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A dozen years of N-confusion: From synthesis to supramolecular chemistry*

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Abstract: The chemistry of N-confused porphyrin (NCP) and its analogs started in 1994. Since then, considerable progress has been made in understanding the unique properties of NCP and its analogs, which confer characteristic reactivity and metal complex formation. The evolved isomers, multiply NCPs, and expanded N-confused derivatives, have opened up new realms of NCP chemistry. *Cis*- and *trans*-doubly N-confused porphyrin (N_2CP) stabilizes higher oxidation states such as Cu^{III} in square-planar fashion in the core. Confused isomers with five or more pyrrole rings can coordinate several cations owing to their larger cavities compared to tetrapyrrolic system. The peripheral nitrogen(s) of NCP and its analogs can serve as hydrogen-bonding donor and acceptor, and metal coordination site as well. For example, NCP forms versatile dimers with the assistance of metal ions. The square-planar divalent metal complexes of C_6F_5-substituted NCP act as efficient anion-binding receptors. Furthermore, Cu^{III} complexes of N_2CP, possessing both N and NH at the periphery, form self-assembled one-dimensional (1D) hydrogen-bonding networks, whose orientations differ in *cis* (zigzag) and *trans* (straight) isomers.

Keywords: porphyrins; supramolecular chemistry; anion binding; metal coordination; core-modified.

INTRODUCTION

Porphyrin is a widely studied functional pigment that can coordinate with a variety of metals in a square-planar arrangement in the core. In biotic systems, porphyrin derivatives play essential roles like chlorophyll in photosynthetic reaction centers and hemes in hemoglobin that serve as oxygen carriers in a red hemocyte of vertebrates. Porphyrin also acts as a useful biomimetic molecule in artificial systems. On the other hand, very few porphyrin analogs are observed in biotic systems, with the exception of vitamin B_{12} [1]. What happens if the porphyrin core is modified? How do their properties differ from conventional porphyrins? To answer such questions, new realms of porphyrinoid chemistry, such as expanded, contracted, and isomeric analogs, are being developed (Chart 1) [2].

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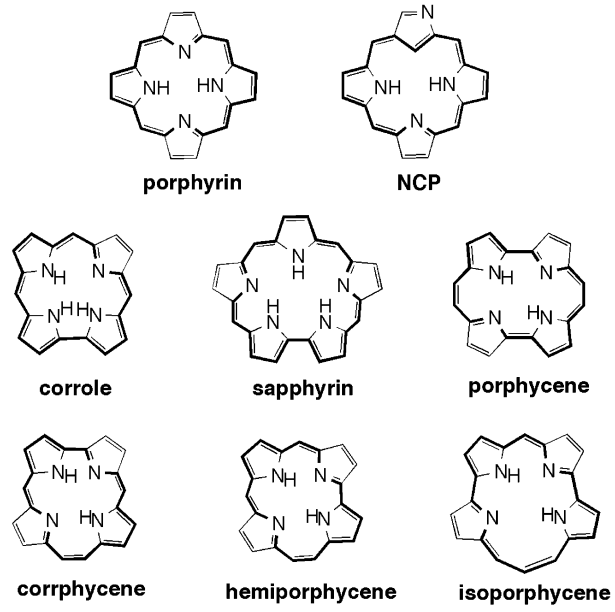
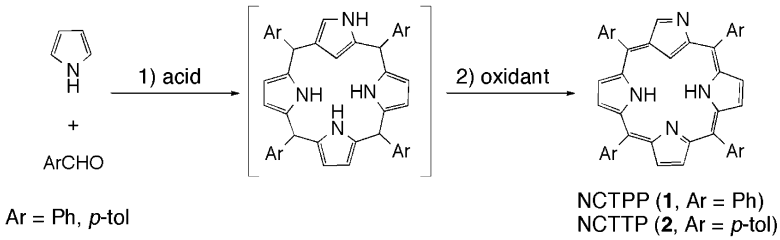


Chart 1 Porphyrin and its analogs.

Porphyrin analogs, whose frameworks and properties differ from normal ones, have been discovered serendipitously or synthesized by rational routes. Sapphyrin, the first expanded porphyrin with a 22π-electronic system, reported by R. B. Woodward in 1966, was produced as a byproduct during the total synthesis of vitamin B_{12} [3]. Up to date, various kinds of expanded porphyrins, including disk-like cyclo[8]pyrrole ([30]octaphyrin-(0.0.0.0.0.0.0.0)) by Sessler et al. [4] are synthesized. In 1964, Johnson et al. synthesized the first contracted porphyrin with an 18π-aromatic system, corrole, wherein one of the *meso*-carbons was missing in the skeleton [5]. Since the report of porphycene ([18]porphyrin-(2.0.2.0)) by Vogel et al. in 1986 [6], isomeric porphyrins like corrphycene ([18]porphyrin-(2.1.0.1)) [7], hemiporphycene ([18]porphyrin-(3.0.1.0)) [7a,8], and isoporphycene ([18]porphyrin-(2.1.1.0)) [9], whose core macrocycles have the same chemical formula, $C_{20}H_{14}N_4$, have been synthesized. Here, a peculiar nomenclature system consisting of the number of π-electrons, the general compound's name, and the number of C atoms between the pyrrole units was used. These isomeric porphyrins were known as reference macrocycles, compared to normal porphyrins with a view of annulene chemistry.

Apart from those analogs, in 1994, the groups of Furuta and Latos-Grażyński independently and almost simultaneously reported a new porphyrin isomer, N-confused porphyrin (NCP), in which one of the pyrrole rings is connected to *meso*-carbons at α and β' positions with an almost identical framework of normal porphyrin ([18]porphyrin-(1.1.1.1)) [10]. The discovery of N-confused tetraphenylporphyrin (NCTPP, **1**) or N-confused tetra-*p*-tolylporphyrin (NCTTP, **2**) as a byproduct of the reaction for normal porphyrin was serendipitous, but derived from a reasonable result under the consideration of the process of cyclization into normal porphyrin, e.g., the Rothemund-type reaction (Scheme 1) [11]. Latos-Grażyński's group used a large amount of pyrrole compared to *p*-tolaldehyde in the ratio of 7:4 to afford NCTTP **2** in 4 % yield. In Furuta's strategy for NCP, hydrobromic acid was used as an anion template, in the presence of hydrophilic solvent such as *tert*-butyl alcohol and CH_2Cl_2 (1:1), to afford NCTPP **1** in 5-7 %. The facile and efficient one-pot reaction conditions, which improved the NCTPP yield up to ca. 40 %, were reported by Lindsey in 1999 [12]. Here, the methanesulfonic acid was used as a catalyst for NCP, but the synthesis of other analogs including multiply and expanded NCPs requires stepwise reactions.



Scheme 1 One-pot synthesis of NCPs **1** and **2**.

Up to date, various properties of NCP and its analogs have been elucidated for 12 years since the first reports, some of which have also been described in the previous reviews [13]. NCP analogs containing hetero-atoms such as O, S, and Se were synthesized by the groups of Lee [14], Latos-Grażyński [15], and Chandrashekar et al. [16]. Furthermore, Lash and coworkers reported syntheses of a series of CNNN- and CNCN-core porphyrins, including "true" carbaporphyrins, which contain a cyclopentadienyl unit in the macrocycle [17]. Here, CNNN is defined as the core structure consisting of one carbon and three nitrogens, and the macrocyle with CNCN has the two core carbons at the opposite side. Similar CNNN configurations were observed in benziporphyrins, which act as versatile coordination ligands [18]. These compounds could serve as good references for the study of NCP chemistry, but they are not "genuine" isomers of conventional porphyrins like NCP. Therefore, we describe the synthesis and unique properties of NCP and its analogs, and, especially, focused on "evolved" multiply NCPs (Fig. 1). The peripheral nitrogen of a series of N-confused porphyrinoids behaves as a binding site with various cation, anion, and neutral species, to form supramolecular architectures in some cases.

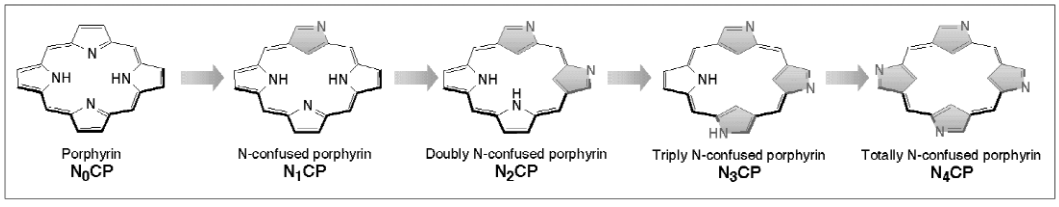


Fig. 1 Evolution of the NCP family.

SYNTHESIS OF N-CONFUSED PORPHYRIN

For almost 60 years since the report of one-pot synthesis of tetraphenylporphyrin (TPP) by Rothemund [11], there had been no reports on the isolation of NCTPP **1** from the reaction tar. Actually, the yields of NCP and other analogs were too low to be isolated by the chromatography techniques of that time. NCTPP **1** would have been missed because it is much more polar than TPP, and requires methanol(2–3 %)/CH_2Cl_2 for successful elution on silica gel. This implies that there may be future scope for isolating further porphyrin analogs by varying acid-catalysts and oxidants. As an example, in 2001, the modified procedures using the mixture of acetone and benzaldehyde as electrophiles and pyrrole in 1:3:4 ratio yielded 3 % of N-confused calix[4]phyrin (NcCP), wherein the sp^3 *meso*-carbon atom was present in the framework regioselectively, and 19 % of NCTPP **1** [19].

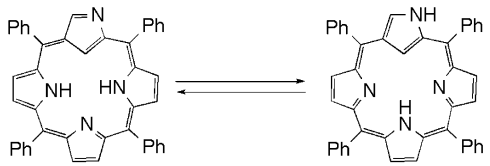
Lindsey's reaction conditions for NCTPP **1**, which are efficiently applicable to various electron-donating aryl groups such as *p*-tolyl, *p*-anisyl, etc. as *meso*-substituents. Synthesis of NCP with electron-withdrawing aryl groups such as 4-cyanophenyl and 2,6-dichlorophenyl moieties are performed by the procedures from pyrrole and arylaldehyde using $BF_3{\cdot}OEt_2$ as an acid catalyst with tetrabutylammonium iodide as possibly a cyclization template. However, for synthesizing C_6F_5-bearing NCP,

stepwise synthesis is necessary due to the formation series of expanded porphyrins in one-pot reaction [20]. [2+2]-Condensation reaction using biscarbinol of bis(pentafluorobenzoyl)-substituted N-confused dipyrromethane and normal dipyrromethane afforded N-confused tetrakis(pentafluorophenyl)-porphyrin (C_6F_5-NCP, **3**) in 21 % yield [21]. In addition, NCP possessing several kinds of substituents at *meso*-positions requires rational stepwise route rather than the reaction in one pot. For example, partially *meso*-free NCP **4** with only two phenyl groups was synthesized from [3+1]-type condensation from diol of 2,4-dibenzoylpyrrole and *meso*-free tripyrrane in 7 % yield [22]. Very recently, NC-porphine, completely unsubstituted NCP, was synthesized by similar procedure [23]. Stepwise procedures are required to make versatile kinds of functional NCP.

Apart from the synthesis of *meso*-"aryl"-substituted NCP, some examples of *meso*-free β-alkyl-type NCP were also reported in 1996 and 1999 [24]. These porphyrinoids were also prepared in a stepwise manner using MacDonald-type [2+2] and [3+1] condensation by Dolphin's and Lash's groups in 25 and 61 % yields, respectively. Here, β-alkyl-substituted N-confused dipyrromethane and 2,4-diformylpyrrole were used as key precursors in order to incorporate confused pyrrole unit in the macrocycle.

FLEXIBILITY AND REACTIVITY OF CONFUSED PYRROLE

Owing to the presence of the core and the peripheral nitrogens, NH tautomerism of NCP can take place between inner and outer nitrogens, and the tautomeric equilibrium changes with solvents [25]. In nonpolar solvents like $CHCl_3$, an inner 3H tautomer of an 18π aromatic system (**1-H$_3$**) predominates, whereas an inner 2H tautomer (**1-H$_2$**) predominates in polar and hydrogen-bonding accepting solvents like dimethylformamide (DMF) (Scheme 2). As a result, the colors of NCTPP solutions differ greatly, red in $CHCl_3$ and green in DMF. The two tautomers also differ in structure, absorption spectra, and aromaticity. The X-ray single-crystal analysis of **1-H$_2$** (obtained from DMF/MeOH) revealed that the molecule was fairly flat and the confused pyrrole ring was tilted only 4.7°, reflecting less crowding in the core compared with **1-H$_3$**, 26.9° [10a]. In the solid state, a DMF molecule was hydrogen-bonded with outer NH of the confused pyrrole.



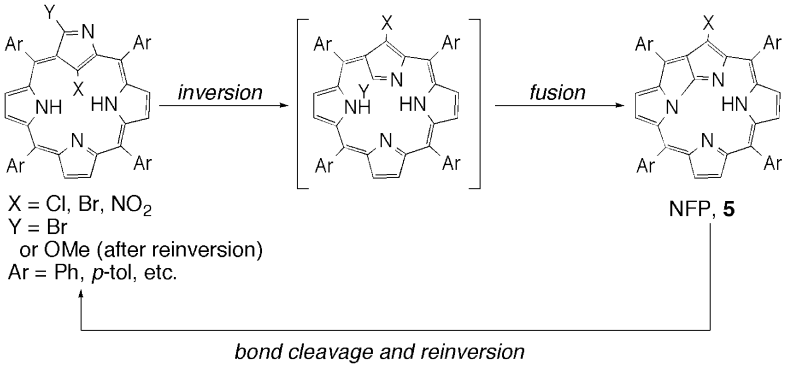
1-H$_3$ **1-H$_2$**

Scheme 2 NH tautomerism of NCTPP, **1**.

The ^{1}H NMR signals derived from the inner CH and NH of **1-H$_3$** in $CDCl_3$ resonated at –4.99 and –2.41 ppm, respectively. On the other hand, the corresponding signals of **1-H$_2$** in DMF-d_7 are shifted to 0.76 and 2.77 ppm, respectively, in addition to the appearance of an outer NH signal at 13.45 ppm. The downfield shifts of inner protons in DMF-d_7 are attributable to disruption of the 18π system. The dynamic process of NH tautomerism of NCTPP was studied by ^{1}H NMR saturation transfer experiments in pyridine-d_5 solution, where both the tautomers could exist in comparable amounts. Based on the large negative value of the activation entropy, the drastic conformational change in the transition state, where the confused pyrrole ring *inverts* to draw the "outer" nitrogen nearer to the inner NH to receive the proton, was postulated.

The observation of the tilting of the confused pyrrole ring in NCTPP **1** [10a] and NO_2-substituted NCTTP [26] drove us to a further study on the core modification with expectation of more tilting and

flipping of the pyrrole ring. During the halogenation of NCTPP **1**, a new type of porphyrinoid, N-fused porphyrin (NFP, **5**), with a tripentacyclic ring in the core was obtained (Scheme 3) [27]. This product is possibly derived from the ring inversion of the confused pyrrole ring. NFP was found to return to NCP by *reinversion* of the pyrrole ring by treatment with base, which can readily introduce various kinds of substituents at the outer α-carbon. Such transformation using alkoxide affords the β_{inner}-β_{inner}-linked NCP dimer from NFP dimer, obtained by oxidative coupling reaction [27d].

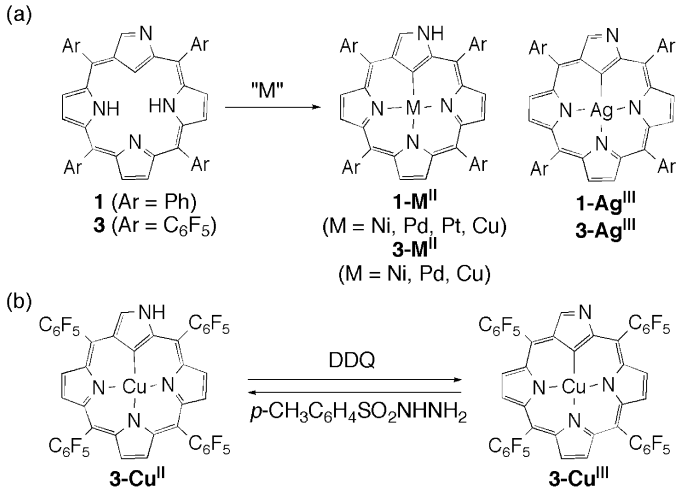


Scheme 3 Transformation between NCP and NFP **5**.

As seen in the halogenation of NCP, α-carbon of confused pyrrole ring shows unique reactivity [27a,b]. Air oxidation of NCTPP **2** using HBr in refluxing toluene/CH_2Cl_2 afforded α-α-linked NCP dimer [28]. Apart from the substitution and reaction at the carbons, outer N-alkylation, which makes the preorganized dianionic NCP, was performed by methylation reagents such as methyl iodide [29].

METAL-COORDINATED DIMERS OF N-CONFUSED PORPHYRIN

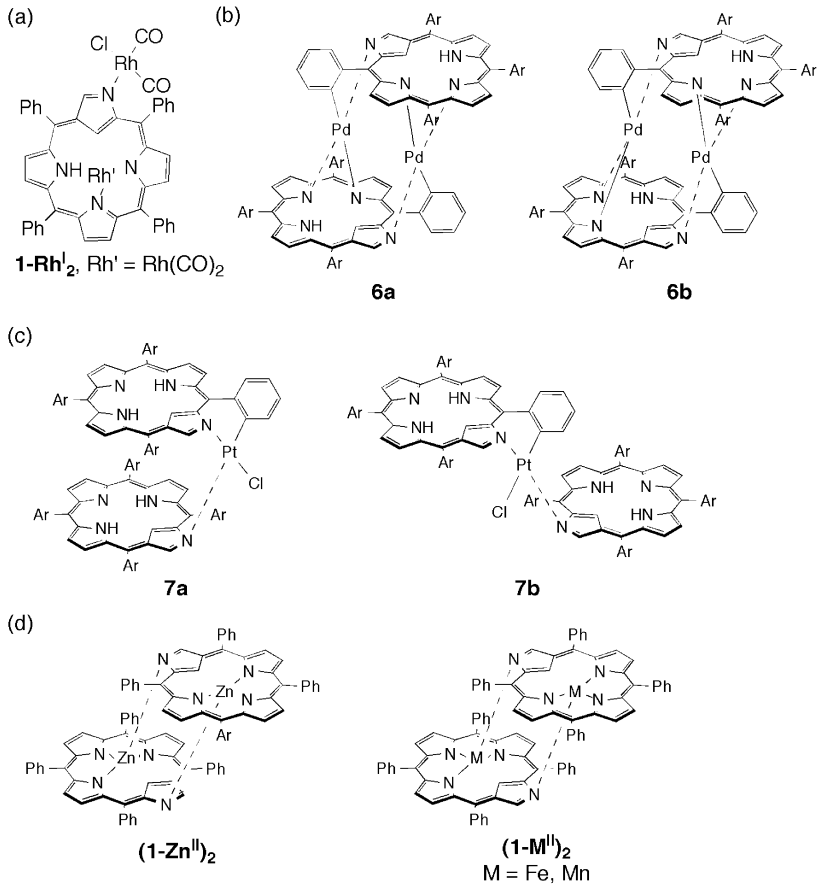
NCP can complex with a variety of metal cations, as expected from the structural resemblance to the normal porphyrins. Since the report on the efficient synthesis of NCTPP **1** [10], the investigations on the coordination chemistry of NCP have been carried out progressively. Like porphyrins, NCP coordinates metal cations in the core to form square-planar complexes. According to the NH tautomers, divalent metals like Ni^{II} [10b], Pd^{II} [30], Pt^{II} [31], and Cu^{II} [21,32], and trivalent one such as Ag^{III} [33] are chelated by the three nitrogen atoms and one inner carbon of NCP (Scheme 4a). The Cu^{II} complex of C_6F_5-substituted NCP (**3-Cu^{II}**) was transformed into the same square-planar Cu^{III} complex (**3-Cu^{III}**) by chemical oxidation (Scheme 4b) [34]. This is the first example of NCP metal complexes, whose ligand valences can be changed by protonation and deprotonation at the peripheral nitrogen.



Scheme 4 (a) Inner metal coordination of NCP (**1**, **3**) and (b) transition between Cu^{II} and Cu^{III} in C_6F_5-substituted NCP **3**.

The nitrogen atom at the periphery of NCP participates in the metal coordination to assist the formation of a supramolecular assembly (Scheme 5). A monomeric bis-Rh^I complex (**1**-$\mathbf{Rh^I_2}$) with inner- and outer-N coordinations was obtained from the reaction of NCP and $[RhCl(CO)_2]_2$ (Scheme 5a) [35]. Two Pd^{II} cations were chelated by the two NCP ligands at both the outer and inner nitrogens simultaneously, to form double-decker-type dimers (**6a**,**b**) along with the inner-core-metallated monomer (Scheme 5b) [30]. These Pd^{II} cations were coordinated in a distorted square-planar fashion, by the two inner nitrogen atoms of NCP, and an outer nitrogen atom and an *ortho* carbon atom of the neighboring aryl group in the counter NCP. In **6a** and **6b**, the relative geometries around Pd^{II} cations between two NCP planes are different: symmetrical (**6a**) and unsymmetrical (**6b**). On the other hand, in Pt^{II} case, two kinds of dimer complexes (**7a**,**b**), in which one Pt^{II} cation is coordinated by the outer nitrogen, *ortho* carbon atom of *meso*-aryl group, a chloride atom and the peripheral nitrogen of the countered NCP, were isolated along with the monomeric complex (Scheme 5c) [31]. In **7a**, the positions of the outer nitrogen atoms are in the same side (*cis*-form), and those of **7b** are opposite (*trans*-form). The cyclometallation by the Pd^{II} and Pt^{II} cations were generally seen in the NCP derivatives with phenyl, *p*-tolyl, and 4-*tert*-butylphenyl substituents at *meso* positions.

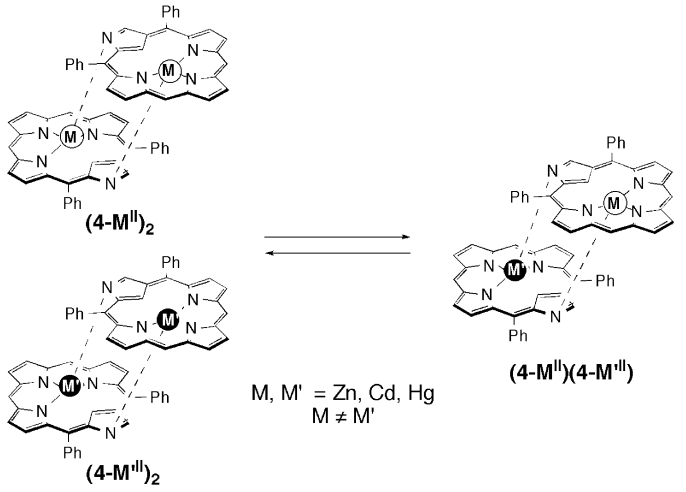
The distorted monomer complexes from a square-planarity were reported for Zn^{II} [22b,36], Fe^{II} [37], and Mn^{II} [38] cations. In the absence of covalent metal–carbon bond in these metal complexes, the center cation was coordinated by three inner nitrogen atoms and one axial ligand, and a side-on η^1- or an agostic η^2-interaction of inner C–H was suggested in the solid state. Oxidation of Fe^{II} complex gave a pentacoordinated Fe^{III} complex with a covalent Fe–C bond [39]. Moreover, several face-to-face sandwich-type dimers [(**1**-$\mathbf{M^{II}})_2$], wherein each metal cation is connected to one outer nitrogen and three inner nitrogen atoms as well as the inner carbon or C–H bond, were synthesized along with the monomeric complexes of Zn^{II} [36], Fe^{II} [37a], and Mn^{II} [38a,b] metals (Scheme 5d). The relative orientation of the two NCP planes is different: *syn* (C_2 symmetry) in the Zn^{II} dimer and *anti* (C_i symmetry) in the Fe^{II} and Mn^{II} dimers. In the refluxing toluene, the Mn^{II} dimer complex [(**1**-$\mathbf{M^{II}})_2$] was transformed into another dimer, where one of the porphyrin rings is reduced at the two opposite *meso* positions while the second poprhyrin ring remains unchanged [38b]. Another type of outer coordination was also observed in the tetranuclear Zn^{II} dimer complex, where the two outer Zn atoms form a 6-membered ring with a hydroxy and an acetate group, and the remaining two Zn atoms are coordinated with the inner three nitrogen atoms and another acetate group [36]. For the dimerization of Fe^{II} complex



Scheme 5 Outer coordination of NCP in (a) Rh^{I}, (b) Pd^{II}, (c) Pt^{II} complexes (substituents on the aryl groups of **6a,b** and **7a,b** are omitted for clarity), and (d) face-to-face NCP dimers [**(1-M^{II})$_2$**] of Zn^{II}, Fe^{II}, and Mn^{II}.

[37a], in addition to a normal μ-hydroxo iron dimer, the formation of a novel inner-oxo NCP dimer was clearly observed under the aerobic conditions.

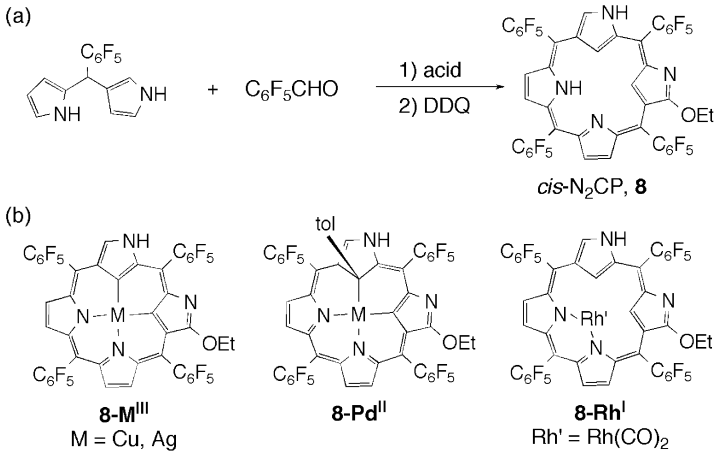
The ligand exchange reactions between the bis-aryl substituted NCP **4** [22a] and the metal cations such as Zn^{II}, Cd^{II}, and Hg^{II} in solution were also investigated (Scheme 6) [22b]. In $CHCl_3$, the homo-dinuclear dimers including the same cations [**(4-M^{II})$_2$**, **(4-M'^{II})$_2$**] changed to the "hetero"-nuclear dimer [**(4-M^{II})(4-M'^{II})**] in the equilibrium. The equilibrium constant obtained was lower than the statistical value 4, which indicated that the formation of hetero-dimer was less favorable due to the unbalance of the two kinds of metal coordination environments. During the transmetallation, only the bond between the metal cation and the outer nitrogen is dissociated, while the other metal-inner nitrogen bonds are intact. As the coordination at the peripheral nitrogen seems to be relatively weak in solution, NCP ligands would be usable as the transporters for the group 12 metals.



Scheme 6 Equilibrium between homo-dimers [$(\mathbf{4\text{-}M^{II}})_2$, $(\mathbf{4\text{-}M'^{II}})_2$] and hetero-dimers [$(\mathbf{4\text{-}M^{II}})(\mathbf{4\text{-}M'^{II}})$].

SYNTHESIS AND METAL COORDINATION OF DOUBLY N-CONFUSED PORPHYRIN

As inspired by the first reports of NCP [10], the possibility of the multiply NCPs, which contains two or more confused pyrrole rings in the core, was highlighted by Sessler [40]. Before then, in 1989, Franck had reported a totally α,β'-linked pentaphyrinogen, *invertopentaphyrinogen*, which failed to be dehydrogenated to the corresponding conjugated porphyrinoid [41]. In 2000, six years after the discovery of singly N-confused isomer, the first doubly NCP (N_2CP) as *cis*-regioisomer (**7**) was synthesized by [2+2] acid-catalyzed condensation of N-confused dipyrromethane and C_6F_5CHO in 0.4-2 % yields, according to the substituents of dipyrromethane (Scheme 7a) [42].

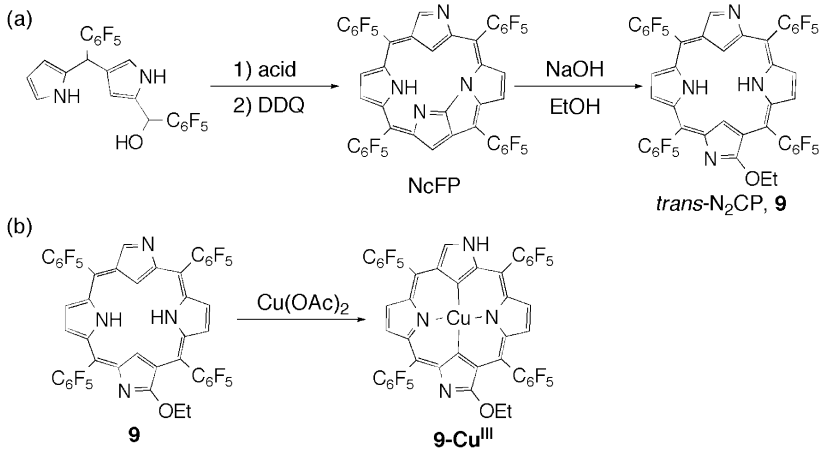


Scheme 7 Synthesis of (a) *cis*-N_2CP **8** and (b) its metal complexes.

Cis-N_2CP **8**, as a trianionic ligand, can coordinate Cu and Ag as rather higher oxidation states (+III), which are chelated by the two electron-donating inner carbons as well as two inner nitrogens (Scheme 7b). The presence of two air-stable metal–carbon bonds, in these metal complexes, promote these materials as the catalysts for electrochemical H_2O-splitting and sensitizers for singlet oxygen gen-

eration [43]. With Pd^{II} salts, *cis*-N_2CP **8** forms a distorted square-planar Pd^{II} complex (**8-Pd^{II}**), where the toluene is connected at one of the inner carbons [44]. In the case of Rh salts, **8** forms Rh^{I} complex using two inner N and CO, not inner carbons [45], as seen in the Rh^{I} coordination of NCP [35].

Just three years later, in 2003, the other type of doubly N-confused isomer, *trans*-N_2CP **9**, was synthesized by [2+2] self condensation of biscarbinol derivative of pentafluorobenzoyl-substituted N-confused dipyrromethane [46]. Surprisingly, first synthesized macrocycle is not *trans*-N_2CP, but N-fused derivative [N-confused, N-fused porphyrin (NcFP)] (Scheme 8a). The yields of condensation reaction and cleavage of tripentacyclic ring by nucleophilic base like alkoxide (EtO^-) are modest, 11 and 53 %, respectively. In contrast to *cis*-N_2CP **8**, *trans*-N_2CP **9** shows the tautomer with four protons in the core, and, thus, 18π aromatic forms, which is consistent with the theoretical speculation [47]. In ^{1}H NMR ($CDCl_3$), two inner CH and NH protons appear at –4.36, –4.34, –3.21, and –2.73 ppm, respectively, which are in the high field region compared to those of *cis*-N_2CP (inner CH: 3.22 and 3.52 ppm; inner NH: 6.40 ppm). Inferred by X-ray analyses, confused pyrrole rings of both N_2CP tilt at 18.9 and 16.4° in *cis* (**8**) and 21.2 and 21.9° in *trans* (as a *methoxy* derivative instead of **9**) compared to normal one (4.4 and 7.1°, and 6.8 and 9.3°), respectively.



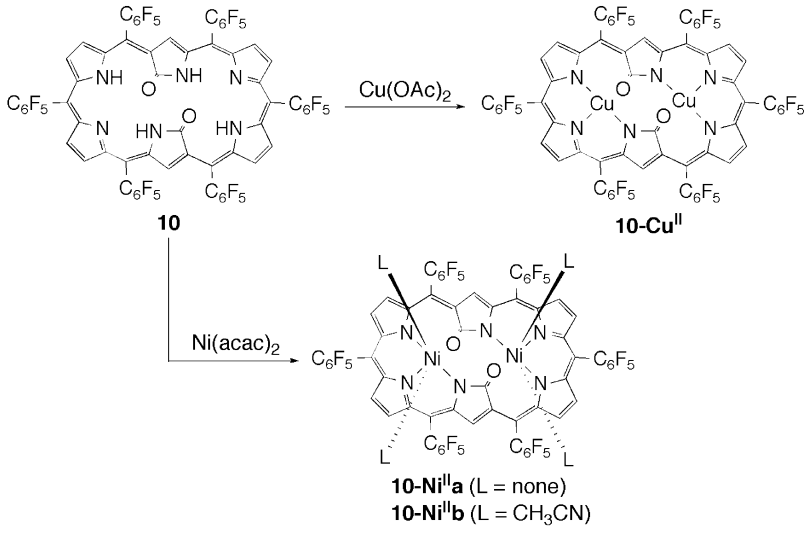
Scheme 8 Synthesis of (a) *trans*-N_2CP **9** via NcFP and (b) Cu^{III} complex **9-Cu^{III}**.

Like *cis*-isomer **8**, *trans*-N_2CP **9** coordinates Cu as tricationic metal in the core (Scheme 8b). While not clarified yet, the absorption spectra of Cu^{III} complexes of *cis*- and *trans*-N_2CP show the significant distinction, which is possibly derived from the differences in the symmetry and coordination geometries (CCNN and CNCN).

SYNTHESIS AND METAL COORDINATION OF N-CONFUSED EXPANDED PORPHYRIN

The peripheral coordination observed in the NCP complexes dramatically changes to "inward" chelation in the confused expanded porphyrin complexes. Owing to the facile inversion of the pyrrole ring in the expanded porphyrins, the nitrogen atoms of the confused pyrrole ring can be located inside the core. In 2003, one of the hexapyrrolic confused analogs, doubly N-confused hexaphyrins, are obtained from N-confused tripyrrane and C_6F_5CHO by acid-catalyzed condensation [48]. Here, several macrocycles, α-oxo/α-CH and aromatic/nonaromatic ones, were formed according to the amounts of the oxidants. The two confused pyrrole rings are *inverted* into the core center, thus, six nitrogen atoms and two carbon atoms (or carbonyl oxygens) in total could provide two metal coordination sites in the core. The dioxo-derivative **10** chelates two Cu^{II} and Ni^{II} cations, respectively, in the corresponding cavities

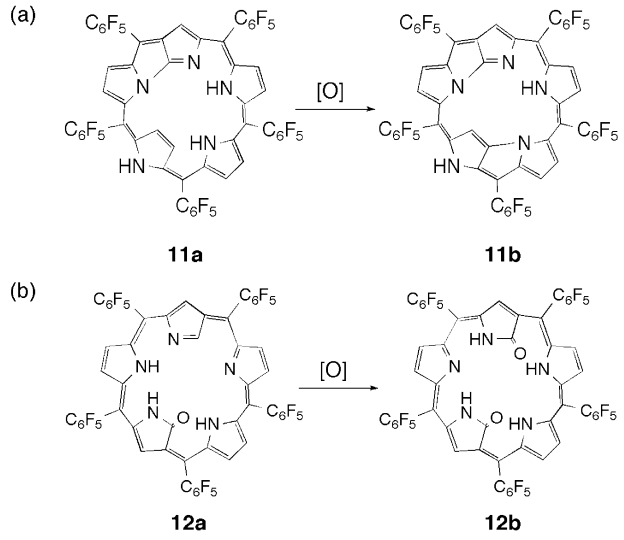
(Scheme 9). Interestingly, the Ni^{II} complexes (**10-Ni^{II}a**,**b**), which are distorted (**a**) and rather flat (**b**), respectively, differ largely in the structures and the electronic absorption spectra. In the latter complex (**b**), the solvent CH_3CN molecules are coordinated to the Ni^{II} metals as the axial ligands.



Scheme 9 Metal coordination of doubly N-confused hexaphyrin **10**.

In 2004, a series of pentapyrrolic macrocycles with one and two confused pyrroles were reported. N-Confused pentaphyrins (**11a,b**), synthesized by acid-catalyzed condensation of C_6F_5-substituted N-confused tripyrrane and diol of bis(pentafluorobenzoyl)-substituted *normal* dipyrromethane, have a fused tripentacyclic moiety at the confused pyrrole in the core [49]. Further oxidation of this mono-fused pentaphyrin **11a** resulted in the formation of doubly fused derivative **11b** (Scheme 10a), wherein one of the fused units is derived from confused pyrrole like NCP [27], and the other new one is transformed from normal pyrrole under conjugative oxidation similar to N-fused pentaphyrin [20b]. The oxidized aromatic intermediate (which is not shown here) from **11a** to **11b** is of 22π electronic system. In contrast, the mono- and doubly-fused (**11a** and **11b**) are, however, anti-aromatic circuits consisting of 24π systems, which indicate the aromaticity is not necessarily required for expanded porphyrins [50].

Similar inward coordination as observed in the doubly N-confused hexaphyrin **10** is also present in the doubly N-confused pentaphyrin **12a,b** [51]. Pentaphyrin **12a** can be transformed into bis-oxo derivative **12b** by chemical oxidation (Scheme 10b). The above examples strongly suggest that the confused analogs of the expanded porphyrins are promising functional macrocycles.

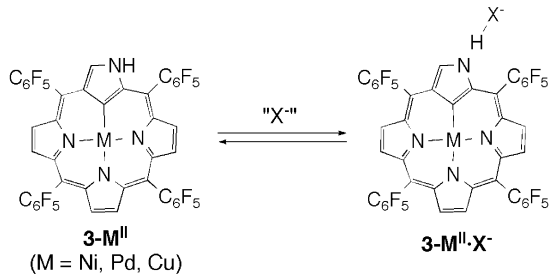


Scheme 10 Oxidative transformation of (a) N-confused pentaphyrin **11a,b** and (b) doubly N-confused pentaphyrin **12a,b**.

ANION BINDING AT THE PERIPHERAL NITROGEN OF N-CONFUSED PORPHYRIN

Apart from the coordination with metal cations at the peripheral nitrogen, NCP can also bind anions at the outer NH in the solid state. Sb^V NCP complexes bearing two monoanionic axial ligands are promising conductive materials [52]. The changes of the axial bond length in Sb^V complexes with dibromide ligands by the protonation/deprotonation were confirmed by X-ray single-crystal analysis. Interestingly, the distance between the uncoordinated Br^- anion and the protonated outer-N of NCTPP was 3.771(9) Å, which was in the range of weak N-H···Br^- hydrogen-bonding interaction [52b]. The intermolecular hydrogen bonding between N-H···Br was also observed in the Fe^{II} monomer complex in the crystal, wherein the axial bromide was associated with the peripheral NH of the other NCP, forming a dimeric structure [37a].

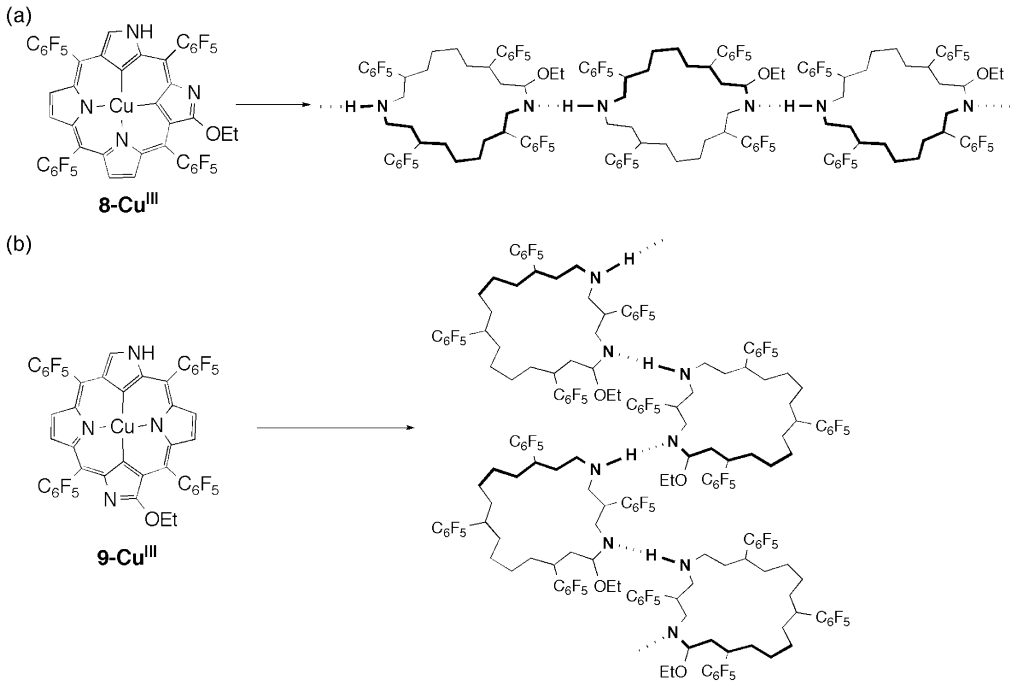
In the case of divalent metal complexes of C_6F_5-substituted NCP (**3-M^{II}**, M = Cu, Ni, Pd) [21], the efficient binding of anions such as halide (F^-, Cl^-, Br^-, and I^-), ClO_4^-, and PF_6^- was observed in nonpolar solvent like CH_2Cl_2 (Scheme 11) [34,53]. For example, the binding constants of **3-Cu^{II}** for Cl^-, ClO_4^-, and PF_6^- were estimated as 4.9×10^4, 360, and 50 M^{-1} in CH_2Cl_2, respectively. The ^1H NMR signal of the outer NH proton of Ni^{II} complex (**3-Ni^{II}**) at 10.05 ppm in $CDCl_3$ shifted to a lower field at 14.65 ppm, and the doublet signal of the peripheral α-CH at 8.45 ppm (J = 3.3 Hz) changed into a singlet at 8.80 ppm upon the addition of 1 equiv of Cl^- as a tetrabutylammonium salt. The divalent metal complexes of NCTPP (**1-M^{II}**) with fewer electron-withdrawing substituents showed smaller binding constants for anions (e.g., <10 M^{-1} for Cl^-). In the case of Cu^{II} complex (**3-Cu^{II}**), the redox potential coupled with Cu^{III}/Cu^{II} can be modulated by the anions of supporting electrolytes [34]. Here, the tightly bound anion, Cl^-, decreases the oxidation potential (0.03 V vs. Fc^+/Fc) compared to ClO_4^- (0.14 V) and PF_6^- (0.15 V) in CH_2Cl_2. The sources of unusually high association constants derived from only one hydrogen-bonding interaction (N-H···X^-) have been clarified by further investigation on anion binding behaviors of Cu^{III} complexes of *cis*- and *trans*-N_2CP (**8-Cu^{III}**, **9-Cu^{III}**) [54].



Scheme 11 Anion binding of divalent metal complexes of C_6F_5-substituted NCP **3-M^{II}**.

SUPRAMOLECULAR NETWORK OF DOUBLY N-CONFUSED PORPHYRIN

As described in the previous sections, the peripheral nitrogen of NCP serves as an interaction site for negatively charged species. The two peripheral interaction sites of both *cis*- and *trans*-Cu^{III} complexes **8-Cu^{III}** and **9-Cu^{III}** have a similar nitrogen arrangement as "imidazole", where one nitrogen is hydrogen-bonding donor (NH) and the other one is acceptor (N), which could serve as the scaffolds of the building subunits for the supramolecular architecture. Actually, one-dimensional (1D) hydrogen-bonding chains of Cu^{III} complexes of both *cis*-N_2CP[41a,55] and *trans*-N_2CP[46] are constructed in the solid state (Scheme 12). The intermolecular configurations are different in *cis*- and *trans*-N_2CP, in which zigzag and straight assemblies are formed with the dihedral angles between two macrocycles of 67.71 and 83.74°, respectively. In the *cis* case, free base and Ag^{III} complex **8** and **8-Ag^{III}** also form such hydrogen-bonding networks, but, in the *trans* case, free base **9** shows no interaction due to the absence of hydrogen-bonding donor NH at the periphery. The geometries of N_2CP affect the electronic states of the core and the shapes of the molecular assembly as well.



Scheme 12 1D hydrogen-bonding networks of Cu^{III} complexes of *cis*- and *trans*-N_2CP (**8-Cu^{III}**, **9-Cu^{III}**).

At present, further N-confused analogs, triply and totally confused ones, which would be promising substructures of 2D and 3D supramolecular networks, are not yet synthesized. According to the density functional theory (DFT) calculations, the stability of the confused analogs is inferred to decrease about 18 kcal/mol by the introduction of every confused unit [47]. Whether it is true or not, the efforts toward triply and totally NCPs will be continued to disclose the entire picture of the NCP chemistry.

CONCLUDING REMARKS

Since the first reports, NCP and other analogs with confused pyrrole ring(s) have exhibited characteristic properties on coordination behavior, host-guest chemistry, etc., which are derived from the inward pointing carbon(s) and outward nitrogen(s). Introduction of *confusion* into the normal bond-linking system, thus, not only changed the properties of the compounds largely, but also served as a novel concept to unveil or create a rich porphyrin chemistry. At present, NCP is regarded as a mutant of the normal porphyrin. However, we believe the time will come when the *normal* porphyrin is classified as one of the isomers among the NCP family.

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