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Review on *N*-confused porphyrin

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Abstract: We all know how vital porphyrin is to our body, from binding haemoglobin and iron to carrying oxygen to our organs and tissues. Recently, there has been a discovery about a new isomer of porphyrin called N-confused porphyrin. Its chemistry is very different and exciting. From there, scientists have explored many corners of this confusion chemistry, from doubly confused coordination to its supramolecular architecture, it has an identical backbone structure as porphyrin (1,1,1,1). NCP, on the other hand, has an additional pyrrolic moiety called a "confused pyrrole" that is linked to the surrounding meso-carbons at the α and β-positions. The position of pyrrolic N-H and β-CH are shifted as a result of this unusual linkage. Resulting, NCP contains an NNNC core and an outward-pointing N atom. When a metal is co-ordinated in the core, a kind of organometallic complex having a carbon-metal bond is formed. On the other hand, the peripheral nitrogen atom serves as a H-bonding donor/acceptor and a metal coordination site.

Introduction

Porphyrin is a functional pigment that has received extensive study and can coordinate with a wide range of metals with square-planar geometry. In biological systems, porphyrin derivatives have important roles such asin the photo synthetic process, chlorophyll centres and hemes in haemoglobin that act as oxygen transporter in a red haemocyte of vertebrates (Biscaglia et al., 2018). Porphyrin also behaves as a compelling bio-mimetic molecule in synthetic arrangements. However, there aren't many porphyrin congeners in biotic systems, with vitamin B_{12} as an exception (Ishihara et al., 2014). Later on, the preparation of further novel porphyrin isomers to be a point of interest for chemists due to their chemical (Stone et al., 1968), structural (Saito et al., 2011), physical (Lavi et al., 2002) and spectral (Fan et al., 1999) properties, in comparison to the parent porphyrin structure. There are now just two different forms of porphyrin isomers. Both have the formula $C_{20}H_{14}N_4$ and feature an internal macro-cyclic ring with 18-electron conjugated electrons; in the case of the first one, all the pyrrole nitrogen (N4) in the ring that is different from the positioning of the pyrrole-connecting different carbon atoms than a typical porphyrin. The original form of such type, porphycene, was prepared in 1986 by Vogel et al. (Vogel et al., 1986). Following this, isoporphycene (Sessler et al., 1994), corrphycene and hemiporphycene (Vogel et al., 1999) were also explored. The second one possesses one pyrrole ring inverted or confused to form an N3C core, which is explained as a "true porphyrin isomer," as it comprises four meso-carbon atoms like the normal one. N-confused porphyrin (NCP), the first isomer of this type, was independently documented by us and Latos Grazùyn'ski's team, in 1994 (Chmielewski et al., 1994). Later, doubly N-confused porphyrins (N_2CP), the second generation of the confused isomers (Fig **1**), were also produced (Maeda et al., 2003a).

Additionally, Latos-Grazùyn' ski et al. later reported on porphyrins that contain heteroatoms and have one or more pyrrolic nitrogen atoms that have been replaced by Se, O, Te, or S (Ulman et al., 1978).

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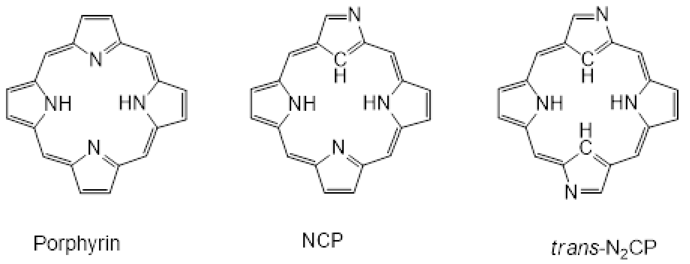


Figure 1. Porphyrin isomers

In 1994 the study of N-confused porphyrin and its analogues were started. So far, advancements have been made to comprehend its distinctive properties and parallel compounds. The porphyrin isomer known as N-confused porphyrin (NCP) differs significantly from the parent porphyrin, especially in the physical (Ziegler et al., 2013), structural (Srinivasan et al., 2005), chemical and coordination properties (Liu et al., 2013). The development of the confused porphyrinoids with a high potential for diversification is accelerated by establishing the confused pyrrole within the common and expanded porphyrins. As a result, we list some recently synthesized N-confused porphyrinoids and analyze their properties. A new realm of NCP chemistry has been opened up by the produced isomers, multiplied NCPs, and expanded N-confused derivatives (Chmielewski, 2004). In the core of the doubly N-confused porphyrin (N_2CP), the *cis* and *trans* isomers remain stable at higher oxidation numbers, such as Cu (III). Because they have more space than tetrapyrrolic isomers, confused isomers with five or more pyrrole rings can coordinate a high number of cations (Maeda et al., 2003b). The outlying nitrogen(s) of N-confused porphyrin and its congener can serve as a hydrogen bond donor, acceptor, and location for metal coordination. Through the use of metal ions, NCP produces many-sided dimers. Additionally, Cu (III) complexes of N2CP with N and N-H at the margin generate one-dimensional hydrogen-bonding webs that self-assemble and have different positions in the *cis* and *trans* isomers (Skorey et al., 1986).

The tautomerism of porphyrins and their analogues has been studied in detail due to their importance in biological fields and their interest in the associated mechanism. Usually, the tautomerism of porphyrins happens very fast with the four nitrogen in the nucleus, and each tautomer with the same stability exists in the equilibria (Maity et al., 2000). Furthermore, N-confused porphyrin (NCP), among the porphyrin isomers with an upside-down pyrrole ring, contains three nitrogen in the nucleus and one at the margin. As a consequence, the tautomer (**A**, **B** and **C**) (Fig **2**) have different stability and structure provided they exist (Furuta et al., 2001).

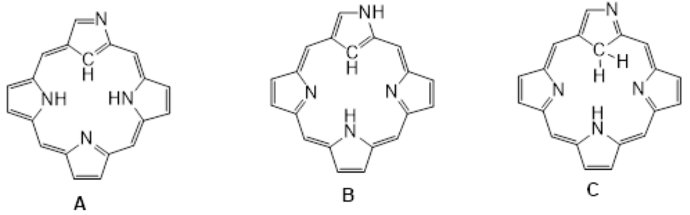
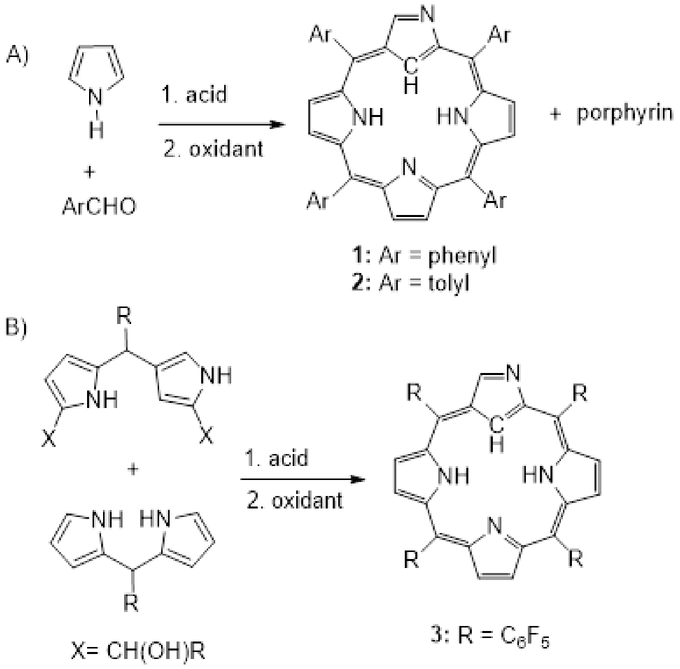


Figure 2. Tautomer of N-confused porphyrin

Discussion

Synthesis of N-confused Porphyrin

The first NCP was synthesized via the Rothemund-type procedure, which condenses benzaldehyde and pyrrole catalysed by an acid while also producing regular porphyrin. The yields reported were low [N-confused tetra-phenylporphyrin (NCTPP, **1**), 5 to7%, and N-confused tetra-tolylporphyrin (NCTTP, **2**), 4%] (Scheme 1A) (Furuta et al., 2001).



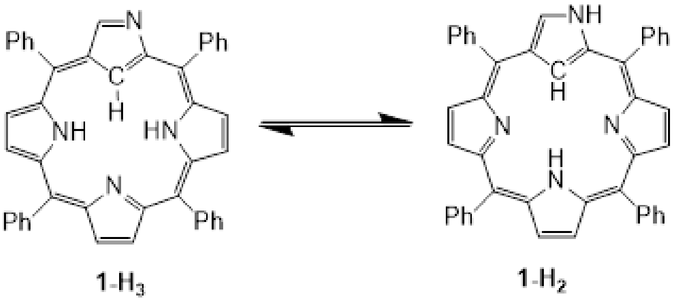
Scheme 1. One-pot synthesis of NCP 1, 2 and 3

In 1999, Lindsey and his team reported a better synthesis of **1** by catalyzing this reaction by methanesulfonic acid, and the yield of the reaction was increased to 39% (Furuta et al., 2002). A closer look at the document also describes how meso-free -alkyl type NCP was created, which involved McDonald type acid-catalyzed [2+2] and [3+1] condensation by the specific predecessor's Dolphin and Lash group, followed by oxidation (Lash et al., 1999). To incorporate the confused pyrrole unit into the macrocycle, β-alkyl-substituted N-confused dipyrrolo methane and 2,4-diformylpyrrole were utilized as lead precursors (Maeda et al., 2004). For the preparation of penta-fluorophenyl-substituted NCP**3**, Since Lindsey's modified technique proved ineffective, they ended up with an [2+2] acid-catalyzed condensation process (Scheme **1B**) (Maeda et al., 2003).

Many aryl electron donors, such as *p*-anisyl, *p*-tolyl, etc., as *meso*-substituents, are correctly suited to Lindsey's reaction conditions for NCTPP **1**. By employing $BF_3.OEt_2$ as an acid catalyst and tetra-butylammonium iodide as a cyclization template, it is possible to synthesize NCP containing electron-withdrawing aryl groups, such as 2,6-dichlorophenyl and 4-cyanophenyl component. Stepwise synthesis is crucial for producing C_6F_5-carrying NCP since it develops several enlarged porphyrins in a single process (Shin et al., 2001). A [2+2] condensation reaction with bis-carbinol of bis(penta-fluorobenzoyl)-substituted N-confused di-pyrromethane and unsubstituted di-pyrromethane resulted in the production of N-confused tetrakis-(pentafluorophenyl)-porphyrin (C_6F_5-NCP) with a yield of 21% (Furuta et al., 2004). Furthermore, NCP with various types of substituents at meso-positions requires a logical sequential approach rather than being synthesized in a single pot. As an example, [3+1] type condensation with meso-free tri-pyrrane and diol of 2,4-di-benzoylpyrrole resulted in the formation of partially meso-free NCP with only two phenyl groups in a 7% yield (Furuta et al., 2003). Recently, a similar approach was used to create NC-porphine, an unsubstituted form of NCP. To develop effective NCP types that are adaptable, stepwise methods are required (Morimoto et al., 2005).

Flexibility and reactivity of confused pyrrole

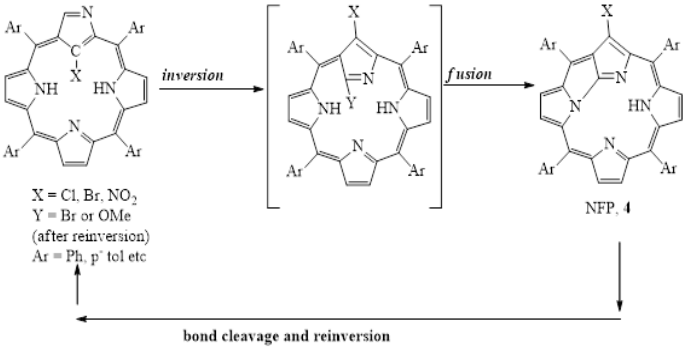
The NH tautomerism of NCP can occur between the inner and outer nitrogen due to the nitrogen in the core and peripheral, and the tautomeric equilibrium alters with various solvents (Shin et al., 2001). For example, an inner 2-H tautomer (**1-H$_2$**) predominates in polar solvents and solvents that tolerate hydrogen bonding, such as dimethyl formamide (DMF). Still, an inner 3-H tautomer of an 18-aromatic system (**1-H$_3$**) is found in most nonpolar solvents like $CHCl_3$ (Scheme **2**).



Scheme 2. NH tautomerism of NCTPP, 1

As a result, NCTPP solution's colours vary widely, red in $CHCl_3$ and green in DMF. The aromaticity, structure, and absorption spectra of the two tautomer also differ. The X-ray single-crystal study of 1-H_2 (from DMF/MeOH) showed the molecule was justly flat, and the confused pyrrole ring was leaning only 4.7°, reflecting less crowding in the centre compared with 1-H_3, which is 26.9°. In the solid state, a dimethyl formamide (DMF) molecule is hydrogen bonded with the peripheral N-H of the confused pyrrole (Szterenberg et al., 1997).

It has been observed that if the confused pyrrole ring is tilted in NCTPP **1** (Jasat et al., 1997) and NO_2 substituted NCTTP (Kiran et al., 2002) leads them to a study where they can modify the core and expectation of more flipping and tilting of the pyrrole ring. By halogenation of NCTPP **1**, N-fused porphyrin (NFP,4), A novel form of porphyrinoid with an inner tri-pentacyclic ring was discovered (Scheme **3**) (Furuta et al., 2000).



Scheme 3. Transformation between NCP and NFP, 4

Now, the confused pyrrole ring may invert to generate this product. NFP was converted back to NCP by reinverting the pyrrole ring through base treatment, which can incorporate various substituents at the outer α-carbon. The β-inner-β-inner linked NCP dimer is produced by an alkoxide transformation of the NFP dimer, produced by an oxidative coupling reaction (Ishizuka et al., 2004). The α-carbon of the confused pyrrole ring exhibits a distinct reactivity during the halogenation of NCP (Toganoh et al., 2004). α-α-linked NCP dimer was obtained when air oxidation of NCTPP utilizing HBr in toluene/CH_2Cl_2 that is refluxing (Chmielewski, 2005). Aside from the substitution and reaction at the carbons, methyl iodide was used to perform outer N-alkylation, creating the arranged di-anionic NCP (Sternberg et al., 1998).

Metal co-ordinated dimmers of N-confused Porphyrin

The structural similarity to conventional porphyrin indicates that NCP can mix with various metal cations. Since the NCTPP has been successfully synthesized, studies on the coordination chemistry of NCP have been conducted. NCP coordinates metal cations in the core to create square planar complexes, much like porphyrins. As per the N-H tautomer, divalent metals like Ni(II), Pd(II) (Furuta et al., 2000), Pt(II)(Hiroyuki Furuta, Katsuyuki Youfu, Hiromitsu Maeda, 2003) and Cu(II) (Chmielewski

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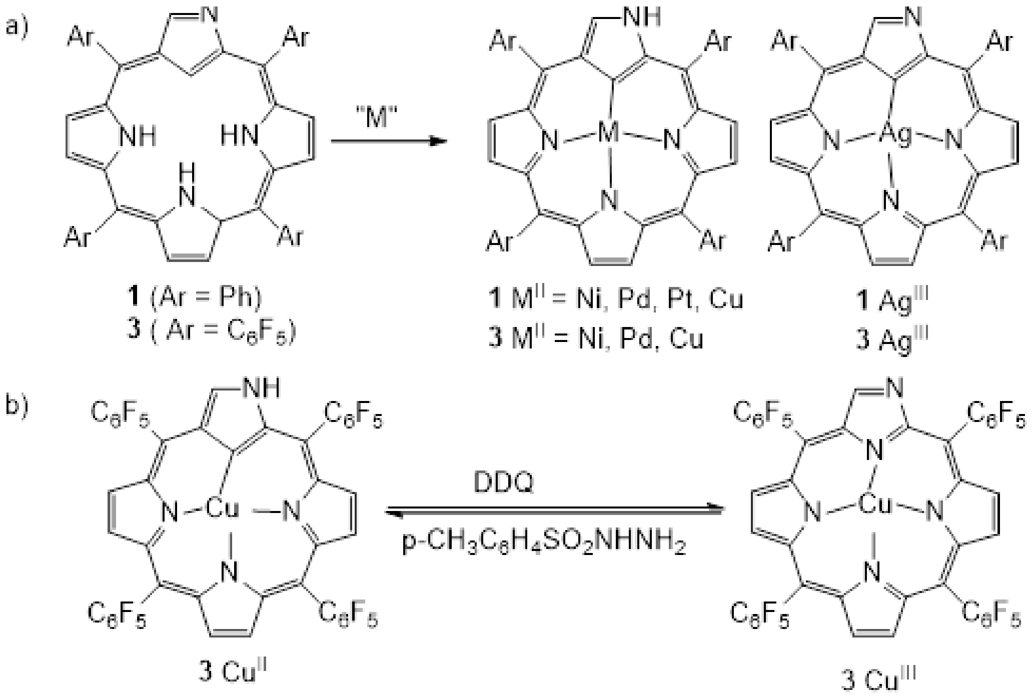
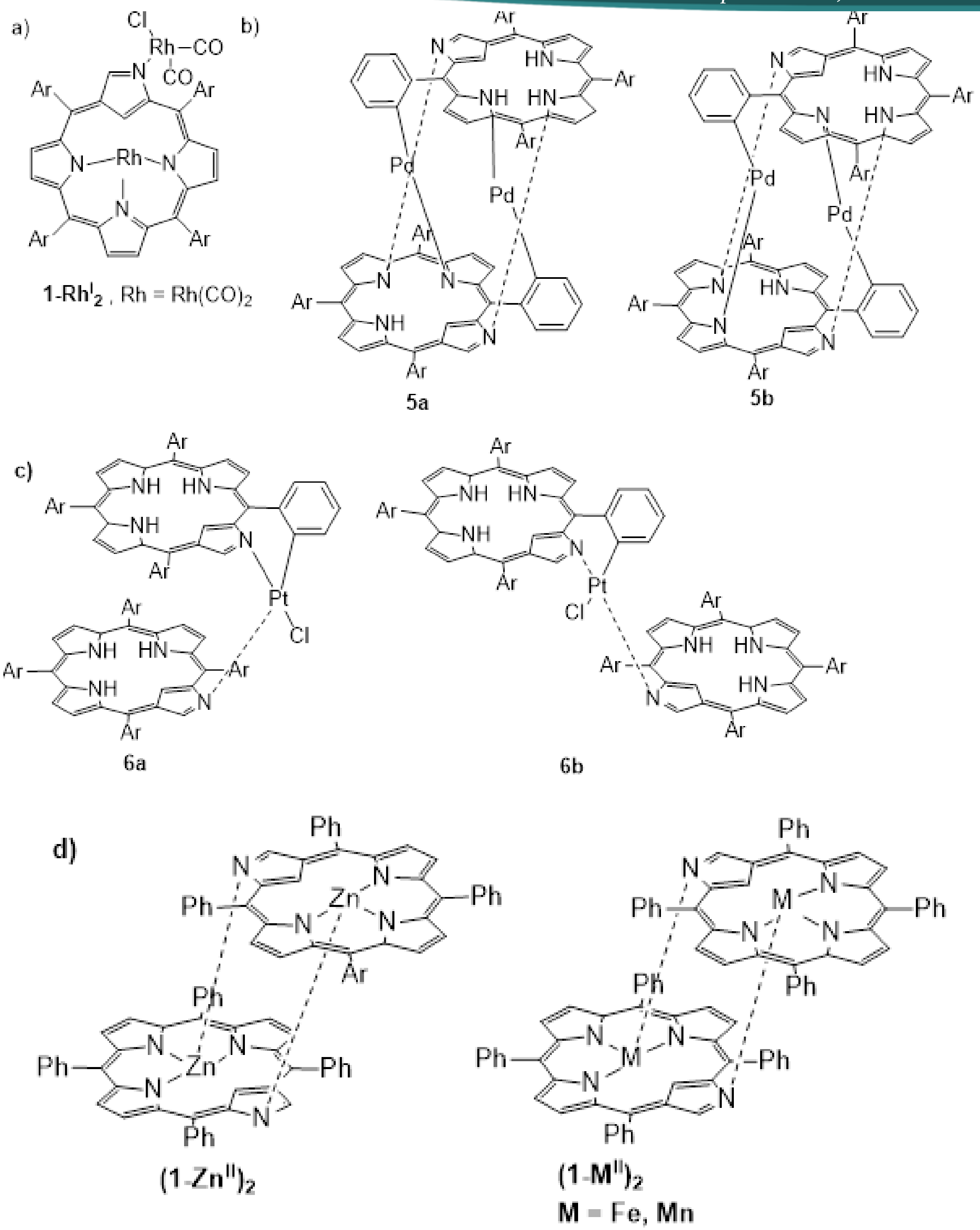
et al., 2000) and trivalent ones such as Ag(III) (Furuta et al., 1999) the three nitrogen atoms and one carbon atom at the centre of NCP to form a chelate complex (Scheme **4a**) (Maeda et al., 2003). Once more, the square planar Cu(III) complex [**3-Cu(III)**] was created from the Cu(II) complex of C_6F_5-substituted NCP [**3-Cu(II)**] via oxidation in chemicals (Scheme **4b**). The valences of the ligands can be changed by protonation and deprotonation at the outlying nitrogen in the first instance of NCP metal complexes.

monomeric complex, where one Pt(II) cation is coordinated with peripheral nitrogen, ortho carbon atom of the *meso*-aryl group, a Cl^- and the outer N of the opposing NCP (Scheme **5c**) (Mitrikas et al., 2005). The peripheral nitrogen atom locations in **6a** are on the same side (*cis*-form), whereas they are on the opposite side in **6b** (*trans*-form). In the NCP derivatives containing phenyl, *p*-tolyl, and 4-*tert*-butylphenyl substituents at the meso sites, the Pd(II) and Pt(II) cations commonly exhibited cyclo-metallation. The distorted monomer complexes from a square planarity were reported for Mn(II) (Harvey et al., 2003), Zn(II) (Furuta et al., 2002) and Fe(II) cations. The cation at the centre of the metal complexes was coordinated by three inner nitrogen atoms, one axial ligand without a covalent metal-carbon bond, and a side-on η^1-or an agnostic η^2-interaction of C-H at the core was hypothesized in the solid state. By oxidizing the Fe(II) complex, a covalent Fe-C bond and a penta-coordinated Fe(III) complex were produced (Rachlewicz et al., 2004). However, various face-to-faces and dimers $[(1\text{-}M^{II})_2]$, where in the monomeric complexes were created together with the metal cations, which are each attached to one peripheral nitrogen, three nitrogen at the core, and the inner carbon or CH bond of Fe(II) (Hung et al., 2002), Mn(II) (Harvey et al., 2005) and Zn(II) (Bohle et al., 2002) metals (Scheme **5d**). Various NCP planes have different relative orientations: syn (C_2 symmetry) in the case of the Zn(II) dimer and anti (C_i symmetry) in the case of the Fe(II) and Mn(II)



Scheme 4. (a) Coordination complexes of NCP (1,3) and (b)ChangesfromCu(II)to Cu(III)in C_6F_5- substituted compound.

The nitrogen at the NCP's periphery may be coordinated with metals to create a supramolecular assembly (Scheme **5**). When NCP and $[RhCl(CO)_2]_2$ reacted, a monomeric bis-Rh(I) complex $(1\text{-}Rh^I{}_2)$ complete N coordination was formed. (Scheme **5a**) (Srinivasan et al., 2008). To create double-decker-type dimers (**5a**, **5b**), two Pd(II) cations were chelated simultaneously at the outer and inner nitrogen with the assistance of two NCP ligands. The inner core was metallated (Scheme **5b**) (Chen et al., 2001). These Pd (II) cations were coordinated with the two central nitrogen atoms of NCP and a peripheral nitrogen atom with an ortho carbon atom of the adjacent aryl group in the counter NCP in a deformed square-planar fashion. The relative configuration surrounding the Pd(II) cations between the planes of two NCP are distinct in **5a** and **5b**, being both symmetrical (**6a**) and unsymmetrical (**5b**). However, in the instance of Pt(II), two distinct dimer complexes (**6a,b**) were isolated along with the



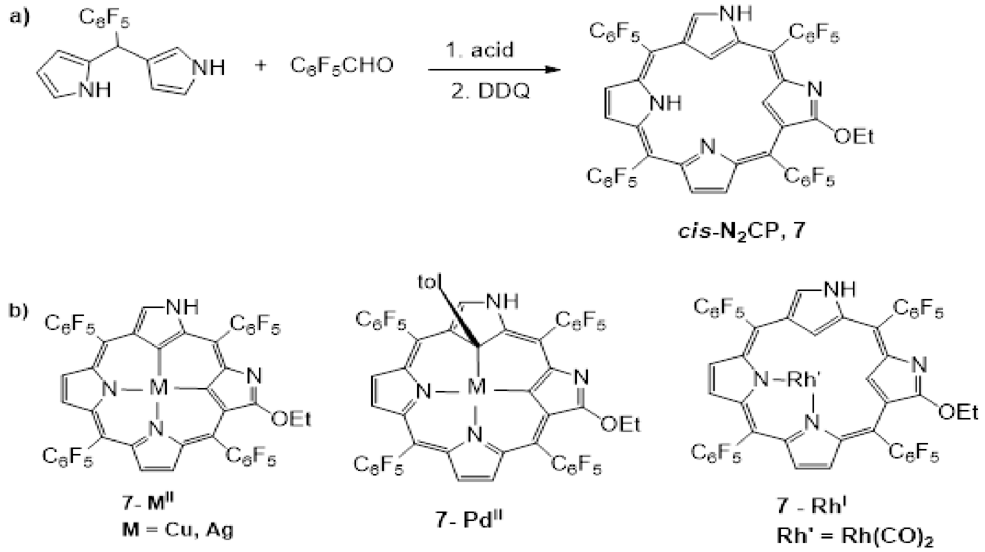
Scheme 5. Outer coordination of NCP in (a) Rh^{I}, (b) Pd^{II}and (c) Pt^{II}complexes (substitution in the aryl groups of 5a,b and 6a,b are not shown for clarity) and (d) face-to-face NCP dimers[(1-M^{II}$_{2}$)] of Zn^{II}, Fe^{II} and Mn^{II}

dimers. The Mn(II) dimer complex [(1-M^{II})$_2$] was converted into a new dimer in the refluxing toluene; however, the second porphyrin ring remained intact, and one of the porphyrin rings was reduced at the two opposing meso locations (Rachlewicz et al., 2003). Another example of peripheral coordination was reported in the tetra-nuclear dimer complex of the Zn(II) ion. The remaining two Zn atoms are coordinated with the inner three nitrogen atoms and other acetate groups. In contrast, the two outside Zn atoms form a 6-membered ring with an acetate and a hydroxy group (Furuta et al., 2002).

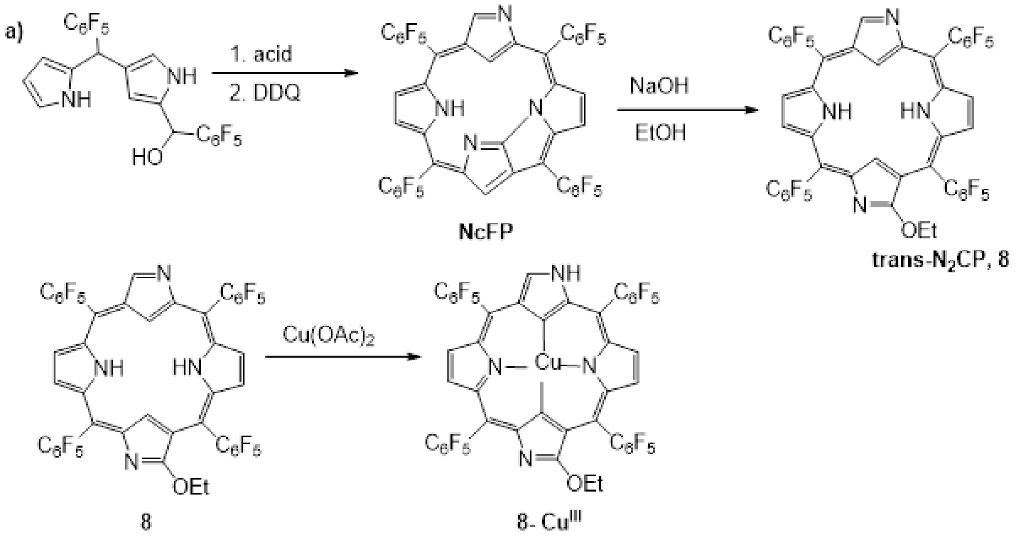
A distinct inner-oxo NCP dimer was generated during the aerobic dimerization of the Fe^{II} complex (Chen et al., 2001) in addition to the normal hydroxo iron dimer.

Doubly N-confused Porphyrin

From the NCP's initial reports (Chmielewski et al., 1994), Sessler brought up the potential of multiple NCPs, which would have more than two confused pyrrole rings in the inner section (Sessler, 1994). Invertopenta-phyrinogen, which Franck discovered in 1989, is a fully, *α,β′*-linked penta-phyrinogen that does not dehydrogenate to its comparable conjugated porphyrinoid (Schumacher et al., 1989). The first doubly NCP (N_2CP) as a *cis*-regio isomer **(7)** was prepared through the [2+2] acid-catalyzed condensation reaction of N-confused dipyrrolomethane and C_6F_5CHO with a yield ranging from 0.4-2 %, based on the substituents of dipyrrolomethane (Scheme **6a**) (Furuta et al., 2001a).



Scheme 6. Synthesis of (a) cis-N_2CP, 8 and (b) its metal complexes.



Scheme 7. Synthesis of (a) trans-N_2CP, 8 via NcFP and (b) Cu^{III} complex 8-Cu^{III}

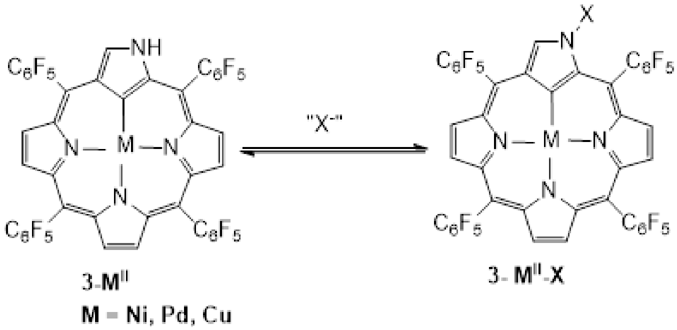
With the support of the two core nitrogen’s and two core electron-donating carbons, the *cis*-N_2CP **7** functions as a tri-anionic ligand that may coordinate with Ag and Cu at a higher oxidation state (+III) (Scheme **6b**). Due to the presence of two stable metal-carbon bonds, these substances are encouraged to act as sensitizers for the production of singlet oxygen and catalysts for electrochemical H_2O splitting (Araki et al., 2003). Toluene is attached to one of the inner carbons in the distorted square-planar Pd(II) complex (**7**-Pd^{II}) that is produced by *cis*-N_2CP **7** with the aid of Pd(II) salts (Furuta et al., 2000). During the case of salts of Rh, **7** forms Rh(I) complex through two core N and CO and not core carbons (Engelmann et al., 2004), seen in the Rh(I) coordination of NCP (Srinivasan et al., 2005).

After just three years, in 2003, another doubly N-confused isomer, *trans*-N_2CP **8**, was prepared by [2+2] self-condensation of bis-carbinol which is the derivative of penta-fluoro-benzoyl-substituted N-confused dipyrromethene (Maeda et al., 2003b). Surprisingly, the first macrocycle synthesised is not *trans*-N_2CP, but N-fused derivative (Scheme **7a**). The condensation reaction and the cleavage of the tri-pentacyclic ring by a nucleophilic base such alkoxide (EtO^-) have moderate yields of 11 and 53%, respectively. *Trans*-N_2CP **8** contrasts with *cis*-N_2CP **7** by displaying the tautomer with four protons in the inner section and, consequently, 18 aromatic forms, which is consistent with theoretical research (Furuta et al., 2001b). Two core C-H and N-H protons may be seen in the ^1H NMR ($CDCl_3$) at -4.36, -4.34, -3.21, and -2.73 ppm; in contrast to *cis*-N_2CP, they are in the high field region (inner CH: 3.22 and3.52 ppm; inner NH: 6.40 ppm). The confused pyrrole rings of both N_2CP incline 21.2° and 21.9° in trans (as a methoxy derivative instead of **8**) and 18.9° and 16.4° in cis (**7**), respectively, as revealed by X-ray analysis, as opposed to the normal one's 4.4°, 7.1° and 6.8°, 9.3° respectively.

Trans-N_2CP **8** coordinates with Cu as a tri-cationic metal in the core, similar to the *cis*-isomer **7** (Scheme **7b**). Although it has not been documented yet, the absorption spectra of *trans* and *cis*-N_2CP Cu(III) complexes exhibit a noticeable variation, which may be due to the difference in the coordination geometries (CCNN and CNCN).

Anion binding at the N-confused porphyrin's peripheral nitrogen

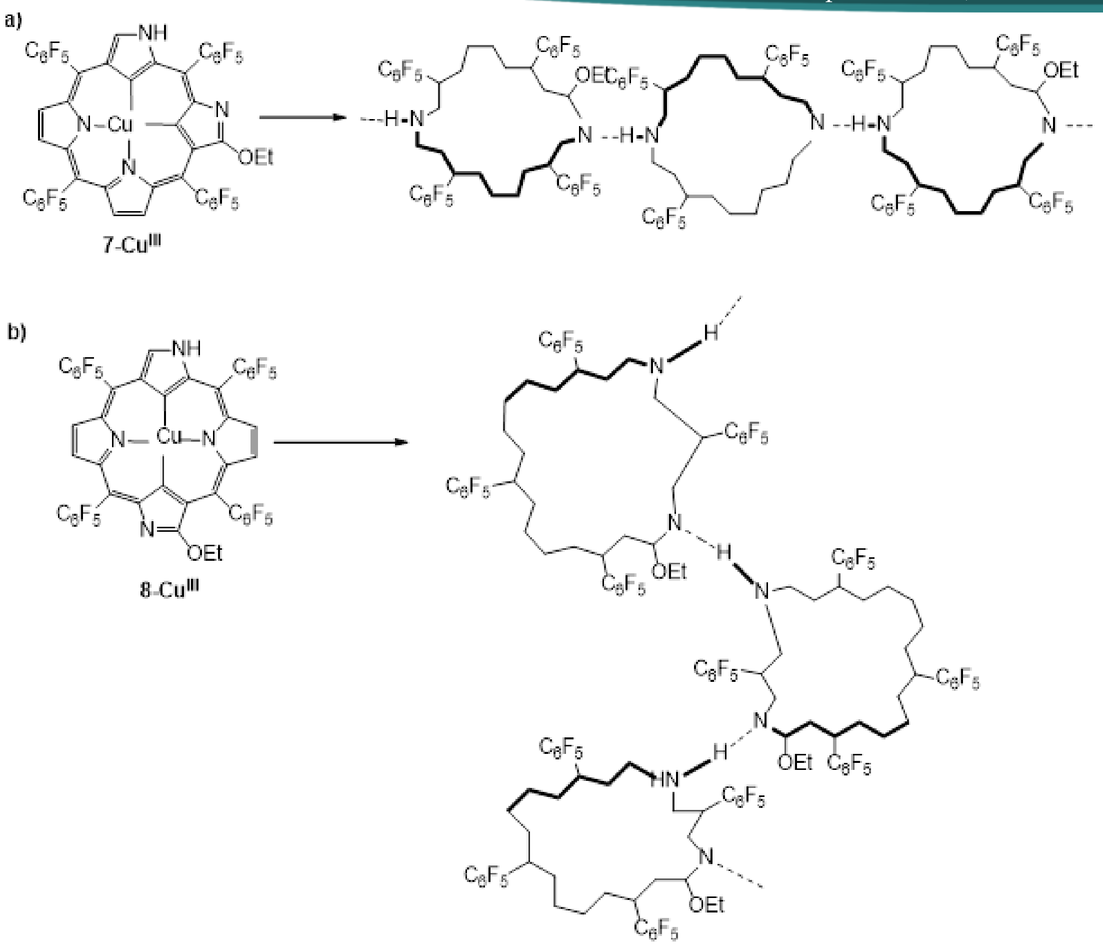
NCP in its solid form, in addition to binding with metal ions by outward nitrogen, it can also recognise anions by the peripheral N-H. Sb(V) NCP compounds with two mono-anionic axial ligands make good conductors of electricity (Ogawa et al., 2000). Through X-ray single-crystal analysis, it was confirmed that protonation or deprotonation can change the bond length of axial substituent in Sb(V) complexes containing dibromide ligands (Liu et al., 2003). X-Ray studies of monomeric Fe(II) complex, where the axial Br^- was H-bonded to the outer N-H of the other NCP, which results the formation of the dimeric compound (Szyszko et al., 2015). The well-organized binding of anions such as halides, ClO_4^-, and PF_6^- was seen (Scheme **8**) (Ikawa et al., 2008) in the case of divalent metal complexes with C_6F_5-substituted NCP (**3-M^{II}**, M = Cu, Ni, Pd) (Maeda et al., 2003). For instance, it was observed binding constants of **3**-Cu(II) for ClO_4^-, Cl^-, and PF_6^- were 4.9×10^4, 360, and 50 M^{-1} respectively in CH_2Cl_2. It was also observed that the binding constants for anions are reduced in the case of divalent complexes of NCTPP (1-M^{II}) with only a few electron-withdrawing substituents (e.g.,<10 M^{-1} for Cl). The anions of the supporting electrolytes can be used to modify the redox potential that is associated with Cu(III)/Cu(II) in the instance of the Cu(II) complex (3-Cu^{II}) (Maeda et al., 2003). In contrast to PF_6^- (0.15 V) and ClO_4^- (0.14 V) in CH_2Cl_2, the tightly bound Cl^- has a lower oxidation potential (0.03 V *vs* Fc^+/Fc). Further research on the anion recognition behaviours of Cu(III) complexes of *cis* and *trans*-N_2CP has clarified the origins of extraordinarily high association constants observedfor only one H-bonding interaction (N-H⋯X^-) (**7**-Cu^{III}, **8**-Cu^{III}) (Maeda et al., 2006).



Scheme 8. Anion binding of divalent metal complexes of C_6F_5-substituted NCP 3-M^I

Doubly N-confused Porphyrin and its supramolecular network

Negatively charged organisms can interact with the nitrogen's in the NCP's outer portion. One nitrogen atom acts as a H-bonding donor (N-H), and at the two external contact sites of the cis and trans-Cu(III) metal complexes like 7-Cu(III) and 8-Cu, the other atom acts as an acceptor (N), which may serve as the podium for the supramolecular superstructure's building blocks(III). Literally, 1D H-bonding chain of Cu(III) complexes of the cis-N2CP (Maeda, Osuka, & Furuta, 2003a) and trans-N2CP (Maeda et al., 2003b) are built in the solid state (Scheme 9) as well. In cis and trans-N2CP, the intermolecular configurations are distinct; straight and zigzag units are created with dihedral angles of 67.71° and 83.74° between the two macrocycles. In the case of trans form, as there is no H-bonding donor, N-H at the outer section of the free base 8 exhibits virtually no interaction, but for cis form, where the free base construct H-bonding networks with Ag(III) complex 7. The molecule aggregation as well as the electronic states at the core are both influenced by the geometries of N2CP. The preparation of N-confused congeners, including triply and fully confused ones that could make excellent substructures for 2D and 3D supramolecular architecture, is still pending. Based on calculations utilising the density functional theory (DFT), it is believed that confused congeners destabilises at around 18 kcal mol-1 with the introduction of each confused unit (Suzuki et al., 2006). Whether authentic or not, research into triply and complete NCPs will continue to shed light on NCP chemistry.



Scheme 9. H-bonding networks (1D) of Cu^{III}-complexes of cis- and trans-N2CP (7-Cu^{III} and 8-Cu^{III}).

Conclusion

The unintentional finding of N-confused porphyrin opened our eyes to new fields outside of the confusion method. The researcher investigated inversion followed by fusion using the "single confusion strategy." Numerous peripheral nitrogen coordination, particularly those linked to second- and third-row transition metals and various anions, were employed to create the recognisable confused pyrrole in NCP. Molecular switches and anion sensors are just a few applications that can be made possible by managing the metal valences by outer boosts. Second-generation NCPs, also known as "*cis* and *trans*-N_2-CP", have been created by the "double confusion technique." It is possible to understand the introduction of extra confusion in oligo-pyrrolic macrocycles in activating macrocycles for further mutation. Thus, the "confusion approach" to the study of novel porphyrinoids has an auspicious future, especially in the areas of 2-D and 3-D supramolecular structures.

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