scheme 1. General process for the synthesis of porphyrin.

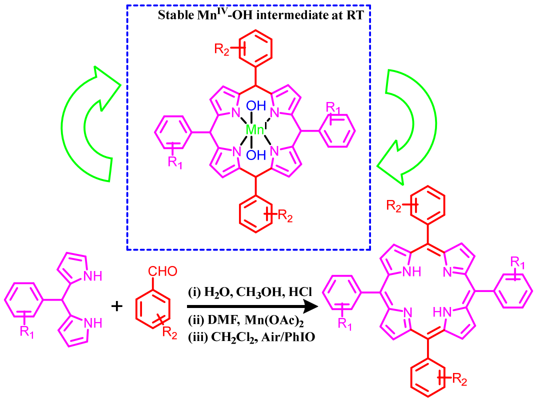
Moreover, the chemical properties of MPs have been applied for demolition of tumor cells in cancer patient. Therefore, porphyrins are crucial for life and have significant clinical application [12]. Although the catalytic applications of porphyrins have been comprehensively reviewed [13-21], but in this spotlight as a mini-review, it has been attempted to present some of the catalytic application of porphyrins and MPs in chemical processes. In this regard various important applications of porphyrins have been studied in several scientific fields (Scheme 2).



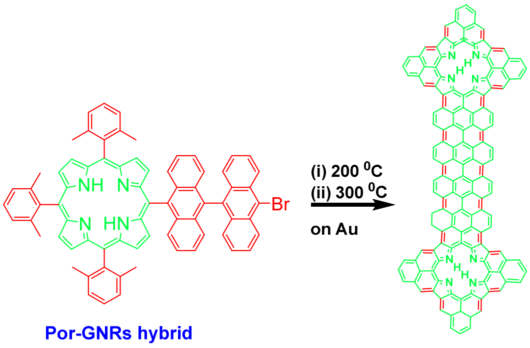
Scheme 2. Applications of porphyrins (Pors).

Abstracts

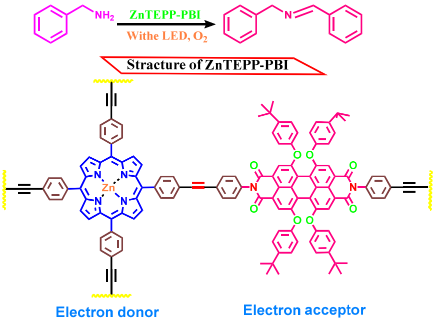
(**A**) In 2020, Mondal et al., [22] have been reported an efficient synthesis of porphyrin *via* a putative *trans*-manganese(IV) dihydroxide intermediate.



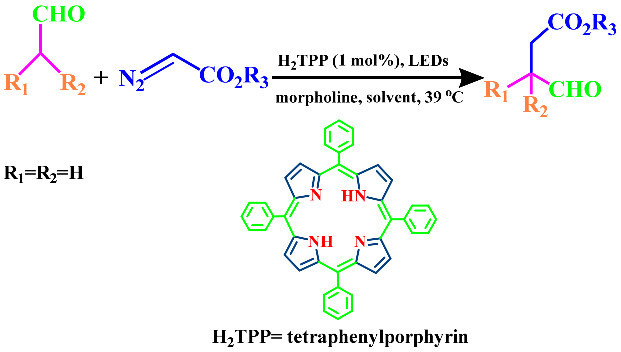
(**B**) It has been investigated the selective on-surface synthesis of a Por-GNR hybrid containing of two porphyrin(por) related to a short graphene nanoribbones (GNRs) segment [23].



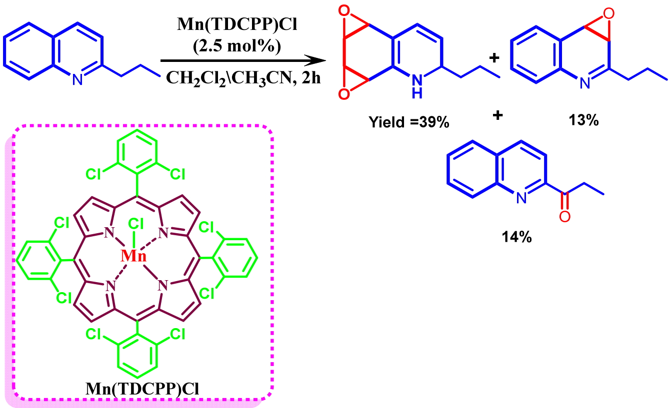
(**C**) Metalloporphyrin can be used as a facile homogenous photocatalyst [24]. Zinc porphyrin (ZnTEPP) and perylene bisimide (PBI) have been produced based previously reported procedure [25,26]. In 2019, Gua et al., [27] have been investigated a zinc-porphyrin-based porous organic polymer bearing an electron donor and an electron acceptor (ZnTEPP-PBI). This compound has been used as a heterogeneous photocatalyst for oxidative homocoupling of amines to imines under visible light.



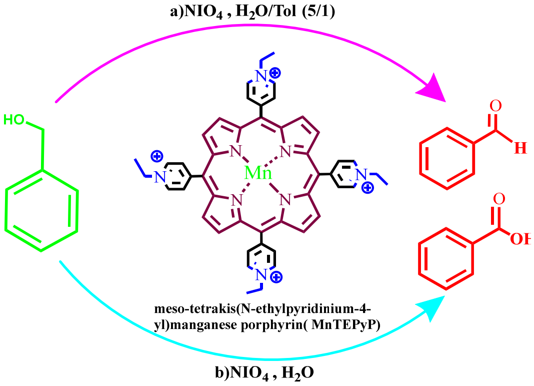
(**D**) Under light irradiation porphyrin not only are able to transfer energy but also participate in electron transfer procedure, producing an enamine cation and carbene in the triplet state, thus, facilitating functionalization of aldehydes at the α-position. As result, porphyrins are strongly believed to be as photoredox catalysts in C-C bond forming reaction [28].



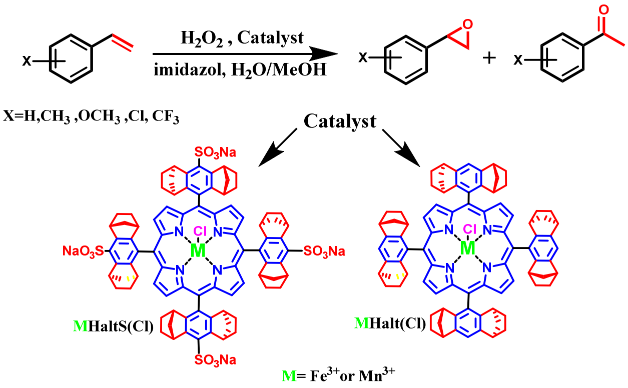
(**E**) the epoxidation of alkenes is one of the processes of great importance in the fine chemical industry from an economic point of view, because epoxide is useful intermediate in the production and manufacture of high-value commercial polymers like polyurethane, polyamide, resins, and polyester [29]. In addition, this transformation is used to carry out bioinspired oxidation [30] to produce drug candidates or metabolites.



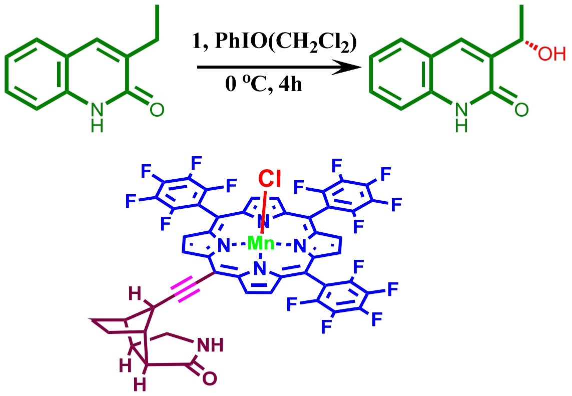
(**F**) Metalloporphyrins have been used as oxidative agents. Manganese porphyrin is appropriate catalyst for transformation of primary alcohols to the corresponding aldehyde and carboxylic acids [31].



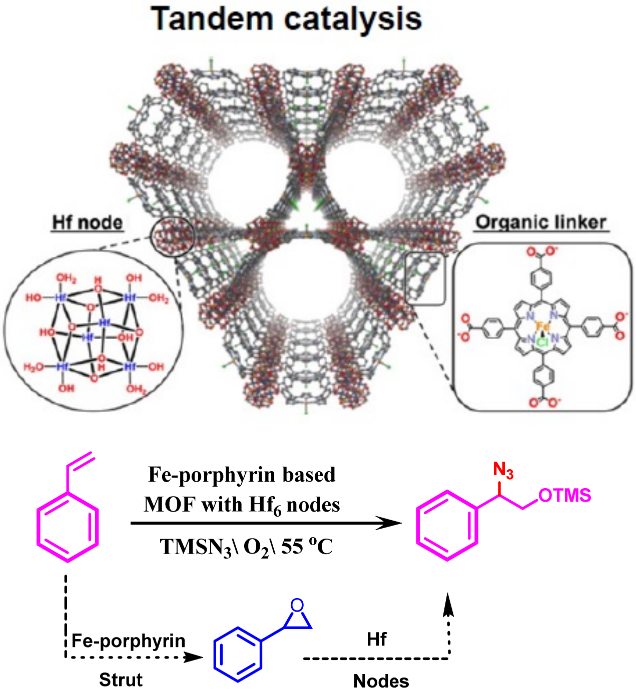
(**G**) Simonneaux et al., [8,9] have studied enantioselective epoxidation of styrene derivatives by using H_2O_2, in water-methanol solution through chiral water-soluble manganese and iron porphyrin as catalysts.



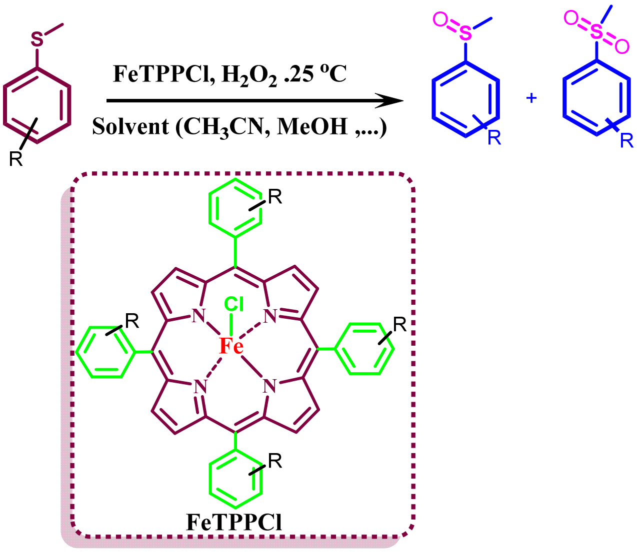
(**H**) Burg et al., [32] have been investigated enantioselective oxygenation of exocyclic methylene groups by using manganese porphyrin catalyst with a chiral recognition site.



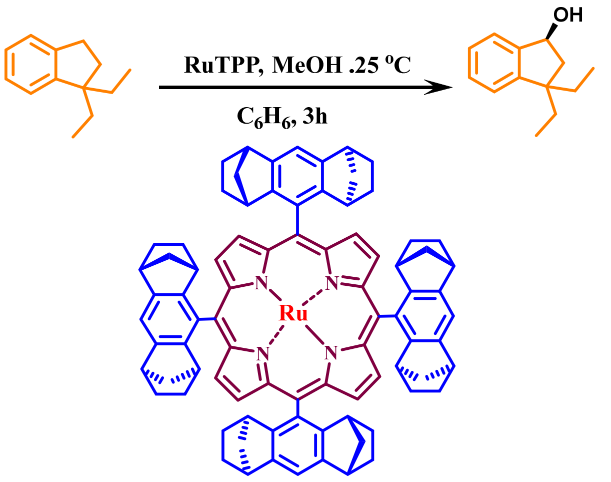
(**I**) Porphyrins with unsaturated metal centers within framework compounds can function as efficient Lewis acid catalysts by offering available coordination sites and facilitating the catalytic transformation within open pore spaces of framework compounds. In this regard, one model reaction is the ring-opening of styrene epoxide with trimethylsilylazide ($TMSN_3$). Takaishi, and coworkers have been reported a Zn-based porphyrin MOF (ZnAl-RPM) that could catalyze this ring-opening reaction efficiently due to the strong Lewis acidity of Al(III) sites in the porphyrin linkers [33]. Later, Stoddart, and coworkers have been also designed a tandem catalytic system that couples a Fe-porphyrin catalyzed epoxidation of styrene with a subsequent Hf6 cluster catalyzed epoxide ring opening by using a recyclable heterogeneous PCN-222/MOF-545(Hf) catalyst [14].



(**J**) Sulfoxidation is commonly presented as being a direct pathway for generating sulfoxides, however, most of the reagents that have been used for this reaction are such as iodosylbenzene, peroxyacids, and stoichiometric oxo-metal oxidants are unsatisfactory due to their high toxicity and low chemoselectivity between sulfoxide and sulfone products [34]. One successful example of a green protocol has been described by Baciocchi and co-workers, so that the oxidation of sulfides with an ethanolic solution of H_2O_2 and iron tetrakis(pentafluorophenyl)porphyrin as catalyst, thus giving the corresponding sulfoxides on a gram-scale [35].

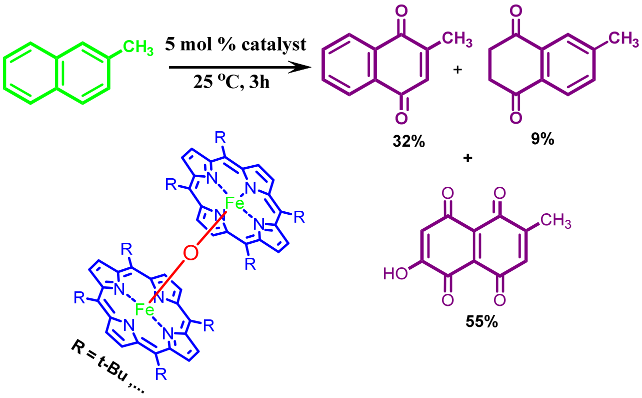


(**K**) In 2012 Simonneaux and co-workers have been reported examples of enantioselective hydroxylation of alkanes, with a chiral iron porphyrin as a catalyst and using hydrogen peroxide as an oxidant in methanol and water, to give optically active secondary alcohols (ee up to 63%) [8].



Catalytic enantioselective hydroxylation of a alkene

(**L**) In 2009 Neu et al., have been reported metalloporphyrins as oxidative agents. Manganese porphyrin is an appropriate catalyst for the oxidation of 2-methylnaphthalene by the $(FePct\text{-}Bu_4)_2$ O-polymeric iodosylbenzene system [17].



References

[1] (a) J. T. Groves, J. Inorg. Biochem. 100 (2006) 434-447; (b) L. Que Jr, W. B. Tolman. Nature. 455 (2008) 333; (c) J. P. Collman, J. I. Brauman, T. R. Halbert, K. S. Suslick, Proc. Natl. Acad. Sci. U.S.A. 73 (1976) 3333-3337; (d) D. Dolphin. Biochem.7 (2012) 33.

[2] Harper, Douglas, Buglione, Drew Carey, "porphyrian., The Online Etymology Dictionary, Retrieved 14 September 2014.

[3] A.S. Ivanov, A.I. Boldyrev. Org. Bio. chem. 12 (2014) 6145-50.

[4] T.D. Lash. J. Porphyr. Phthalocyanines.15 (2011) 1093-115.

[5] T. Tanaka, A. Osuka. Chem. Soc. Rev. 44 (2015) 943-69.

[6] S. Hiroto, Y. Miyake, H. Shinokubo. Chem. Rev. 117 (2017) 2910-3043.

[7] M. Costas. Chem. Rev. 255 (2011) 2912–2932.

[8] P. Le Maux, H.F. Srour, G. Simonneaux. Tetrahedron. 68 (2012) 5824-5828.

[9] H. Srour, P. Le Maux, G. Simonneaux. Inorg. Chem. 51 (2012) 5850–5856.

[10] P. Le Maux, G. Simonneaux. Chem. Commun. 47 (2011) 6957–6959.

[11] J. Cossy, D. Belotti. Tetrahedron Lett. 42 (2001) 4329–4331.

[12] B. Whittney, Sh. Lindsey, Sh. Mark. Handbook of Porphyrins: Chemistry, Properties and Applications. 2014.

[13] L. Feng, K. Wang, E. joseph, H-C. Zhou. Trends in Chemistry. Article in Press (2020), Review.

[14] C.F. Pereira, M.Q. Simoes, J.P.C. Tome, F.A.A. Paz. Molecules. 21 (2016) A126.

[15] J.C. Barona-Castano, C.C. Carmona-Vargas, T.J. Oliveira, K.T. Graca, M. Neves, P.M.S. Amparo, F. Faustino. Molecules. 21 (2016) no.310.

[16] A.B. Sorokin. Inorg. React. Mech. 8 (2012) 89-84.

[17] M.P. Doyle. Angew. Chem. Int. Edit. 48 (2009) 850-852.

[18] B. Boitrel, V. Baveux-Chambenoit, P. Richard. Helv. Chim. Acta. 87 (2004) 2447-2464.

[19] A. B. Solovieva, S.F. Timashev. Russ. Chem. Rev. 72 (2003) 965-984.

[20] G.B. Maravin, M.V. Avdeev, E.I. Bagrii. Pet. Chem. 40 (2000) 1-18.

[21] F. Bedioui. Coord Chem Rev. 144 (1995) 39-68.
[22] S. Mondal, K. Sahu, B. Patra, S. Jena, H.S. Biswal, S. Kar. Dalton Trans. 49 (2020) 1424-1432.
[23] L.M. Mateo, Q. Sun, S.X. Liu, J.J. Bergkamp, K. Eimre, C.A. Pignedoli, P. Ruffieux, S. Decurtins, G. Bottari, R. Fasel, T. Torres. Angew. Chem. Int. Ed. 59 (2020) 1334-9.
[24] P. Kar, T. K. Maji, P. K. Sarkar, P. Lemmens, S. K. Pal. J. Mater. Chem. A. 6 (2018) 3674–3683.
[25] A. R. McDonald, N. Franssen, G. P. M. van Klink, G. van Koten. J. Organomet. Chem. 694 (2009) 2153-2162.
[26] H. Y. Wang, K. Y. Pu, S. Huang, F. Liu, B. Peng, W. Wei. Funct. Polym. 69 (2009) 117–123.
[27] X.X. Guo, J. Jiang, Q. Han, X.H. Liu, X.T. Zhou, H.B. Ji. Appl. Catal. A. 590 (2020) 117352.
[28] K. Rybicka-Jasińska, W. Shan, K. Zawada, K.M Kadish, D. Gryko. J. Am. Chem. Soc. 138 (2016) 15451-8.
[29] S. Nakagaki, G. Ferreira, G. Ucoski, K. Dias de Freitas Castro. Molecules. 18 (2013) 7279–7308.
[30] B. Akagah, A.T. Lormier, A. Fournet, B. Figadère, Org. Biomol. Chem. 6 (2008) 4494–4497
[31] Q.G. Ren, S.Y. Chen, X.T. Zhou, H.B. Ji. Bioorg. Med. Chem. 18 (2010) 8144-8149.
[32] F. Burg, S. Breitenlechner, C. Jandl, T. Bach. J. Chem. Sci. 2020.
[33] S. Takaishi, Chem. Sci. 4 (2013) 1509–1513.
[34] N. Wojaczy, E. Wojaczy. Chem. Rev. 110 (2010) 4303–4356.
[35] E. Baciocchi, M.F. Gerini, A. Lapi. J. Org. Chem. 69 (2004) 3586-3589.