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Pradip B Gujarathi

Department of Chemistry

Shri Shivaji College Kandhar,

Nanded, Maharashtra, India

Recent emerging applications of porphyrins and Metalloporphyrins and their analogue in diverse areas

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Abstract

In recent years, scientific advancements have constantly increased at a significant rate in the field of biomedical science is gaining substantial importance. Porphyrins are most widely studied tetrapyrrole - based compound because of their importance role in biological processes. The cavity of porphyrins containing four pyrrolic nitrogens is well suited for binding majority of metal ions to form metalloporphyrins. Porphyrins and metalloporphyrins possess peculiar photochemical, photophysical, and photoredox properties which are tunable through structural modification, have drawn interest to discover new dimension in the field of biomedical. Applications of porphyrins and metalloporphyrins have been pursued in the perspective of contrast agents for magnetic resonance imaging (MRI), photodynamic therapy (PDT) of cancer, and bioimaging.

This purpose of this review is to accumulate the recent study on applications of porphyrins and metalloporphyrins - base materials.

Keywords: Porphyrins, metalloporphyrins, corrole, photosensitizers, bioimaging, drug delivery, catalysis

1. Introduction

Porphyrins represent a unique class of heterocyclic tetrapyrrolic organic molecule which are the most ubiquitous compound found in nature. Porphyrins are of fundamental significance on this planet to sustain life in various ways like storage and transport of oxygen, chlorophyll for photosynthesis –different type of enzyme and vitamins ^[1-2]. Synthetic porphyrins and metalloporphyrins have inspiring biological photophysical, photochemical properties and are promising candidates for diseases treatment ^[3] biological imaging ^[4], industrial ^[5], analytical ^[6] photocatalytic ^[7] nonlinear optical ^[8] and molecular photovoltaics ^[9-10].

In few last decades, researches have expanded the use of porphyrins –base compounds for medical, drug delivery, biosensing, and bio-imaging purpose ^[11-12]. The work synthesized of porphyrins arrays for light harvesting application using Wittig chemistry, which allow construction of covalently bound system of conjugated stable and easy to characterized. this is achieved with dendrimers strategy utilizing tetraaryl porphyrins as buiding blocks.

The main applications in this case has been in the well established PDT of tumor cell where porphyrins can selectively binds cancer cell and destroy them by oxidation (by singlet O₂ formation) after photoexcitation ^[13-14]. These methods no side effect causes by classical methods (surgery, radiotherapy, chemotherapy).

Porphyrins can also be useful in other medical conditions such as spinal cord compression where antioxidants properties of low valent metalloporphyrins (Mn(II) porphyrin can be exploited ^[15].

Another major field of single porphyrin applications in catalysis. for example Fe(II) porphyrin have been employed to catalyze reduction of highly polyhalogenated alkane pollutants ^[16]. Ru and Os porphyrin have shown highly regioselectivity in oxidation of many olefins ^[17].

The emission properties of metalloporphyrins includes the use of electroluminescence devices ^[18, 19]. Other applications includes use of porphyrins in new kinds of memory devices ^[20] in the field of optoelectronic ^[21].

Synthesis of dyads composed of Fe (II) and Zn porphyrin of new artificial photosynthetic systems and also for protein binding. The use of porphyrin array necessary for light harvesting artificial photosynthesis, photonics and optoelectronics are connected through mesopositions ^[22, 23]. In order to create large antenna dendrimers strategy is simplest approach ^[24-25]. Monosubstituted tetraarylporphyrins is important candidate for this dendramers strategy.

Corresponding Author:**Pradip B Gujarathi**

Department of Chemistry

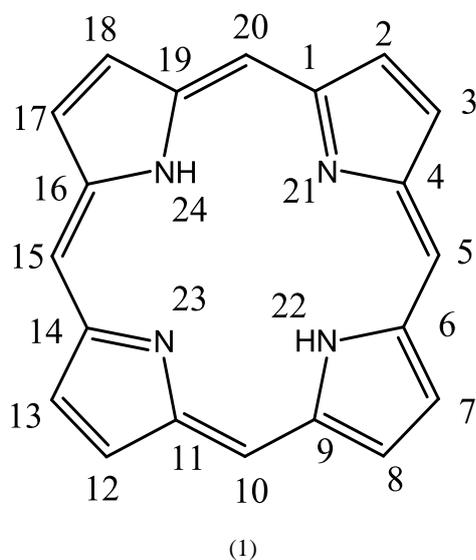
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The meso substituted unsymmetrical porphyrins have more applicability as potential bioactive compound, in our earlier work we have synthesized meso substituted unsymmetrical porphyrins and metalloporphyrins by using two different aldehydes [26-30].

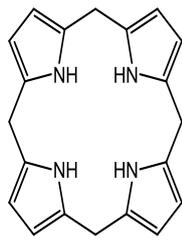
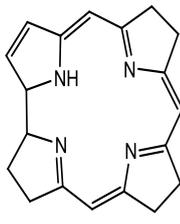
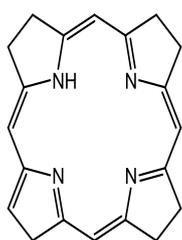
1.1 Structural Features

The porphyrin nucleus (1) consists of four 'pyrrole-type' rings joined by four methine bridges to give a macrocycle. The porphyrin (1) system is completely conjugated. The system possesses total twenty two electrons, out of which eighteen electrons are in conjugation to satisfy Huckel ($4n + 2$) aromaticity. The four nitrogen atoms with lone pair of electrons chelated with most of the metal ions in the periodic table. The system is reactive like simple aromatic compounds since it possesses Huckel ($4n + 2$) π electrons.



The ring atoms are numbered from 1 to 20 (and / or 24 during inclusion of the positions of nitrogen atoms). Generally the 5,10,15, and 20 positions become *meso* positions. The positions 2,3,7,8,12,13,17 and 18 are the peripheral (β) positions of the porphyrin ring. Depending upon the substitution arrangement of peripherals as well as *meso* positions the symmetrical and unsymmetrical porphyrins were generated. Porphyrins are highly coloured their main absorption bands have very high extinction coefficients, the intense 'Soret' band found around 400 nm is a characteristic of macrocyclic conjugation.

Examples of more highly reduced macrocycles are known. Corphin (2), Corrin (3) and Porphyrinogen (4). The importance of these materials lies in the fact that they are intermediate biosynthetic precursors of the porphyrins, plant pigments, PDT as well as vitamin β_{12} .



2. Importance of porphyrins and metalloporphyrins in diverse areas

The importance of complexity of porphyrin rings in nature attracted many researchers to study the fundamental chemistry of these macromolecules. A vital part of such research is the design and synthesis of these macromolecular system.³¹ Synthesis and functionalization of porphyrins are scientific matters which in recent years have received much attention. This has been mainly due to the use of these macromolecules in

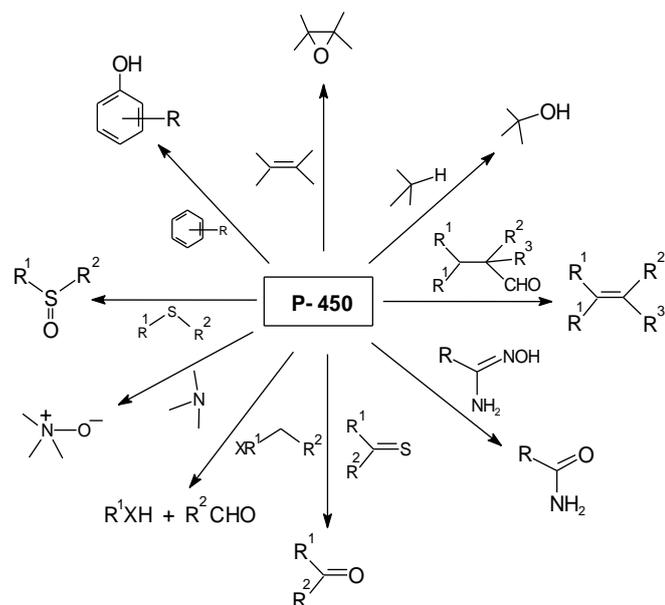
1. Biological catalysis,
2. Photodynamic therapy
3. Photosynthetic and electron transfer role
4. Porphyrins and Metalloporphyrins as Opto-materials
5. Artificial Photosynthetic Systems
6. Porphyrins for Optoelectronics
7. Synthetic Light-Harvesting Antenna
8. Material chemistry
9. Porphyrins as a catalyst in scalable reaction:
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11. Bio - Imaging application of porphyrins and metalloporphyrins
12. Porphyrins and metalloporphyrins for drug delivery

2.1 Biological Catalysis

In organic chemistry, oxidation belongs to the most important process. An advancement towards the development of an efficient catalyst for oxidation process has great importance. "The right to development must be fulfilled in such a way that, in fair way it should correspond to the environmental needs of today's and future generation". The knowledge around this circumstance has led to the development of intensive catalysis. The design of catalysts often orients itself by naturally occurring examples, since nature presents many models for extremely efficient and selective catalyst. These "Bio-mimetic chemistry" contain one of the most extensive areas: porphyrin catalyzed reactions. This is based on the large extent on the discovery of called mono and dioxygenase enzymes which are able to catalyze oxidation of substrate by incorporating one or two oxygen atoms. The P-450 cytochromes ubiquitous membrane bound mono-oxygenase enzymes that homogeneously catalyze oxygen atom transfer to entrapped non-polar substrates [31]. Many heme catalyzed reactions were reported by S. A. Hahatscher [32].

The catalyst reductively activates dioxygen by using NADPH as an electron source. One oxygen atom is then reduced to water atom and the other atom is transferred to a substrate resulting in the hydroxylation of alkanes and arenes, the epoxidation of alkenes, formation of N-oxides, S-oxides from amino and sulphur compounds. Other P-450 reactions include N-dealkylation, O-dealkylation and reductase-like dehalogenation of halocarbons [33].

The enzyme is also responsible for oxidation cleavage of carbon-carbon bonds in the biosynthesis of certain steroids. Substrates processed by P-450 include endogenous compounds such as steroids, fatty acids, leukotrienes and prostaglandins, as well as exogenous drugs, pesticides, anaesthetics, solvents and chemical carcinogens. In contrast to its beneficial roles in biosynthesis, metabolism and detoxification, cytochrome P-450 initiates many chemical carcinogens. Some catalyzed reactions are illustrated in (Scheme -1).



Scheme-1: P-450 Catalyzed reactions ^[32].

Metal complexes of synthetic tetraaryl porphyrins especially those of Fe (III), Mn (III), Ru (III) and Cr (III) porphyrins are efficient models of cytochrome P-450 monooxygenase enzymes in the presence of single oxygen donor. ^[34] The oxygen donors NaOCl and H₂O₂ are particularly interesting for alkene epoxidation.

2.2 Photodynamic therapy

Synthetic porphyrin, especially, *meso*-tetraphenylporphine derivatives substituted in para positions with soluble acidic, basic, neutral groups are of potential interest in medicinal chemistry because they can form chelates either with some toxic heavy metals or with gamma ray emitting radioisotopes. They are also used as fluorescent indicators for delineation of neoplastic tissue in cancer patient. In the past year it was found that such compounds may be used as tumor selective radiation sensitizers and are used in cancer therapy. Several functionalized porphyrins are used as drugs to treat diseases such as central nervous system disorder, ulcer, glaucoma and amnesia. More recently Sn (IV) porphyrin complexes and also tin porphyrinoids are good candidates for photodynamic therapy. The coordination chemistry of tin porphyrin complexes has been reviewed ^[35].

In connection with photodynamic therapy (PDT) of cancer during which the administered sensitizer necessarily interacts with the biological material. Recently reviewed surveys ^[36] highlight the changes in photophysical behaviour of porphyrins, metalloporphyrins and other porphyrinoid sensitizers induced by their interaction with biopolymers (i.e. proteins, nucleic acids), liposomes or synthetic sensitizer carriers (i.e. cyclodextrins, calixarenes). The structure, charge, and physicochemical properties of the sensitizer predetermine the type of interaction with surrounding microenvironment and are manifested by changes in absorption, fluorescence, kinetics of deactivation of the excited states and generation of singlet oxygen.

Several reviews exist ^[37-45] for porphyrinoid as a sensitizer for PDT. Synthetic porphyrin (1) are often substituted in *meso* positions. Chlorin and bacteriochlorin are partly hydrogenated porphyrins. Hydrogenation shifts absorption band above 600 nm. Purpurins are degradation product of chlorophylls.

Among novel type of porphyrinoid compounds which are sensitizers PDT. The cationic sensitizer TMPyP intercalates into DNA at G-C base pairs ^[46].

Three binding modes have been distinguished for interaction of cationic porphyrins with DNA Interaction, Outside groove binding, Outside binding with porphyrin self stacking. Porphyrin derivatives depending upon their structure, central metal and axial ligand prefer not only a particular binding modes but also certain DNA sequence.

2.3 Photosynthetic and electron transfer role

The importance and complexity of electron transfer reactions in Nature have lead many researchers to look for ways to study the fundamental chemistry of these processes in simplified model systems. A significant part of this effort has been devoted to the study of photoinduced charge separation reactions as a means of capturing and storing solar energy. A long-term goal of this research is to develop an understanding of photoinitiated electron-transfer reactions that is sufficiently advanced to enable one to design laboratory systems for conversion of solar energy into chemical potential. A vital part of such research is the design and synthesis of complex molecular systems which are comprised of electron donors and acceptors that mimic the charge separation function of photosynthetic proteins and these complex molecules are usually referred as supramolecular system. The review ^[47] describes the work in this field on supramolecular system that utilize porphyrins in their electron-transport schemes.

2.4 Porphyrins and Metalloporphyrins as Opto-materials

In photosynthesis, the chlorophylls and pheophytins (i.e. close cousins of metalloporphyrins and porphyrins respectively) play key roles in absorbing light energy over wide spectral range. Also, they helps in covering light energy into the highly directional transfer of electrons ^[48-50]. It is highly complex process that has inspired considerable interest in the synthesis of porphyrin arrays. A biomimetic approach to the photosynthetic apparatus may also lead to application as opto-electronic devices.

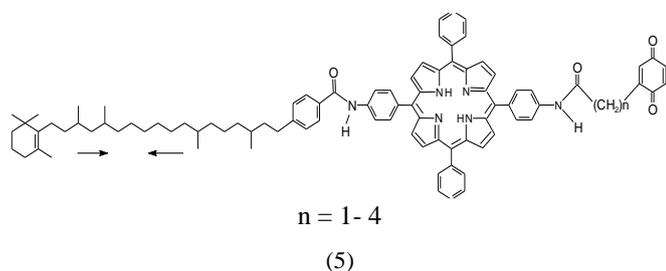
Most research of artificial photosynthetics has been directed towards mimicry of the natural reaction center (RC). The center functions as a molecular-scale solar photovoltaic device that converts light energy into chemical energy. This chemical energy can be transported, stored for maintenance, growth, and reproduction of the organism The artificial reaction center requires some kinds of chromophore that can absorb light and acts as an electron donor/ electron acceptor/ organized super structure that controls the electron interaction between the donor and the acceptor.

2.5 Artificial photosynthetic systems

Achieving a long-lived charge separation after photoinduced electron transfer is the key to realizing artificial photosynthesis. The ultimate goal here is to create a sufficiently long-lived excited state that chemical reactions can compete with the back reaction and convert the excited state free energy in to less volatile form. The first such system was developed in the 1970s, were molecules consisting of synthetic porphyrins covalently linked to the quinones. Following absorption of light, the porphyrin (p) transfers an electron to quinone (Q) resulting a charge-separated state consisting of a cationic radical P^{•+} and an anionic Q^{•-}. The life time of P^{•+}- Q^{•-} is usually very short because of the back reaction. The electron rapidly returns to the porphyrin

molecule, losing energy as heat, and the ground state of the molecule is restored.

Substantial success has been made in using these complexes for biomimetic studies. In the 1980s, Gust and Moore have shown that the back reaction could be slowed substantially using "triad" molecular composed of a tetraphenylporphyrin covalently linked to both carotenoid and quinone. Distance dependence of the electron transfer reaction was studied in the "triad" having 1 to 4 methylene groups between the quinone and porphyrin (5).



A spectacular example of long-lived charge separation donor acceptor triad was demonstrated by Gust and Moore.^[51] Triad consisting of diaryl porphyrin (P) covalently linked to a carotenoid polyene (c) and a fullerene (C-60).

2.6 Porphyrins for Optoelectronics

An ultimate goal in microelectronics is the design of electronic switches, wires, transistors and gates made of single molecules. This goal borrows heavily from the photosynthetic reaction center, both in physics and chemistry. In principle, porphyrin arrays connected with conducting or insulating molecular wires could be converted into such molecular photo-electronic devices.

2.7 Synthetic Light-Harvesting Antenna

A light harvesting antenna should be multicomponent assembly including chromophores that can absorb strongly in the blue and red regions of the solar spectrum and an energy-acceptor component to accept it. Synthetic porphyrin arrays are obvious candidates for the design of artificial antenna since chlorophylls are the main natural chromophores. However, their number has been limited by lack of appropriate synthetic methodology for their preparation.

Many groups are also pursuing light harvesting porphyrin arrays, an excellent examples of employing pigment to enhance the absorption of the porphyrin was reported by Lindsey and others^[52]. They synthesized light-harvesting arrays comprised of a central porphyrin with one, two, or eight boron-dipyrrin (BDPY) pigments.

In an effort to prepare new biomimetic light-harvesting system, Therien *et al.* have adopted metal-mediated cross-coupling methodologies and synthesized new class of arrays^[53]. The porphyrins are linked together by yne and polyynyl units as multichromophoric system.

2.8 Material Chemistry

Since, porphyrin possess extended π electron system and exhibit high stability, they are used in material chemistry as: Photonic materials, Nonlinear optical materials, Opto-materials (i.e. artificial photosynthetic system, optoelectronics, synthetic light harvesting antenna), Porphyrinic solids (i.e. porous molecular porphyrin structures, metal ion coordination network materials, porphyrin-incorporated zeolites, clay and layered materials incorporating

porphyrins), Conductive polymers, Ferroelectrics, Component in organic metals, Molecular wire and other devices, Porphyrin-based chemical sensors (i.e. gas sensors and sensor for solution spaces).

The attachment of redox active molecules such as porphyrins to electro- active surface provides an attractive approach for electrically addressable molecular based information storage.

Porphyrin and related macrocycles provide an extremely versatile synthetic base for variety of material applications. The exploration of metalloporphyrin assemblies as building blocks for tailored material properties has found rapid growth during the past decade^[54].

Porphyrins and metalloporphyrins have found broad applications as field-responsive materials, particularly for optoelectronic applications (e.g. the facile substitution of the periphery of various porphyrins has generated series of unusual liquid crystalline materials). The porphyrin ligands serve as a platform on which one can erect desirable molecular and material properties, including very large dipole moments, polarizabilities, and hyperpolarizabilities. The nonlinear optical properties of these materials are of special interest, in part of energy transfer with molecular control, and in part of potential applications in optical communications, data storage and electrooptical signal processing.

In contrast to their interaction with applied electric, magnetic or electromagnetic fields, porphyrins and metalloporphyrins can also interact with other chemical species. Such interactions were chemo-responsive rather than field-responsive. As an example of such applications porphyrin solids are often highly porous and the intentional development of molecularly-based molecular sieves or shape-selective solid catalysts is currently under development. Sensor applications is another chemo-responsive materials.

High thermal and chemical stability, thin films if metalloporphyrins can be obtain by using organic molecular beam deposition technique, which enable better potential to build molecular spintronic devices^[55-60], applications in this field have been reviewed^[61].

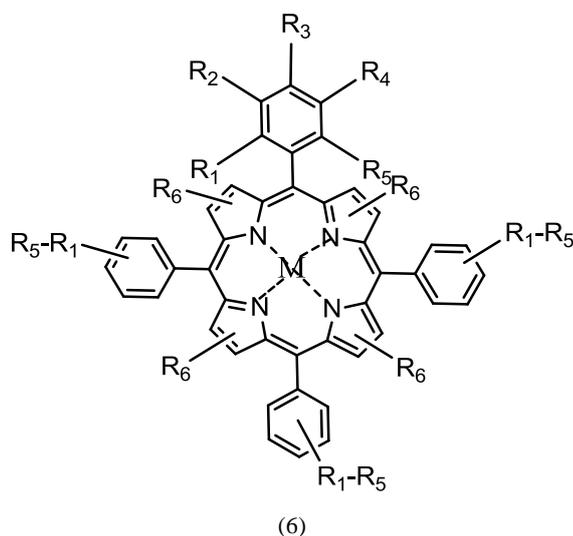
2.9 Porphyrins as a catalyst in scalable reaction

Catalysis is topic of continuous interest since it was discovered in chemistry centuries ago. Porphyrin and metalloporphyrin are fascinating compound which are involved in number of synthetic transformation of great interest for industry and academy. The review on recent progress in reaction catalysed by porphyrins in epoxidation, sulphoxidation, oxidation of alcohol to carbonyl compound and C-H functionalisation reported by Juanc Barona Castano and *et al.*^[62].

Porphyrins and their derivatives are the class of naturally occurring macrocyclic compounds, intense color and special aromatic 18π electron structure. A suitable example are chlorophyll a, heme group and cyanocobalamine.

Porphyrins that introduction of phenyl or related groups at meso position is a good strategy which provide efficient catalytic oxidation^[63].

Meso phenyl substituted metalloporphyrins bearing electronegative groups where classified as second generation porphyrins. oxidation reactions are important synthetic tools and number of application can be found in chemical industry^[64]. The inert nature of C-H bond requires use of highly reactive reagents. Porphyrins and metalloporphyrins with ruthenium, iron, manganese among other metals constitute family of catalyst.



Third generation catalyst of metalloporphyrin R_1 - R_5 represents EWG or bulky groups and R_6 halogen.

2.9.1 Epoxidation of alkenes

First industrial scale bioinspired oxidation of cyclohexane with COTPP, oxidation of alkene is a great importance in fine industry and commercial polymers. Iron porphyrins are effective catalyst for epoxidation [65]. Dendritic Ru porphyrins catalyzed epoxidation reactions was reported by Juanc *et al.* [66].

2.9.2 Sulphides to sulfoxides

Sulfoxides are chiral synthons in the synthesis of bioactive compounds [67, 68]. Metalloporphyrins catalyzed epoxidation for the enantioselective synthesis of sulindac.

2.9.3 Oxidation of alcohol to carbonyl compounds

Ji and co workers reported gram scale selective oxidation of alcohols to carbonyl compounds meso tetraphenyl ruthenium complex [69].

2.9.4 Iridium porphyrin catalyzed cyclopropanation: C-H insertion, and N-H insertion reaction has been reported by Bernie Joe Anding [70].

2.10 Porphyrins and metalloporphyrins as Contrasting agent for magnetic resonance Imaging

Tetrapyrrolic based macrocyclic systems are getting more attention in biomedical field due to their low toxicity in absence of light, tunable photophysical properties and superior tumor uptake of these chemical entities [71], has been observed in this area in the 21st century. Generally contrast agents are of two categories, which are paramagnetic and superparamagnetic materials [72]. Researchers have prepared expanded porphyrins which are known as texaporphyrins and their metal chelates for potential application in MRI [73-75].

Moreover, the efficiency of contrast agents can be enhanced by structural modifications to optimize relaxation time. Most importantly, the future of MRI technique must be based on molecule having multiple functionalities for excellent tissue contrast and tissue penetration.

2.11 Bio-Imaging application of porphyrins and metalloporphyrins

The field of medical imaging is developing at a significant rate with the advent of noninvasive *in vivo* technologies, like

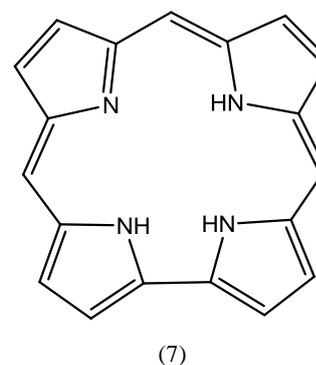
fluorescence imaging to speed up drug design and development progression. Many researchers have reported bio imaging application. [76-78] Porphyrin and a porphyrin zinc complex as a dual function molecular imaging platform for MRI and fluorescence imaging sensing has been reported [79].

2.12 Porphyrins and metalloporphyrins for drug delivery

The delivery of drug at a specific points in the body has vital importance in disease treatment. porphyrin based metal organic frame work reported for this application. [80-81]

3. Novel aspect of Corrole based applications

Despite of many similarities between corrole and porphyrins, the chemistry of the former remained undeveloped for decades because of served synthetic obstacles. The recent discoveries of facile methodologies for synthesis of triarylcorroles and their corresponding metal complexes allow for their utilization in various fields. The survey reveals many examples where corrole were used as key components in catalysis, sensing of gaseous molecules and medicine oriented research. The corrole has special features such as stabilization of high valent transition metal ions, unique photophysical properties, large N-H acidity, facile synthetic manipulation and distinct catalytic properties.



Basic structure of Corrole

Corrole is a contracted version of porphyrins, is more anionic in nature and have smaller cavity size, one meso carbon is less than porphyrin. Thus it stabilizes higher oxidation states of chromium, manganese and iron corrole trianionic ligand has great potential. Ruijie D. Teo *et al.* [82] predicted corrole anticancer research.

4. Conclusion

In summary, porphyrins and metalloporphyrins and its derivatives present wide range of applications, therefore synthesis of new compounds containing this core represent an interesting proposal for chemist in both academic and industrial laboratories. In view of what has been highlighted herein, we believe that the construction of new derivatives of porphyrins is an alternatives to the future development as potential pharmacophore, fluorophore, chromophore with use in chemical, medical and technological applications.

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