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Review: Comparative Analysis of Structures, Functions, Coordination and Applications of N-Fused and N-Confused Porphyrins

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ABSTRACT

Porphyrins and their structural analogues occupy a central position in bioinorganic chemistry, materials science, and catalysis, largely because of their adaptable macrocyclic frameworks. Two structurally modified variants — N-fused porphyrins (NFPs) and N-confused porphyrins (NCPs) — have attracted sustained interest as aza-modified macrocycles with distinct electronic, coordinative, and structural profiles. Although both classes involve nitrogen-based modifications to the classical tetrapyrrolic core, the nature and consequences of those modifications differ considerably between them.

In NFPs, a pyrrole ring is fused to the meso nitrogen, yielding enhanced aromatic conjugation and a more rigid framework. NCPs, by contrast, arise from an inversion at the β-position of one pyrrole unit, which repositions a nitrogen atom to the periphery of the macrocycle and generates an unusual coordination pocket. This review systematically compares the structural and electronic characteristics of NFPs and NCPs, surveys their metal coordination behaviors, and examines their functional applications.

Keywords- Porphyrins, N-Confused Porphyrin, N-Fused Porphyrin, Porphyrinoids.

I. INTRODUCTION

Porphyrins and their derivatives occupy a well-established place in bioinorganic and coordination chemistry. Their conjugated macrocyclic frameworks allow direct coordination with metal ions and participation in photochemical and redox processes across a wide range of conditions [1–3].

The parent porphyrin consists of four pyrrole subunits joined by methine bridges, forming an 18 π-electron conjugated system with pronounced aromatic character. Modifications to this scaffold can substantially alter both the physicochemical and functional behavior of the resulting compounds, opening pathways toward purpose-built molecular architectures for specific applications [4].

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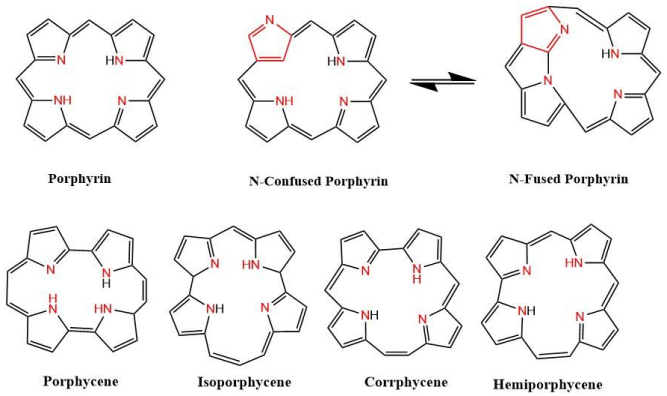

Figure 1: Porphyrin isomers

Among structurally modified porphyrins, NFPs and NCPs have occupied the foreground of research attention for several decades. NCPs incorporate an unusual pyrrolic nitrogen inversion in which one nitrogen atom is displaced to the exterior of the macrocyclic core, disrupting classical symmetry and modifying coordination behavior [5,6]. NFPs, by contrast, carry an additional fused heterocyclic ring at the periphery, extending π-conjugation and reinforcing the rigidity of the macrocyclic scaffold [7–9].

NCPs are formally defined by the external repositioning of a pyrrolic nitrogen away from the interior coordination core, leaving the confused nitrogen at the perimeter of the macrocycle [5,6]. This structural irregularity distorts the macrocyclic framework into saddle-shaped or ruffled conformations, weakening planarity and interrupting aromatic conjugation [4]. The resulting expanded and flexible coordination cavity enables NCPs to bind metal ions in non-standard geometries, stabilize uncommon oxidation states, and support dynamic ligand exchange. The peripheral confused nitrogen also serves as an auxiliary binding site capable of protonation or axial coordination to metal centers and other ligands, adding considerable chemical versatility [10].

These features make NCPs attractive scaffolds for molecular recognition, biomimetic catalysis, and stimulus-responsive systems. A direct comparison with NFPs is instructive: NFPs maintain higher planarity and extended conjugation, which translates into good thermal and photochemical stability alongside well-defined coordination geometries. NCPs, in contrast, offer greater structural flexibility, non-classical metal coordination modes, and modified aromaticity — properties that give rise to distinctive reactivity and functional behavior [3,4,6,10]. Examining these two classes side by side reveals how targeted structural modifications to the porphyrin core translate into divergent chemical outcomes, and how that knowledge can guide the design of next-generation porphyrinoid functional materials.

This review examines recent developments in the structural and electronic properties, coordination chemistry, aromaticity, reactivity, bioactivity, and functional applications of NFPs and NCPs, including their roles in catalysis, sensing, and photodynamic therapy. By drawing out the contrasts between these two families, we aim to highlight their complementary strengths and to identify productive directions for future research in porphyrinoid chemistry

II. STRUCTURAL OVERVIEW OF N-FUSED AND N-CONFUSED PORPHYRINS

The classical porphyrin framework consists of four pyrrole rings connected through methine bridges, generating a planar, highly conjugated, and nearly symmetric 18 π-electron system [1,11]. This planarity and conjugation underlie both the strong aromatic character of classical porphyrins and their capacity to coordinate metal ions through four inward-facing nitrogen donors [2].

NCPs deviate from this arrangement by inverting one pyrrolic nitrogen outward from the macrocyclic plane, effectively replacing an internal carbon donor with a peripheral nitrogen [2,5,6]. Work by Białek et al. established that this inversion produces distorted macrocycles — saddle-shaped, ruffled, or twisted — with significantly reduced planarity relative to conventional porphyrins. Crystallographic and spectroscopic data confirm that the confused nitrogen is markedly more accessible to coordination, giving rise to binding modes and reactivities that are simply not available in the standard framework [4,12].

The structural flexibility introduced by the inversion also perturbs electronic conjugation and aromaticity, creating a ligand environment well suited to a broad range of coordination and catalytic applications [13].

Synthetically, NCPs are typically prepared by dipyrromethane cyclization under conditions that favor nitrogen inversion, or through directed modification of preformed porphyrins [6]. The nature of peripheral substituents can be tuned to adjust both structural flexibility and electronic character, providing a practical handle for controlling coordination behavior [2].

NFPs carry additional heterocyclic rings fused at the β–β or meso–β positions of the macrocycle, which extends π-conjugation and increases molecular rigidity [7,9]. X-ray crystallographic studies confirm the high degree of planarity and

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restricted conformational motion characteristic of NFPs, both of which help stabilize their electronic structure [8]. The fused rings also introduce new reactive sites and modify the steric and electronic environment around the macrocycle, with downstream effects on metal coordination geometry and photophysical behavior [4,6].

NFPs are commonly synthesized by palladium-catalyzed intramolecular cyclization, which permits precise control over ring fusion geometry and macrocycle topology [7]. The planar, conformationally constrained frameworks that result are thermally and chemically robust — properties that are well matched to demanding applications in catalysis and materials science [8].

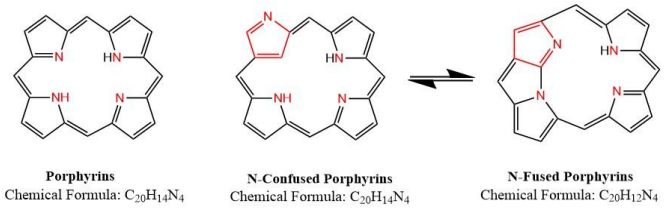

Figure 2: Illustration of porphyrin, N-confused porphyrin, and N-fused porphyrin structures

III. AROMATICITY

Aromaticity in porphyrins stems from the cyclic delocalization of 18 π-electrons, in accordance with Hückel's 4n + 2 rule, and confers both thermodynamic stability and characteristic spectroscopic signatures [14–16]. The classical macrocycle sustains a strong diatropic ring current, which is reflected in pronounced NMR chemical shift patterns and the intense Soret and Q-band absorptions visible in UV–Vis spectra [2].

In NCPs, aromaticity is attenuated. The outward displacement of one pyrrolic nitrogen disrupts macrocyclic planarity and interrupts the continuous conjugation pathway [6]. Computational analyses using nucleus-independent chemical shift (NICS) and anisotropy of induced current density (AICD) methods reveal ring currents that are weaker and more spatially dispersed than in conventional porphyrins [12,17]. Experimentally, this manifests as shifted NMR signals and altered UV–Vis absorption profiles — evidence of diminished but structurally meaningful aromatic stabilization. Białek et al. (2023) showed that the reduced aromaticity also enhances conformational flexibility and reshapes electron density distribution, establishing an electronic landscape that supports non-classical coordination and redox chemistry [4].

NFPs display enhanced aromaticity relative to the classical porphyrin. The extension of π-conjugation through the fused heterocyclic rings strengthens diatropic ring currents and broadens electronic delocalization, as confirmed by NICS and AICD calculations [7–9]. These features stabilize excited states and produce bathochromic shifts in absorption spectra. The rigid planar structure of NFPs also suppresses non-radiative decay pathways, resulting in higher fluorescence quantum yields and improved photostability — qualities that are particularly valuable in photophysical and photochemical applications [18,20,27].

In summary, NFPs benefit from stronger aromatic systems with greater electronic and photophysical stability, while NCPs exhibit attenuated aromaticity paired with conformational adaptability [19,20]. These contrasting aromatic characters underpin many of the functional differences discussed in subsequent

IV. COORDINATION CHEMISTRY

a) Coordination Modes and Metal Binding

These Coordination chemistry is fundamental to porphyrin function, governing their behavior in catalysis, sensing, and materials science. The structural modifications inherent in NFPs and NCPs produce markedly different coordination environments and metal-binding profiles, which have been studied extensively as a basis for understanding structure–function relationships and for exploiting these systems in advanced applications [2,4,6].

In classical porphyrins, four inward-facing nitrogen donors form a planar tetradentate cavity that binds transition metals with precision, yielding square-planar or octahedral complexes depending on the extent of axial ligation [21,22]. NFPs largely preserve this binding motif; the core nitrogen arrangement remains intact, even as the fused heterocyclic rings extend π-conjugation and modulate electron density distribution [7,8].

NCPs diverge from this picture. The inversion of one pyrrolic nitrogen toward the periphery generates a non-classical ligand with an accessible external nitrogen donor [23,24]. This "confused" nitrogen, relatively unhindered sterically, can participate in axial or bridging coordination, expanding the repertoire of binding modes well beyond standard tetradentate chelation [6]. The consequence is a family of NCP complexes with unusual geometries — square pyramidal, distorted octahedral, and multinuclear arrangements — that arise from the involvement of the peripheral nitrogen [4].

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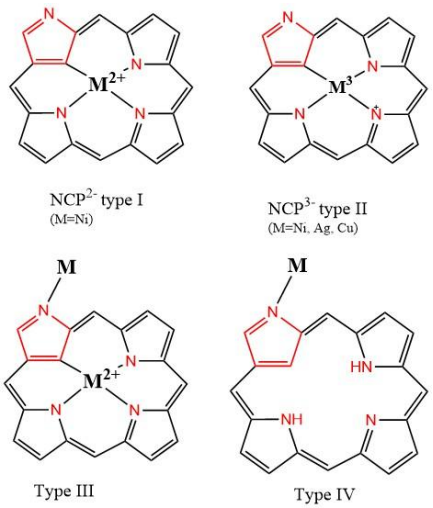

Figure 3: Metal binding modes of NCPs

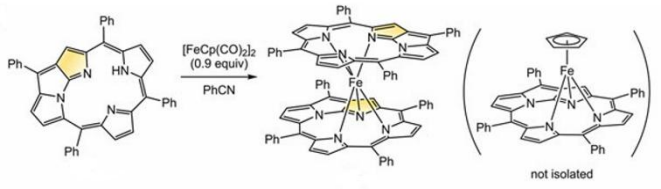

Figure 4: Metal binding example of NFPs

b) Structural and Electronic Implications

The divergent structures of NCPs and NFPs have wide-ranging consequences for their electronic character, coordination geometry, and chemical function. These differences affect macrocyclic planarity, π-conjugation, ligand field properties, and electron density distribution — and through these, they shape coordination geometry, redox behavior, and reactivity [4,26].

• Macrocyclic Distortion and Planarity

The near-planar geometry of classical porphyrins maximizes π-electron delocalization and stabilizes the 18-electron aromatic system, providing a symmetric ligand field and uniform electronic distribution across the four pyrrolic nitrogen donors. The result is predictable, stable metal coordination and consistent reactivity.

In NCPs, relocating one pyrrolic nitrogen to the periphery introduces significant geometric distortion, producing saddle-shaped, ruffled, or twisted macrocycles [4,6]. Crystallographic data show that this distortion breaks macrocyclic planarity and creates asymmetry in both the spatial arrangement of donor atoms and the overall conjugation pathway [32]. While the resulting strain can destabilize certain electronic states, it simultaneously confers conformational flexibility — enabling the macrocycle to adapt dynamically to different coordination environments and substrates [12,21]. This flexibility accommodates a range of metal coordination geometries, including distorted square-pyramidal and octahedral configurations, and allows the peripheral confused nitrogen to act as an axial or bridging ligand [30,36,38].

NFPs present the opposite character. The fusion of additional heterocyclic rings at the β–β or meso–β positions reinforces planarity and restricts conformational motion [7,8]. This rigidity supports extended π-conjugation across the macrocycle and the fused rings, stabilizes electronic states, and limits non-radiative decay — all of which are advantageous for photophysical applications [9].

• Electronic Conjugation and Delocalization

The electronic consequences of these structural differences are substantial. In NCPs, the peripheral placement of the confused nitrogen disrupts the classical conjugation pathway and redistributes electron density within the macrocycle. DFT calculations and NICS analyses confirm perturbation of the delocalized π-electron system, with diminished aromaticity and spatially anisotropic ring currents as the outcome. UV–Vis spectra reflect these changes through red-shifted and broadened absorption bands, which signal altered HOMO–LUMO gaps and modified electronic transitions. The redistributed electron density also affects ligand field strengths and metal–ligand covalency, with downstream effects on redox potentials and catalytic activity.

NFPs show the opposite trend. The fused heterocyclic rings extend π-conjugation beyond the traditional porphyrin boundary, narrowing the HOMO–LUMO gap and producing bathochromic shifts accompanied by enhanced molar absorptivity. Stronger electronic communication between the metal center and the macrocycle benefits electron-transfer processes and photoredox catalysis. The extended delocalization also reduces non-radiative losses, improving fluorescence

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quantum yields and photostability — attributes that matter considerably for photodynamic therapy and organic electronics applications.

• Ligand Field Effects and Metal Center Properties

The asymmetry and peripheral nitrogen of NCPs create ligand field environments that depart substantially from those of classical porphyrins or NFPs. Deviations in crystal field splitting alter metal d-orbital energies and spin-state preferences, enabling stabilization of uncommon oxidation states and spin configurations. High-spin Fe(III) and low-spin Co(II) states can coexist within NCP complexes, supporting multi-electron redox catalysis and oxygen activation.

NFPs impose ligand fields that broadly resemble those of classical porphyrins, but with subtle modulation arising from electron donation or withdrawal by the fused rings. This allows fine-tuning of metal redox potentials and spin states without sacrificing the predictability of the coordination environment. The robust ligand field also stabilizes reactive intermediates and supports fast electron-transfer kinetics, which are essential for photoredox and electrocatalytic applications.

• Implications for Reactivity and Function

The reactivity of NCPs and NFPs is shaped by the interplay of macrocyclic geometry, electronic conjugation, and ligand field characteristics. The flexible, electronically perturbed character of NCPs enables adaptive substrate binding, dynamic coordination equilibria, and stabilization of reactive species — making them well suited to bioinspired catalysis and responsive sensing. The extended conjugation and structural rigidity of NFPs, by contrast, support stable, well-defined electronic states that underpin efficient photophysical processes, durable catalytic cycles, and reliable sensor performance. Their electronic and structural robustness makes NFPs particularly attractive for demanding applications such as solar energy conversion, photocatalysis, and photodynamic therapy.

c) Metal Ion Specificity and Complex Stability

Metal ion selectivity and complex stability are two practical criteria that determine how useful a porphyrinoid can be in real applications. NCPs and NFPs differ markedly on both counts, as a direct consequence of their different structural and electronic frameworks.

• Metal Ion Specificity

The externally inverted pyrrolic nitrogen of NCPs provides a coordination site outside the conventional macrocyclic cavity, substantially widening the range of accessible metal ions [6,37]. According to Białek et al. (2023) and Shaikh & Ghosh (2015), NCPs can bind a broad array of metals across multiple oxidation states — including first-row transition metals (Fe, Co, Ni, Cu), heavier metals (Ru, Rh, Pd), and even lanthanides and actinides — by exploiting the peripheral confused nitrogen as an axial or bridging donor.

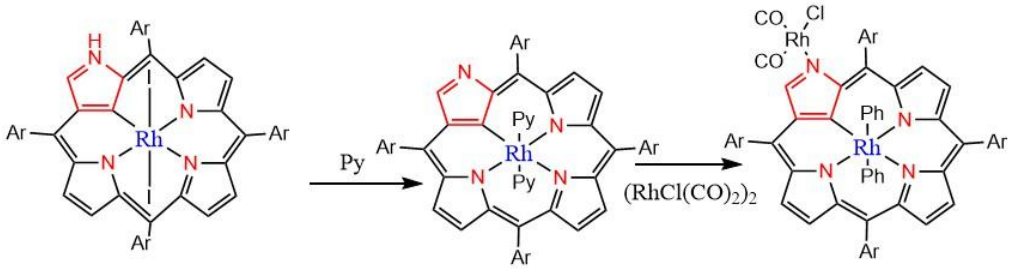

Figure 5: Rhodium N-confused porphyrin complex

The enlarged coordination environment of NCPs facilitates selective metal binding that can be difficult or impossible to achieve with standard porphyrins. For example, NCPs show high affinity for strongly Lewis acidic metals such as lanthanides, which tend to coordinate preferentially at the peripheral confused nitrogen, forming stable complexes that are not readily accessible through conventional porphyrin chemistry. This selectivity has practical value in luminescent lanthanide compounds designed for sensing and imaging. The distorted macrocycle and confused nitrogen also generate a distinctive ligand field that can stabilize unusual oxidation states and coordination geometries, enabling metal centers to access reactive intermediates suited to multi-electron redox processes. Iron-oxo species stabilized within NCP frameworks, for instance, have demonstrated relevance to oxygen activation and hydroxylation catalysis, illustrating the bioinspired catalytic potential of this class [38,12].

NFPs retain the classical inward-facing tetradentate nitrogen donor set, with metal binding governed by the steric and electronic character of the fused macrocycle [7,34].

The fused heterocycles introduce modest differences in electron density and steric shielding that shift metal ion preferences toward late transition metals — particularly Fe(III), Co(II), Ni(II), and Pd(II). The rigid planar framework tends to exclude larger or more labile metal ions that require flexible or expanded coordination spheres, yielding a narrower but highly selective binding profile. This selectivity is advantageous where well-defined metal centers with predictable electronic and catalytic properties are required.

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• Complex Stability

Stability in metal-porphyrinoid complexes directly determines their practical utility in catalysis, sensing, and biomedical contexts. NCPs and NFPs show distinct stability profiles that mirror their structural and electronic differences.
NCP complexes often display dynamic coordination behavior: the peripheral confused nitrogen supports reversible metal binding and facile ligand exchange [6].

Białek et al. (2023) noted that this dynamism, while functionally valuable, can result in lower thermodynamic stability compared with classical porphyrins or NFP complexes. Nevertheless, the flexibility of NCP coordination spheres allows stabilization of catalytically relevant intermediates under mild conditions that would otherwise be inaccessible. Electronic perturbations introduced by the confused nitrogen can also extend the lifetime of high-energy oxidation states that are typically transient in classical systems, thereby prolonging the activity of catalytic species [13].

NFP complexes, in contrast, display exceptional thermodynamic and kinetic stability. The extended conjugation and rigid macrocyclic framework strengthen metal–ligand bonds and slow ligand dissociation [8]. As Zhao et al. (2015) demonstrated, the fused rings suppress conformational rearrangements, reducing pathways to degradation by oxidative cleavage or demetalation. The practical outcome is longer catalytic lifetimes, higher turnover frequencies, and greater tolerance to harsh reaction conditions — attributes that make NFPs well suited to electrocatalysis, photodynamic therapy, and advanced materials applications. The stable coordination environments of NFPs also enable precise tuning of metal redox potentials and spin states, allowing fine control over catalytic selectivity.

d) Functional Consequences in Catalysis and Sensing

The different coordination environments and electronic structures of NCPs and NFPs translate into distinct functional strengths in catalysis and sensing.

• Catalysis

NCPs offer exceptional versatility as catalysts. The peripheral confused nitrogen provides an additional, readily accessible coordination site that supports the formation of dynamic, often multi-dentate coordination environments around the metal center, facilitating substrate binding and activation as well as the stabilization of reactive intermediates that are less accessible in conventional porphyrin systems [6,38]. The macrocyclic distortion and attenuated aromaticity of NCPs also create an electronic environment that accommodates redox flexibility, enabling the metal center to cycle through multiple oxidation states during multi-electron transfer processes. Iron and cobalt NCP complexes have shown strong performance in hydrocarbon oxidation and olefin epoxidation under mild conditions, mimicking the chemistry of enzyme active sites [4, 10]. The peripheral nitrogen can also participate directly in substrate activation through cooperative coordination, improving both rates and selectivity [12].

NFPs bring complementary strengths to catalysis. Their extended conjugation and rigid planar frameworks stabilize charged intermediates and support the rapid electron-transfer kinetics required for redox catalysis [8, 9]. This electronic robustness is reflected in the high durability and turnover numbers characteristic of NFP-based catalytic systems, particularly under oxidative or otherwise demanding conditions. The well-defined coordination geometry of NFPs also enables thorough mechanistic characterization — an important practical advantage. Ruthenium and iridium NFP complexes have performed impressively in photoredox applications including water splitting and CO_2 reduction [39], and the extended π-system facilitates photoinduced charge separation, making NFPs useful photosensitizers for solar energy conversion and oxidative degradation of environmental pollutants.

• Sensing

NCPs are well positioned for metal ion detection. The accessible confused nitrogen serves as an additional binding site that directly coordinates analytes, producing measurable changes in the macrocycle's electronic and spectroscopic properties [6]. These changes typically manifest as significant shifts in absorbance or fluorescence, enabling turn-on or turn-off signaling with favorable signal-to-noise characteristics. The reversibility of NCP coordination also allows analyte binding and release to be cycled, which is essential for reusable and real-time sensing platforms [12].
NFPs are better suited to fluorescence-based sensing and imaging. Their rigid planar structure and extended conjugation generate intense, tunable fluorescence — including emission in near-infrared regions useful for biological imaging and in vivo sensing [8].

The photostability of NFPs extends sensor lifetimes and resists photobleaching during prolonged or repeated use. NFPs can also serve as FRET-based sensing platforms, where the fused macrocycle functions as an efficient energy donor or acceptor for the sensitive detection of biomolecules and reactive species [9]. The ability of NFPs to generate singlet oxygen upon photoexcitation is additionally exploited for reactive oxygen species detection, linking them to the growing field of theranostic probe development [20].

e) Multinuclear and Supramolecular Assemblies

The structural characteristics of NCPs and NFPs strongly influence their capacity to form multinuclear coordination complexes and supramolecular assemblies — architectures with important implications for molecular electronics, magnetism, and catalysis.

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• N-Confused Porphyrins: Bridging and Multinuclear Complexes

The peripheral confused nitrogen is one of the most distinctive structural features of NCPs, functioning as a flexible coordination site capable of bridging metal centers. This property makes NCPs natural building blocks for multinuclear complexes in which multiple metal ions are connected through the macrocyclic scaffold, often giving rise to cooperative catalytic and electronic behavior [10,6]. The accessible ligand environment supports bridging modes that are essentially unavailable in classical porphyrins, allowing the assembly of dinuclear and higher-nuclearity clusters incorporating lanthanides, actinides, and first-row transition metals such as Fe, Co, Ni, and Cu [4]. These multinuclear assemblies exhibit synergistic properties arising from electronic communication and magnetic coupling between metal centers, with relevance to catalysis, molecular magnetism, and small-molecule activation.

For example, dinuclear iron and cobalt NCP complexes have outperformed their mononuclear analogues in oxidation catalysis, a result attributed to cooperative substrate binding and electron transfer between metal sites linked by the confused nitrogen [38]. The ability to tune metal–metal distances and geometries through the flexible confused nitrogen coordination also allows the manipulation of magnetic exchange interactions, which is relevant to molecular spintronics and quantum computing.

NCP-based metallosupramolecular frameworks have been assembled using bridging metal ions, yielding structures with considerable diversity in topology and function [10]. The variable porosity and redox-active sites within these frameworks make them promising candidates for heterogeneous catalysis, gas storage, and separation. Additionally, the peripheral placement of the confused nitrogen encourages intermolecular interactions — including hydrogen bonding and π–π stacking — that can stabilize supramolecular assemblies and give rise to stimulus-responsive behaviors relevant to smart materials and chemical sensors [6].

• N-Fused Porphyrins: Discrete Complexes and Extended Conjugation

NFPs favor the formation of discrete, mononuclear complexes. The structural rigidity and steric constraints imposed by the fused-ring architecture limit the accessibility of peripheral coordination sites, making multinuclear assembly through metal bridging uncommon [7,8]. Within these well-defined mononuclear complexes, however, the extended π-conjugation of the fused rings facilitates efficient intermolecular electronic communication when NFPs are assembled in the solid state or within supramolecular frameworks. This makes NFPs attractive components for materials with efficient charge transport, relevant to molecular electronics, organic photovoltaics, and optoelectronics [9,39].

Supramolecular assemblies of NFPs can be formed through non-covalent interactions — π–π stacking, hydrogen bonding, and van der Waals forces — yielding ordered aggregates or thin films with anisotropic electronic properties [8]. Such ordered morphologies can improve exciton diffusion and charge carrier mobility in device architectures. Although NFPs rarely form multinuclear coordination complexes through metal bridging, their capacity for host–guest chemistry and molecular recognition is notable: the planar, electronically rich macrocyclic cavity can accommodate guest molecules or ions, enabling the design of supramolecular sensors and catalysts with enhanced selectivity.

• Functional Implications

The contrasting assembly behaviors of NCPs and NFPs highlight their complementary roles in advanced materials. NCPs, with their tendency to form metal-bridged multinuclear clusters, serve as adaptable platforms for catalysis that exploits metal–metal cooperativity and dynamic coordination chemistry — useful in biomimetic catalysts, magnetic materials, and molecular machines. NFPs, by contrast, are distinguished by their electronically delocalized, structurally robust frameworks, which favor the formation of highly ordered supramolecular aggregates with efficient charge transport properties. The fusion of heterocycles enhances photostability and allows electronic tunability through supramolecular engineering, giving precise control over material properties [26].

V. REACTIVITY

The reactivity of NCPs and NFPs reflects their underlying structural and electronic differences, with direct consequences for catalysis and other functional applications.

The exposed confused nitrogen atom of NCPs functions as a nucleophilic and coordinatively active site, endowing these compounds with high chemical reactivity [6]. NCP-based systems are able to perform catalytic transformations — including oxidation, oxygenation, and hydroxylation reactions — that closely parallel enzyme mechanisms [4,19]. NCP–metal complexes also display dynamic coordination equilibria and redox-switchable behavior, enabling stimulus-responsive catalysis and molecular sensing [12]. The structural flexibility of NCPs supports adaptive catalytic cycles and selective substrate activation [6].

NFPs are less conformationally flexible, but their extended conjugation and rigid framework confer superior photostability and electron transport capability [7]. These properties make NFPs well matched to photodynamic therapy, solar energy conversion, and photochemical catalysis [8,9]. The photophysical character of NFPs allows efficient reactive oxygen species generation for biological applications, and the stability of reactive intermediates supports durable and selective redox catalysis.

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In short, NCPs favor chemically dynamic, multifunctional catalytic processes, while NFPs provide robust platforms for photochemical and redox catalysis with excellent long-term stability [6].

VI. BIOACTIVITY

The structural properties of NCPs and NFPs have measurable consequences for their biological activity, shaping their utility in medicinal chemistry and biomedicine. Their respective electronic environments, coordination flexibility, and capacity to generate reactive oxygen species (ROS) support a range of biological functions, including antibacterial, anticancer, and photodynamic therapeutic activity.

NCPs have shown notable bioactivity, attributable to their non-planar macrocyclic structure and expanded coordination sites. Metal complexes derived from NCPs have demonstrated promising antibacterial activity, including against drug-resistant bacterial strains, likely through membrane disruption and lethal ROS generation [40]. NCPs have also been investigated as photodynamic therapy (PDT) agents: macrocyclic distortion promotes efficient intersystem crossing and singlet oxygen ($^1O_2$) generation, which is critical for PDT-induced cytotoxicity against cancer cells [35]. The flexible coordination chemistry and peripheral nitrogen binding sites of metalated NCPs additionally enable enzyme inhibition and chemosensing of biologically relevant species [10].

NFPs offer complementary strengths in biomedical contexts. Their extended π-conjugation and planar structure facilitate cellular uptake and generate strong photophysical responses. NFP metal complexes — particularly those incorporating zinc and palladium — have shown significant anticancer activity, driven by high singlet oxygen quantum yields and photostability [8]. The rigid macrocyclic architecture of NFPs also promotes selective engagement with clinically relevant enzymes, making them interesting candidates in drug discovery [41]. In antimicrobial contexts, NFPs have demonstrated the ability to destroy bacterial biofilms through photoactivated mechanisms, underscoring their potential against persistent infections [42].

VII. APPLICATIONS AND FUNCTIONAL PERSPECTIVES

The structural, electronic, and coordination properties of NCPs and NFPs have positioned both classes as adaptable platforms across a wide range of advanced applications. Their complementary characteristics enable targeted use in catalysis, sensing, photodynamic therapy, molecular electronics, and materials science [43-45].

• Catalysis

Catalysis is one of the most actively investigated application domains for NCPs and NFPs, where differences in coordination chemistry and electronic structure lead to different mechanistic strengths and catalytic efficiencies [46,47].

NCPs excel as biomimetic catalysts. Their flexible coordination spheres and peripheral nitrogen sites facilitate substrate binding, activation, and stabilization of high-valent intermediates, including metal–oxo and metal–peroxo species used in hydroxylation, epoxidation, and oxygen reduction [4,10,38]. The dynamic nature of metal coordination promotes adaptive catalysis under mild conditions, aligned with goals for environmentally sustainable chemistry.

NFPs are effective catalytic platforms for redox and photoredox reactions, owing to their extensive π-conjugation and structural rigidity [8]. Their stable complexes support efficient electron transport and charge separation, making them suitable catalysts for solar energy conversion, water splitting, and CO_2 reduction [10,39]. The photostability of NFP complexes is a practical asset in photocatalytic systems that require sustained irradiation.

• Sensing

Sensing applications draw on the distinct coordination environments and photophysical properties of NCPs and NFPs to achieve selective, sensitive detection of ions, molecules, and reactive species.

The peripheral nitrogen coordination site of NCPs enables direct analyte binding, which produces clear spectroscopic changes suited to selective sensing of metal ions and small molecules [6]. The reversible and dynamic nature of this coordination improves sensor reusability and response time — important for real-time monitoring in environmental and biological settings [12].

NFPs' strong fluorescence, photostability, and tunable emission wavelengths make them well-suited for fluorescence-based sensing and imaging [Lee et al., 2010]. Their ability to generate singlet oxygen efficiently upon photoexcitation supports the development of dual-function theranostic agents capable of both detection and photodynamic therapeutic action [20].

• Photodynamic Therapy

Photodynamic therapy (PDT), a minimally invasive approach to cancer treatment, takes advantage of the propensity of both NCPs and NFPs to generate ROS upon light exposure. NFPs are particularly strong candidates, with high singlet oxygen quantum yields and robust absorption in the therapeutic window (600–800 nm), enabling deep tissue penetration and efficient tumor destruction [39].

The flexible coordination chemistry of NCPs enables conjugation with targeting ligands and biomolecules, enhancing selectivity and therapeutic efficacy. This adaptability also supports integration into multifunctional nanoplatforms that combine imaging, drug delivery, and therapy [4].

• Molecular Electronics and Materials

The extensive π-conjugation and structural stability of NFPs make them well matched to organic electronic devices, including photovoltaics, field-effect transistors, and light-emitting diodes [8,9]. Their ability to form ordered supramolecular assemblies improves charge mobility and device performance.

NCPs contribute to molecular electronics through the formation of multinuclear and supramolecular complexes with magnetic and conductive properties [10]. The flexible coordination environment allows tuning of electronic coupling and spin states, which is relevant to spintronic devices and quantum information processing [4].

• Environmental Applications

Both classes have been explored for environmental remediation, including catalytic pollutant degradation and sensing of toxic metal ions [12]. NFPs' photostability and strong catalytic activity support long-term use in solar-powered water purification and pollution degradation systems [9]. The ability of NCPs to coordinate and reduce CO_2 and other greenhouse gases under mild conditions contributes to ongoing efforts in sustainable energy research and carbon capture [48].

VIII. CONCLUSION

N-fused and N-confused porphyrins represent two structurally distinct but complementary branches of porphyrinoid chemistry, each with a characteristic set of properties that shapes their aromaticity, coordination chemistry, reactivity, and functional applications. The outward nitrogen inversion of NCPs creates flexible macrocycles capable of non-classical coordination modes and dynamically adaptive catalytic behavior. The fused-ring architecture of NFPs, by contrast, enhances conjugation, rigidity, and photophysical stability, supporting robust catalysis and phototherapy. Together, these two variants significantly extend the functional landscape of porphyrin chemistry, providing versatile platforms for research in catalysis, sensing, materials science, and biomedicine. Continued investigation of structure–function relationships in NFPs and NCPs holds real promise for the rational design of new porphyrinoid molecules with meaningful scientific and technological impact.

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