

"Unlocking the Potential of Porphyrin-MOFs: Advances in Materials Science"

Dr. Mohammed Saleh Al Ansari¹

¹Associate Professor (College of Engineering, Department of Chemical, Engineering, University of Bahrain, Zallaq, Bahrain

malansari.uob@gmail.com ;

Abstract

The remarkable photo physical and electrochemical properties of porphyrins and their derivatives have led to extensive exploration of these compounds for a variety of applications. Porphyrin-based metal-organic frameworks (MOFs) have garnered important consideration in latest years due to their unique structural characteristics and versatile applications. These substances are constructed by coordinating metal ions with organic ligands, forming highly porous and ordered networks with huge surface areas. This study presents a top level view of the synthesis techniques and structural capabilities of porphyrin-primarily based MOFs, emphasizing the diverse range of metal ions and natural linkers employed to tailor their residences for particular applications. The exceptional porosity and surface area of those materials permit diverse functionalities, in gasoline storage and separation packages, porphyrin-primarily based MOFs showcase high adsorption capacities and selectivity for gases which include hydrogen, methane, carbon dioxide, and volatile organic compounds, making them promising applicants for strength storage and environmental remediation. Additionally, their catalytic activity has been exploited in organic transformations, photo catalysis, and electro catalysis, offering sustainable solutions for chemical synthesis and energy conversion processes. Porphyrin-based MOFs represent a versatile class of materials with immense potential across diverse fields, paving the way for innovative solutions in energy, environmental, and biomedical applications.

Keywords: Porphyrin-based Metal-Organic Frameworks (MOF), Synthesis Strategies, Photo Catalysis, Sensing, Photo Dynamic Therapy.

1. Introduction

In nature, metal ions are found everywhere. When combined with biological ligands like proteins and nucleic acids, metal ions can produce biological proteins. In biological processes, they have significant physiological and biochemical roles[1]. Metal ions, particularly ions made up of heavy metals, which are released into the ecosystem through waste residues, waste gas, and industrial and domestic wastewater, will seriously harm both life and the environment due to the swift growth of modern manufacturing and urbanization. Thus, from an environmental and biological standpoint, effective metal ion detection is still necessary challenge. Porphyrins are macromolecular heterocyclic compounds that are created when different functional groups replace porphyrin (C₂₀H₁₄N₄) in the center or β position. Metallic composites, often referred to as metalloporphyrin, are created when freebase porphyrins combine with

a lot of metal ions or secondary building units (SBUs) in the porphyrin center. Porphyrins are key ecologically benign bionic catalysts with excellent catalytic efficiency and selectivity that function as the active site of many biological enzymes. In contrast to other structures, metalloporphyrin structures exhibit a distinct electronic structure that makes them more active since it can catalyse a wider range of processes. Scheme 1 displays the structure diagrams of the porphyrin core, porphyrins, and metalloporphyrin. As metalloporphyrin and porphyrins are synthesized, they become more significant and have applications in biomimetic chemistry, among other fields. However, the instability, ease of deactivation, and difficulty of recycling of the porphyrin electro-/photo-catalyst hindered the advancement of EC technologies. . In order to provide an exceptional performance of the electro-/photo-catalyst, scientists therefore envisaged the incorporation of porphyrins as organic

ligands into highly engineered, controlled, and structurally stable framework elements such as MOFs and COF. Metal porphyrin frameworks (MPFs) and covalent porphyrin frameworks (CPFs) are the terms used to describe the MOFs and COFs that directly correlate porphyrins with metal ions or SBUs. Metal-organic frameworks, or MOFs for short, are crystalline nonporous hybrid substances made up of organic ligands connecting metal nodes [2]. With the right inorganic and organic building blocks, they can be modularly constructed to create functional frameworks with desired topologies, modifiable porosity, and other characteristics[3]. In contrast to other porous materials like zeolites, MOFs are easily customizable.

The products have good selectivity and specificity since they can be produced under very basic circumstances. By varying their composition, MOFs' extensive coordination chemistry allows for the modification of their photoelectric characteristics [4]. Given this, MOFs applications, such as ion exchange, storage of gases and isolation, photo catalysis, sensor, degradation of pollutants, and so on. Furthermore, because of their repeating and ordered arrangement, MOFs are thought to provide the perfect foundation for sunlight absorption and energy transmission in artificial photosystems. [5]. In addition to being able to be controlled by the structure of the porphyrin molecule, co-structure design of combined ligands in MOFs and co-assembly doping layout with different compounds, especially for the discovery of new photo catalytic materials, can also be used to enhance the photo catalytic ability of porphyrin-based MOFs. Porphyrin-based framework materials have been investigated in great detail after years of development[6], and they often display a variety of activities. Porphyrin-based framework materials' easy production and great chemical stability have made them useful in a variety of catalytic processes[7]. Porphyrins are a type of heterocyclic macromolecules that are created when four pyrrole-like subunits' α -carbon atoms are joined by a methine bridge. With 26 π electrons, the Porphyrin ring is a strongly conjugated structure. Strong optical absorption and emission properties are seen, particularly upon complication with metal ions[8]. Porphyrins are sensitive to minute changes that can be found by UV, luminescence, and other spectroscopic methods because they have

chromophores and a vast conjugated system. In the UV-visible spectrum, Porphyrins are characterized by 4 weak peaks of absorption in the 500–700 nm range (Q band) and a high peak of absorption in the 400–420 nm region (Soret band). The π/π^* electron transport of porphyrin unsaturated ligand is connected to these peaks. The outermost ring of porphyrin can have different substituents added to it, which can be used to create a variety sensors. It is possible to alter the core metal and graft different molecules or groups onto the porphyrin ring. Porphyrins often have excellent stability, are easily modified, and carry out a variety of biological tasks. Thus, biomolecule, anion, and cation detection can be accomplished with porphyrin-based sensors. In addition to being a direct sensor for analyte detection, the porphyrin molecules can also be employed as a dopant to create a composite sensor that is extra steady and effective[9].

Composite sensors based on porphyrins can offer quick, on-location, real-time analysis. Porphyrin has good optical characteristics because of its vast planar conjugated system. As a result, a useful category of metal ions probes is the porphyrin molecule. Unfortunately, the majority of porphyrins are insoluble in water, which restricts their use in the investigation and detection of metal ions. Due to the risk of embolisms, intravenous administration of medications containing insoluble solutions was previously thought to be impossible. The therapeutic index has increased in the modern period due to advancements in nanoparticle (NP) solutions, including Nano-drugs. Novel Nano drugs that target sick tissues and have better action and lower toxicity have been developed. Even so, a large number of nanoparticles are still composed of solid macromolecules that are typically smaller than 200 nm in diameter, too dispersed to be polymers. Since the late 1970s, the issue of polymers' lack of biodegradability has plagued the use of nanomaterial as drug delivery systems. Porphyrins are a type of heterocyclic macro cyclic compounds. The building blocks of these chemical compounds are four linked pyrrole rings organized in a circle. Methylene bridges hold the pyrrole α -carbon atoms together[10]. Out of the 26 π -electrons in porphyrins, 18 π -electrons are in a continuous, planar macro cycle[11]. The knowledge of porphyrin structure has significantly increased in the last few years, as evidenced by the numerous articles

that have documented the precise structures of metalloporphyrin and porphyrin molecules as well as their various functions in biological applications. Porphyrins are a type of macro cyclic tetrapyrroles that typically have a 1-D, 2-D, or occasionally 3-D structure. Porphyrins' characteristics and potential uses in medicine can be significantly altered by substituting nitrogen atoms for α , β , and other carbon atoms in the compound[12].

Aspects of porphyrin chemistry also pertain to how they function as ligands in coordination complexes, which is determined by their structural characteristics, which are influenced by the angles of bonds and bond distances, as well as by the type of metal and the existence of functional groups. In general, toxicity is reduced to the barest minimum when transition metals from the first row are used in the structure of porphyrins; however, certain transition metals from the second and third rows, like Pt, Pd, and Ru, also have minimal cellular toxicity. The biomedical uses of these compounds in drug administration, gene transfer, and photodynamic treatment are expanded by employing amine-based ligands or linkages as the substituents. But because carboxy-based linkers have the ability to form hydrogen bonds with a variety of medicines, they are also effective for drug delivery.

Because of the diverse photo physical and photochemical characteristics of porphyrins, porphyrin-based nanomaterial have garnered a lot of attention lately [13]. Through the central metalation process, the porphyrins can be expanded to generate additional molecules, further adjusting their photo physical characteristics. While the porphyrin family is well-known for producing singlet oxygen and other extremely reactive oxygen species when exposed to light, the majority of porphyrin-based compounds also exhibit strong photo acoustic and fluorescence characteristics, making them viable options for simultaneous imaging and therapy applications known as "theranostics". Because of their potent photosensitizing qualities, capacity to amass specifically inside tumours and other aberrant cells and tissues, and propensity to stay inside tissues for extended periods of time, porphyrins and their related chemicals have piqued the interest of researchers. Their characteristics have made them suitable for use in diagnostic imaging and other biomedical applications. Thus, medicines that have

the ability to manage tumours locally and have fewer adverse reactions than surgery or alternative treatments for cancer can make use of porphyrins and their derivatives. Additionally, porphyrins are capable of carrying metallic radioisotope for application in cancer radiation therapy since they work well as metal chelators. Because majority these substances are hydrophobic and favour an aggregate form, which could affect the treatment result through decreased single-molecule O₂ generation and lowering fluorescence quantum yields, many porphyrin Nanoparticle carriers have been explored as photosensitive substances for PDT applications.

One of the porphyrin derivatives utilized in cancer treatment as a photosensitizing agent is photofrin. Visudyne is another porphyrin derivative that has been approved by the US FDA for use as a pharmacological agent in ophthalmology. Porphyrins and their derivatives are nonetheless subject to the drawback of low aqueous solubility, which renders them hydrophobic and prone to aggregation. The primary cause of the decline in healing efficiency is this aggregation, as only monomeric entities typically exhibit photochemical activity. Metal-organic frameworks (MOFs) have emerged as a flexible elegance of substances with promising packages throughout diverse fields due to their tunable systems and amazing houses. Among those, porphyrin-based MOFs have garnered huge interest because of their unique structural functions and multifunctionality. This take a look at offers a comprehensive overview of synthesis strategies and structural traits of porphyrin-primarily based MOFs, laying the muse for understanding their numerous programs. By highlighting their roles in gas storage and parting, catalysis, sensing, and biomedical applications, this research underscores the versatility of porphyrin-primarily based MOFs in addressing critical societal and business demanding situations. Moreover, the observe emphasizes the top notch homes exhibited by way of these materials, which include excessive adsorption capacities, catalytic activity, and sensing talents, which similarly decorate their attraction for realistic implementation. Importantly, by way of identifying key research instructions focusing on synthesis optimization, fundamental insights, and real-world packages, this study ambitions to catalyse improvements within the field of porphyrin-based MOFs, driving their

transition from laboratory curiosities to impactful technologies with huge utility.

The study's Key Contributions are as follows:

- Overview of synthesis techniques and structural features of porphyrin-primarily based MOFs.
- Highlighting various applications inclusive of gas storage and separation, catalysis, sensing, and biomedical programs.
- Emphasis on the excellent properties of porphyrin-primarily based MOFs which includes excessive adsorption capacities, catalytic interest, and sensing abilities.
- Identification of destiny studies directions focusing on synthesis optimization, fundamental understandings, and practical implementation of porphyrin-based MOFs for actual-world programs.

The following is the arrangement of the remained sections in this article: A summary of relevant studies is given in Section 2. In Section 3 of the study, Synthesis Methods, Structural Characteristics and Characterization Techniques are described. The Construction and design of Porphyrin-Based MOFs presented in Section 4. Section 5 discusses Application of Porphyrin-Based MOFs. The conclusion and future scope of the study is discussed in Section 6.

2. Related Works

A 2d lanthanide metal-organic framework with metal-node-dependent photo catalytic performance was proposed by Jiang et al.[14] In a controlled synthesis. It is very difficult to synthesize (2D MOFs) in great yields and to rationally modify their characteristics in a predictable way for particular applications. Now, in a home microwave oven, a range of porphyrin-based 2Dlanthanide MOFs with varying thicknesses were effectively synthesized. When 1, 5-dihydroxynaphthalene (1,5-DHN) was photo oxidized to create jug lone, the photo catalytic performances of heas-prepared 2DLn-TCPP Nano sheets were thickness-dependent. In particular, the Yb-TCPP produced O₂@ and IO₂ with exceptional photodynamic activity. This work not only lays the groundwork for novel approaches to enhance photo catalytic performance, but it also offers essential insights into the design of 2D MOFs Nano sheets and their property customization. This work provides fresh insights for photo catalysis

property tailoring and illuminates a new lighthouse for the controlled synthesis of 2DMOFs.

By sonicating its bulk crystals, Qin et al. [15] presented a method for achieving a highly dense assembly of porphyrin in porphyrin-integrated MOF Nano sheets generated by an ionic liquid: sonication exfoliation. First, the ionic liquid aided synthesis approach was used to synthesize the 2D layered structure MOF, [BMI]2[Ca3(H₂TCPP)2(μ₂-OH₂)2(H₂O)2] (1). 1's laminated layers make it evident that there is a strong metal-carboxylate connection between the layers but there is no strong interlayer non-covalent interaction. This bonding helps 1 exfoliate to create 2D MOF Nano sheets. High-resolution transmission electron microscopy, powder X-ray diffraction, and fast Fourier transform (FFT) patterns demonstrated that one NS's crystalline structure could be preserved following exfoliation. When exposed to light, these MOF Nano sheets against MCF-7 cells demonstrated significant cytotoxicity, good water dispersibility, and biodegradability.

Because of the exceptional photo physical and electrochemical capabilities of porphyrins and their derivatives, there has been a lot of attention in the areas of gas storage, bio sensing, solar cells, biomedical applications, and catalysis. However, a number of intrinsic drawbacks, including self-quenching, inadequate absorption in the biological spectrum window, and low chemical and optical stability, seriously impede their biological applicability, particularly in treating and diagnosing cancer. A class of new hybrid porous coordination polymers known as porphyrin-based metal organic frameworks (MOFs) was created to address the drawbacks of porphyrins and facilitate their use in medicinal applications. With the ability to be loaded or altered with biological molecules or pharmaceuticals to give therapeutic and imaging capacities, porphyrin-based MOFs retain the unique features of porphyrins. The research by Wang et al. [16] covered the various synthesis methods for porphyrin-based MOFs and thoroughly examined the most recent advancements and successes of MOFs based on porphyrin in the realm of biomedical applications, including cancer therapy and bio imaging. Lastly, we address the difficulties encountered in the biological uses of porphyrin-based MOFs and outline potential avenues for future

study to get extremely effective therapeutic effects and superior imaging for theranostics in cancer.

Though chemically strong frameworks which are required for applications, have been obtained much more recently, porphyrin-based MOFs have been successfully developed for the past thirty years, and this sector is growing. The synthesis with different coordination groups has contributed to this advancement by enabling related MOFs to move beyond metal carboxylates and acquire new topologies and characteristics. A concise summary of the synthetic processes leading to basic porphyrins and phthalocyanines containing these complexation elements was provided in the De et al.[17] Study. The associated MOF molecules are then described, and their stability, physical characteristics, and structural and textural attributes are explored. A summary of the resultant nets and topologies is presented, highlighting the differences associated with the alternate coordinating groups as well as the parallels with metal-carboxylate phases. Ultimately, the prospects presented by this emerging field of study are examined, encompassing synthesis routes, pore shape and size modification, stability, and physical characteristics.

Porphyrins are significant compounds that are widely distributed in nature as units that absorb visible light and as active sites for enzymes. Because it is so simple to manipulate the positions and spacing between the porphyrin units in these porous crystalline substances, there has been a recent surge in interest in employing these useful molecules as components for the creation of MOFs. With atomically accurate structures, porphyrin-based MOFs offer a perfect platform for studying their structure-function correlations in the solid state without sacrificing the porphyrin building blocks' fundamental features. The work by Zhang et al. [18] included a historical account of the creation and uses of porphyrin-based MOFs, from early research on their structures and designs to more recent attempts to use them in biomimetic catalytic processes. Applications in biomedicine, sensing, photo catalysis, and electro catalysis will be emphasized.

It is critical to create new, ecologically friendly energy conversion technologies since the growing fuel demand is seriously polluting the environment. However, good, affordable materials for electrodes and other components are needed for

these energy conversion devices. Porphyrins' multifunctional properties, such as their easy synthesizing, high chemical stability, abundance of metallic sites of activity, adjustable crystalline structure, and high specific surface area, make them suitable for use in energy conversion devices. Examples of these framework materials are metal-organic structures and covalent organic frameworks. Here is a quick summary of the several porphyrin structural blocks found in the Gu et al. [19] study. High-performance electro- and photo-catalysts can be created by directly assembling them with framework materials or by using them as organic ligands. Additionally, a summary and introduction are provided for the various kinds of catalysts used in electro- and photo-catalytic water splitting, carbon dioxide reduction, and oxygen reduction processes. The difficulties with porphyrin-based frameworks materials in the aforementioned application are discussed, along with appropriate solutions, at the conclusion of the paper.

Over the past few decades, there has been a portion of attention in the study of MOFs, an intriguing and practical family of coordination polymers made up of coordination bonds between metal ion/cluster nodes and functional organic ligands. MOFs have found widespread applications in a variety of fields, including drug delivery, desalination, biological imaging and sensing, water vapour capture, magnetic and electronic devices, hydrogen/methane storage, catalysis, nonlinear optics, biological imaging, with large surface areas, flexible porosity, and tunable biocompatibility. Notably, smart MOF-based Nano composites with superior bio-related properties have been devised and manufactured to fulfil the growing needs of materials made from MOF for biomedical applications. This is due to the swift growth of synthetic methodologies and surface functionalization strategies. The work of Yang et al. [20]describes the synthesis, functionalization, and recent developments of MOFs in medical domains, such as the transport of cargo (drugs, proteins, nucleic acids, and dyes) for cancer treatment, bio imaging, bio sensing, antibacterial, and biocatalysts. There is also discussion of the opportunities and difficulties in the field developing MOF-based biomedical materials.

The literature on porphyrin-based metal-organic frameworks (MOFs) offers valuable insights

but faces some limitations. There's a lack of standardized synthesis methods, hindering reproducibility and scalability. Secondly, while these MOFs show promise, their stability in real-world conditions, such as biological environments or under light exposure, needs further study. Moreover, there's a gap between lab-scale demonstrations and practical use, requiring solutions for scalability, cost, and regulatory compliance. Additionally, environmental impacts and sustainable synthesis methods are overlooked. Finally, interdisciplinary collaboration is needed to fully exploit the potential of porphyrin-based MOFs. Addressing these limitations is crucial for practical application and societal impact.

3. Porphyrin-Based MOFs: Synthesis Methods, Structural Characteristics and Characterization Techniques

Porphyrin-based totally Metal-Organic Frameworks (MOFs) constitute a burgeoning area at the vanguard of substances technology, offering exceptional versatility and functionality for numerous applications. Synthesizing those MOFs includes a various array of strategies which includes solvothermal and microwave-assisted strategies, each offering particular advantages for tailoring the shape and properties of the ensuing materials. The macro cyclic nature of porphyrin molecules lends itself nicely to integration inside MOF frameworks, supplying opportunities for precise manage over pore size, and connectivity between metal ions and organic linkers. Structural characterization strategies provide valuable insights into the pore length distribution, area of surface, and framework topology of porphyrin-based MOFs, crucial for optimizing their overall performance in various packages. This convergence of synthesis techniques and characterization techniques paves the manner for the layout and fabrication of custom designed porphyrin-primarily based MOFs with tailor-made properties, driving innovation throughout disciplines ranging from catalysis to biomedical studies. Figure 1 shows the overall flow of the proposed study.

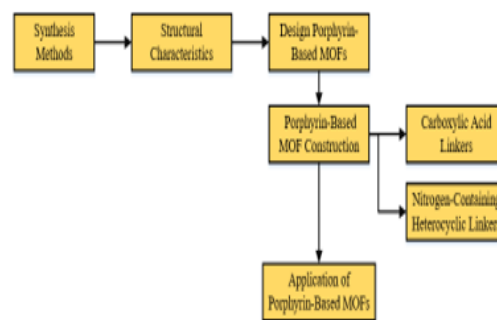


Figure 1: Overall Flow Diagram

3.1 Synthesis Methods

A class of chemical molecules known as porphyrins is distinguished by its macro cyclic structure, which is made up of four pyrrole rings. These molecules are well known for playing crucial roles in biological systems. Specifically, they are necessary building blocks of myoglobin, haemoglobin, and chlorophyll, which respectively enable oxygen transport and photosynthesis. Porphyrins have a wide range of synthetic uses in addition to their biological importance. They act as catalysts in a number of chemical processes, such as reduction and oxidation. Porphyrins are also essential parts of sensors because of their extraordinary sensitivity to environmental changes, which allows for very specific identification of gases that are ions, and biomolecules.

Numerous MOFs have been successfully synthesized. These include ZIFs, MILs, and UiOs. These MOFs offer effective platforms for encapsulating or delivering drugs, imaging agents, and enzymes. The shrinking of MOFs into the Nano scale (10–100 nm) is crucial for the development of biomedical Nano platforms due to its substantial impact on the size-dependent functionality and bio distribution of delivered particles. Numerous approaches have been put out thus far for the synthesis of NMOFs, and these have been compiled in a number of reviews. [23] Numerous effective techniques have also been developed, specifically for the synthesis of NMOFs: reverse micro emulsion, microwave-assisted synthesis, hydrothermal, sono chemical, and mechanochemical approaches. In solvothermal synthesis, organic linkers and ions from metals or clusters react in a solvent at high pressures and temperatures. The size, shape, and crystallization of the resultant MOF crystals may all be precisely

controlled using this approach. Solvothermal synthesis facilitates the integration of porphyrin molecules into the framework of porphyrin-based MOFs, resulting in the formation of customized hybrid materials. Similar to solvothermal synthesis, hydrothermal synthesis uses water as the solvent and usually takes place at lower pressures and temperatures. Benefits of this approach include easy scaling and mild reaction conditions. Hydrothermally produced porphyrin-based MOFs have regulated porosity and area of surface, which makes them excellent options for storing gases and separation applications. In microwave-assisted synthesis, the reaction mixture is heated with microwave radiation, which produces quick and unique heating of vessel.

Comparing this method to traditional heating methods, you should expect faster reaction kinetics and shorter synthesis periods. Microwave-assisted porphyrin-based MOFs frequently show better homogeneity and crystallinity, which improves their performance in catalysis and sensing applications. Free-based porphyrins link with ions of metal or SBUs to function as organic linkers in porphyrinic MOFs. Porphyrinic MOFs can also be used to create multifunctional platforms by combining them with other functional elements including fluorescent quantum dots, photo thermal agents, and magnetic nanoparticles. For biomedical applications, porphyrin-based MOFs' morphology, framework, and composition are essential, and a lot of work has gone into creating porphyrin-based MOFs that satisfy these needs. During synthesis, a number of critical factors affect the structure and characteristics of MOFs based on porphyrins. The coordination of the environment and durability of the MOF structure are dictated by the selection of metal ions, which affects the catalytic in nature adsorptive, and optoelectronic capabilities. The linkage and porosity of the MOF framework are mostly determined by organic linkers, with porphyrin-containing linkers frequently offering extra functionality designed for particular applications. Furthermore, the nucleation, development, and crystalline of porphyrin-based MOFs are greatly influenced by reaction conditions, including pressure, temperature, solvent composition, and reaction time. As a result, optimization is required to achieve the desired structures and attributes. In conclusion, these critical

parameters and synthesis techniques are essential to the design and fabrication of customized porphyrin-based MOFs with specific structures and attributes, enabling their use in a variety of applications such as sensing and catalysis. Figure 2 shows the synthesis of porphyrinic MOFs in two or three dimensions involves controlling the growth of the framework in specific directions, leading to different structural architectures.

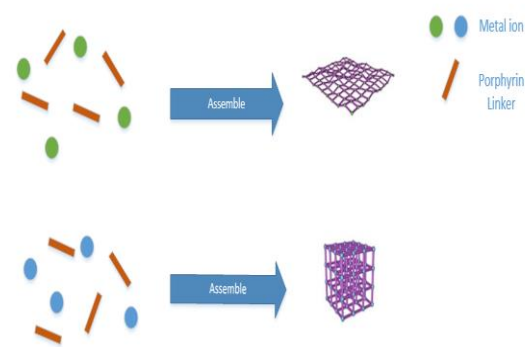


Figure 2: **Porphyrinic MOF Synthesis in Two or Three Dimensions.**

3.2 Structural Characteristics and Characterization Techniques

Porphyrin-based Metal-Organic Frameworks (MOFs) exhibit unique structural characteristics crucial for their diverse applications. These characteristics include pore size, surface area, and the connectivity between metal centres and organic linkers. Porphyrin-based MOFs offer tunable pore sizes, ranging from Angstrom-scale micropores to larger mesopores. The pore size significantly impacts the adsorption and diffusion properties of gases and other molecules within the MOF structure. Characterization of pore size distribution is often achieved through techniques like gas sorption analysis and small-angle X-ray scattering. High surface area is a defining feature of porphyrin-based MOFs, essential for applications such as adsorption and catalysis. Surface area analysis, typically conducted via gas sorption techniques like nitrogen adsorption-desorption isotherms, reveals the extent of internal surface available for interactions. The surface area varies based on factors including metal ions, organic linkers, and synthesis conditions. The connectivity between metal ions and organic linkers dictates the framework topology and stability of MOFs. Metal

ions serve as nodes, coordinating with the nitrogen atoms of porphyrin rings and carboxylate groups of linkers. Understanding this connectivity is crucial for designing MOFs with desired structural rigidity and porosity. X-ray diffraction (XRD) is a key technique for elucidating the coordination environment and connectivity within porphyrin-based MOFs, providing insights into crystal structure and bonding distances. Various techniques are employed to characterize the structural properties of porphyrin-based MOFs. X-ray Diffraction reveals crystal structure and symmetry, while Scanning Electron Microscopy (SEM) offers insights into surface morphology and particle size distribution. Nitrogen Adsorption-Desorption Analysis is utilized to measure area of surface and size of pores distribution, aiding in understanding the porous nature of MOF materials.

4. Design and Construction of Porphyrin-Based MOFs

4.1 Design of Porphyrin-Based MOFs

The large-scale application of MOFs in photo catalysis is hindered by certain drawbacks, such as their swift recombination and deactivating photo-generated charges and poor cycling stability. MOFs and their combined materials offer advantages such as adjustable pores, a high level of porosity, and an extensive surface area. These restrictions make it more difficult for MOFs to be used effectively and sustainably in photo catalytic processes. Addressing these issues with MOFs is made easier by porphyrins and their derivatives' exceptional light absorption capability and ease of coordination with metal ions. Thus, the advantages of both MOF materials and porphyrin molecules are combined when porphyrins are included into them. Furthermore, MOFs with different structures can be created by varying the porphyrin linker's connectivity and geometry.

The incorporation of distinct groups of function onto porphyrin molecules can also modulate their chemical characteristics and coordination capabilities. For instance, adding different substituents or modifying peripheral groups might alter the electron affinities of porphyrins. By achieving the proper band gaps and orbital energy levels, this alteration enables the creation of porphyrin-based MOFs that have remarkable light-harvesting qualities as well as

effective separation of charges and transfer efficiencies. The most often utilized organic linker in porphyrin-based MOFs is 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (TCPP). Additionally, metal ions aids in addressing the problems with MOFs' instability, weak dispersion, and easy aggregation, and leads to enhanced performance.

4.2 Porphyrin-Based MOF Construction

Porphyrin molecules attach themselves to ions from metals or clusters of metals as organic ligands. The main components of the porphyrin links in porphyrin-based MOFs include carboxylic acid, the pyridines, and polyazole groups.

4.2.1 Porphyrin-Based MOFs with Carboxylic Acid Linkers

Porphyrin-based MOFs incorporating carboxylic acid linkers offer unique opportunities for the design of functional materials with tunable properties. The presence of carboxylic acid groups in the linker molecules facilitates the coordination with metal ions or clusters, contributing to the framework's stability and structural diversity. MOFs with carboxylic acid linkers construction, the carboxylic acid groups serve as binding sites for metal ions, forming metal-carboxylate coordination bonds. These bonds play a crucial role in connecting the metal-porphyrin nodes and auxiliary linkers, thus dictating the topology and porosity of the resulting framework.

The porphyrin ligand containing an acidic carboxyl linker is the most often used ligand for porphyrin-based MOFs. It is linked to the metal core by a changeable coordination mode, which results in a flexible and regulated ligand structure. These MOFs based on porphyrins have strong structural stability and controllability and can be employed for photo catalysis, gas absorption, and catalysis.

By employing tetra carboxylic porphyrin (H₂TCPP) to connect Al(OH)O₄ chains by a hydrothermal reaction and subsequent Pt(II) metalation, a fundamentally Pt-dispersed aluminium-porphyrin-based MOF was created. With the help of the extremely effective electron transmission channel that platinum (Pt) atoms provide, the hybrid Al-TCPP-Pt MOFs demonstrated noticeably increased photo catalytic activity. Similar to this, [Sr₄(TCPP)₂(DMF)₈]_n and

[Ba₄(TCPP)₂(DMF)₈]_n were produced by hydrothermal reaction with H₄TCPP ligand and Sr²⁺/Ba²⁺ ions. The PMOFs had outstanding fluorescence characteristics. Four porphyrin alkaline earth-based MOFs were generated by substituting 5,15-bis(4-carboxyphenyl) porphyrin (H₂DCPP) for the TCPP ligand, which changed the MOFs' size and shape. They demonstrated superior methylene blue adsorption ability.

4.2.2 Porphyrin-Based MOFs with Nitrogen-Containing Heterocyclic Linkers

Porphyrin-based metal-organic frameworks (MOFs) incorporating nitrogen-containing heterocyclic linkers offer a diverse range of structural and functional possibilities due to the unique coordination chemistry of these ligands. Heterocyclic ligands that include nitrogen include pyridine, imidazole, polyazole, pyrazole ligands, and more. Compared to the atoms of oxygen and metal ions, the atoms of nitrogen and metal ions have a stronger coordination. As a result, MOFs made of heterocyclic ligands containing nitrogen show similar thermal and chemical stability to MOFs based on carboxylic acids.

A coordinating structure substance comprising Cu (II) and neutral pyridyl-substituted porphyrin groups was initially reported by Robson and co-authors [87] in 1994. Since then, there have been more and more reports of MOFs based on porphyrins. By encasing Pt (II) TMPyP in a rho-ZMOF via a post-modification technique, pyridine-containing porphyrin-based MOFP was created. The limit of detection was significantly increased as a result of their outstanding ability to discriminate for different anions under both aqueous and methanol conditions [88]. With eight peripheral pyridines, the newly developed porphyrin molecule may communicate to up to nine metal centres.

Utilizing a solvothermal technique, several MOFs were created utilizing TDPAP and different metal ions. With the exception of the MOFs made from Mn²⁺, these materials exhibit exceptional fluorescence characteristics. Similar to imidazole, pyrazole carboxylate is another heterocyclic group that contains nitrogen. The interaction among the linker and the metal clusters in the pyrazole carboxylate connection is facilitated by the sp-hybridized nitrogen atoms and the hydrogen bonding between the metal cluster's

carbonyl moiety and the nearby NH group. For instance, even under extremely alkaline circumstances, the pyrazole carboxylate-based porphyrin MOFs PCN-601 and PCN-602 show exceptional stability. They remain porosity and crystallinity even after being treated at 100°C with a saturating NaOH solution.

Porphyrin-based MOFs are flexible materials with a broad range of uses because of their complex structural design and chemical composition, which give rise to a multitude of unique features. Because porphyrin chromophores are included in the framework, these qualities include outstanding photo physical traits like potent fluorescence emissions and effective photosensitization capabilities. Porphyrin-based MOFs are excellent choices for photodynamic treatment, solar energy conversion, and fluorescence-based monitoring and imaging applications because of their photo physical activity. Porphyrin-based MOFs also show strong chemical stability in a range of environmental settings, which guarantees their durability and dependability in real-world uses. The robust framework structure and the strong coordination connections between organic linkers and metal ions are responsible for this stability. Furthermore, the porphyrin ligands' inherent qualities and the framework's accessible metal centres provide these MOFs with catalytic activity. They are heterogeneous catalysts that are used for a wide range of chemical reactions, providing possibilities for energy conversion, precise chemical synthesis, and environmental clean-up. Porphyrin-based MOFs have a number of benefits, one of which is their tenability via sensible design and functionalization techniques. Through careful manipulation of metal ion selection, organic bonds, and synthetic conditions, scientists can customize the molecular organization, porosity, and chemical response of MOFs to fulfil distinct application needs. Porphyrin-based MOFs' utility in sophisticated materials and applications for devices is further expanded by functionalization techniques like post-synthetic alteration and guest's molecules encapsulation, which allow for the inclusion of additional functionalities like sites for catalysis and sensing probes.

To summarize, porphyrin-based MOFs are very promising materials for a variety of applications, including energy conversion,

biomedical research, sensing, and catalysis. They also have particular photo physical characteristics, chemical stability, and catalytic activity that can be adjusted through functionalization and thoughtful design.

5. Application of Porphyrin-Based MOFs

5.1 Photo Catalytic Evolution of Hydrogen

The production of hydrogen from sun energy-driven water splitting has enormous potential as a clean and efficient energy supply. The introduction of porphyrin ligands efficiently broadens the ability to absorb visible light of MOFs. In addition co-catalysts, added to the bigger MOFs pore size, giving MOFs based on porphyrin a lot of advantages and possibilities when it comes to harnessing solar energy to make hydrogen. Fateeva and associates [21] documented the growth of photo catalytic hydrogen over porphyrin-based metal oxide films in 2012. Using the Al (OH) O₄ chain node and the tetra (4-carboxy) porphyrin (H₂TCPP) linker, Al-PMOF was created. In H₂ evolution, the photo catalytic activity of Al-PMOF including zinc metalloporphyrin and free-based porphyrin was investigated. The MOF/EDTA/Pt combination is utilized to capture the excited state of energy of the porphyrin; specifically, Pt serves as a co-catalyst to speed up the reaction while EDTA serves as a sacrificial electron donor. The findings suggested that a zinc-porphyrin-based MOF may be created by introducing Zn²⁺ into the porphyrin core. A renewable energy-driven water-splitting reaction can be exploited to create hydrogen using both porphyrin and Zn based MOFs.

Active metals can be included into MOF frameworks to increase the activity of photo catalytic hydrogen evolution. High stability and photo catalytic hydrogen production effectiveness characterize porphyrin-based MOFs. The iron hydride enzymes serves as a catalytic site for the evolution of hydrogen in this system. The quick transmission of photo-generated carriers is made possible by the chemical bonding and the close proximity of the two components. The materials' inherent chemical linkages can create powerful hydrogen elution systems, doing away with the requirement for electron mediators to transfer electron from the photosensitive agents to the

catalyst. MOFs' photo catalytic activity can also be influenced by their structure and form. 2D lamellar structures in MOFs are more favourable than bulk MOFs for maximizing the light-absorbing capacity of porphyrin units within the framework. This increases the possibility of contact among the substrate and the sites that are active, hence enhancing catalytic activity. Because 2D MOF materials can lessen the recombination process of photo-generated electron-hole pairs, they also exhibit considerable potential in photo catalytic hydrogen evolution. The shape and form of MOFs can potentially affect their photo catalytic activity. 2D lamellar structures in MOFs are more favourable than bulk MOFs for maximizing the light-absorbing capacity of porphyrin units within the framework. This increases the possibility of contact among the base material and the active sites, hence enhancing catalytic activity.

Utilizing metalloporphyrin as a link and Cu₂ (COO)₄ as a metal node, thin a two-dimensional MOF Nano sheets were created via a surfactant-stabilized coordination method. Under natural light irradiation, just-one Pt atom-coordinated MOFs set an entirely novel historical record in photo catalytic H₂ creation using water as the solvent and ascorbic acid as the sacrificial ingredient. The MOF Nano sheets are simply drop-cast able to form a thin film with a wide range of practical applications on solid surfaces.

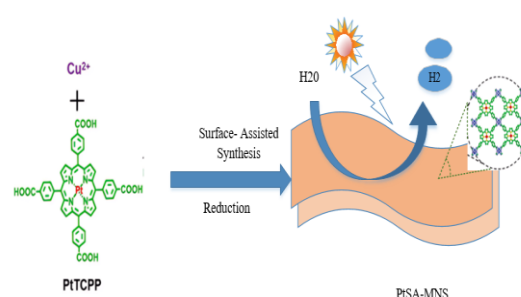


Figure 3: **Synthesis of Pt Ultrathin MOF Nano Sheets with Single-Atom Coordination for Photo Catalytic Hydrogen Generation**

Figure 3 shows the synthesis of Pt ultrathin MOF Nano sheets with single-atom coordination represents a significant advancement in photo catalytic hydrogen generation. By precisely controlling the arrangement of platinum atoms

within the MOF structure, this approach enhances catalytic efficiency and stability, promising substantial potential for clean energy applications.

5.2 Catalytic Photolysis of CO₂

Every day, enormous volumes of fossil fuels are utilized, and excessive carbon dioxide emissions into the atmosphere result in a growing number of environmental issues. As a result, scientists and businesspeople worldwide are very interested in the gathering and transformation of carbon dioxide into high-value-added molecules or renewable energy fuels, and a number of methods for doing so have been developed. Among them, the photo catalytic elimination of carbon dioxide powered by solar energy is one of the most effective and affordable techniques. For instance, the process of photo catalytic decrease of carbon dioxide can yield a variety of fuels, including hydrocarbons, CO, and formic acid [22].

The initial stage in the photo catalytic elimination of CO₂ is the synthesis of MOFs with suitable organic linkers to enhance light absorption. Fu and colleagues initially demonstrated the use of MOF photo catalysts for photo catalytic degradation of CO₂ to HCOO⁻ in 2013 [23]. Researchers created an aminated MOF photocatalyst and assessed its photo catalytic efficacy in an acetonitrile electrolyte with triethanolamine, which acting as the electron donor. The findings support the notion that MOFs' amino functionalization enhances photo catalytic function for CO₂ reduction. Because porphyrin-based MOFs produce charge carriers and efficiently absorb visible light, they are well suited for photo catalytic reduction of CO₂. For instance, the zirconium-based MOF PCN-222's porphyrin ligand functions as a visible light harvesting unit. Because PCN-222 and holes have a deep electron trap state, it can inhibit harmful, radioactive electron-hole recombination and increase the catalytic function of photo-reduced CO₂.

Different porphyrin contents in BUT-110 MOFs shown varying increases in chemical stability when compared to BUT-109(Zr). At a pH range of 1 to 10, the BUT-110 material showed remarkable stability as soon as the porphyrin level surpassed 50%. Moreover, greater photo catalytic capacity in the CO₂ conversion to CO was demonstrated by the BUT-110 series including metalloporphyrin ligands. It is thought that BUT-110-50%-Co represents the

optimal trade-off between chemical stability, photo catalytic effectiveness, and synthesis cost by varying the kind and quantity of metal porphyrins in BUT-110. In CO₂ reduction, the MOFs with a two-dimensional lamellar structures likewise demonstrate strong catalytic activity. Because of its superior charge transfer capacity and extended lifetime of photo-generated charges, an ultra-thin a two-dimensional Zn-MOF Nano sheets the photo catalyst demonstrated exceptional photo catalytic activity and good CO selectivity under slight circumstances. In the occurrence of Zn-MOF Nano sheets, the TON of CO is 26.2 over six hours, demonstrating their enhanced capacity to reduce CO₂.

MOFs may also be mixed with additional functional components to create photo catalytic composites, which will increase their capacity for photo catalytic CO₂ reduction even further. A novel hybrid catalyst was created by combining zero-dimensional-carbon nitride quantum dots with two-dimensional (2D) ultrathin porphyrin MOFs, as Figure 9a illustrates. The coordination of g-CNQDs with Co active sites in PMOF significantly reduces the migratory paths of gaseous substrates and photo-generated charges. Because of the successful separation of pairs of electron-holes and long-term absorption of electron in the Co core, the material shows more activity in the decrease of CO₂ and superior selectivity towards CH₄. At a feed ratio of 1:6, the mean longevity (τ) of g-CNQDs/PMOF is 5.25 ns, a considerable reduction from the mean lifetime (τ) of g-CNQDs, a value of 7.73 ns. In addition to increasing 6.02 times, the rate of methane (CH₄) generation also rose. When it came to CO₂ reduction, the composite showed exceptional activity; the amount of CO released was around seven times that of pure TiO₂. The separation of electron-hole pairs was aided by the light-induced carriers that were situated between the TiO₂ and MOF constituents. Consequently, in the photo catalytic decrease of CO₂ to CO, CTU/TiO₂ shown good catalytic ability and recyclability [24].

5.3 Photo Catalytic Fixation of Nitrogen

The significant regular processes in the nitrogen phase of the Earth is nitrogen fixation, which transforms nitrogen from the atmosphere into n-containing molecules that are utilized by all living things, including humans. The most widely used

commercial chemicals and free of carbon energy storage molecule is ammonia (NH_3)[25]. The method of industrially preparing NH_3 is quite energy-intensive and not good for the environment. An alternative sustainable approach for the effective synthesis of NH_3 from N_2 under moderate conditions is desperately needed. Porphyrin-based MOFs can efficiently improve N_2 adsorption because they are large surface area, extremely porous crystalline substances with highly organized pores.

Because porphyrin molecules are a potent photosensitive linker, they can greatly increase MOFs' light responsiveness. Moreover, well-thought-out porphyrin-based MOFs can greatly increase the efficiency of photo catalytic nitrogen fixation by improving the separation of charges created by photosynthesis [68]. As a result, porphyrin-based MOFs have an exciting future in photo catalytic fixation of nitrogen and perform exceptionally well[26]. For instance, a comparative analysis revealed that $\text{NH}_2\text{-MIL-125 (Ti)}$ performed best in nitrogen reduction, with the Ti^{3+} sites increasing the efficiency of N_2 adsorption and reduction and the amine-functionalized linker effectively enhancing light absorption. Porphyrin molecules are particularly effective at photo catalytic nitrogen fixing because they serve as excellent absorbers of light and may be used as linkers to construct MOFs, Fe is the core of activity for the uptake of N_2 and decrease, and Al serves as a metallic node that sustains the MOF frameworks. The Al-PMOF (Fe) exhibits exceptional effectiveness in nitrogen fixation, with an ammonium yield of $127 \mu\text{g g}^{-1} \text{ h}^{-1}$ that is 50% higher than that of Al-PMOF, at a nitrogen dioxide flow rate of 20 mL min^{-1} .

5.4 Photo Catalytic Removal of Pollutants

Pollution and clean energy-related environmental challenges have gained prominence. Due to development and growing populations, a significant amount of impurities have been released into the atmosphere. Because of their variable resistance to oxidation and photodecomposition, organic dyes constitute a major environmental hazard and are challenging to eliminate from the environment. Adsorption, biological oxidation, treatment with chemicals, and photo-degradation are just a few of the numerous methods that have been

created and put to use thus far to eliminate dangerous pollutants from the environment. Among these, photo catalytic techniques are often inexpensive, have good selectivity for organic contaminants, and do little harm to ecosystems.

Using Zr-oxide complexes and porphyrin groups in various geometries, MOF-525 and MOF-545 can be used for the adsorption and elimination of the organic contaminant sulfamethoxazole. The mesopores nature of both MOFs allowed them to adsorb SMX. The maximal adsorption capacities of MOF-545 and MOF-525 are 690 and 585 mg/g, respectively. It is feasible to enhance the removal of pollutants by augmenting the materials' capacity to absorb organic contaminants on them through the addition of additional materials containing porphyrin-based MOFs. For instance, porphyrin, ZrCl_4 , and nano- TiO_2 were used to create Zr-porphyrin-based MOFs (PCN-224- TiO_2). They displayed strong photocurrent and notable absorption of visible light. In terms of removing methylene blue under bright light, PCN-224- TiO_2 performed better than a combination of TiO_2 and PCN-224. Methylene blue was removed at a rate of 93.2% after 4 hours of low-power light exposure. Additionally, the cycling reactions maintained the stability of the PCN-224- TiO_2 photocatalyst[27].

Furthermore, the choice and assembly of metal nodes and porphyrin ligands can control the photo catalytic breakdown rate of organic contaminants over MOFs. Furthermore, porphyrin-based MOFs demonstrated superior inorganic pollution removal capabilities. With a capacity for adsorption of 412.5 mg g^{-1} , the Zr-MOF-SH/MF composite can be employed to selectively eliminate Hg^{2+} from water. Additionally, Zr-MOF-SH/MF composite could be used to remove Hg^{2+} and oil from water at the same time, and the effectiveness of Hg^{2+} removal improved as the amount of oil in the combination of oil and water rose. Furthermore, the composites exhibit a negligible drop in adsorption during five cycles of recycling and reuse.

5.5 Photo Catalytic Synthesis of Organic Compounds

The utilization of photo catalysis for the synthesis of organic compounds, particularly in the oxidation of sulfides and amines, holds significant promise due to its environmentally friendly nature and efficiency. Reactive oxygen species, such as

singlet oxygen, play a crucial role in these catalytic processes. However, to ensure the effectiveness of photo oxidation reactions, it is essential for photo catalysts to efficiently produce singlet oxygen and prolong its lifetime. Reactive oxygen species like singlet oxygen are useful for a variety of catalytic processes. To be used in photo oxidation reactions like sulfide oxidation and amine oxidation, photo catalysts must be able to produce singlet oxygen efficiently and extend its lifetime. Sulfoxide is often oxidized using strong oxidants as potassium permanganate, which causes significant environmental contamination. The oxidation process of Sulfoxide can benefit greatly from porphyrin-based metal-organic frameworks because of its broad absorption from the ultraviolet to light area, strong chemical resistance, and friendly to the environment. The findings indicate a positive correlation between the singlet oxygen quantum yield and the oxidation rate of CEES. This correlation is contingent upon the Zr-based MOF linker, specifically porphyrin < pyrene < perylene. Porphyrins and metal atoms also work well together to enhance the stability of their chemicals and streamline the recovery procedure. This integration in photo catalytic processes offers a sustainable and efficient approach for the synthesis of organic compounds, providing a greener alternative to traditional oxidation methods.

5.6 Bio Sensing

Numerous physiological species are important for controlling physiological activities and cellular processes; variations in their kinds and concentrations point to pathogenic or disruptive alterations in physiological settings. As a result, the usage of precise and sensitive bio sensing technologies has increased in order to identify and track changes in biological processes and illness diagnosis in living things. Because porphyrins and derivatives of them have outstanding physicochemical properties that can be employed for signal interaction with their host molecules, they have been extensively explored as small-molecule biosensors. Porphyrins can also imitate a wide range of biological processes. Porphyrins, for instance, have the ability to reversibly bond with gaseous molecules and go through redox and/or photo physical processes that are driven by the desired analytes. MOFs' large specific surface area and porous structure, in particular, contribute to their

high catalytic activity. Furthermore, MOFs have a high degree of selectivity for the molecules they are targeting due to their intended size and structure as well as unique chemical interactions with guest molecules. Porphyrins can be added to MOFs to prevent their self-quenching and to combine their many functions with MOFs' excellent sensitivity, resolution, and precise for bio sensing. Porphyrin-based MOFs have been extensively used in bio sensing applications up to this point. Numerous investigations have shown that porphyrin-based MOF-based biosensors are capable of sensing a wide range of biological materials and conditions, primarily ions, small molecules, bio macromolecules, and pH levels.

5.7 Photodynamic Therapy with Porphyrin-Based MOFs

PDT is a promising approach for treating various illnesses, including cancer. It involves the use of photosensitizing agents, which are activated by light of a definite wavelength to produce ROS that induce cell death. Porphyrin-based metal-organic frameworks (MOFs) have garnered significant interest in recent years for their potential applications in PDT due to their unique properties. Three crucial elements are needed for photodynamic treatment to be effective: photosensitive agent, light, and oxygen molecules in cells. Therefore, when exposed to light, PDT produces extremely harmful reactive oxygen species (ROS). ROS, such as hydroxyl radical (COH), superoxide anion radical (O_2^-), and singlet oxygen (1O_2), can cause tumor immunity in addition to apoptosis and/or necrosis. Through the use of localized light exposure at tumor sites and the intravenous infusion of photosensitizers to accumulate in tumor tissue, photodynamic therapy (PDT) is able to specifically kill tumor cells with minimal harm to adjacent normal cells and tissues. Compared to traditional surgery, irradiation, and chemotherapy, this method is advantageous since it is non-invasive and has less adverse effects (such as drug toxicity and radiation damage). Additionally, MOFs' biocompatibility and biodegradability improve biosafety during PDT. Many MOFs were developed for PDT since Lin et al.'s 2014 study, which was the first to discuss porphyrinic NMOFs for possible tumor PDT.

5.8 Photodynamic Therapy with Porphyrin-Based MOFs

Because fluorescence imaging is non-invasive and has a high signal sensitivity, it has proven to be an effective imaging modality for both in vitro and in vivo studies. The capacity of fluorophores to absorb light energy in a specific wavelength band and subsequently release additional photon energy in a longer wavelength band is the basis for fluorescence imaging. Fast and appropriate for high-throughput screening is fluorescence imaging. MOFs have integrated porphyrins, a common fluorophores, for fluorescence imaging in vivo as well as in vitro. Fluorescence imaging enables the visualization of tumor/particle distribution and evolution during treatment, ensuring highly efficacious and safe therapy that is selectively controllable. Porphyrins are organic molecules known for their excellent photosensitizing properties[27].

Because porphyrins combine photosensitivity and fluorescence, it is easy to build fluorescent imaging-guided treatment nanotechnology using porphyrin-based MOFs for effective therapy. The initial compatible porphyrinic NMOFs for fluorescent imaging-guided tumor therapy were created in 2017 by Yin and colleagues. Porphyrinic NMOFs (NPMOFs) were able to achieve fluorescence imaging with high TCPP content (59.8%). According to the findings, when TCPP was stimulated at 514 nm, its fluorescence was seen at 651 nm with a weak shoulder at 710 nm; however, NPMOFs only displayed one emissions peak at 689 nm. Because of the lengthy Stokes shift, strong red emission, and low excitation interference caused by the biological tissue's scattering light, NPMOFs allowed for fluorescence imaging with high resolution and signal-to-noise ratios.

NPMOFs were examined by following the fluorescent trajectory in a mouse model, proving the NPMOFs' biological compatibility for mammals. Furthermore, porphyrinic NMOFs show swear as sites for luminescence imaging-guided treatment for diagnosis and therapy, as demonstrated by the unmistakable validation of NPMOF distribution patterns in cancers with better recovery and signal-to-noise ratio in HepG2 tumor-carrying mice through in vivo luminescence. Nevertheless,

fluorescence imaging-guided therapy also led to the construction of composite porphyrinic NMOFs.

The addition of porphyrinic NMOFs enabled the Nano composites to be used in fluorescence imaging, chemotherapeutic, and PDT, and AuNRs demonstrated superior PTT characteristics. Furthermore, fluorescent imaging-guided therapy can be utilized to further enhance therapeutic efficacy and prevent under- or overtreatment by providing actual time tracking and evaluation of the efficacy of treatment based on changes in fluorescence signals.

5.9 Sensing of PH

PH Indicator In general, pH is crucial for preserving the stability, typical shape, and functionality of living cells and organisms. Because the spectral characteristics of porphyrins vary with pH due to the protonation and deprotonating processes of the pyrrole compounds ring in porphyrins, porphyrin-based MOFs have the likely to be used in the construction of pH sensors, which could be very useful for measuring pH, diagnosing diseases, and even assessing the effectiveness of treatments. Zhou et al. (2013) initially reported on the use of metalloporphyrin MOF PCN-225(Zn) and Zr-based porphyrinic MOF PCN-225 for pH sensing. Within the pH range of 0–10.2, there is a high association between the fluorescence level of PCN-225 and the solution's pH. The pH 10.2 solution displayed the strongest fluorescence, while the maximum acidic solution displayed the weakest. Moreover, the pH range with the highest sensitivity for intensity response was 7–10. Additionally, fluorescence confocal imaging might be utilized to track pH variations in living cells, and fluorescence spectroscopy could be employed to ascertain the pH levels in real water samples.

6. Conclusion and Future Scope

Porphyrin-based totally metallic-natural frameworks (MOFs) have occurred as a tremendously hopeful class of substances with diverse programs in electricity, environmental remediation, and biomedical fields. The specific structural characteristics and versatile functionalities of porphyrins lead them to superb building blocks for MOF synthesis. The synthesis methods discussed in this observe, along with the structural characteristics and characterization

strategies, offer insights into the layout and production of porphyrin-based totally MOFs with tailored properties. These materials exhibit fantastic porosity, floor place, and stability, making them perfect for gas garage and separation applications, catalysis, sensing, and drug shipping. The programs of porphyrin-based totally MOFs, such as photograph catalytic hydrogen evolution, CO₂ photolysis, nitrogen fixation, pollutant removal, natural synthesis, bio sensing, photodynamic remedy, and fluorescence imaging-directed intervention, underscore their versatility and ability impact across diverse domain names. Their excessive adsorption capacities, selectivity, catalytic interest, and sensing capabilities offer sustainable answers to pressing demanding situations in electricity, surroundings, and healthcare. Future Scope of the study involves moving ahead, several avenues for similarly exploration and development in porphyrin-based totally MOFs can be envisaged. Firstly, persisted research efforts are needed to beautify the synthesis techniques, making an allowance for precise control over the shape, morphology, and residences of MOFs to obtain superior overall performance in unique programs. Additionally, the exploration of recent metal ions and organic linkers, as well as progressive meeting techniques, can expand the scope of porphyrin-primarily based MOFs and uncover novel functionalities. Furthermore, comprehensive research at the fundamental mechanisms underlying the particular homes and functionalities of porphyrin-based MOFs are vital to unlock their complete capability and optimize their overall performance. This includes elucidating the interactions among porphyrin ligands and metal ions, to information the dynamics of gas adsorption, catalytic reactions, and molecular reputation processes within MOF frameworks. The interpretation of porphyrin-primarily based MOFs from laboratory-scale synthesis to sensible packages calls for addressing demanding situations associated with scalability, reproducibility, and long-time period balance under real-international conditions. This includes collaborative efforts between researchers from multidisciplinary fields, such as chemistry, substances technological know-how, engineering, and biomedicine, to conquer technical obstacles and accelerate the commercialization of MOF-based totally technologies.

References

1. L. A. Finney and T. V. O'Halloran, "Transition Metal Speciation in the Cell: Insights from the Chemistry of Metal Ion Receptors," *Science*, vol. 300, no. 5621, pp. 931–936, May 2003, doi: 10.1126/science.1085049.
2. W.-R. Cai et al., "Enhanced Electrochemiluminescence of Porphyrin-Based Metal–Organic Frameworks Controlled via Coordination Modulation," *Anal. Chem.*, vol. 92, no. 2, pp. 1916–1924, Jan. 2020, doi: 10.1021/acs.analchem.9b04104.
3. M. Eddaoudi et al., "Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal–Organic Carboxylate Frameworks," *Acc. Chem. Res.*, vol. 34, no. 4, pp. 319–330, Apr. 2001, doi: 10.1021/ar000034b.
4. R. C. Rodrigues, C. Ortiz, Á. Berenguer-Murcia, R. Torres, and R. Fernández-Lafuente, "Modifying enzyme activity and selectivity by immobilization," *Chem. Soc. Rev.*, vol. 42, no. 15, pp. 6290–6307, 2013, doi: 10.1039/C2CS35231A.
5. C. Lin et al., "Porphyrin-Based Metal–Organic Frameworks for Efficient Photocatalytic H₂ Production under Visible-Light Irradiation," *Inorg. Chem.*, vol. 60, no. 6, pp. 3988–3995, Mar. 2021, doi: 10.1021/acs.inorgchem.1c00041.
6. Jessica et al., "Design components of porphyrin-based photocatalytic hydrogen evolution systems: A review," *Coordination Chemistry Reviews*, vol. 467, p. 214599, Sep. 2022, doi: 10.1016/j.ccr.2022.214599.
7. H.-C. Kim, J. Yoon, S. Yoon, Y. Kim, S. Joong Lee, and S. Huh, "N-doped porous carbons derived from Zn-porphyrin-MOF," *RSC Advances*, vol. 12, no. 10, pp.

- 5979–5989, 2022, doi: 10.1039/D2RA00327A.
8. W.-R. Cai et al., “Enhanced Electrochemiluminescence of Porphyrin-Based Metal–Organic Frameworks Controlled via Coordination Modulation,” *Anal. Chem.*, vol. 92, no. 2, pp. 1916–1924, Jan. 2020, doi: 10.1021/acs.analchem.9b04104.
9. Liberman, R. Shimoni, R. Ifraemov, I. Rozenberg, C. Singh, and I. Hod, “Active-Site Modulation in an Fe-Porphyrin-Based Metal–Organic Framework through Ligand Axial Coordination: Accelerating Electrocatalysis and Charge-Transport Kinetics,” *Journal of the American Chemical Society*, Jan. 2020, doi: 10.1021/jacs.9b11355.
10. Y. Tian et al., “Oriented Growth of In-Oxo Chain Based Metal-Porphyrin Framework Thin Film for High-Sensitive Photodetector,” *Advanced Science*, vol. 8, no. 14, p. 2100548, Jul. 2021, doi: 10.1002/advs.202100548.
11. B.-X. Xie et al., “Boosting Antibacterial Photodynamic Therapy in a Nanosized Zr MOF by the Combination of Ag NP Encapsulation and Porphyrin Doping,” *Inorganic Chemistry*, Aug. 2023, doi: 10.1021/acs.inorgchem.3c01785.
12. Y. Zhao, X. Cai, Y. Zhang, C. Chen, J. Wang, and R. Pei, “Porphyrin-based metal–organic frameworks: protonation induced Q band absorption,” *Nanoscale*, vol. 11, no. 25, pp. 12250–12258, 2019, doi: 10.1039/C9NR02463H.
13. J. Yang and Y.-W. Yang, “Metal–Organic Frameworks for Biomedical Applications,” *Small*, vol. 16, p. 1906846, Feb. 2020, doi: 10.1002/sml.201906846.
14. Z. W. Jiang, Y. C. Zou, T. T. Zhao, S. J. Zhen, Y. F. Li, and C. Z. Huang, “Controllable Synthesis of Porphyrin-Based 2D Lanthanide Metal–Organic Frameworks with Thickness- and Metal-Node-Dependent Photocatalytic Performance,” *Angew Chem Int Ed*, vol. 59, no. 8, pp. 3300–3306, Feb. 2020, doi: 10.1002/anie.201913748.
15. J.-H. Qin et al., “Ionic liquid induced highly dense assembly of porphyrin in MOF nanosheets for photodynamic therapy,” *Dalton Trans.*, vol. 49, no. 48, pp. 17772–17778, Dec. 2020, doi: 10.1039/D0DT03031G.
16. Wang et al., “Recent advances in porphyrin-based MOFs for cancer therapy and diagnosis therapy,” *Coordination Chemistry Reviews*, vol. 439, p. 213945, Jul. 2021, doi: 10.1016/j.ccr.2021.213945.
17. S. De, T. Devic, and A. Fateeva, “Porphyrin and phthalocyanine-based metal organic frameworks beyond metal-carboxylates,” *Dalton Trans.*, vol. 50, no. 4, pp. 1166–1188, 2021, doi: 10.1039/D0DT03903A.
18. X. Zhang et al., “A historical perspective on porphyrin-based metal–organic frameworks and their applications,” *Coordination Chemistry Reviews*, vol. 429, p. 213615, Feb. 2021, doi: 10.1016/j.ccr.2020.213615.
19. J. Gu, Y. Peng, T. Zhou, J. Ma, H. Pang, and Y. Yamauchi, “Porphyrin-based framework materials for energy conversion,” *Nano Res. Energy*, vol. 1, p. e9120009, Jun. 2022, doi: 10.26599/NRE.2022.9120009.
20. Das, L., Anand, P., Anjum, A., Aarif, M., Maurya, N., & Rana, A. (2023, December). The Impact of Smart Homes on Energy Efficiency and Sustainability. In *2023 10th IEEE Uttar Pradesh Section International Conference on Electrical, Electronics and Computer Engineering (UPCON)* (Vol. 10, pp. 215-220). IEEE.
21. Abd Algani, Y. M., Caro, O. J. M., Bravo, L. M. R., Kaur, C., Al Ansari, M. S., & Bala, B. K. (2023). Leaf disease identification and classification using optimized deep learning. *Measurement: Sensors*, 25, 100643.

22. Mishra, M. K., Selvaraj, K., Santosh, K., Aarif, M., Mary, S. S. C., & Bala, B. K. (2024, March). The Impact of 5G Technology on Agile Project Management: A Cross-Industry Analysis. In *2024 5th International Conference on Intelligent Communication Technologies and Virtual Mobile Networks (ICICV)* (pp. 119-126). IEEE.
23. Kaur, C., Kumar, M. S., Anjum, A., Binda, M. B., Mallu, M. R., & Al Ansari, M. S. (2023). Chronic kidney disease prediction using machine learning. *Journal of Advances in Information Technology*, 14(2), 384-391.
24. Lohiya, A., Aggarwal, V., Dixit, A., Srivastav, R., Yadav, S., & Aarif, M. (2023). An Exploring the Relationship Between Consumer Knowledge and Adoption of Energy-Efficient Home Technologies. *Journal of Informatics Education and Research*, 3(2).
25. P. Soundarraj, M. Aarif, S. Gangadharan, S. R. Naqvi, N. K. AssiHalaf and A. Salih Mahdi, "Smart Product Packing and IoT Marketing: Enhancing Customer Interaction," 2023 *International Conference on Innovative Computing, Intelligent Communication and Smart Electrical Systems (ICESSES)*, Chennai, India, 2023, pp. 1-6, doi: 10.1109/ICESSES60034.2023.10465408.
26. Khan, S. I., Kaur, C., Al Ansari, M. S., Muda, I., Borda, R. F. C., & Bala, B. K. (2023). Implementation of cloud based IoT technology in manufacturing industry for smart control of manufacturing process. *International Journal on Interactive Design and Manufacturing (IJIDeM)*, 1-13.
27. Ambashtha, K. L., Vijayalakshmi, N. S., Aarif, M., Jeevalatha, R., Kuchipudi, R., & Reddy, T. S. K. (2023, December). Integrating a Neural Network Model based on LSTM and Auto Encoder into the Travel and Tourism Industry. In *2023 2nd International Conference on Automation, Computing and Renewable Systems (ICACRS)* (pp. 623-628). IEEE.
28. Abd Algani, Y. M., Caro, O. J. M., Bravo, L. M. R., Kaur, C., Al Ansari, M. S., & Bala, B. K. (2023). Leaf disease identification and classification using optimized deep learning. *Measurement: Sensors*, 25, 100643.
29. Chaudhary, J. K., Aarif, M., Rao, N. R., Sobti, R., Kumar, S., & Muralidhar, L. B. (2023, December). Machine Learning Strategies for Business Process Optimization. In *2023 10th IEEE Uttar Pradesh Section International Conference on Electrical, Electronics and Computer Engineering (UPCON)* (Vol. 10, pp. 1743-1747). IEEE.
30. Ratna, K. S., Daniel, C., Ram, A., Yadav, B. S. K., & Hemalatha, G. (2021). Analytical investigation of MR damper for vibration control: a review. *Journal of Applied Engineering Sciences*, 11(1), 49-52.
31. Das, L., Salman, R., Sabeer, S., Ansari, S. K., Aarif, M., & Rana, A. (2023, December). Customer Retention Using Machine Learning. In *2023 10th IEEE Uttar Pradesh Section International Conference on Electrical, Electronics and Computer Engineering (UPCON)* (Vol. 10, pp. 221-225). IEEE.
32. Naidu, K. B., Prasad, B. R., Hassen, S. M., Kaur, C., Al Ansari, M. S., Vinod, R., ... & Bala, B. K. (2022). Analysis of Hadoop log file in an environment for dynamic detection of threats using machine learning. *Measurement: Sensors*, 24, 100545.
33. Almahairah, M. S. Z., Goswami, S., Karri, P. N., Krishna, I. M., Aarif, M., & Manoharan, G. (2023, December). Application of Internet of Things and Big Data in Improving Supply Chain Financial Risk Management System. In *2023 10th IEEE Uttar Pradesh Section International*

- Conference on Electrical, Electronics and Computer Engineering (UPCON)* (Vol. 10, pp. 276-280). IEEE.
34. Abd Algani, Y. M., Ritonga, M., Kiran Bala, B., Al Ansari, M. S., Badr, M., & Taloba, A. I. (2022). Machine learning in health condition check-up: An approach using Breiman's random forest algorithm. *Measurement: Sensors*, 23, 100406. <https://doi.org/10.1016/j.measen.2022.100406>
 35. Muda, I., Shah, J. A., Jarudin, J., Arnone, G., Aarif, M., & Sravan, I. (2023, November). An improved analysis of cryptocurrencies for business trading deterministic with deep learning techniques. In *AIP Conference Proceedings* (Vol. 2930, No. 1). AIP Publishing.
 36. J. Yang and Y. Yang, "Metal–Organic Frameworks for Biomedical Applications," *Small*, vol. 16, no. 10, p. 1906846, Mar. 2020, doi: 10.1002/sml.201906846.
 37. Fateeva et al., "A Water-Stable Porphyrin-Based Metal–Organic Framework Active for Visible-Light Photocatalysis*," *Angew. Chem.*, 2012.
 38. Tang et al., "Porphyrin-Based Metal-Organic Framework Materials: Design, Construction, and Application in the Field of Photocatalysis," *Molecules*, vol. 29, no. 2, Art. no. 2, Jan. 2024, doi: 10.3390/molecules29020467.
 39. Sun et al., "Studies on Photocatalytic CO₂ Reduction over NH₂-Uio-66(Zr) and Its Derivatives: Towards Better Understanding of Photocatalysis on Metal-Organic Frameworks.," *Chemistry (Weinheim an der Bergstrasse, Germany)*, vol. 19, Oct. 2013, doi: 10.1002/chem.201301728.
 40. Wang et al., "In-situ incorporation of Copper(II) porphyrin functionalized zirconium MOF and TiO₂ for efficient photocatalytic CO₂ reduction," *Science Bulletin*, vol. 64, no. 13, pp. 926–933, Jul. 2019, doi: 10.1016/j.scib.2019.05.012.
 41. M. Cheng, C. Xiao, and Y. Xie, "Photocatalytic nitrogen fixation: the role of defects in photocatalysts," *J. Mater. Chem. A*, vol. 7, no. 34, pp. 19616–19633, 2019, doi: 10.1039/C9TA06435D.
 42. [Y.-H. Liu, C. A. Fernández, S. A. Varanasi, N. N. Bui, L. Song, and M. C. Hatzell, "Prospects for Aerobic Photocatalytic Nitrogen Fixation," *ACS Energy Lett.*, vol. 7, no. 1, pp. 24–29, Jan. 2022, doi: 10.1021/acsenergylett.1c02260.
 43. Amirreza Talaiekhosani, "Recent advances in photocatalytic removal of organic and inorganic pollutants in air," *Journal of Cleaner Production*, vol. 278, p. 123895, Jan. 2021, doi: 10.1016/j.jclepro.2020.123895.