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## **Editorial on Synthesis and Application of Porphyrin based complexes**

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Porphyrins constitute a highly important class of macrocyclic organic compounds characterized by a planar, aromatic structure composed of four pyrrole units interconnected through methine bridge (1-2). This extended pi - conjugated system endows porphyrins with remarkable optical, electronic and redox properties, making them a central subject of research in chemistry, material science and biology (3). The structural rigidity and symmetry of the porphyrin framework also allow for extensive chemical modifications and metal coordination, further enhancing their functional versatility (4).

Porphyrins play a vital role in nature, where they serve as the core structural units of several essential biomolecules.

For example, iron porphyrin forms the active centre of heme proteins (5), which are responsible for oxygen transport (7) and electron transfer in biological systems, similarly magnesium containing porphyrin such as chlorophyll are crucial for light absorption and energy conversion in photosynthesis (6). These naturally occurring systems have inspired extensive research into synthetic porphyrins as biomimetic models for understanding and replicating complex biological processes (8-12).

The aim of this review is to systematically summarize and critically analyse the recent development in porphyrin chemistry, including their classification, synthesis, properties and application. By highlighting key advances and identifying current challenges the review seeks to provide valuable insights and future directions for

researchers working in the field of porphyrin based functional material.

Paollesse and co-workers (13) reported a well-designed synthetic strategy for the development of a zinc (II) phthalocyanine derivative bearing a 2-(2,4-dichlorobenzyl)-4-(1,1,3,3-tetramethyl butyl) phenoxy substituent(14). The synthesis was initiated from a Clofocetol-derived moiety (15), a synthetic antiviral compound known for its activity against SARS-CoV-2. In this approach, phthalonitrile precursors were synthesized through a nucleophilic aromatic substitution reaction between 4-nitrophthalonitrile and 2-(2,4-dichlorobenzyl)-4-(1,1,3,3-tetramethylbutyl) phenol (Clofocetol). The resulting intermediates underwent cyclotetramerization in the presence of zinc (II) salts to afford the corresponding zinc phthalocyanine complex. The synthesized compound demonstrated good solubility in common organic solvents. Furthermore, comprehensive photochemical and electrochemical studies were carried out, revealing its suitability as a solid-state sensing material for gravimetric chemical sensors, thereby highlighting its potential application in gas-sensing technology.

The self-assembly process refers to the spontaneous organization of small molecular or structural building blocks into well-defined nanostructures with controlled morphology. This organization is governed by different non-covalent intermolecular forces, including hydrogen bonding,  $\pi$ - $\pi$  stacking interactions, hydrophobic effects, electrostatic attractions, and van der Waals forces. In the case of porphyrins, self-assembled nanostructures retain the intrinsic properties of the porphyrin monomer while simultaneously exhibiting enhanced functional characteristics such as efficient electronic buffering, photoelectric conversion ability, strong photosensitivity, and remarkable chemical stability. Owing to these unique features, porphyrin-based self-assembled nanos(16).

Zilong Zhang and co-workers studied on 3d-metalloporphyrin. The nature of the central metal ion in 3d-metalloporphyrins plays a crucial role in

governing their structural features as well as their photophysical, electrochemical, and spin-related properties. In this context, a series of symmetrically meso-substituted porphyrins incorporating first-row transition metals, denoted as TPA-MPs (M = 2H, Mn, Fe, Co, Ni, Cu, and Zn), were successfully synthesized and systematically characterized using various spectroscopic techniques. Density functional theory (DFT) calculations of the electrostatic potential surface revealed that the positive electrostatic potential is mainly concentrated on the triphenylamine substituent, whereas the negative electrostatic potential localized on the porphyrin macrocycle varies depending on the nature of the coordinated metal ion (17).

Tetrapyrrolic porphyrins and their related compounds are commonly used as model systems to mimic the active sites of mononuclear metalloenzymes. Because of this ability, these molecules have gained considerable importance, especially in catalytic applications (18-20).

In recent years, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have received remarkable research attention owing to their well-defined architectures and versatile physicochemical properties. These frameworks now represent one of the most intensively explored areas in materials chemistry, as reflected by the growing number of high-impact publications in leading international journals (21-26).

Porphyrin chemistry has gained renewed attention in recent years owing to its wide-ranging applications in photodynamic therapy, solar energy conversion, and catalysis. The increasing relevance of these systems necessitates a concise evaluation of recent progress in the field. While the fundamental aspects and early developments of porphyrin chemistry have been comprehensively documented in *The Porphyrins* edited by Dolphin, the present review focuses on advances reported over the past two decades. To provide a clear and systematic overview, this review is organized into two sections: the first discusses porphyrin synthesis involving

functional group incorporation during macrocycle formation, and the second addresses post-synthetic functionalization of pre-assembled porphyrin frameworks (27).

As part of our ongoing efforts to build porphyrin molecular theranostics (28–31). Additionally, the inherent structural versatility of porphyrins provides a robust platform for precise molecular tailoring, enabling their systematic conversion into multiplicands architectures. Such design flexibility plays a crucial role in the development of advanced multifunctional materials, which can be assembled through well-defined coordination interactions or strategically implemented covalent crosslinking approaches (32-33).

Porphyrin-based compounds have attracted significant attention in recent years due to their remarkable chemical as well as biological properties. Extensive research efforts have been devoted to modifying the porphyrin core in order to enhance structural diversity, improve stability, and achieve better selectivity. Various chemical alterations in the porphyrin framework have led to the development of advanced functional systems. This review presents a comprehensive overview of different porphyrin-based derivatives and discusses recent progress in their structural modification. Particular emphasis is placed on their emerging applications in organic solar cells, functional materials and devices, as well as their promising role in cancer therapy (34).

Porphyrins and their related derivatives, commonly referred to as porphyrinoids, are macrocyclic compounds composed of pyrrole units interconnected through extended  $\pi$ -conjugation. This highly delocalized electronic framework is responsible for their intense and characteristic colors visible to the naked eye. A well-known biological example is chlorophyll A, a porphyrinoid pigment that imparts the green color to plants due to its selective light absorption. During autumn, the degradation of chlorophyll leads to the prominence of other chromophores, resulting in yellow, orange, and brown shades in foliage. Beyond their visual appeal, porphyrinoids play indispensable roles in biological systems

owing to their distinctive photophysical and chemical properties. They are central to crucial processes such as photosynthesis, oxygen transport in blood, and various oxidative biochemical reactions. In living systems, the porphyrinoid core is typically embedded within protein environments, where specific interactions with surrounding macromolecules regulate and fine-tune their and functional performance. Reactivity Apart from their traditional significance in photophysical and photochemical research—including electron transfer studies, solar energy conversion, and artificial light-harvesting systems—porphyrins have gained considerable attention in biomedical research. In particular, they function effectively as photosensitizers in therapeutic applications such as photodynamic therapy (PDT) and photodynamic antimicrobial chemotherapy (PACT). Furthermore, they have been explored in photothermal therapy (PTT) and as efficient chromophoric probes for biological imaging, highlighting their versatile applicability in modern medicine and materials science (35).

Structurally, porphyrins consist of four pyrrole subunits that are interconnected through methine (=CH-) bridges at their  $\alpha$ -positions, giving rise to a highly conjugated and planar macrocyclic framework. Each pyrrole unit contributes one nitrogen atom directed toward the inner cavity of the ring, which plays a crucial role in metal coordination. As early as 1912, Küster and co-workers proposed the cyclic tetrapyrrolic architecture of porphyrins. Later experimental studies confirmed this structural model and further demonstrated that the trans-NH tautomer represents the most thermodynamically stable form of the free base porphyrin (36).

Porphyrins constitute an important class of naturally occurring macrocyclic compounds that play a crucial role in various biological processes. These molecules are fundamentally composed of four pyrrole units interconnected through methine (=CH-) bridges, forming a highly conjugated cyclic framework (Fig. 1). The central cavity of the porphyrin ring acts as a tetradentate ligand, providing four nitrogen donor atoms capable of

coordinating with metal ions. The size of this cavity is well suited for metal incorporation, with an approximate maximum diameter of about 3.7 Å. During metallation, two inner pyrrolic protons are removed, generating a dianionic ligand that strongly binds to the incoming metal ion. The extensive conjugation within the macrocycle imparts significant aromatic stability to the porphyrin system. As a result, porphyrins form highly stable complexes with transition metal ions. For example, the stability constant of ZnTPP (tetraphenylporphyrin) is reported to be as high as  $10^{29}$ , reflecting the remarkable binding affinity of the porphyrin core toward metal ions (37).

The covalent integration of two porphyrin or phthalocyanine macrocycles through extended  $\pi$ -conjugated linkers significantly amplifies interchromophoric electronic communication. This enhancement primarily arises from the enforced coplanarity of the coupled units, which facilitates efficient orbital overlap and promotes long-range  $\pi$ -electron delocalization across the entire framework. As a consequence, strong excitonic coupling and modulation of frontier molecular orbitals (HOMO–LUMO levels) are typically observed. Such conjugated architectures have attracted sustained attention owing to their distinctly altered photophysical characteristics. These systems commonly display pronounced bathochromic shifts in absorption spectra, shortened excited-state lifetimes due to rapid energy or charge redistribution, and enhanced third-order nonlinear optical responses. Collectively, these features render them promising candidates for applications in molecular electronics, photodynamic systems, and optoelectronic device engineering (38).

However, when 9-anthranylboronic ester was employed as the coupling partner, the transformation proceeded with only modest efficiency, affording the desired product in comparatively low yield. This observation suggests that the boronic ester counterpart may suffer from limited reactivity or competing side processes under the applied conditions. In a related strategy, Anderson and co-workers demonstrated a more effective approach toward

the construction of bis-anthracene-fused porphyrin architectures (54.3a and 54.3b). Their methodology involved the cross-coupling of a meso-borylated porphyrin precursor (54.1Zn) with either 9-anthryl triflate or 9-bromoanthracene. The reaction was carried out in the presence of a catalytic system comprising  $\text{Pd}_2(\text{dba})_3$  and SPhos, which facilitated efficient C–C bond formation at the meso position of the porphyrin core. This palladium-catalyzed protocol provided a viable synthetic route to extended  $\pi$ -conjugated porphyrin systems, enabling the successful fusion of anthracene units onto the macrocyclic framework. Such structural modification is particularly significant for tuning the electronic communication and photophysical characteristics of the resulting conjugated assemblies (39).

Selective monobromination at the meso-positions of 5, 15-disubstituted porphyrins remains a significant synthetic challenge. This difficulty primarily arises from the nearly identical electronic environment and comparable reactivity of the two unsubstituted meso sites, which often leads to poor regioselectivity. When these porphyrins are treated with N-bromosuccinimide (NBS), the reaction typically proceeds in an uncontrolled manner, affording a mixture of mono- and dibrominated derivatives. Consequently, extensive and often laborious purification steps are required to isolate the desired monobrominated product in pure form. To address this limitation, Arnold and co-workers strategically exploited the intermediacy and reactivity of  $\sigma$ -complex species, enabling improved control over the bromination process and achieving enhanced selectivity at a single meso position (40).

The photophysical and photobiological characteristics of a number of trans-C6F5 meso-substituted corroles were examined by Iglesias and colleagues (41). These corroles, which contain various groups (phenyl, naphthyl, 4-(hydroxy) phenyl, or 4-(thiomethyl) phenyl) connected to their meso locations, are interesting for possible use in PDT and other photo-related procedures. Several approaches, including

electrochemical methods and photophysical features including absorption and emission characteristics, as well as their behavior in various solvents, were used to characterize these compounds for the study.

To learn more about their characteristics, theoretical computations were done. According to the research, these substituted corrole chemicals prefer to bind to DNA in the minor grooves and interact with HSA, suggesting that they have potential for a variety of photo induced activities. Human serum albumin (HSA) and the non-charged synthetic porphyrin 5,10,15,20-tetra(pyridin-4-yl)porphyrin (4-TPyP) were investigated by Chaves, Serpa, and colleagues (42) using in vitro assays conducted under physiological conditions using spectroscopic techniques (UV-vis, circular dichroism, steady-state, time-resolved, synchronous, and 3Dfluorescence) in conjunction with molecular docking calculations. The same average fluorescence lifetime for HSA without and with 4-TPyP corroborated the lack of any dynamic fluorescence quenching, whereas the UV-vis and steady-state fluorescence parameters showed a ground-state relationship between HSA and 4-TPyP. Consequently, the binding affinity is reflected in the Stern–Volmer quenching (KSV) constant, which shows a moderate interaction that is enthalpically, spontaneously, and entropically driven. Only a very slight disruption of albumin's secondary structure is caused by binding. The Trp-214 residue is located in the subdomain IIA (site I), which is the only major binding site for 4-TPyP ( $n = 1.0$ ) in HSA. Despite 4-TPyP interacting through hydrogen bonds and van der Waals forces, the microenvironment surrounding this fluorophore appears to be unaffected. Waals forces with subdomain IIA's amino acid residues. Additionally, molecular docking calculations were performed for the three primary albumin binding sites (subdomains IIA, IIIA, and IB) in order to provide a molecular-level explanation of the binding HSA: 4-TPyP.

The reported work significantly advances the sustainable transformation of renewable aromatic molecules through a carefully designed oxidative

strategy. In this study, a one-pot oxidation protocol was established that proceeds efficiently at ambient temperature. The system utilizes hydrogen peroxide ( $H_2O_2$ ) as a clean and environmentally compatible oxidant, while ethanol serves as a green solvent medium. An electron-deficient iron(III) porphyrin complex was applied as the catalyst in very low loading ( $<2 \text{ mol}\%$ ), demonstrating both catalytic efficiency and economic feasibility.

To better understand the nature of the transformation, detailed mechanistic studies were also performed. These investigations helped clarify the probable reaction pathway and the role of the catalytically active iron–oxo species involved in the oxidation process.

The substrate scope was evaluated using three comparatively stable aromatic compounds, namely acridine, o-xylene, and quinoline. Interestingly, the study revealed an unusual initial activation step involving epoxidation of the aromatic ring, which is not commonly observed under such mild conditions (43).

Over the last decade, advances in nanoscience and nanotechnology have been significantly influenced by the ability of organic molecules to organize into well-defined supramolecular architectures. The strategic assembly of molecular units into controlled two-dimensional and three-dimensional frameworks has become a central approach in designing functional nanomaterials.

In this regard, porphyrins represent an exceptionally versatile class of building blocks. Their rigid, planar  $\pi$ -conjugated core promotes efficient  $\pi$ – $\pi$  stacking interactions, while the possibility of diverse peripheral substitutions allows fine control over intermolecular aggregation. Owing to these structural attributes, porphyrins can self-assemble into a broad spectrum of nanostructures, including columns, sheets, nanotubes, nanowires, and other complex geometrical arrangements.

Notably, such supramolecular assemblies demonstrate superior sensitivity and selectivity in

sensor-based applications, properties that are difficult to achieve with individual porphyrin molecules. This collective behaviour highlights the importance of organized molecular architectures in enhancing functional performance (44).

In conclusion, a contemporary viewpoint on the synthesis and modification of porphyrins, metalloporphyrins, and related compounds can be found in the Special Issue titled "Synthesis and Application of Porphyrin based Complexes". A wide range of significant applications are revealed in this editorial, which also improves our grasp of synthetic techniques in light of the difficulties in this fascinating topic. These applications span important areas like biological applications (such as radiopharmaceuticals, interactions between DNA and proteins, cancer treatments, and microbial inactivation), sensors, improved materials, catalysis, and computational research.

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